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Appleton, Wisconsin

Doctor's Dissertation

An Investigation of the Vibrational  
Spectra of the 1,5-Anhydropentitols

Larry James Pitzner

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AN INVESTIGATION OF THE VIBRATIONAL  
SPECTRA OF THE 1,5-ANHYDRO-PENTITOLS

A thesis submitted by

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To My Wife, Marilyn

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## SUMMARY

The 1,5-anhydropentitol compounds (namely, 1,5-anhydroxylitol, 1,5-anhydro-ribitol, and 1,5-anhydro-D- and L-arabinitol) are a logical class of compounds with which to begin a systematic analysis of carbohydrate vibrational spectra. These compounds form a model system that is structurally similar to the pentoses, although simpler because they lack a hydroxyl group at the C1 position of the ring. The vibrational spectra of these compounds are quite complex, complicated by extensive vibrational coupling. As a result, a complete interpretation of the vibrational spectra can be accomplished only by detailed normal coordinate analyses.

The laser Raman and infrared spectra of the crystalline 1,5-anhydropentitol compounds were measured in the region from 4000 to 150  $\text{cm}^{-1}$  (wave number). (The infrared spectra were only recorded down to 300  $\text{cm}^{-1}$ ) The solid state spectra were assigned and interpreted with the aid of detailed normal coordinate calculations, performed for each compound in the class. In the normal coordinate analyses, a series of computer programs were employed to construct and solve the vibrational secular equation by the Wilson  $\overline{GF}$  method. An iterative nonlinear least squares technique based on the Fletcher-Powell method was adapted to refine an initial set of force constant parameters for each of the 1,5-anhydropentitol models simultaneously; whereby, the difference between the calculated and experimental frequencies were minimized. The result was an overall average error of 6.2  $\text{cm}^{-1}$

The comparative differences in band location (i.e., frequency) between the 1,5-anhydropentitol spectra are demonstrated to be primarily the result of a kinetic energy effect ( $\overline{G}$  matrix) rather than a potential energy effect ( $\overline{F}$  matrix) and are related to the hydroxyl group orientation, i.e., axial or equatorial.

The Raman spectra of the water and dimethyl sulfoxide-d<sub>6</sub> solutions of the 1,5-anhydropentitol compounds were observed to be very similar upon exclusion of the solvent bands. This observation suggests that the type of solvent, amphiprotic versus aprotic, has little effect on the vibrational spectra of these saccharide model compounds. The solution spectra were noted to correlate quite favorably with the crystalline spectra; however, the bands were greatly broadened in the solution spectra. Several additional bands were observed in the solution spectra for 1,5-anhydroribitol and 1,5-anhydro-L-arabinitol that were not evident in the crystalline spectra. Conformational free energy calculations and normal coordinate computations support the argument that these bands originate from a significant portion of the molecules that exist in the alternate chair conformation in solution.

The infrared and Raman spectra of crystalline 1,5-anhydro-DL-arabinitol were recorded. The 1,5-anhydro-DL-arabinitol spectra were not identical to the spectra of the D and L isomers. Several spectral bands appeared to be shifted in frequency, and the relative intensities of a number of bands were not the same. The hydrogen bonding and crystal geometry are suspected of differing in the two systems; however, the influence of these factors upon the spectra was not investigated.

In addition to providing important vibrational information about a class of compounds previously unstudied, the investigation of the 1,5-anhydropentitol spectra has also made available the necessary data to assist in the spectral interpretation of other carbohydrate compounds. The normal coordinate computations for these compounds have generated a force field which should simplify the mathematical analyses of the monosaccharides, especially the pentoses.



## INTRODUCTION<sup>1</sup>

The saccharides are a broad class of naturally occurring compounds composed of such groups as the pentoses (xylose, ribose, arabinose), hexoses (glucose, mannose, galactose), oligomers (lactose, fructose, sucrose), and polysaccharides (glycogen, pectin). Derivatives (glucosamine) and substituted polysaccharides (mucopolysaccharides) are also members of this group.

The saccharides are important elements in biological systems. They form the subunits of more complex molecular systems such as the glycoproteins and glycolipids (1-3), are important structural components in a variety of living tissues, and are involved in a number of complex metabolic pathways (4,5). In addition, saccharides enter into a number of important biological mechanisms, and they are constituents of some of the clinically important antibiotics (6).

The saccharides, especially the polymers of anhydroglucose, are also the basic raw material for several industries. For example, the starch industry utilizes the  $\alpha$ -1,4-linked polymer (7), while the cotton textiles and paper industries depend upon cellulose, the  $\beta$ -1,4-linked polymer, as the basic raw material (8,9). The rayon, cellophane, sugar, and fermentation industries are further examples of areas of technology where saccharides are important.

Recently, polysaccharides have been determined as important elements in pollution abatement problems. The dewatering of sludges from municipal sewage treatment systems appears to be influenced by their waste cellulose fiber content and by the hydration properties of the capsular polysaccharides of microorganisms.

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<sup>1</sup>The Introduction, Background, and Thesis Objectives sections are based on an unpublished review by Dr. Rajai Atalla, The Institute of Paper Chemistry, Appleton, Wisconsin.

In view of the widespread importance of the saccharides, it is evident that an expansion of our basic understanding of these compounds through physical chemical investigations will result in potential applications in biochemistry, medicine, industrial technology, and environmental protection programs.

To date, physical chemical investigations of the saccharides have employed optical rotation (10), x-ray crystallography (11,12), and nuclear magnetic resonance spectrometry (13,14) as important sources of information. Vibrational spectroscopy, primarily infrared spectroscopy, has also been used extensively in the investigation of saccharides; however, its use has been almost entirely as an analytical tool, based on the group frequency approach. In recent years, the potential of vibrational spectroscopy as a physical chemical tool has been greatly expanded due to the increasing availability of laser Raman spectrometers and the development of computer methods for normal coordinate calculations. Laser Raman spectrometers provide complementary spectral information to infrared absorption measurements, and the computational methods allow the investigation of the vibrational dynamics of large molecules. Therefore, it now appears certain that detailed vibrational analyses of the spectra of well-chosen saccharides can add significantly to the fund of basic information developed utilizing other physical chemical techniques.

## BACKGROUND

The vibrational spectra of the saccharides, their derivatives, and related compounds have been studied by many workers in this area of chemistry. Although some progress has been made in the interpretation of these spectra, the full potential of vibrational spectroscopy utilizing modern techniques has not been attained.

Coblentz (15) appears to have been the first person to critically examine the infrared spectra of the saccharides. He studied D-fructose and D-glucose in the region from  $3200 \text{ cm.}^{-1}$  to  $833 \text{ cm.}^{-1}$ . The series was expanded by Rogers and Williams (16) to include D- and L-arabinose, D-galactose, and D-mannose. The spectra of several other simple sugars were examined by other workers (17). However, the work of Kuhn (18) represents the first effort to correlate the spectra with structure. His work was followed by a series of significant contributions published by a number of groups throughout the decade of the 1950's. Whistler and House (19) were the first workers to employ infrared spectra to differentiate between sugar anomers. A significant series of publications followed by a group of workers at The University of Birmingham (20-22). The spectral region from  $670 \text{ cm.}^{-1}$  to  $1000 \text{ cm.}^{-1}$  was investigated for many monosaccharides and their derivatives. They observed that the spectral features in this region could be correlated with structure, particularly at the C1 position. They found, however, that the fingerprint region was too complex for systematization.

Tipson and Isbell and their coworkers (23-29), at the National Bureau of Standards, investigated the infrared spectra of a substantial number of monosaccharides and their derivatives. In one of the more unusual applications of infrared spectral measurements in this field, they measured the equilibrium

compositions of aqueous solutions of monosaccharides ( $\alpha$ - and  $\beta$ -anomer distribution and presence of the furanose form after mutarotation had taken place) by measuring the spectra of lyophilized samples of the solutions (28). They also attempted to make some band assignments in the fingerprint region.

A significant contribution to the study of polysaccharide spectra has been made by Marchessault and Liang and their coworkers (30-35). They have recorded the spectra of a number of celluloses, xylans, and chitin. They utilized polarized infrared absorption measurements on oriented samples as an aid to assigning some of the bands. Zhabankov and his coworkers (36) have also made important contributions in this area. They have measured the spectra of a large number of saccharides, especially celluloses from a variety of natural sources. In a more recent publication (37), they have reported low temperature studies of the infrared spectra of various monosaccharides.

Michell and coworkers (38-41) have also substantially contributed to the study of the polysaccharides and have recorded spectra at low temperature (42,43).

While the low temperature studies of Zhabankov and Michell have concentrated on the OH stretching bands, Katon and coworkers (44,45) have more recently demonstrated that low temperatures may also improve resolution in other regions of the spectra.

In the work cited so far, the utilization of infrared spectroscopy has been based on the group frequency approach which has been successful in many areas of organic chemistry, as well summarized by Bellamy (46,47). In this approach, model systems are very important, and the area of saccharide chemistry is no exception. The Birmingham school based their discussion of pyranose spectra on an assignment of the spectrum of tetrahydropyran by Burket and Badger (48).

The assignment of tetrahydropyran was confined to the region above  $700\text{ cm.}^{-1}$  in the spectrum and consequently, did not include the ring bending vibrations. Much of the later discussion of pyranose spectra is also based on this assignment. In later work, the workers at The University of Birmingham expanded the fund of basic information on relevant model compounds by investigating the spectra of tetrahydropyran-2-ol, -3-ol, -4-ol, and also tetrahydro-2-hydroxymethylpyran (49). The assignment of these spectra were also based on Burket and Badger's assignment of tetrahydropyran, which, in turn, was based on analogy with the spectrum of cyclohexane. A normal coordinate analysis of cyclohexane had been reported by Beckett, *et al.* (50).

A more detailed review of the application of vibrational spectroscopy to saccharide chemistry is provided by Spedding (51). A recent review by Tipson (52) is even more exhaustive in its discussion of group frequencies. In summary, it is sufficient to state that most of the spectral investigations of saccharides in the past have been confined to the region above  $700\text{ cm.}^{-1}$ , and have been oriented primarily toward analytical application.

However, since most of this work on saccharides, their derivatives, and related compounds has been undertaken, i.e., since the period of the 1950's and early 1960's, there has been substantial progress in the methodology of vibrational spectroscopy which has made possible more rigorous analyses of the spectra of complex<sup>2</sup> molecules. In particular, the work of Schachtschneider and Snyder on the hydrocarbons (53-55) and of Snyder and Zerbi on the ethers (56), have established the possibility of systematic analyses of the spectra of groups of related

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<sup>2</sup>The term complex is used in this context to indicate the presence of numerous atomic groups in large molecules. For saccharide compounds, this includes atomic groups such as CH, CC, OH, and COC where the last group signifies the ether linkage in the pyranose ring.

compounds with the aid of normal coordinate computations. Their work has established the necessary computational methods for a mathematical analysis of molecular vibrations and demonstrated the applicability of these methods to large molecules. Snyder and Zerbi included the normal coordinate analysis of the vibrations of tetrahydropyran in their study of the ether spectra. (As stated earlier, tetrahydropyran is the basis for several interpretations of saccharide spectra.) More recently, Pickett and Strauss (57) have adapted the methods of Schachtschneider and Snyder in a study of the bending vibrations of cyclohexane and related oxanes, including tetrahydropyran. The normal coordinate analyses of tetrahydropyran, tetrahydropyran-4-ol, -4-Cl, and -4-F are reportedly in progress at The Royal Holloway College in England (58). Tetrahydropyran-4-ol provides an improved model compound relative to tetrahydropyran for many of the saccharides, particularly the pentoses and simple sugars. This results from the addition of a hydroxyl group to the pyranose ring, which is an important element of saccharide molecules.

The availability of more comprehensive data on vibrational frequencies has been essential in the detailed vibrational studies of the saccharides in the past. The recent improvements in infrared instrumentation and the increasing availability of laser excited Raman spectrometers have made the necessary data obtainable. Furthermore, developments in computer systems and computational methods have made possible the mathematical vibrational analyses of large, complex molecules. In view of this progress, both in computational technology and instrumental capabilities, there is now a basis for a new effort at more comprehensive analyses of the saccharide spectra.

## THESIS OBJECTIVES

With respect to what has been outlined in the previous section regarding current knowledge of the vibrational spectra of the saccharides and related model compounds, the next logical effort should be a detailed vibrational study of a model system in more close approximation to the saccharides than tetrahydropyran. The 1,5-anhydropentitol (1,5-AP) compounds provide such a model system.

The compounds in this class are 1,5-anhydroxylitol (1,5-AX), 1,5-anhydroribitol (1,5-AR), 1,5-anhydro-L-arabinitol (1,5-ALA), and 1,5-anhydro-D-arabinitol (1,5-ADA). These compounds are represented in Fig. 1. The 1,5-AP compounds constitute a particularly important model system for several reasons. First, they differ from the pentoses only in the absence of the hydroxyl group at C1. Therefore, they approximate the pentoses more closely than the related model compounds previously studied. Second, the equivalence of C1 and C5 increases the symmetry of 1,5-AX and 1,5-AR, relative to the pentoses, from  $C_1$  to  $C_5$ . This allows the magnitude of the vibrational problem to be reduced by symmetry considerations. This is particularly valuable in exploring effects associated with axial or equatorial orientation of the hydroxyl group at C3. Third, the compounds as a group have melting points which are low enough to permit measurement of the spectra of the melts. Thus, it is possible to distinguish molecular bands from spectral features associated with the solid state. The monosaccharides, in contrast, generally undergo decomposition before melting. Fourth, the absence of the hydroxyl group at C1 eliminates the problems associated with mutarotation in solution. Thus, it is possible to investigate the spectra of aqueous solutions, without the complication of having two or more species present, as is the situation with the monosaccharides. The additional information provided by the solution spectra assists in the assignment of the solid state spectral bands.

In application of vibrational spectroscopy to physical chemical investigations, as distinguished from analytical investigations, it is necessary to begin with comprehensive assignments of the spectral bands in the spectra of the compounds of interest. Therefore, the major objective of this thesis is to achieve the assignment and interpretation of the vibrational spectra of the 1,5-AP compounds based on comparisons of the infrared and Raman spectra, as well as on normal coordinate analyses of the molecular vibrations. In this endeavor, an attempt is made to apply the computational methods of Schachtschneider and Snyder (53-56) to the analyses of the more complex 1,5-AP molecules.



## EXPERIMENTAL

### PREPARATION OF THE 1,5-ANHYDRO-PENTITOL COMPOUNDS

The 1,5-AP compounds are not available commercially and were prepared as part of this investigation. The syntheses of 1,5-AR, 1,5-ALA, and 1,5-ADA from their parent sugar compounds were based on the paper by Gray and Barker (59) and the unpublished laboratory procedures by Schroeder (60). The fourth compound in this class, 1,5-AX, had been previously prepared in sufficient quantity by Dr. Paul Seib, formerly of the Institute staff.

### PREPARATION OF 1,5-ANHYDRO-D- AND L-ARABINITOL

#### Tetra-O-acetyl-D-arabinopyranose

The procedure for the acetylation of D-arabinose was adapted from a method described in Schroeder's laboratory procedures (60).

Acetic anhydride (200 ml.) was added to a 600-ml. beaker equipped with a thermometer and an overhead stirrer. Anhydrous sodium acetate (13.5 g.) and then D-arabinose (30 g.) were added to the beaker with continuous stirring. The mixture was heated to 70-75°C. on a hot plate. At this point the external heat was removed. The temperature of the mixture continued to rise as a result of the heat being produced by the exothermic reaction. The reaction temperature was controlled between 90-100°C. by increasing the rate of stirring and placing the beaker in a pan of chopped ice when necessary. The sodium acetate and D-arabinose went into solution in the acetic anhydride at approximately 90°C. The temperature was maintained between 90-100°C. for 15 minutes, applying external heat when requisite. The solution was then slowly cooled to room temperature. Upon cooling, the reaction mixture solidified. The solidified mixture was transferred, a small

portion at a time, to a beaker containing rapidly stirred ice and water (700 ml.) causing the acetylated arabinose to precipitate. Upon completion of the transfer, the contents of the beaker were stirred for an additional two hours with ice being added when needed. Chloroform (350 ml.) was next added to the mixture and the stirring continued for an additional minute. The entire water-chloroform mixture was transferred to a separatory funnel (2 liter) and the chloroform layer drawn off. Additional chloroform (150 ml.) was added to the separatory funnel containing the water layer; the mixture shaken for a minute; and upon settling, the chloroform layer drawn off. The chloroform extraction solutions were combined. The chloroform solution was next transferred to a separatory funnel (1 liter) and washed with saturated sodium bicarbonate solution (2 x 250 ml.) and distilled water (3 x 250 ml.). The washed chloroform solution was dried over calcium chloride and concentrated in vacuo to a thick sirup. All attempts to crystallize tetra-0-acetyl-D-arabinopyranose from the sirup, using various solvents, were unsuccessful.

#### 2,3,4-Tri-0-acetyl-D-arabinopyranosyl Bromide

The bromination procedure to be described was also adapted from a method in Schroeder's laboratory procedures (60).

The tetra-0-acetyl-D-arabinopyranose sirup (25 g.) was dissolved in 1,2-dichloroethane (60 ml.) and hydrogen bromide in glacial acetic acid (20 ml., 43%) added. The reaction was allowed to progress at room temperature for 45 minutes with occasional stirring of the solution and then the reaction stopped by the additional of chloroform (150 ml.). The diluted solution was poured into a separatory funnel (500 ml.), washed with ice water (3 x 225 ml.), and dried over calcium chloride. The dried chloroform solution was concentrated in vacuo to the point at which 2,3,4-tri-0-acetyl-D-arabinopyranosyl bromide began to

crystallize. The sirup was immediately dissolved in anhydrous diethyl ether (50 ml.) and petroleum ether (b.p. 30-60°C.) added until crystallization was initiated. The mother liquor was put into a refrigerator overnight to allow for further crystallization. The triacetyl-D-arabinosyl bromide crystals were then filtered from the mother liquor, washed with a small amount of diethyl ether, pressed with dental dam, and dried in a vacuum desiccator for ten minutes. A yield of 13.4 g. was recorded. The melting point of the triacetyl-arabinosyl bromide crystals was not measured due to their instability. (The crystals were found to decompose rapidly in air, giving off hydrogen bromide vapors within a few minutes after exposure to the air.)

#### 2,3,4-Tri-O-acetyl-1,5-anhydro-D-arabinitol

The procedure to be described for the reductive dehalogenation was adapted, for the most part, from Gray and Barker (59) with modifications in the choice of catalyst and bromine scavenger.

The crystalline 2,3,4-tri-O-acetyl-D-arabinopyranosyl bromide (13.4 g.) was dissolved in absolute ethyl acetate (160 ml.). Palladium catalyst on charcoal (1 g., 10%) and triethylamine (9 ml.) were added to the solution<sup>3</sup>. The reaction mixture was transferred to a teflon-coated Parr bomb reactor. A magnetic stirring bar was added; the bomb was sealed; hydrogen gas was introduced into the bomb to a pressure of 50 p.s.i.g.; and the bomb was placed on a magnetic stirring motor. The reaction mixture was stirred for 48 hours. Thin-layer chromatography was employed to establish when the reaction had reached completion. The reaction mixture was then filtered through Celite to remove the catalyst. The Celite bed

<sup>3</sup> Gray and Barker suggest using a platinum on charcoal catalyst; however, the palladium catalyst was found to result in higher yields for the 1,5-AP compounds. Triethylamine was found to be an effective bromine scavenger with less tendency to produce side products.

was washed with chloroform. Additional chloroform was added to the filtrate until a total chloroform addition of 150 ml. was attained. The chloroform-ethyl acetate solution was transferred to a separatory funnel (1 liter). The solution was washed with 0.5N hydrochloric acid solution (2 x 200 ml.), saturated sodium bicarbonate solution (2 x 200 ml.), and distilled water (2 x 200 ml.). The washed solution was treated with silver nitrate in acetone (7 ml., 3%) to "strip" bromine from any unreacted triacetylarabinosyl bromide as suggested by Brandon (61). A turbid suspension of silver bromide formed immediately. The mixture was dried over calcium chloride. The suspended material was then removed by filtration through Celite. The solution was concentrated to a sirup in vacuo, and all attempts to crystallize 2,3,4-tri-O-acetyl-1,5-anhydro-D-arabinitol from the sirup were unsuccessful.

#### 1,5-Anhydro-D-arabinitol

The deacetylation procedure was adapted from a method in the unpublished procedures by Schroeder (60).

The 2,3,4-tri-O-acetyl-1,5-anhydro-D-arabinitol sirup (9.5 g.) was dissolved in absolute methanol (100 ml.) in a stoppered flask. Sodium methoxide in methanol (0.5N) was added in 0.5-ml. increments until the methanol solution was basic to phenolphthalein solution. In this case, 1.0 ml. of sodium methoxide solution was required. The deacetylation was monitored by thin-layer chromatography using silica gel G and diisopropyl ether as the developing solvent. The deacetylation was observed to be almost simultaneous with the sodium methoxide solution addition. The methanol solution was deionized by adding Amberlite IR-120 (1.5 g.), a cation exchange resin, stirring, and testing for neutrality with litmus paper. The resin was removed by filtering the solution through Celite. The 1,5-ADA solution

was then concentrated to a sirup in vacuo. The reaction scheme for the synthesis of 1,5-ADA is diagrammed in Fig. 2.

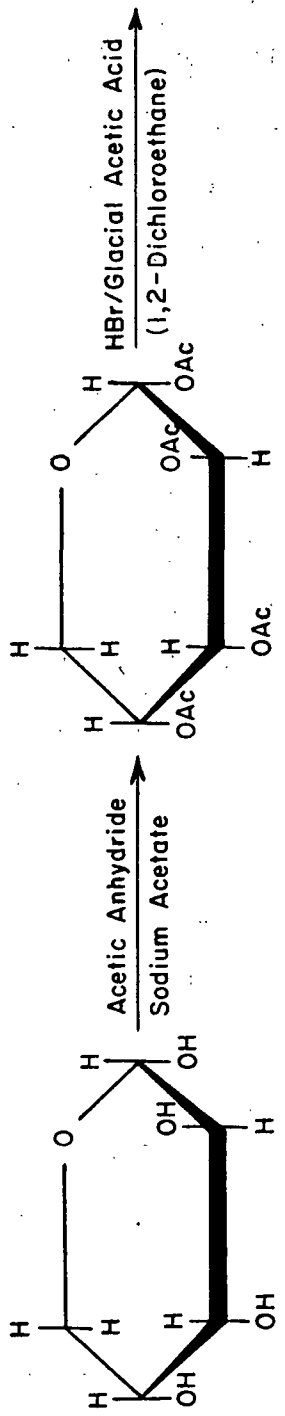
#### Purification of the 1,5-Anhydro-D-arabinitol Sirup

The most probable source of impurity in the 1,5-ADA preparation was suspected to be the parent sugar. A reducing sugar can be removed by alkaline hydrolysis followed by ion-exchange chromatography. Alkaline hydrolysis of a reducing sugar results in the formation of metasaccharinic acids. These acids are then removed by passing the solution through a column containing an anion exchange resin and a cation exchange resin, to remove sodium ions.

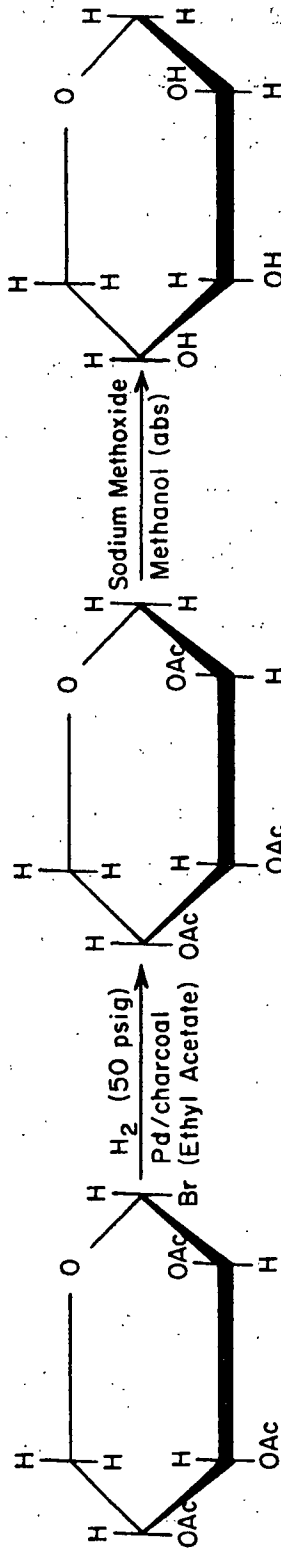
The 1,5-ADA sirup (5 g.) was dissolved in distilled water (25 ml.) and treated with 0.5N sodium hydroxide solution (10 ml.). The solution was refluxed over a steam bath for two hours with the basicity being determined with pH paper at 30-minute intervals. The pH of the solution remained above 12 throughout the hydrolysis. Upon cooling to room temperature, the hydrolysis solution was passed through a column packed with Amberlite MB-3 mixed bed ion exchange resin (50 ml.) followed by distilled water (150 ml.). The deionized solution was decolorized with activated charcoal, filtered through Celite, and concentrated to a sirup in vacuo at 50°C.

#### Crystallization of 1,5-Anhydro-D-arabinitol

The purified 1,5-ADA sirup was dissolved in an absolute ethanol-ethyl acetate mixture (50:50, v./v.) (20 ml.) and crystallization initiated by refrigeration. Two recrystallizations of this material from ethanol-ethyl acetate resulted in 1.8 g. of crystalline product. The melting point of the 1,5-ADA product was determined to be 96-97°C. which is in agreement with the literature value of 96-97°C. reported by Fletcher and Hudson (62). The purified material displayed



Tetra-O-acetyl- $\alpha$ -D-arabinopyranose



2,3,4-Tri-O-acetyl- $\alpha$ -D-arabinopyranosyl Bromide

2,3,4-Tri-O-acetyl-1,5-Anhydro-D-arabinitol

1,5-Anhydro-D-arabinitol

Figure 2. The Reaction Scheme for the Synthesis of 1,5-Anhydro-D-arabinitol

an optical rotation of  $-96.5^{\circ}$  ( $c$ , 1.133) in distilled water, the literature value being  $-98.6^{\circ}$  ( $c$ , 0.8928) (62). An elemental analysis was performed on the 1,5-ADA material by Micro-Tech Laboratories, Inc., Skokie, Illinois. The calculated percentages for C, H, and O based on the formula  $C_5H_{10}O_4$  are 44.77, 7.52, and 47.71%, respectively. The corresponding percentages experimentally determined for the 1,5-ADA product were 44.67, 7.66, and 47.47%, respectively.

#### 1,5-Anhydro-L-arabinitol

The compound 1,5-ALA was synthesized from its parent sugar, L-arabinose, in an analogous manner to the preparation of 1,5-ADA. The product material was also subjected to the purification steps described for the 1,5-ADA preparation. A yield of 2.8 g. of crystalline product was obtained after crystallization followed by two recrystallizations from absolute ethanol-ethyl acetate (50:50, v./v.). The melting point of the material was determined to be  $97^{\circ}C$ . which agrees with the literature value of  $95-96^{\circ}C$ . reported by Rice and Inatome (63). The optical rotation of the 1,5-ALA solution in distilled water was measured to be  $+97.1^{\circ}$  ( $c$ , 1.129) as compared with the literature value of  $+101^{\circ}$  ( $c$ , 1.8) (63). An elemental analysis was also performed by Micro-Tech on the 1,5-ALA product. The C, H, and O percentages were determined to be 44.91, 7.46, and 47.72%, respectively. The corresponding percentages based on the formula  $C_5H_{10}O_4$  were 44.77, 7.52, and 47.71%, respectively, as for 1,5-ADA.

#### PREPARATION OF 1,5-ANHYDRORIBITOL

##### Tetra-O-benzoyl-D-ribopyranose

Gray and Barker (59) state in their paper that triacetylribopyranosyl bromide is quite unstable, and the acetylated products are difficult to isolate. They suggest using benzoylated rather than acetylated intermediates in the

reaction scheme. Thus, in the preparation of 1,5-AR from D-ribose, the reaction scheme employed to prepare 1,5-ALA and 1,5-ADA was followed, with the exception that the intermediate compounds were benzoylated rather than acetylated derivatives. The benzoylation procedure was adapted from a method by Jeanloz, et al. (64).

D-Ribose (28 g.) was added to a beaker containing a chilled mixture (-10°C.) of pyridine (120 ml.), benzoyl chloride (115 ml.), and 1,2-dichloroethane (230 ml.). The beaker was placed in an ice bath; the mixture stirred for 45 minutes at 0°C.; and upon completion of the stirring, the beaker and contents were set in a refrigerator for 24 hours. After this period in the refrigerator, the beaker was removed and allowed to warm to room temperature overnight. The reaction mixture was then poured slowly into a beaker containing rapidly stirred ice and water. The stirring was continued for one-half hour with ice being added when necessary. Chloroform (500 ml.) was next added to the ice-water mixture and the stirring maintained for approximately one minute. The contents of the beaker were then transferred to a separatory funnel (2 liters), the chloroform layer drawn off, and the aqueous layer back extracted with additional chloroform (200 ml.). The chloroform extracts were combined and washed with 2N sulfuric acid solution (1 x 200 ml.), 1N sulfuric acid solution (2 x 200 ml.), saturated sodium bicarbonate solution (2 x 200 ml.), distilled water (2 x 200 ml.), 1N sodium hydroxide solution (1 x 200 ml.), 0.5N sodium hydroxide solution (2 x 200 ml.), and distilled water (3 x 200 ml.). The chloroform solution was dried over calcium chloride, filtered through activated charcoal on Celite, and concentrated in vacuo to a thick sirup.

The procedure for the next steps in the synthesis scheme leading to 2,3,4-tri-O-benzoyl-1,5-anhydroribitol, namely, bromination and reductive dehalogenation, follows the preparation of 1,5-ALA and 1,5-ADA.



### 1,5-Anhydroribitol

The debenzoylation of 2,3,4-tri-O-benzoyl-1,5-anhydroribitol was accomplished in an analogous procedure to the deacetylation of the acetyl derivatives of 1,5-ALA and 1,5-ADA, i.e., by the addition of sodium methoxide in methanol to a methanol solution of the benzoyl derivative of 1,5-AR. However, the rate of debenzoylation was considerably slower than the deacetylations. The process required two hours to reach completion at elevated temperatures near the boiling point of methanol. The product was next carried through the purification steps discussed earlier for 1,5-ADA. Purified 1,5-AR was crystallized from absolute ethanol-ethyl acetate (50:50, v./v.) followed by two recrystallizations. A yield of 3.4 g. of crystalline product was obtained. A melting point of 128°C. was determined for this material. Jeanloz, et al. (64) have reported a melting point of 128-129°C. for 1,5-AR. A solution of 1,5-AR in distilled water was determined to have an optical rotation of 0° (c, 1.144), as it should since the compound has symmetry, and is in agreement with the literature (64). An elemental analysis of the product determined the percentages of C, H, and O to be 44.68, 7.48, and 47.64%, respectively. These values are to be compared with the calculated values of 44.77, 7.52, and 47.71% for C<sub>5</sub>H<sub>10</sub>O<sub>4</sub>.

### PREPARATION OF 1,5-ANHYDROXYLITOL

As stated earlier, 1,5-AX was prepared by Dr. Paul Seib, formerly of the Institute staff, employing the procedure of Gray and Barker (59). The melting point of the crystalline product was determined to be 117°C. which is comparable to the accepted literature value of 116-117°C. (65). The optical rotation for a solution of 1,5-AX in distilled water was determined to be 0° (c, 1.100), which is expected since the compound has symmetry, and is also in agreement with the literature (65). An elemental analysis was performed by Micro-Tech for the

1,5-AX preparation. The percentages of C, H, and O were determined to be 44.73, 7.53, and 47.70%, respectively. These values are to be compared with the calculated values of 44.77, 7.52, and 47.71% for C<sub>5</sub>H<sub>10</sub>O<sub>4</sub>.

The melting points, optical rotation data, and elemental analyses for the four 1,5-AP preparations are summarized in Table I.

TABLE I.

SUMMARY OF PHYSICAL AND CHEMICAL DATA FOR THE  
1,5-ANHYDROPENTITOLS

	M.p., °C.		[α] <sub>D</sub> <sup>25</sup>		%C	%H	%O	Σ%
	Observed	Reported	Observed	Reported				
					44.77	7.52	47.71 <sup>a</sup>	100.00
1,5-AX	117	116-117 <sup>b</sup>	0.0	0.0 <sup>b</sup>	44.73	7.53	47.70	99.96
1,5-AR	128	128-129 <sup>c</sup>	0.0	0.0 <sup>c</sup>	44.68	7.48	47.64	99.80
1,5-ALA	97	95-96 <sup>d</sup>	+97.1	+101.0 <sup>d</sup>	44.91	7.46	47.72	100.09
1,5-ADA	96-97	96-97 <sup>e</sup>	-96.5	-98.6 <sup>e</sup>	44.67	7.66	47.47	99.80

<sup>a</sup>Calculated C, H, and O percentages based on the formula C<sub>5</sub>H<sub>10</sub>O<sub>4</sub>.

<sup>b</sup>Fletcher, H. G., Jr., and Hudson, C. S. (65).

<sup>c</sup>Jeanloz, R., *et al.* (64).

<sup>d</sup>Rice, F. A. H., and Inatome, M. (63).

<sup>e</sup>Fletcher, H. G., Jr., and Hudson, C. S. (62).

DEUTERATION OF THE 1,5-ANHYDROPENTITOL PREPARATIONS

The hydroxyl group protons for the 1,5-AP preparations were exchanged for deuterium by crystallizing the compounds from monodeuteroethanol.

Approximately 300 mg. of the 1,5-AP material was dissolved in a minimum amount of hot monodeuteroethanol (99%, 0.5 ml.) in a 10-ml. Erlenmeyer flask. The solution was then cooled in an ice bath. If crystallization did not occur upon cooling, approximately 0.5 ml. of cold ethyl acetate was added to the solution. In most cases, crystallization was initiated by scratching the bottom of the flask with a glass stirring rod. In the other cases, crystallization took place within a few hours after the mother liquor was refrigerated. The deuterated crystals were separated by filtration, washed with a small amount of cold ethyl acetate, and dried in a vacuum desiccator. The above procedure was then repeated two or more times. The degree of deuteration was not rigorously established.

The melting points of the deuterated 1,5-AP compounds were determined to be 115, 128, and 96.5°C. for 1,5-AX, 1,5-AR, and 1,5-ALA, respectively. These melting points are quite close to the values determined for the undeuterated mother compounds as seen from Table II.

TABLE II

MELTING POINTS FOR THE DEUTERATED AND UNDEUTERATED  
1,5-ANHYDROPENTITOL COMPOUNDS

	M.p., °C.	
	Undeuterated	Deuterated
1,5-Anhydroxylitol	117	115
1,5-Anhydroribitol	128	128
1,5-Anhydro-L-arabinitol	97	96.5
1,5-Anhydro-DL-arabinitol	74	73

## PREPARATION OF 1,5-ANHYDRO-DL-ARABINITOL

The compound 1,5-anhydro-DL-arabinitol (1,5-ADLA) was prepared by initiating crystallization from an ethanol solution of a racemic mixture of the D and L isomers.

Equal amounts of 1,5-anhydro-L- and D-arabinitol (100 mg.) were weighed out into a 10-ml. Erlenmeyer flask. The mixture was dissolved in a minimum of hot absolute ethanol (0.3 ml.). The resulting solution was next cooled in an ice bath, cold ethyl acetate added (0.3 ml.), and the mother liquor refrigerated overnight. The crystalline product was separated by filtration, washed with a small amount of cold ethyl acetate, and dried in a vacuum desiccator. After two recrystallizations, the melting point of the crystalline material remained constant at 74°C. This value is noted to be substantially lower than the melting point measured for either of the D or L isomers (96-97°C.) as listed in Table II.

The 1,5-ADLA product was later deuterated by the method described in the last section. The deuteration procedure was repeated three times, the degree of deuteration was not rigorously established, and the melting point was determined to be 73°C., which is comparable to the undeuterated material (see Table II).

## NUCLEAR MAGNETIC RESONANCE MEASUREMENTS OF THE 1,5-ANHYDROPENTITOL COMPOUNDS

The nuclear magnetic resonance (NMR) spectra for the 1,5-AP compounds in solution in heavy water (D<sub>2</sub>O) and dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) were measured to provide conformational information which might be used to aid the interpretation of the solution vibrational spectra.

The NMR spectra were measured on a Varian A-60A analytical NMR spectrometer.

The infrared spectra of the crystalline 1,5-AP compounds were also recorded in two sample arrangements: 1) as a potassium bromide pellet (KBr pellet) and 2) as a split mull<sup>4</sup>.

MEASUREMENT OF THE INFRARED AND RAMAN SPECTRA OF THE DEUTERATED 1,5-ANHYDRO-PENTITOL COMPOUNDS IN THE CRYSTALLINE STATE

The vibrational spectra of the deuterated 1,5-AP compounds were measured to provide additional information that might assist in the assignment of the solid state 1,5-AP spectral bands, primarily the COH bending vibrations.

The preparation of the deuterated 1,5-AP compounds has already been discussed in an earlier section. The Raman spectra of the deuterated compounds were measured for the crystalline samples in capillary tubes. The infrared spectra were recorded for the potassium bromide pellets.

The pellet preparation sometimes resulted in a significant decrease in the degree of deuteration. This apparently was the result of the hygroscopic nature of potassium bromide and the generation of new crystal surfaces by grinding. Two sample preparation methods were observed to minimize protonation. The first alternative follows as a minor modification of the pellet preparation. That is, the deuterated sample is added to the potassium bromide base and the two materials ground and mixed together with an agate mortar and pestle, rather than the usual practice of grinding the sample first and then adding the potassium bromide. The second alternative is to prepare the sample as Fluorolube and Nujol mulls, since neither of these materials are hygroscopic. The first method was employed for the deuterated 1,5-AP samples.

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<sup>4</sup>The spectral region from 3600 to 1300  $\text{cm}^{-1}$  was recorded employing a Fluorolube mull while the region from 1300 to 600  $\text{cm}^{-1}$  was recorded with a Nujol mull. Sodium chloride windows were used in both cases.

## MEASUREMENT OF THE RAMAN SPECTRA OF THE 1,5-ANHYDRO-PENTITOL SOLUTIONS

The 1,5-AP aqueous solution spectra were measured to provide additional spectral information that might aid in the assignment of the solid state spectral bands. A comparison of the solid state and solution spectra provides a means of distinguishing molecular bands from spectral features associated with the solid state. In addition, the effect of the dissolution of the 1,5-AP compounds upon the vibrational spectra can be investigated. Further, the 1,5-AP DMSO-d<sub>6</sub> solution spectra were recorded. A comparison of the 1,5-AP water and DMSO-d<sub>6</sub> solution spectra will also permit the investigation of the effect of the type of solvent (amphiprotic versus aprotic) on the vibrational spectra.

The Raman spectra were measured for the 1,5-AP solutions in water and in DMSO-d<sub>6</sub>. The spectra were recorded with the samples in each of two sample arrangements, i.e., in a capillary tube and in an intermediate size quartz cell. The concentration of the DMSO-d<sub>6</sub> solutions was approximately 30% by weight (mass), and the concentration of the aqueous solutions was approximately 25%. For comparison, the Raman spectra of the concentrated solutions or sirups were recorded. The sirups resulted from concentrating the 25% solutions through slow evaporation of water at room temperature.

## ATTEMPT TO MEASURE THE RAMAN SPECTRUM OF THE 1,5-ANHYDROXYLITOL MELT

The measurement of the Raman spectra of the 1,5-AP melts would permit the examination of the vibrational spectra of these compounds in the fluid state without the presence of a solvent. A comparison of these spectra with the solid state spectra would provide a means of distinguishing molecular bands from spectral features associated with the solid state.

An attempt was initiated to record the Raman spectrum of the 1,5-AX melt with the assistance of a Harney-Miller variable temperature cell<sup>5</sup>. A capillary tube was packed with the crystalline sample and inserted into the variable temperature cell. The cell was heated and its temperature controlled by passing hot nitrogen gas through it. The cell temperature was increased until the sample melted (117°C.) and then maintained slightly above the melting point. The Raman spectrum was then recorded. Fluorescence from the glass cell walls resulted in an intense background. During the spectral scan, the fluorescence level began to increase, eventually masking the Raman spectrum. The increase in the level of fluorescence was traced to sample or sample impurity decomposition. The melt was observed to darken in color during the scan. In addition, the melting point of the sample after it had cooled and crystallized was determined to be a few degrees lower than the initial value. However, the 1,5-AP compounds are considered to be quite stable to oxidation. This implies that the fluorescence problem may be derived from the decomposition of impurities present in the sample. The presence of only a small amount of fluorescent material will result in a high level of fluorescence which may mask the Raman spectrum. In addition, spurious bands and excessive background noise generated by continual formation of tiny gas bubbles in the melt added to the destruction of the spectrum. The result was a completely unusable vibrational spectrum.

No attempt was made to measure the melt spectra of 1,5-AR and 1,5-ALA.

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<sup>5</sup> A brief description and a diagram of this Raman spectrometer attachment can be found on page 76 in Tobin (67).

DEPOLARIZATION RATIO MEASUREMENTS FOR 1,5-ANHYDROXYLITOL  
AND 1,5-ANHYDRORIBITOL SOLUTIONS

The depolarization ratios were measured for 1,5-AX and 1,5-AR in solution in water and also DMSO-d<sub>6</sub>. Such measurements provide additional data which assist the band assignment in the 1,5-AP solid state spectra.

Discussions of the theory of depolarization ratios and the instrumental technique of their measurement can be found in almost any text treating Raman spectroscopy, for example (66-69). The various instrumental arrangements for measuring depolarization ratios have been discussed and evaluated for accuracy by Allemand (70). He suggests that the polarization of the exciting beam be kept constant and that the analyzer be placed after the sample as the experimental arrangement providing the most accurate depolarization ratios. He further states that in cases where it is impracticable to measure the instrument functions, the use of the scrambler eases the experimental difficulties at relatively little cost in accuracy of the depolarization ratio determinations. In this sample arrangement, the spectrum of the sample in a fluid state, such as in solution, is recorded with the plane of polarization of the analyzer set parallel to the plane of polarization of the incident beam. The spectrum is then measured with all instrument conditions the same except that the plane of polarization of the analyzer is rotated by 90°, so that it is now perpendicular to the plane of polarization of the incident beam. The scrambler is in place after the analyzer and before the entrance slit in both cases. The depolarization ratio of a particular band is then calculated by dividing the intensity of the band, which is proportional to the band height for symmetric band shapes, in the spectrum where the analyzer is in the perpendicular position by the intensity of the same band in the spectrum with the analyzer in the parallel position. In this experimental



arrangement, vibrations that are not totally symmetric have a theoretical depolarization ratio of 0.75, while totally symmetric vibrations have a ratio less than 0.75.

Both 1,5-AX and 1,5-AR belong to the  $C_{\underline{s}}$  molecular point group. They possess a plane of symmetry which bisects the ring and passes through the ring oxygen and third carbon atom. The vibrational bands for these compounds are then expected to belong to either the symmetric ( $A'$ ) or antisymmetric ( $A''$ ) symmetry species which embody the  $C_{\underline{s}}$  point group. The depolarization ratio calculations are seen to aid in the assignment of spectral bands. The spectral bands belonging to the totally symmetric species should have depolarization ratios less than 0.75, while bands of the antisymmetric species should have ratios equal to 0.75. The calculated spectral bands resulting from the normal coordinate calculations may be classified mathematically as belonging to either the symmetric or antisymmetric species. The assigned experimental bands should be of the same symmetry species. In the case of 1,5-ALA, the molecule contains no elements of symmetry; therefore, all vibrational bands would be expected to have depolarization ratios less than 0.75.

Depolarization ratios were calculated for 1,5-AX and 1,5-AR solutions in water and in DMSO- $d_6$ . The experimental arrangement discussed above involving a fixed plane of polarization for the incident beam, a polarization analyzer after the sample, and a polarization scrambler was employed in all cases. The calculated values for a number of bands are questionable, however, because the bands are overlapped with neighboring bands. It is virtually impossible to determine the band intensity of an overlapped band except by some approximation technique. The peak height is no longer strictly proportional to the band intensity, and the measured ratios are no longer accurate. Unfortunately, the solution spectra of 1,5-AX and

1,5-AR possess a number of overlapped bands. (The reader may wish to examine the solution spectra in the next section.)

MEASUREMENT OF THE INFRARED AND RAMAN SPECTRA OF 1,5-ANHYDRO-DL-ARABINITOL AND THE DEUTERATED DERIVATIVE

The Raman and infrared spectra of 1,5-ADLA were measured to investigate the differences, if any, that exist between the 1,5-ADLA vibrational spectra and the spectra of the D and L isomers. The hydrogen bonding and crystal structure are suspected of differing between 1,5-ADLA, 1,5-ALA, and 1,5-ADA. The procedures employed in the preparation of 1,5-ADLA from a racemic mixture of the D and L isomers and in the subsequent deuteration of this material have been described in earlier sections.

The infrared spectrum was recorded for the deuterated material in a mull pressed between sodium chloride windows. The spectral region from 3600-1300  $\text{cm.}^{-1}$  was measured for the Fluorolube mull, and the region from 1300-600  $\text{cm.}^{-1}$  was recorded for the Nujol mull. The mulls were employed because an excessive decrease in the degree of deuteration resulted from the preparation of KBr pellets. This situation was encountered and discussed earlier in relation to the infrared spectra of deuterated 1,5-AP compounds; however, the decrease in the degree of deuteration was much more pronounced with the deuterated 1,5-ADLA compound.

## EXPERIMENTAL RESULTS

### NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE 1,5-ANHYDROPENTITOL COMPOUNDS

The NMR spectra of the 1,5-AP compounds in solution in D<sub>2</sub>O are included in Fig. 3-5 in which sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) is the internal standard. The NMR spectra of the 1,5-AP compounds in solution in DMSO-d<sub>6</sub> are included in Fig. 6-8a in which tetramethylsilane (TMS) is the internal standard. The NMR spectrum of the DMSO-d<sub>6</sub> solution of 1,5-ALA to which a drop of D<sub>2</sub>O has been added and the solution exposed to HCl vapor is presented for comparison in Fig. 8b.

### INFRARED AND RAMAN SPECTRA OF THE 1,5-ANHYDROPENTITOL COMPOUNDS IN THE CRYSTALLINE STATE

The Raman spectrum of 1,5-AX (pellet) is shown in Fig. 9. The corresponding infrared spectrum (KBr pellet) is displayed in Fig. 10. In Table III, the measured frequencies (cm.<sup>-1</sup>) of the bands in the 1,5-AX infrared and Raman spectra, exhibited in Fig. 9 and 10, are listed as well as their relative intensities<sup>6</sup>. The Raman spectrum (pellet) and the infrared spectrum (KBr pellet) of 1,5-AR are reproduced in Fig. 11 and 12, respectively. The observed frequencies and relative intensities of the bands appearing in these spectra are tabulated in Table IV. The Raman spectrum (pellet) of 1,5-ALA is included in Fig. 13. The complementary infrared spectrum (KBr pellet) follows in Fig. 14. The frequencies and relative intensities for these spectra are tabulated in Table V. The Raman and infrared spectra of 1,5-ADA are identical to those of the L isomer,

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<sup>6</sup> The relative intensity of a spectral band is determined by computing the ratio of the peak heights from the background of that particular band to that of the most intense band in the spectrum.

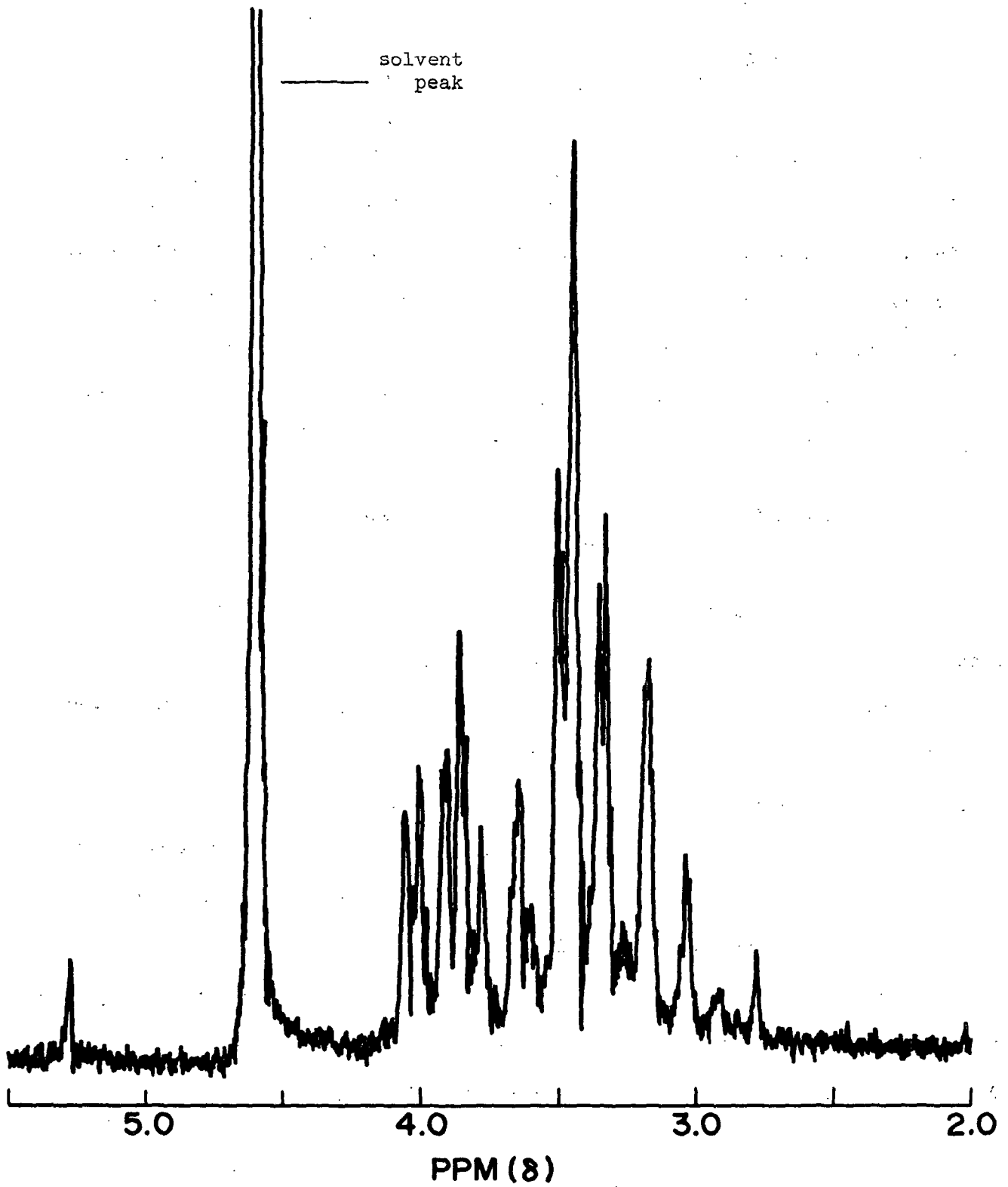


Figure 3. The NMR Spectrum of 1,5-AX in  $D_2O$  with DSS as an Internal Standard

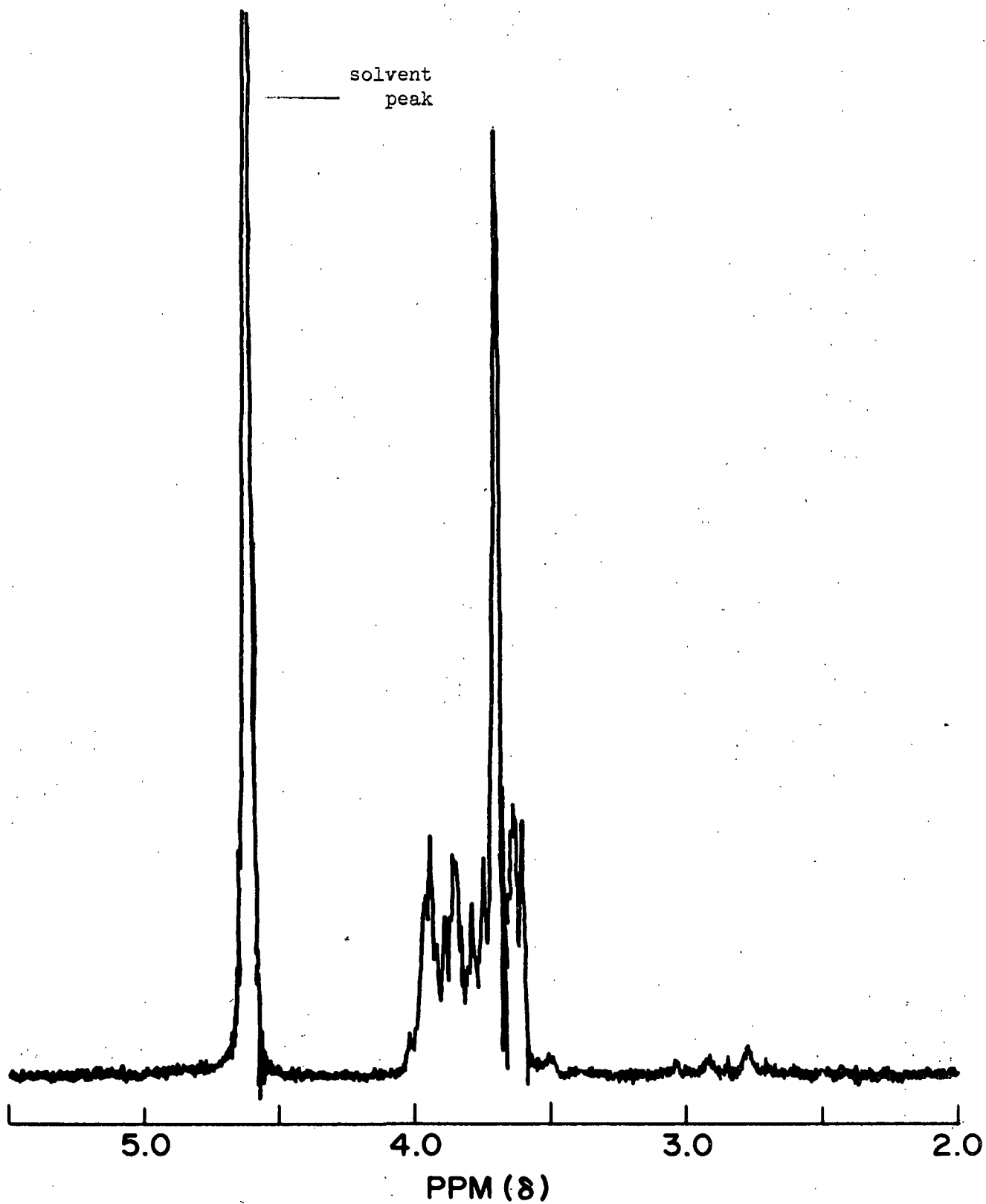


Figure 4. The NMR Spectrum of 1,5-AR in  $D_2O$  with DSS as an Internal Standard

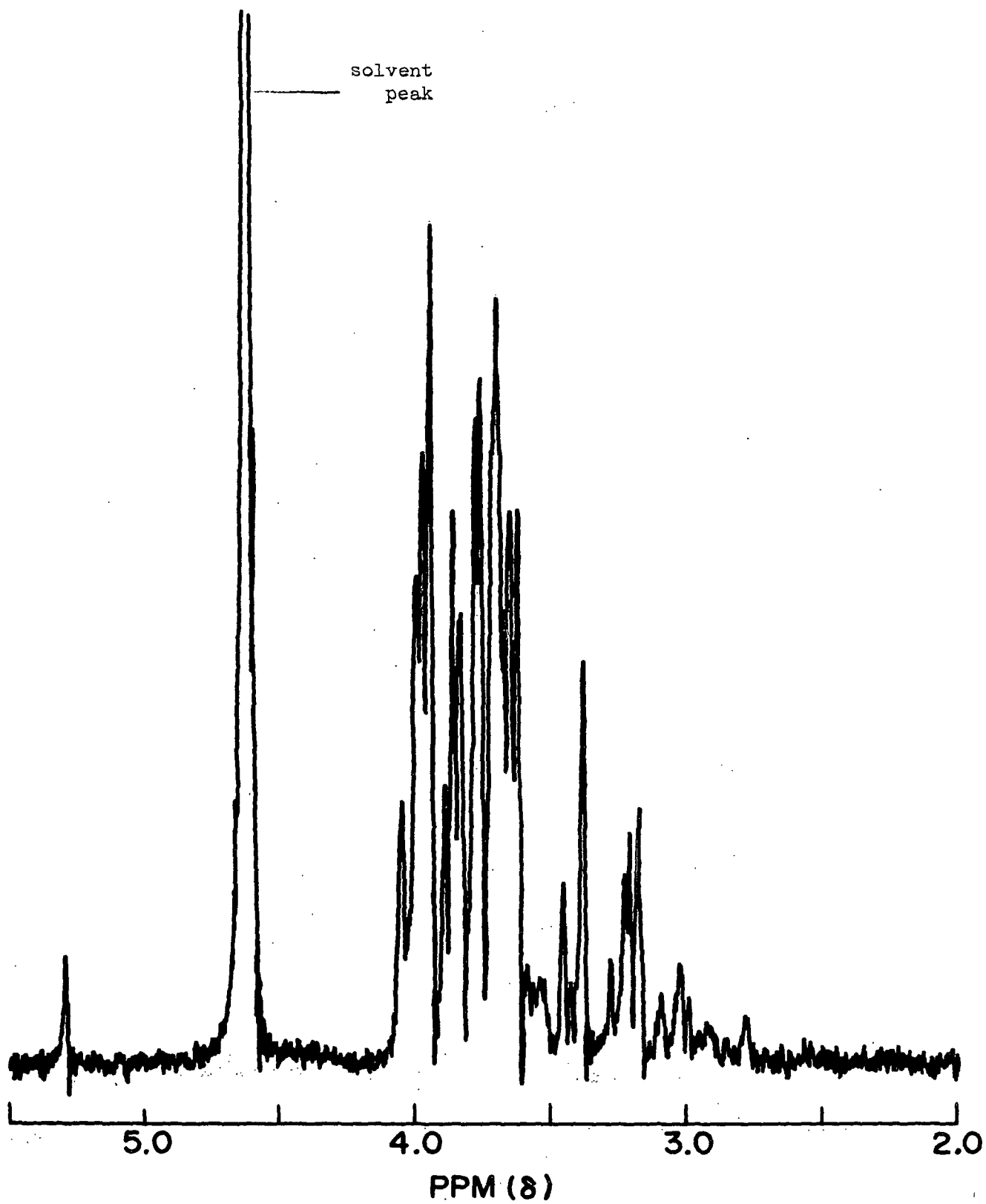


Figure 5. The NMR Spectrum of 1,5-ALA in D<sub>2</sub>O with DSS as an Internal Standard

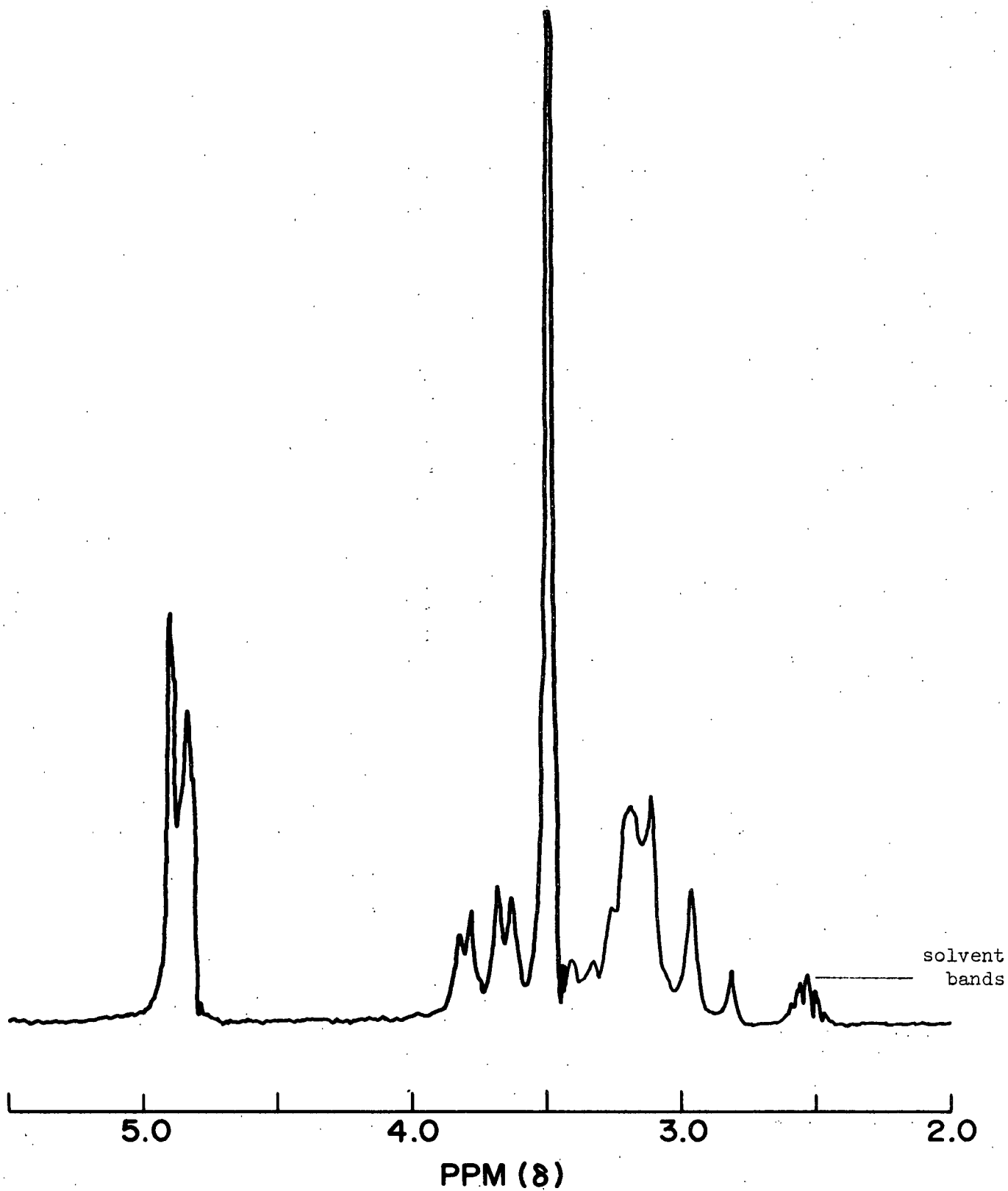


Figure 6. The NMR Spectrum of 1,5-AX in DMSO-d<sub>6</sub> with TMS as an Internal Standard

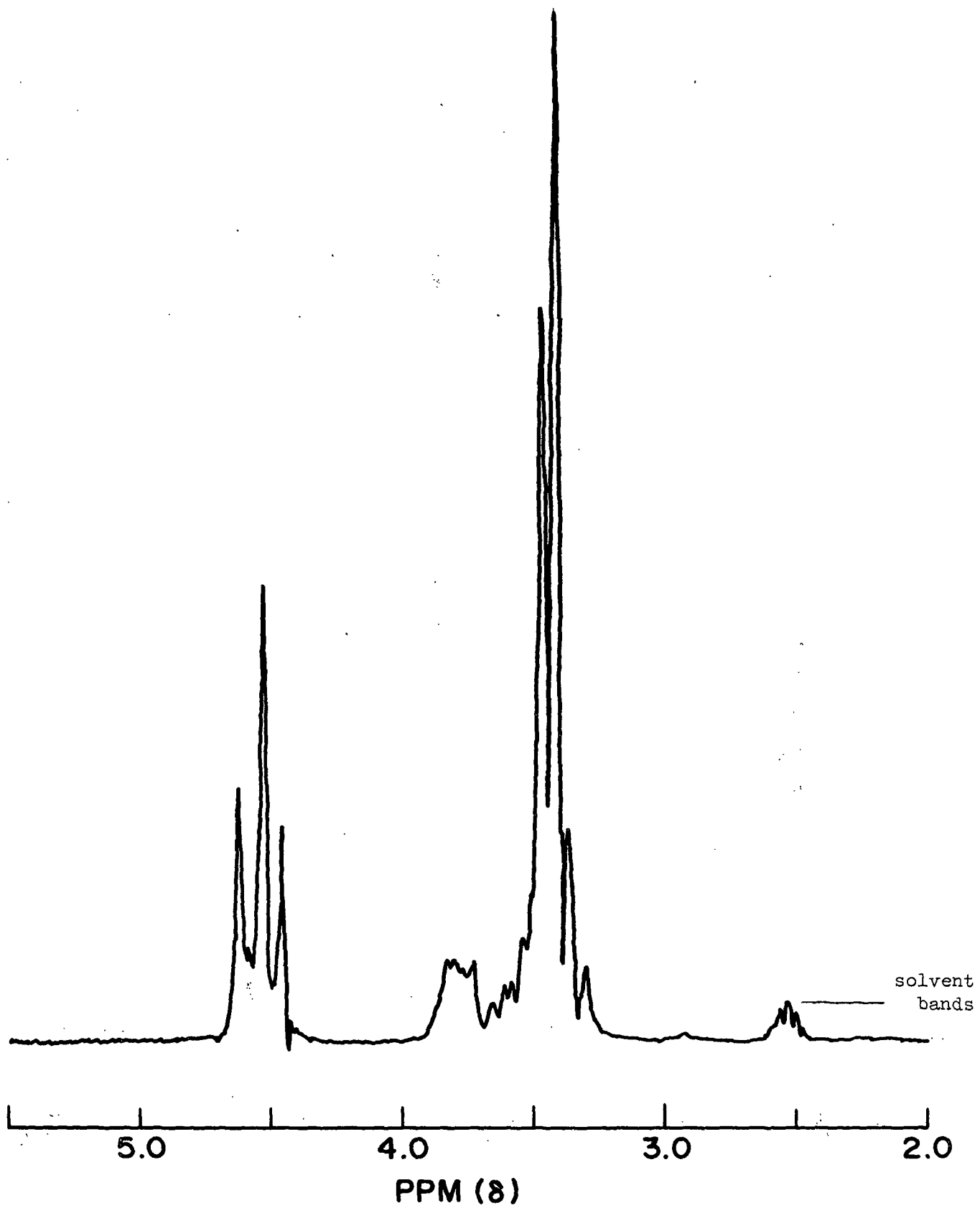


Figure 7. The NMR Spectrum of 1,5-AR in DMSO- $d_6$  with TMS as an Internal Standard



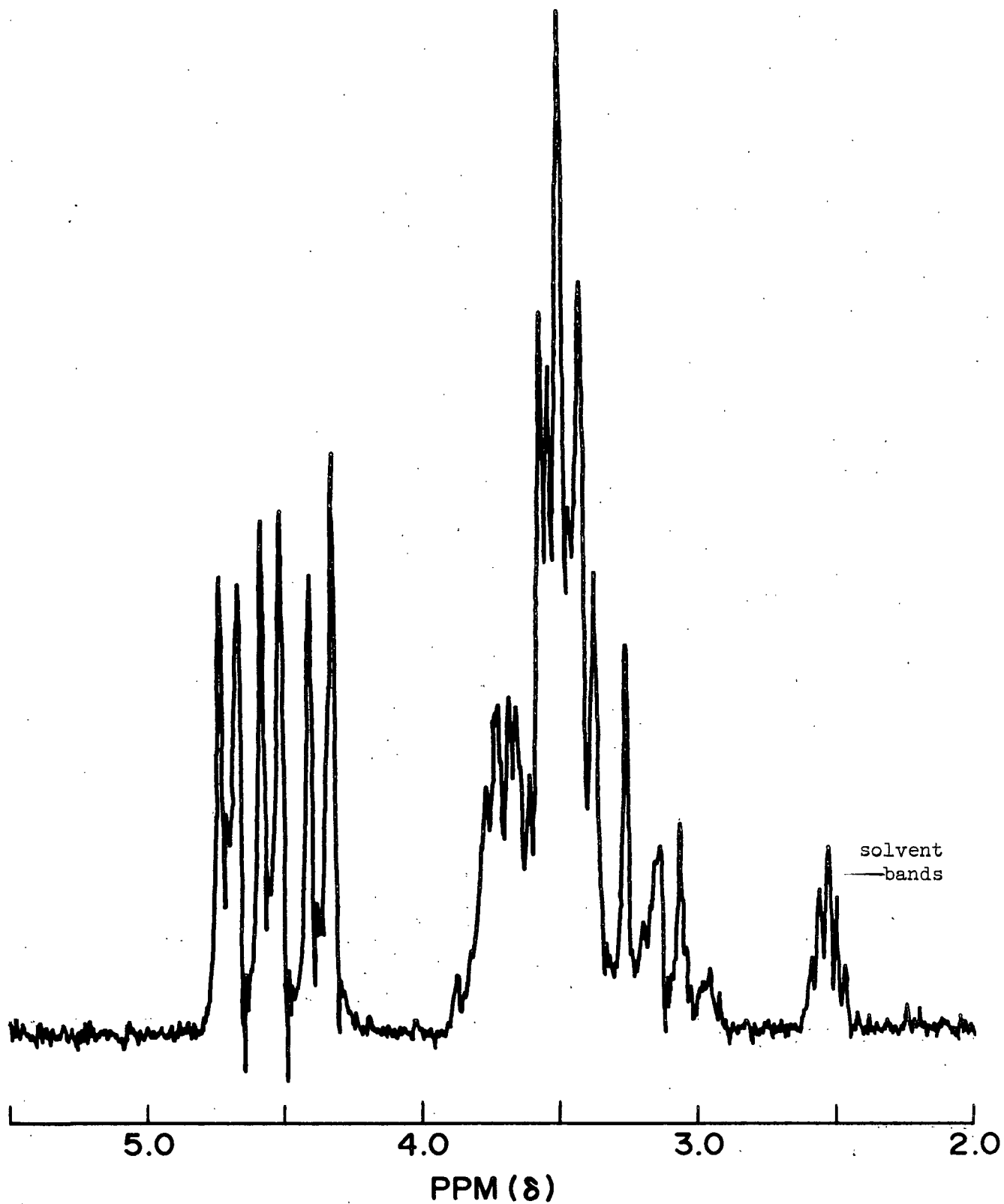


Figure 8a. The NMR Spectrum of 1,5-ALA in DMSO- $d_6$  with TMS as an Internal Standard

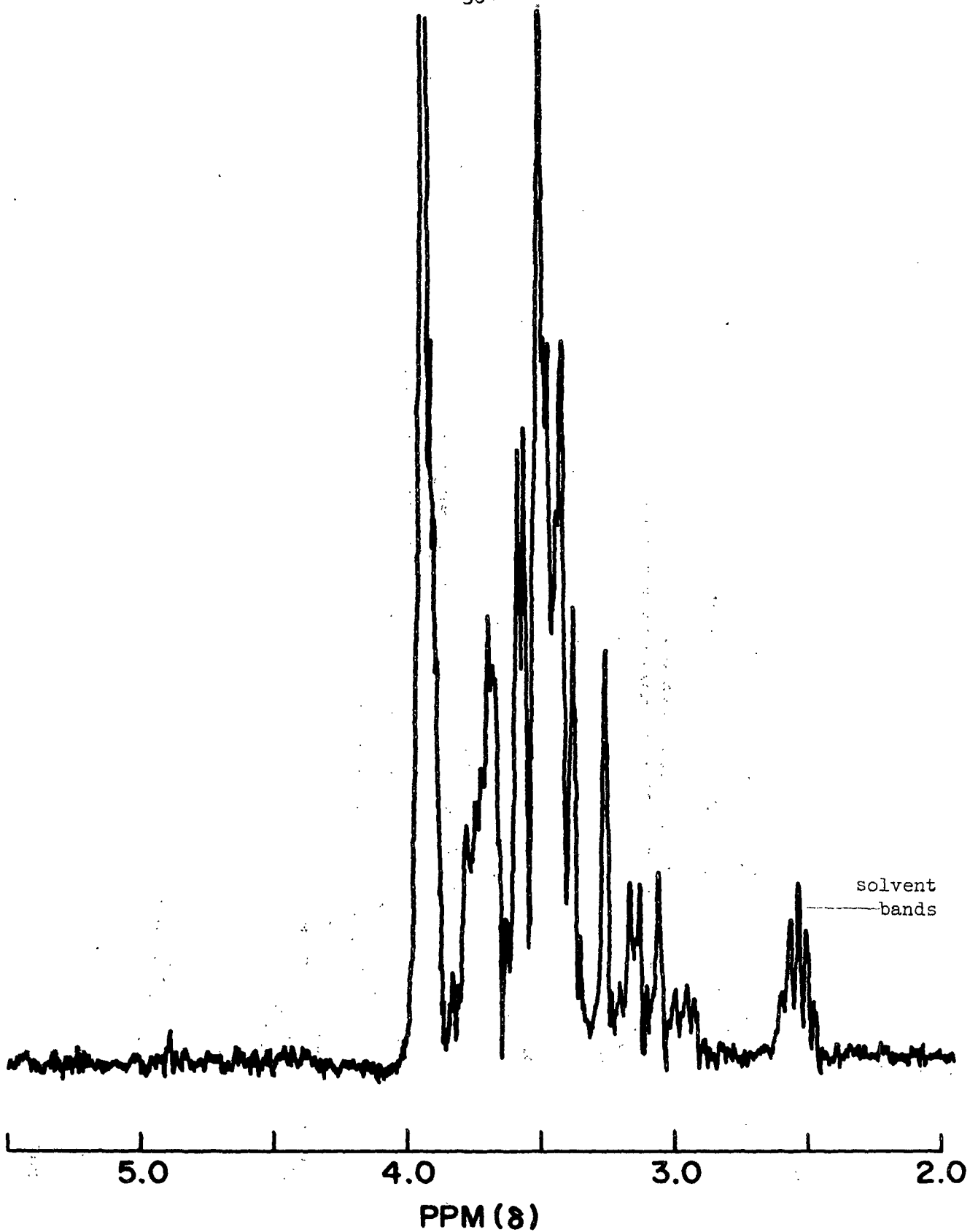


Figure 8b. The NMR Spectrum of 1,5-ALA in DMSO-d<sub>6</sub> with TMS as an Internal Standard After Adding a Drop of D<sub>2</sub>O

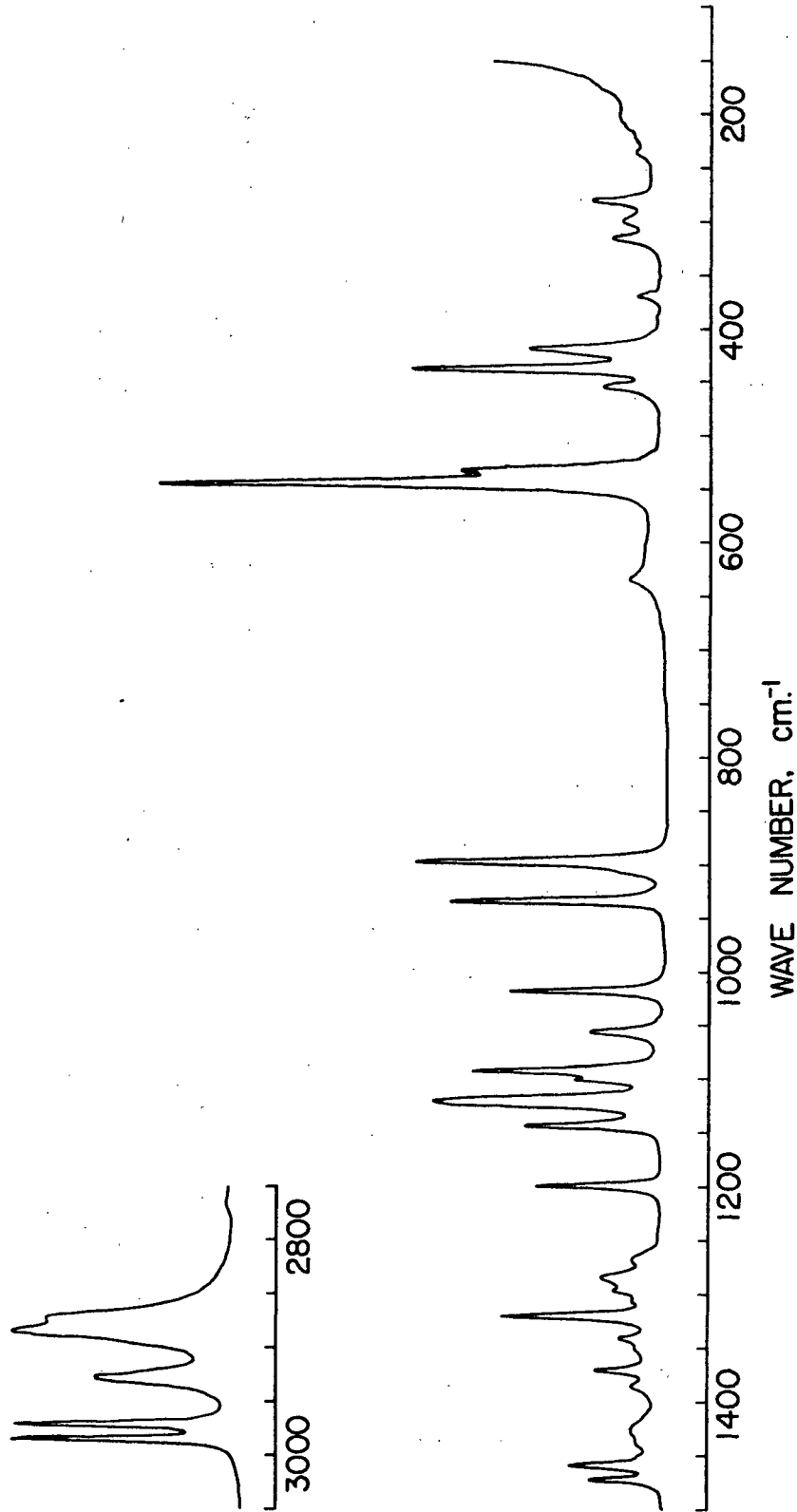


Figure 9. The Raman Spectrum of Crystalline 1,5-Anhydroxylytol

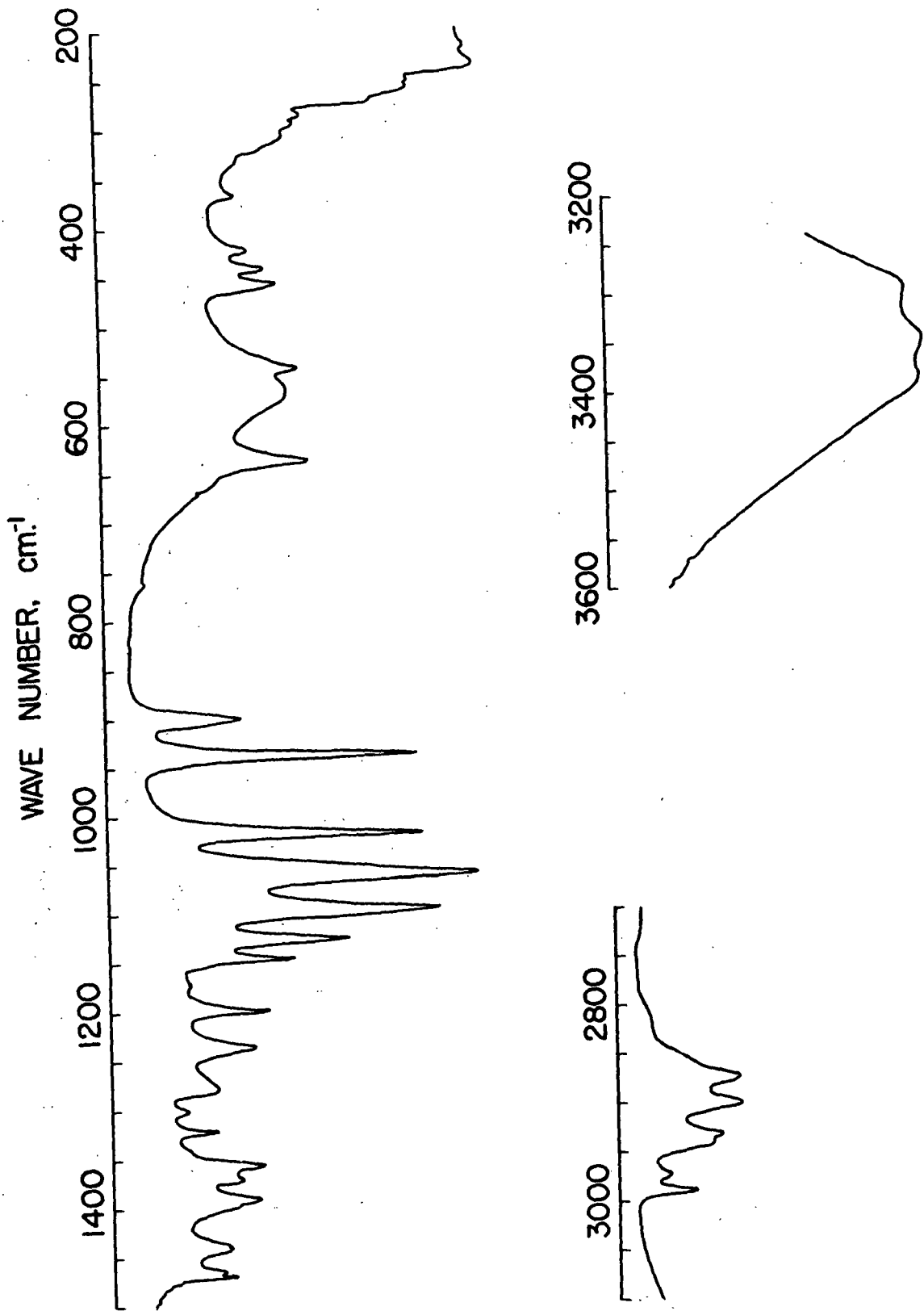


Figure 10. The Infrared Spectrum of Crystalline 1,5-Anhydroxylitol

TABLE III

THE TABULATED FREQUENCIES FOR THE RAMAN AND INFRARED SPECTRA OF CRYSTALLINE 1,5-ANHYDROXYLITOL

$\Delta\nu$ , R, cm. <sup>-1</sup>	a Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	b Relative Intensity	$\Delta\nu$ , R, cm. <sup>-1</sup>	a Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	b Relative Intensity
3383	4	3387	85	1143	30	1145	47
3343	4	3350	87	1120	46	1125	63
3290	4	3300	82	1100 <sup>c</sup>	17	1100 <sup>c</sup>	73
2985	45	2990	17	1092	38	1095	89
2970	45	2973	10	1056	14	1060	100
		2941	22			1052 <sup>c</sup>	73
2928	29	2933	25	1017	31	1018	84
2896 <sup>c</sup>	24			933	43	936	83
2885	46	2900	30			928 <sup>c</sup>	17
2871	39	2873	30	905 <sup>c</sup>	11	904 <sup>c</sup>	26
1472	15	1470	28	896	50	899	32
1459	19	1464	25	635	5	637	29
1439	6	1440	27			565	23
1427	7			544	100	542	27
		1402 <sup>c</sup>	25	533 <sup>c</sup>	40	533 <sup>c</sup>	18
		1397 <sup>c</sup>	29	455	12	456	21
1385	7	1391	36	437	50	440	17
1370	14	1372	31	418	26	420	12
1349	6	1356	37	369	5	366 <sup>c</sup>	9
1340	10	1340	15	315	10	317 <sup>c</sup>	3
1320	33	1321	24	299	8	295	3
1306	7			280	14	285	4
1296	11	1301	15	234	2		
1285	13	1279 <sup>c</sup>	24	225	1		
1268	7	1267 <sup>c</sup>	20	220	1		
		1235	35	214	2		
1199	26	1198	39	202	2		
		1168	15				

<sup>a</sup>Raman spectrometer

operating conditions:

Sample arr.: pellet  
 Laser wavelength: 5145 A.  
 Laser power: 780 mw.  
 Slit width: 250  $\mu$ m.  
 Slit height: 2 mm.  
 Scan: 50 cm.<sup>-1</sup>/min.  
 DC: 0.1 x 10<sup>-6</sup>  
 RT: 1 sec.  
 PM voltage: 1900  
 PM temp.: -20°C.  
 Spike filter used

<sup>b</sup>Infrared spectrometer

operating conditions:

Sample arr.: KBr pellet  
 Slit program: 1000 x 1  
 Gain: 4.6  
 Atten. speed: 1100  
 Scan time: 1 x 32  
 Suppression: 6  
 Scale expansion: 1X  
 Source current: 0.75

<sup>c</sup>Shoulder.

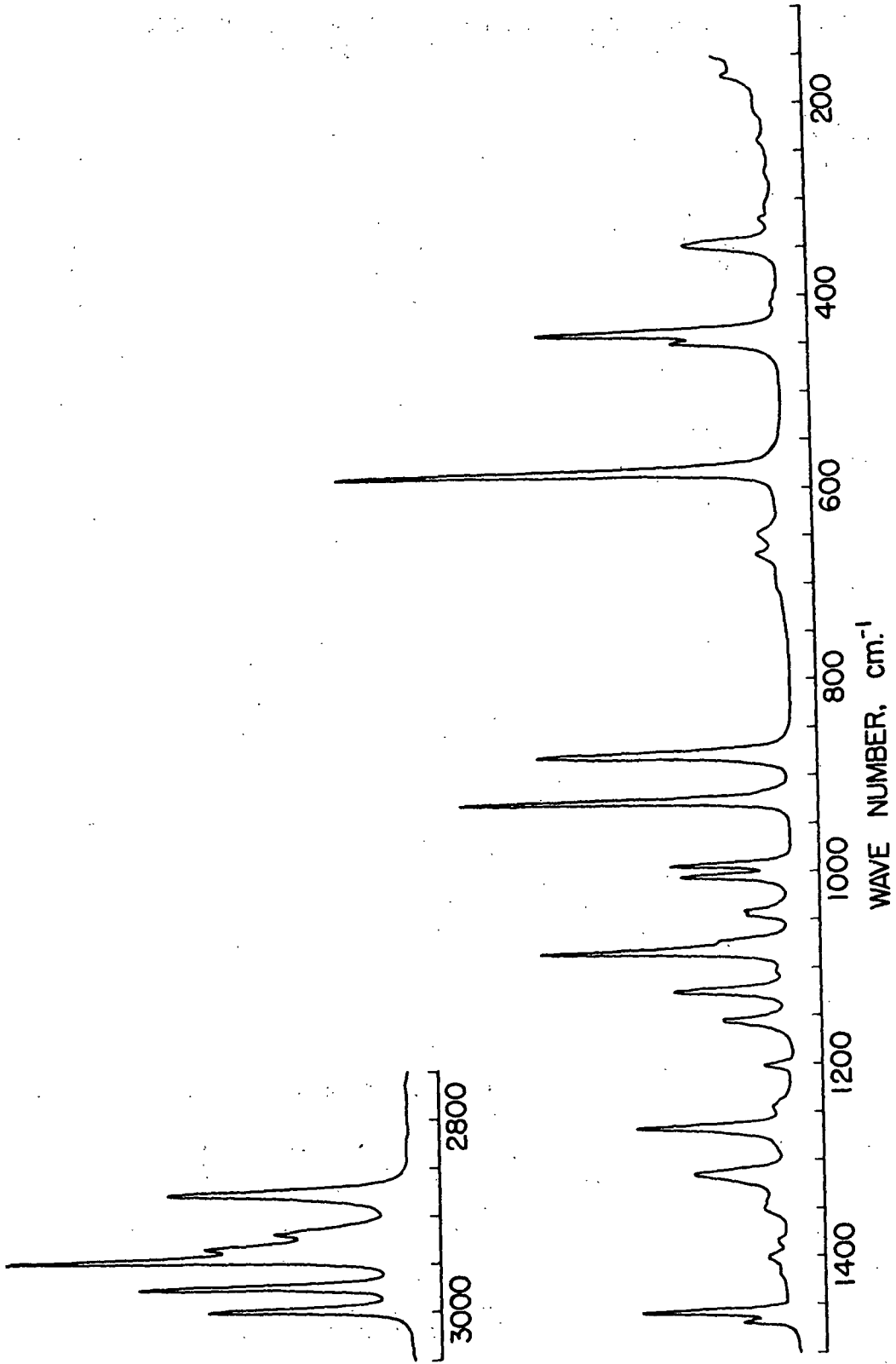


Figure 11. The Raman Spectrum of Crystalline 1,5-Anhydroribitol

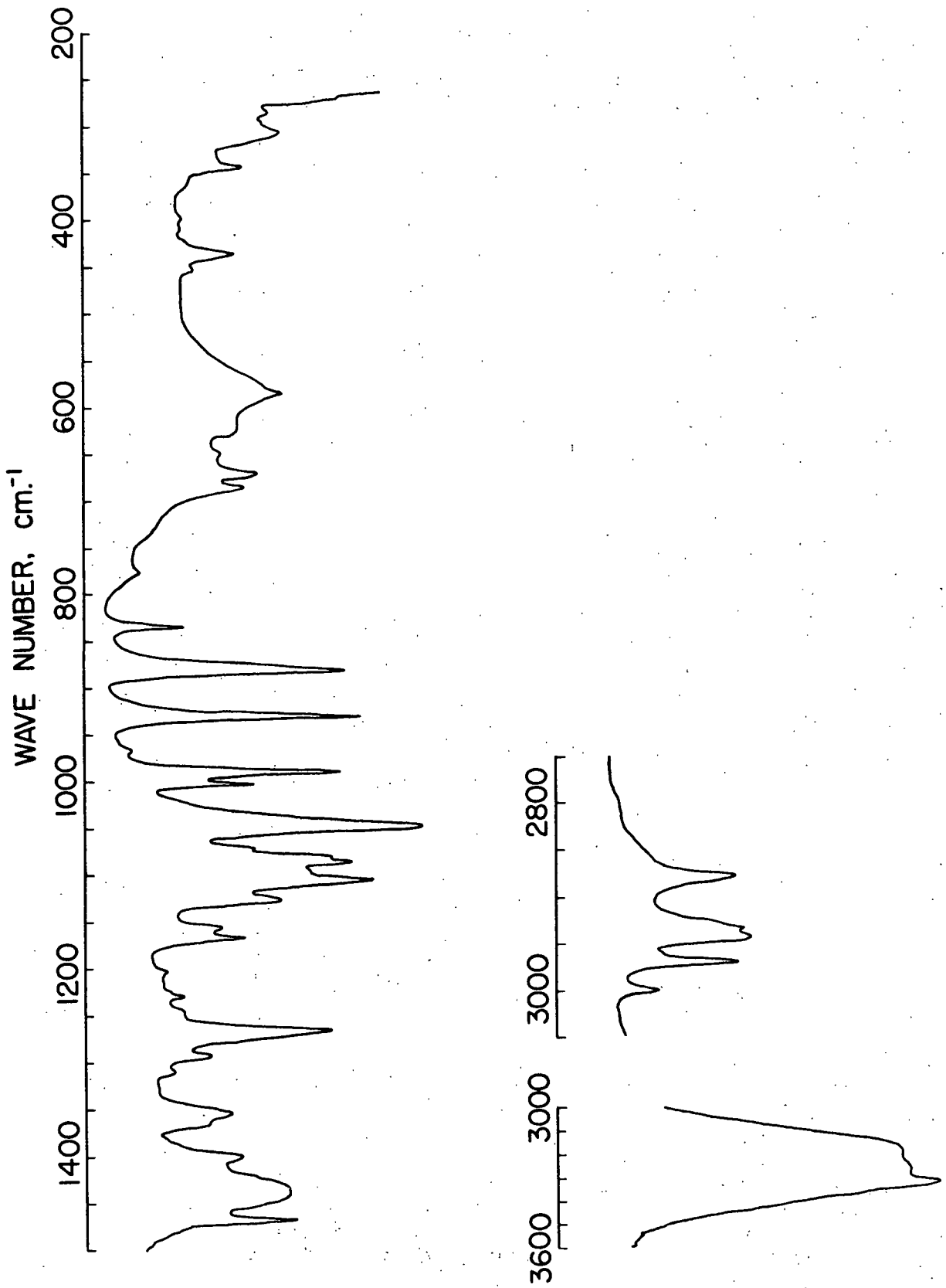


Figure 12. The Infrared Spectrum of Crystalline 1,5-Anhydroribitol

TABLE IV

THE TABULATED FREQUENCIES FOR THE RAMAN AND INFRARED  
SPECTRA OF CRYSTALLINE 1,5-ANHYDRORIBITOL

$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity	$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity
3406	13	3409	100			1077 <sup>c</sup>	63
3350	4	3345	92	1073 <sup>c</sup>	17	1070 <sup>c</sup>	42
3250	3	3279	90	1045	10	1045	89
2997	47	3000	23	1040	11		
2972	63	2970	45	1005	25	1000	42
2943	92	2945	49	993	27	989	66
2932	48	2934 <sup>c</sup>	47			963	8
		2929 <sup>c</sup>	41	925	74	928	71
2918	32			916 <sup>c</sup>	7	916 <sup>c</sup>	11
2875	56	2880	44	878	57	879	67
1468	13	1466	53			873 <sup>c</sup>	47
1458	35					832	22
		1435	52			776	10
1419	5					683	19
1403	9	1400	38	669	7	668	23
1385	5	1388 <sup>c</sup>	21	647	6	649	13
		1365 <sup>c</sup>	29	581	100	582	30
1350	7	1354	36	448 <sup>c</sup>	25	451 <sup>c</sup>	5
1315	23	1310	19	437	55	433	17
1281 <sup>c</sup>	5	1290	30	406	2	406	2
1265	36	1264	63	396	1	395	2
1244 <sup>c</sup>	5	1245 <sup>c</sup>	22			353 <sup>c</sup>	4
		1226	22	345	21	342	14
1202	7	1202	18	319	4		
		1167	39	306	3	305	18
1156	16	1156	33	271	3		
1124	29	1126	50	238	4		
1104	4	1103	75	208	1		
		1093 <sup>c</sup>	57	169	3		
1082	57	1083	69				

<sup>a</sup>Raman spectrometer  
operating conditions:

Sample arr.: pellet  
Laser wavelength: 5145 Å.  
Laser power: 780 mw.  
Slit width: 160 μm.  
Slit height: 5 mm.  
Scan: 50 cm.<sup>-1</sup>/min.  
DC: 0.1 x 10<sup>-6</sup>  
RT: 1 sec.

PM voltage: 1900  
PM temp.: -20°C.  
Spike filter used

<sup>b</sup>Infrared spectrometer  
operating conditions:

Sample arr.: KBr pellet  
Slit program: 1000 x 1  
Gain: 4.6  
Atten. speed: 1100

Scan time: 1 x 32  
Suppression: 6  
Scale expansion: 1X  
Source current: 0.75

<sup>c</sup>Shoulder.



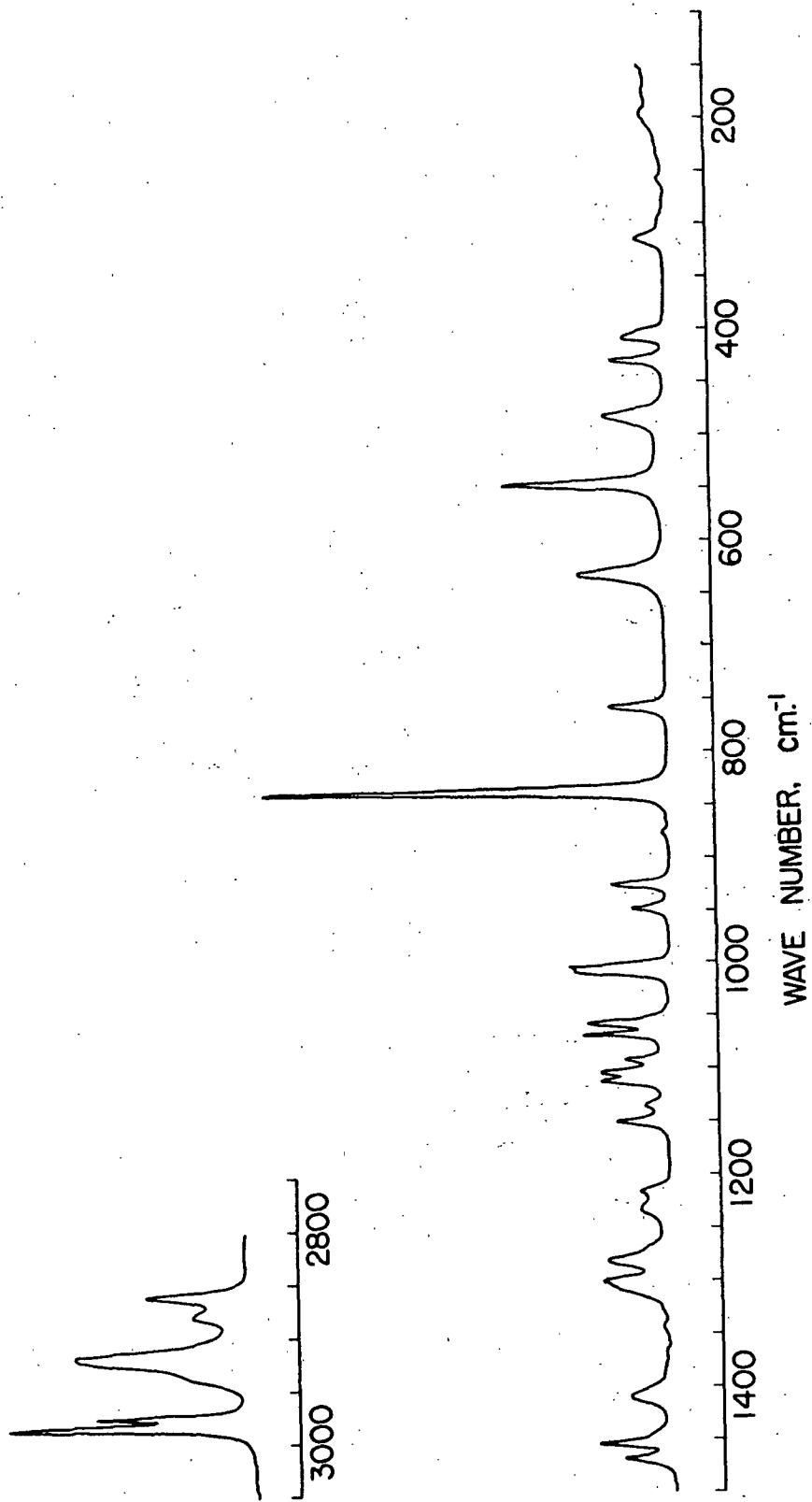


Figure 13. The Raman Spectrum of Crystalline 1,5-Anhydro-L-arabinitol

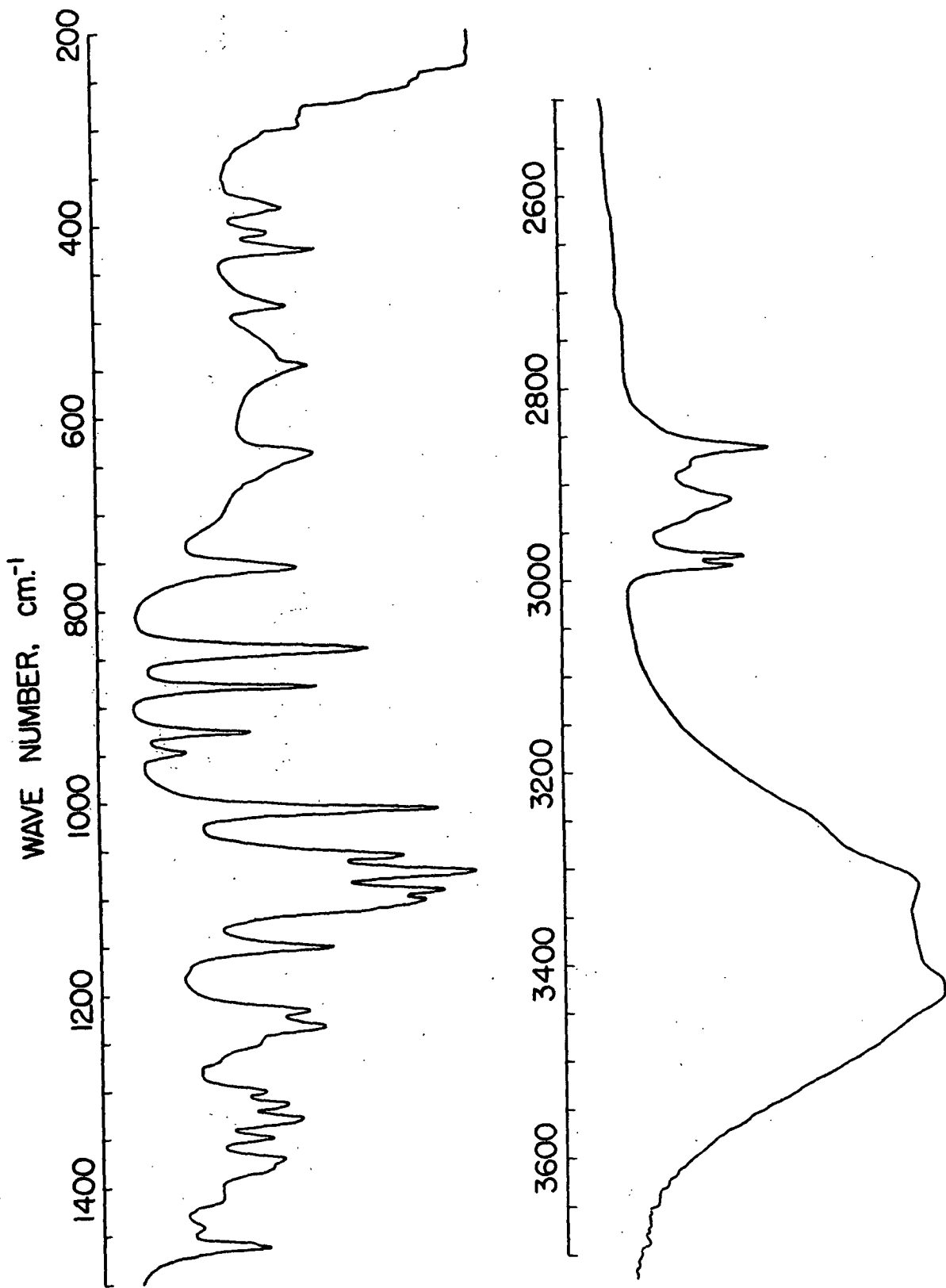


Figure 14. The Infrared Spectrum of Crystalline 1,5-Anhydro-L-arabinitol

TABLE V

THE TABULATED FREQUENCIES FOR THE RAMAN AND INFRARED SPECTRA OF CRYSTALLINE 1,5-ANHYDRO-L-ARABINITOL

$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity	$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity
3425	6	3428	100	1136	7	1145 <sup>c</sup>	38
		3385	93	1112	17	1112 <sup>c</sup>	66
3310	3	3320	94	1104	17	1103	85
2983	60	2985	42	1092	12	1093	90
2973	39	2976	45	1067	21	1074	99
2932 <sup>c</sup>	19	2932 <sup>c</sup>	31	1057	21	1056	79
		2925 <sup>c</sup>	37	1005	25	1008	88
2916	44	2917	42	948	10	947	19
2879	15	2879	31	926	14	927	37
2860	26	2863	55	876	2	880	55
1467	13	1463	41	837	100	840	70
1454	19	1460 <sup>c</sup>	37	758	14	755	50
1446 <sup>c</sup>	6	1442	22	633	23	636	26
1410	12	1410	28	546	41	546	25
1381 <sup>c</sup>	3	1379 <sup>c</sup>	42	483	16	483	19
1369	3	1371	46	430	14	426	27
1343	3	1349	42	408	11	408	14
1325 <sup>c</sup>	4	1329	50	406 <sup>c</sup>	10		
		1313	46			383	19
1302	18	1300	40	371 <sup>c</sup>	1	375 <sup>c</sup>	14
1281	16	1279	23	314	7	306 <sup>c</sup>	2
1269 <sup>c</sup>		1262 <sup>c</sup>	29	296 <sup>c</sup>	2	296 <sup>c</sup>	5
		1248 <sup>c</sup>	40	256	2		
1233	8	1233	57	233	2		
1216	8	1217	53	197	4		
1150	14	1151	60	176	2		

<sup>a</sup>Raman spectrometer  
operating conditions:  
Sample arr.: pellet  
Laser wavelength: 5145 Å.  
Laser power: 780 mw.  
Slit width: 130  $\mu$ m.  
Slit height: 5 mm.  
Scan: 50 cm.<sup>-1</sup>/min.  
DC: 0.1 x 10<sup>-6</sup>  
RT: 1 sec.  
PM voltage: 1900  
PM temp.: -20°C.  
Spike filter used

<sup>b</sup>Infrared spectrometer  
operating conditions:  
Sample arr.: KBr pellet  
Slit program: 1000 x 1  
Gain: 4.6  
Atten. speed: 1100  
Scan time: 1 x 32  
Suppression: 6  
Scale expansion: 1X  
Source current: 0.8

<sup>c</sup>Shoulder.

as one might expect. Therefore, to refrain from repetition the 1,5-ADA spectra are not included.

#### INFRARED AND RAMAN SPECTRA OF THE DEUTERATED 1,5-ANHYDRO-PENTITOL COMPOUNDS IN THE CRYSTALLINE STATE

The Raman and infrared spectra of crystalline deuterated 1,5-AX, 1,5-AR, and 1,5-ALA follow in Fig. 15-20, respectively. The frequencies and relative intensities of these spectra are tabulated in Tables VI-VIII.

#### RAMAN SPECTRA OF THE 1,5-ANHYDRO-PENTITOL SOLUTIONS

The Raman spectra of the 1,5-AP sirups are reproduced in Fig. 21-23. The Raman spectra of the DMSO-d<sub>6</sub> solutions are not included because the spectra, excluding solvent bands, are almost identical with the aqueous solution spectra. However, the frequencies and relative intensities for the DMSO-d<sub>6</sub> solution spectra are tabulated along with the corresponding values for the aqueous solution spectra in Tables IX-XI. The solution spectra of 1,5-ALA and 1,5-ADA are identical and for this reason only the Raman spectrum of the L isomer is included.

#### DEPOLARIZATION RATIOS FOR 1,5-ANHYDROXYLITOL AND 1,5-ANHYDRORIBITOL IN AQUEOUS SOLUTION

The calculated depolarization ratios for the vibrational bands of 1,5-AX and 1,5-AR are listed in Tables XII and XIII, respectively, with the questionable values resulting from overlapped bands designated by footnote c. The OH stretching bands in the region 3400-3200 cm.<sup>-1</sup> are not included because they are too weak and broad to measure depolarization ratios. The CH stretching bands in the region 3000-2850 cm.<sup>-1</sup> are also omitted since they overlap extensively in the solution spectra making measurement of depolarization ratios impossible.

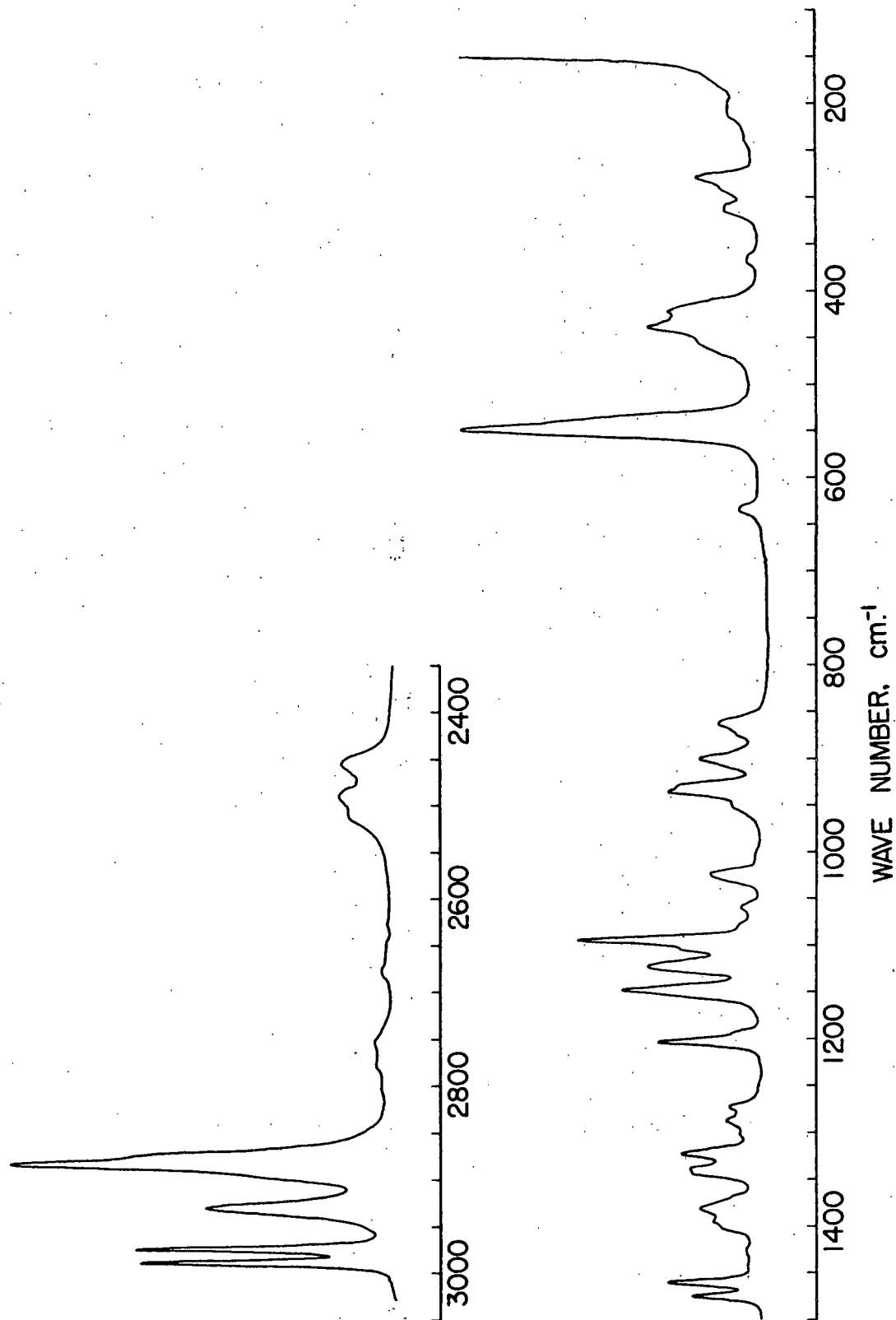


Figure 15. The Raman Spectrum of Crystalline Deuterated 1,5-Anhydroxylitol

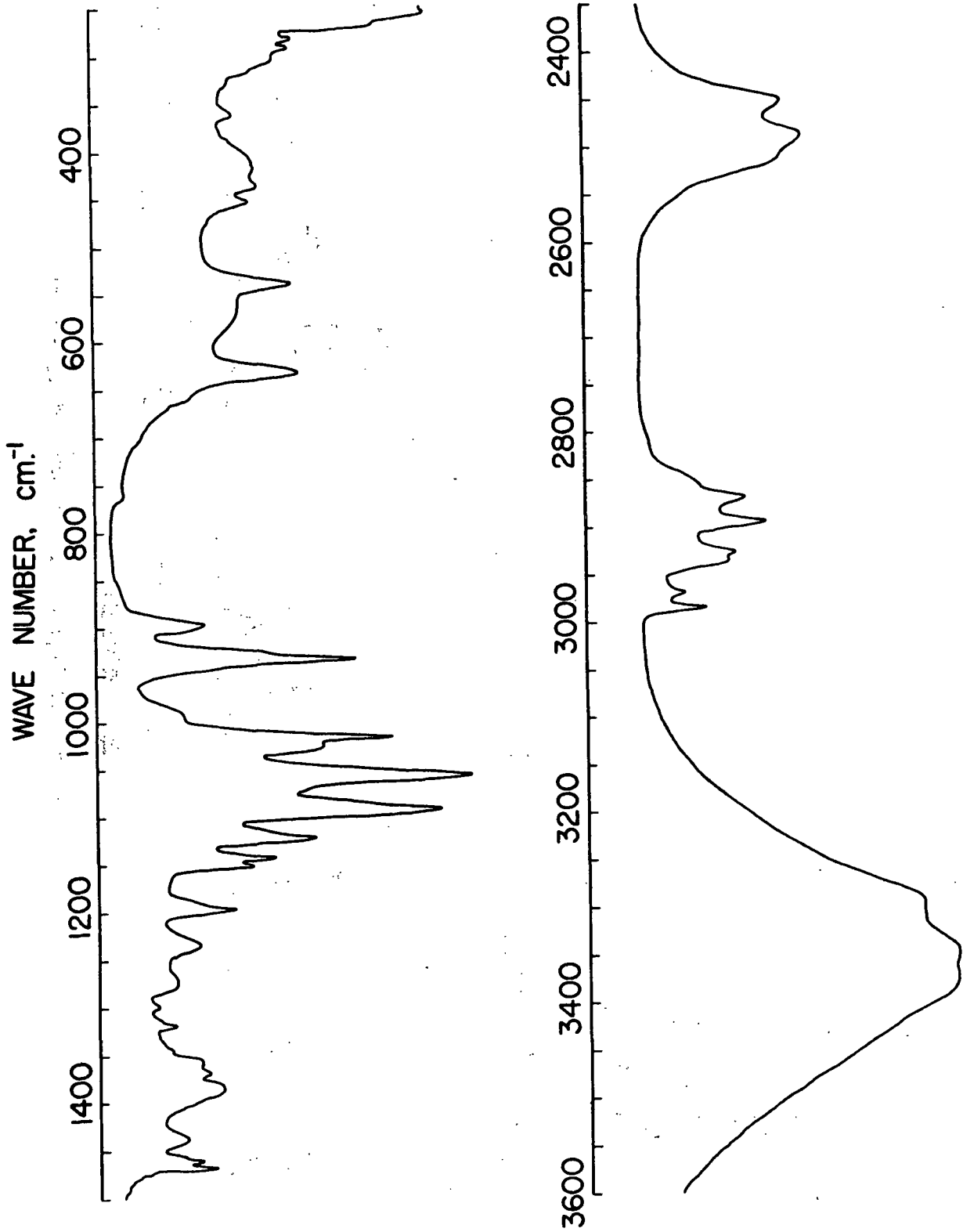


Figure 16. The Infrared Spectrum of Crystalline Deuterated 1,5-Anhydroxylitol

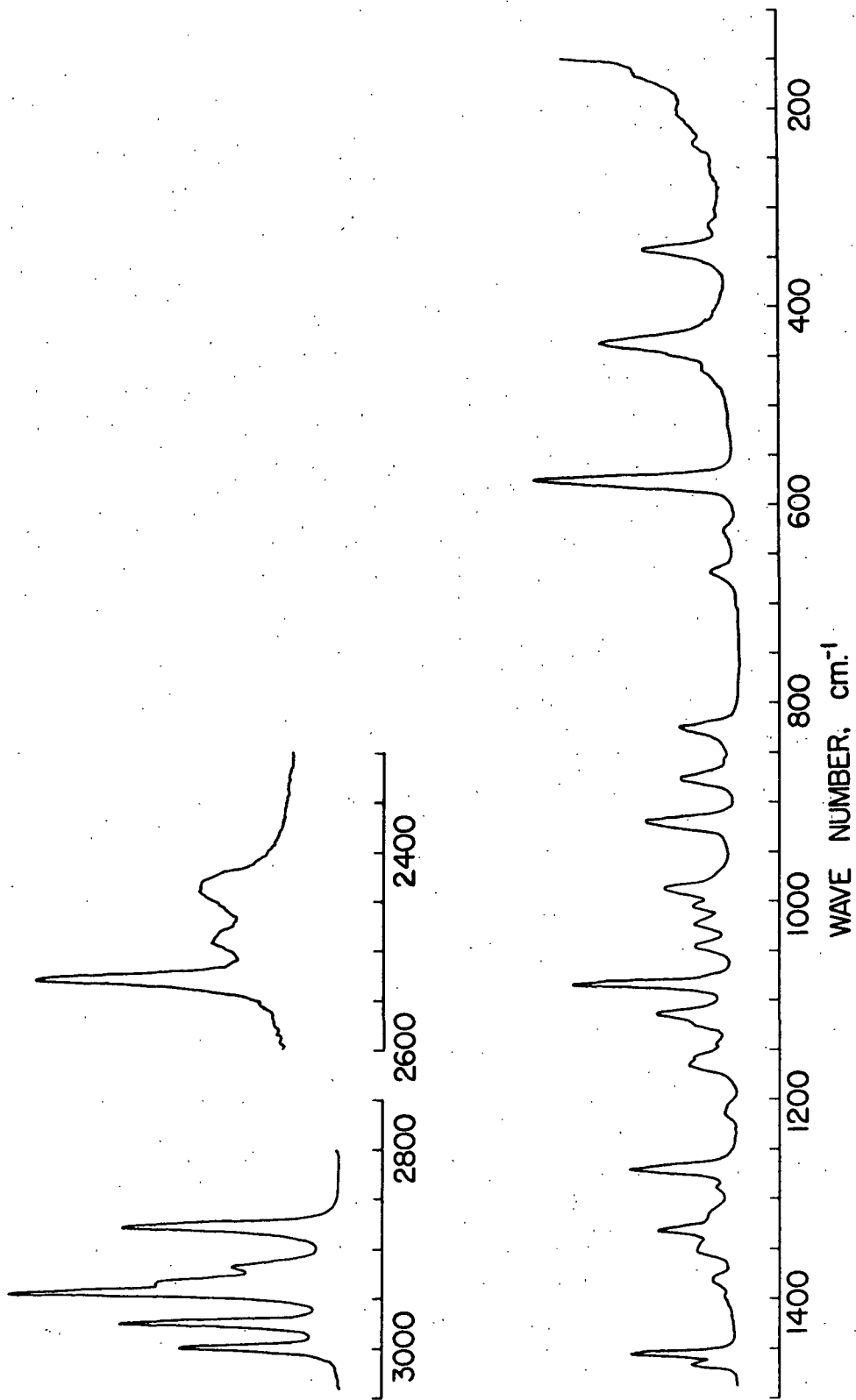


Figure 17. The Raman Spectrum of Crystalline Deuterated 1,5-Anhydroribitol.

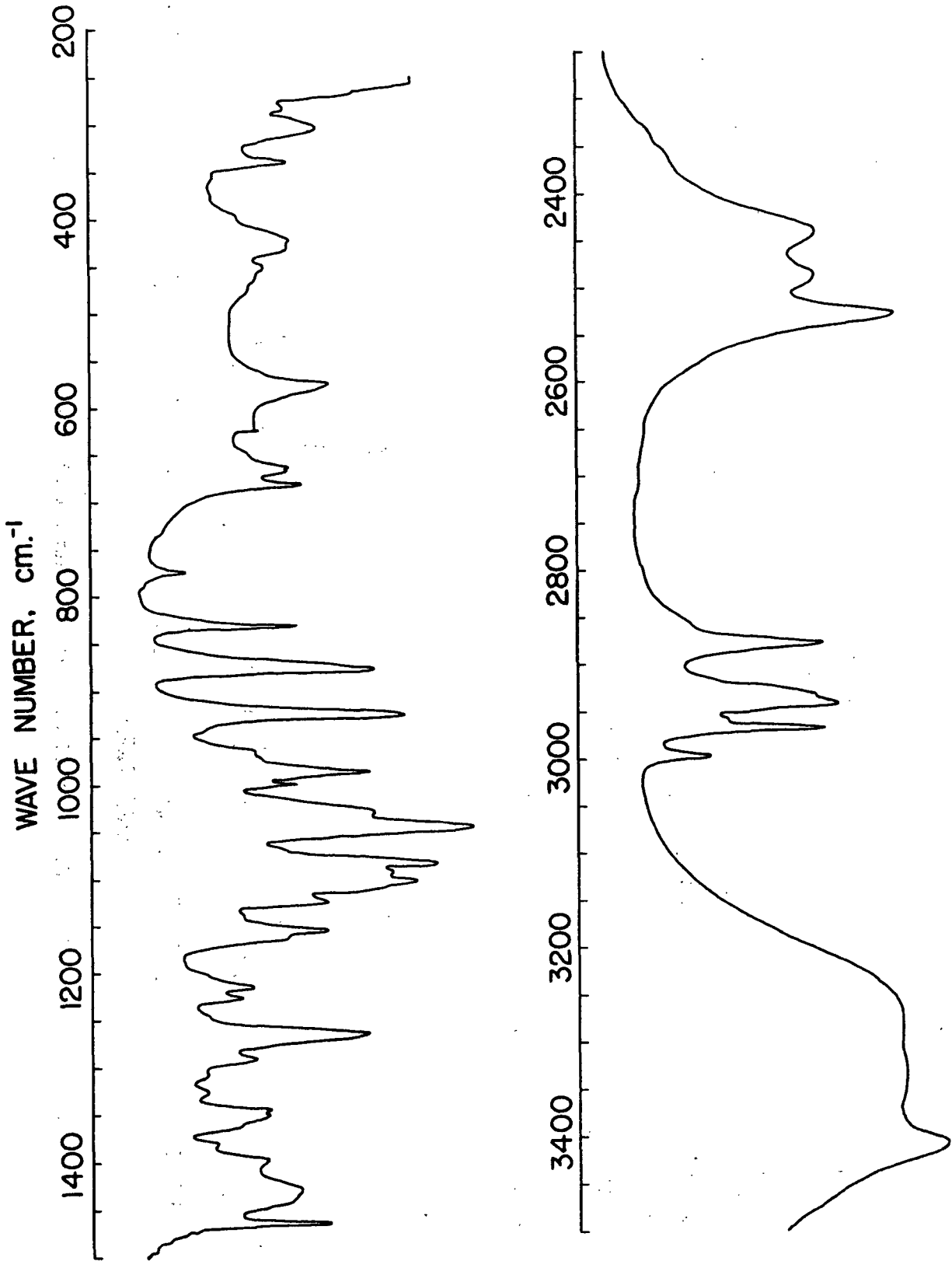


Figure 18. The Infrared Spectrum of Crystalline Deuterated 1,5-Anhydroribitol



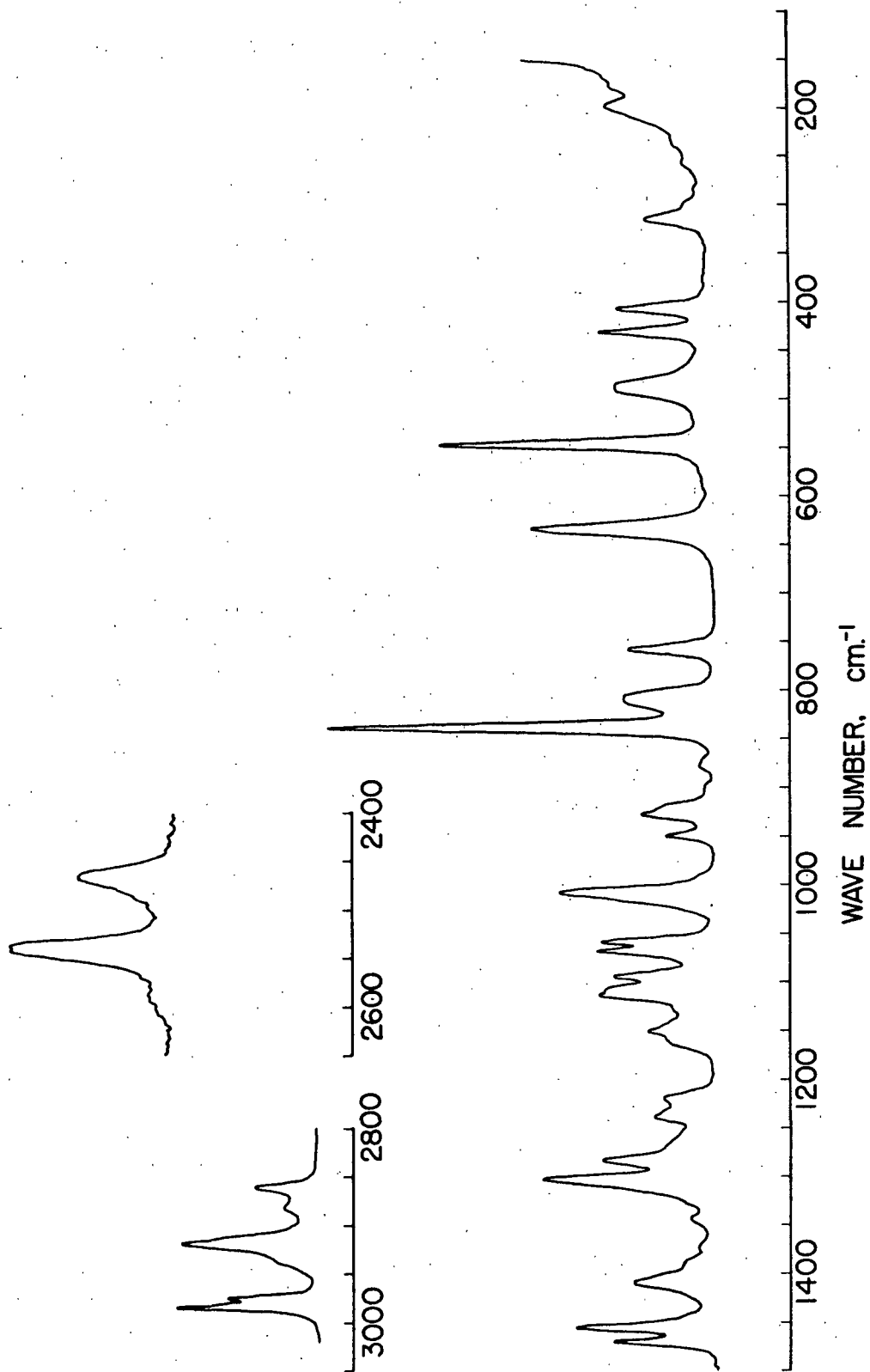


Figure 19. The Raman Spectrum of Crystalline Deuterated 1,5-Anhydro-L-arabinitol

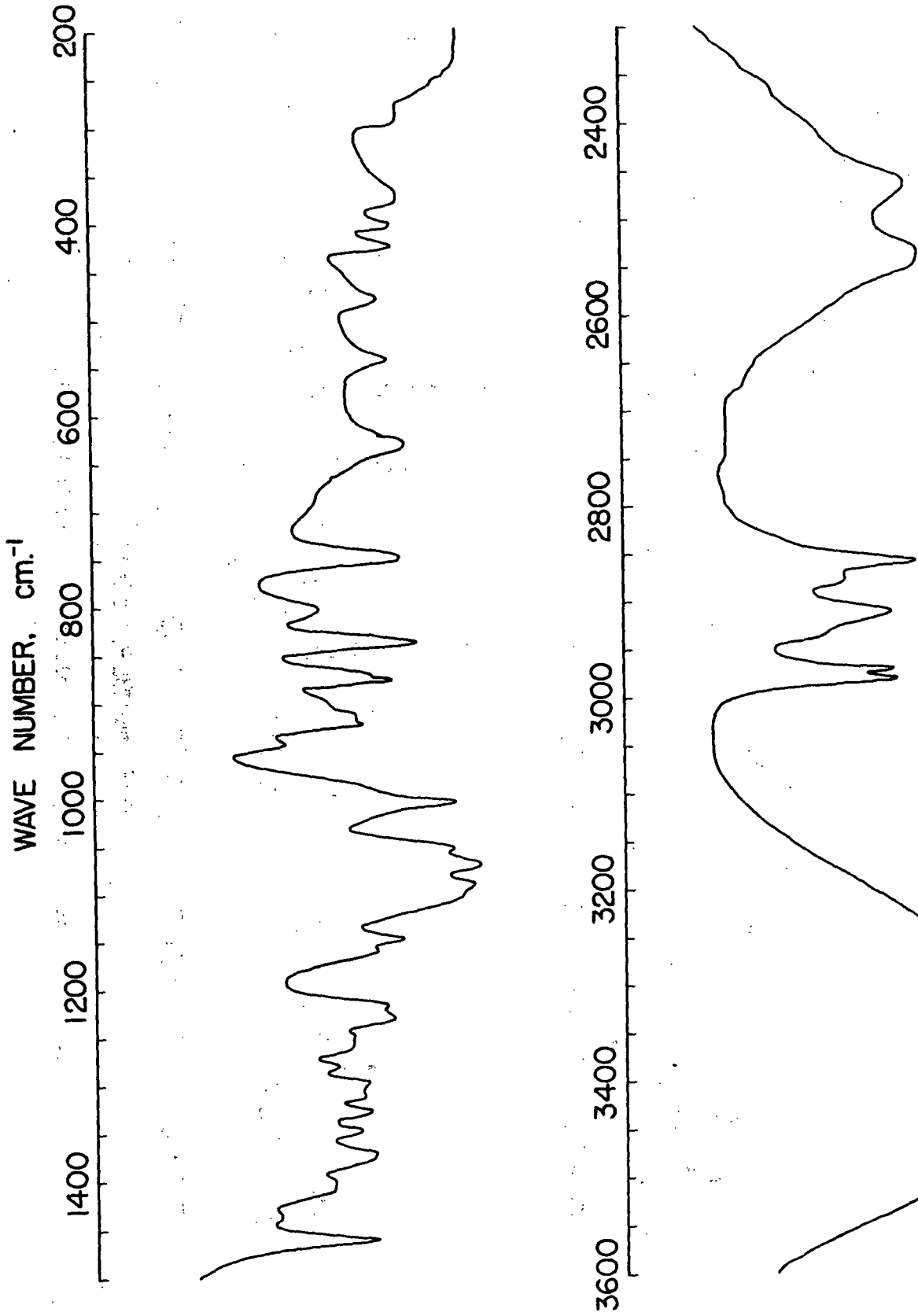


Figure 20. The Infrared Spectrum of Crystalline Deuterated 1,5-Anhydro-L-arabinitol

TABLE VI

TABULATED FREQUENCIES FOR THE RAMAN AND INFRARED  
SPECTRA OF DEUTERATED 1,5-ANHYDROXYLITOL

$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity	$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity
2989	66	2983	29	1122	30	1121	56
2974	67	2969	24			1116 <sup>c</sup>	45
		2935	35	1102 <sup>c</sup>	22		
2931	49	2927	37	1093	49	1093	91
2896 <sup>c</sup>	36	2894	46			1086	73
2883	100			1078 <sup>c</sup>	7		
2874 <sup>c</sup>	68	2869	40			1068 <sup>c</sup>	54
2508 <sup>c</sup>	13	2509	51	1059	6	1057	100
2488	15	2490	56	1021	14	1025 <sup>c</sup>	59
2452	15	2453	51			1016	78
						990 <sup>c</sup>	19
1474	19	1467	38			941 <sup>c</sup>	31
1460	26	1460	24	947 <sup>c</sup>	9	933	68
		1456 <sup>c</sup>	20	936	25	929 <sup>c</sup>	45
1439	4	1438	20	929 <sup>c</sup>	23	900 <sup>c</sup>	25
1427	5			906 <sup>c</sup>	12	897	26
1402 <sup>c</sup>	12	1400 <sup>c</sup>	22	899	17		
1394	14	1396 <sup>c</sup>	24	870 <sup>c</sup>	8		
		1390 <sup>c</sup>	29	861	12		
1381	17	1385	30	633	7	632	29
1373 <sup>c</sup>	13	1369	26			562	12
		1356	24	543	79	539	28
1344	19			532 <sup>c</sup>	48		
1340	20	1342 <sup>c</sup>	16	455 <sup>c</sup>	18	453	15
1320	22	1318	19	435	30	435	18
1300	7	1298	14	420	25	415	17
1287	10			366	4	360	11
1273	9	1273	17			316	1
		1233	24	306	10	304	2
1203	28			289 <sup>c</sup>	12	293	5
1193 <sup>c</sup>	9	1196	34	279	18	284	5
		1189 <sup>c</sup>	24	256	1		
1157 <sup>c</sup>	23			235	1		
1147	37	1150	39	206	3		
		1142	46	200	3		

<sup>a</sup>Raman spectrometer  
operating conditions:

Sample arr.: cap. tube  
Laser wavelength: 5145 Å.  
Laser power: 800 mw.  
Slit width: 250  $\mu$ m.  
Slit height: 2 mm.  
Scan speed: 50 cm.<sup>-1</sup>/min.  
DC: 0.03 x 10<sup>-6</sup>  
RT: 3 sec.  
PM voltage: 1900  
PM temp.: -20°C.

<sup>b</sup>Infrared spectrometer  
operating conditions:

Sample arr.: KBr pellet  
Slit program: 1000 x 1  
Gain: 4.6  
Atten. speed: 1100  
Scan time: 1 x 32  
Suppression: 6  
Scale expansion: 1-5X  
Source current: 0.8

<sup>c</sup>Shoulder.

TABLE VII

TABULATED FREQUENCIES FOR THE RAMAN AND INFRARED SPECTRA OF DEUTERATED 1,5-ANHYDRORIBITOL

$\Delta\nu$ , <sup>a</sup> R, cm. <sup>-1</sup>	Relative Intensity	$\nu$ , <sup>b</sup> IR, cm. <sup>-1</sup>	Relative Intensity	$\Delta\nu$ , <sup>a</sup> R, cm. <sup>-1</sup>	Relative Intensity	$\nu$ , <sup>b</sup> IR, cm. <sup>-1</sup>	Relative Intensity
2999	48	2996	27			1102	84
2975	66	2967	60			1093 <sup>c</sup>	77
		2956	32	1085	51	1082	90
2945	100	2942	64			1078 <sup>c</sup>	72
2935 <sup>c</sup>	55	2931 <sup>c</sup>	57			1069 <sup>c</sup>	46
		2925 <sup>c</sup>	47	1046	14	1045	100
2919	33			1023	14	1029	71
2879	66	2876	60	1005	14	999	49
2533	23	2528	81	988	23	986	70
2491	8	2487	58			972 <sup>c</sup>	39
						962 <sup>c</sup>	37
2437	9	2440	58			931 <sup>c</sup>	25
1467	15			920	28	925	80
		1463	58	877	18	877	71
1457	33			826	19	831	49
		1437	48			776	16
1427	2	1430	49			682	27
1420	2					668	22
1400	5	1396	40	669	9	663	23
1382	9	1380	25			648 <sup>c</sup>	12
		1361 <sup>c</sup>	33	646	2		
1354	13	1350	40	628	5		
1347	12	1345	40	577	62	575	35
1333	25	1326	22			473	12
1319 <sup>c</sup>	10			465 <sup>c</sup>	11		
		1307	22	448 <sup>c</sup>	18	451	16
1289	8	1290	36	438	42	433	22
1272	33					421	23
		1263	70	406	8		
		1248 <sup>c</sup>	23			395	8
		1225	32	343	29	339	23
1215	5	1214	36	318	9		
1209 <sup>c</sup>	4			306	7	304	31
		1200 <sup>c</sup>	22			283	22
1166	16	1161 <sup>c</sup>	46	265	2		
1158 <sup>c</sup>	15	1154	58	237	5		
1143	7			202	3		
1124 <sup>c</sup>	15	1124 <sup>c</sup>	54	165	8		
1114	25	1109 <sup>c</sup>	73				

<sup>a</sup>Raman spectrometer  
operating conditions:

Sample arr.: cap. tube  
Laser wavelength: 5145 Å.  
Laser power: 800 mw.  
Slit width: 250 μm.  
Slit height: 2 mm.  
Scan speed: 50 cm.<sup>-1</sup>/min.  
DC: 10 x 10<sup>-9</sup>  
RT: 3 sec.  
PM voltage: 1900  
PM temp.: -20°C.

<sup>b</sup>Infrared Spectrometer  
operating conditions:

Sample arr.: KBr pellet  
Slit program: 1000 x 1  
Gain: 4.6  
Atten. speed: 1100  
Scan time: 1 x 32  
Suppression: 6  
Scale expansion: 1X  
Source current: 0.8

<sup>c</sup>Shoulder.

TABLE VIII.

TABULATED FREQUENCIES FOR THE RAMAN AND INFRARED SPECTRA OF DEUTERATED 1,5-ANHYDRO-L-ARABINITOL

$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity	$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity
2985	35	2981	63	1109 <sup>c</sup>	29	1102 <sup>c</sup>	95
2975	23	2971	62	1094	27	1091	98
2935 <sup>c</sup>	10	2931 <sup>c</sup>	42	1068	31	1069	100
2919	34	2911	61	1059	30	1053	91
2883	8	2876	46	1017 <sup>c</sup>	26		
2862	16	2858	69	1008	40	1005	92
2538	14	2539	71			995 <sup>c</sup>	67
2465	9	2464	66	950	13	943	36
1470	27			928	20	923	62
		1460	73	921 <sup>c</sup>	15		
1456	36	1456 <sup>c</sup>	58			912 <sup>c</sup>	59
1444 <sup>c</sup>	9	1437	41	900 <sup>c</sup>	3	896 <sup>c</sup>	49
1410	22	1404	58	878	4	877	71
1393 <sup>c</sup>	9					869 <sup>c</sup>	64
		1376 <sup>c</sup>	64	839	100	837	79
1373	5	1371	65	809	24	803	47
1327 <sup>c</sup>	8	1327	64	759	23	750	74
1304	45	1310	62	634	48	631	39
		1297	63	547	71	542	23
1284	30	1280	53	488	26	480	20
1271 <sup>c</sup>	13			431	30	424	25
		1259 <sup>c</sup>	58	407	26	402	25
		1248	58	371 <sup>c</sup>	3	372	13
1239	16			314	18		
		1229	71	300 <sup>c</sup>	8		
1220	15	1215	69	257	3		
1161 <sup>c</sup>	13	1159 <sup>c</sup>	66	232	3		
1151	18	1147	75	198	10		
1141 <sup>c</sup>	13			175	2		
1114	30	1110 <sup>c</sup>	89				

<sup>a</sup>Raman spectrometer  
operating conditions:

Sample arr.: cap. tube  
Laser wavelength: 5145 Å.  
Laser power: 800 mw.  
Slit width: 250 μm.  
Slit height: 2 mm.  
Scan speed: 50 cm.<sup>-1</sup>/min.  
DC: 0.03 x 10<sup>-6</sup>  
RT: 3 sec.  
PM voltage: 1900  
PM temp.: -20°C.

<sup>b</sup>Infrared spectrometer  
operating conditions:

Sample arr.: KBr pellet  
Slit program: 1000 x 1  
Gain: 4.6  
Atten. speed: 1100  
Scan time: 1 x 32  
Suppression: 6  
Scale expansion: 1X  
Source current: 0.8

<sup>c</sup>Shoulder.

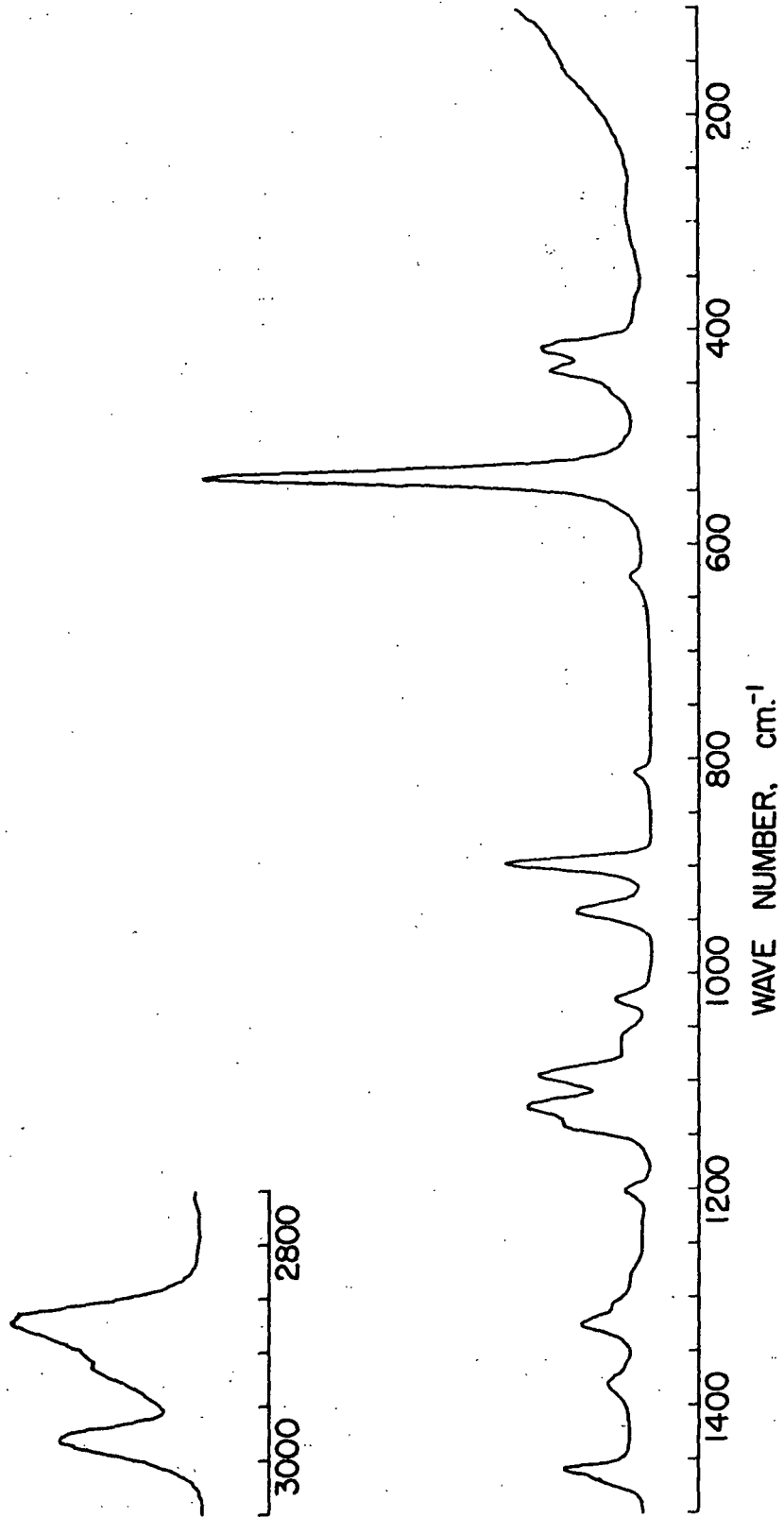


Figure 21. The Raman Spectrum of the Water Solution of 1,5-Anhydroxytolitol

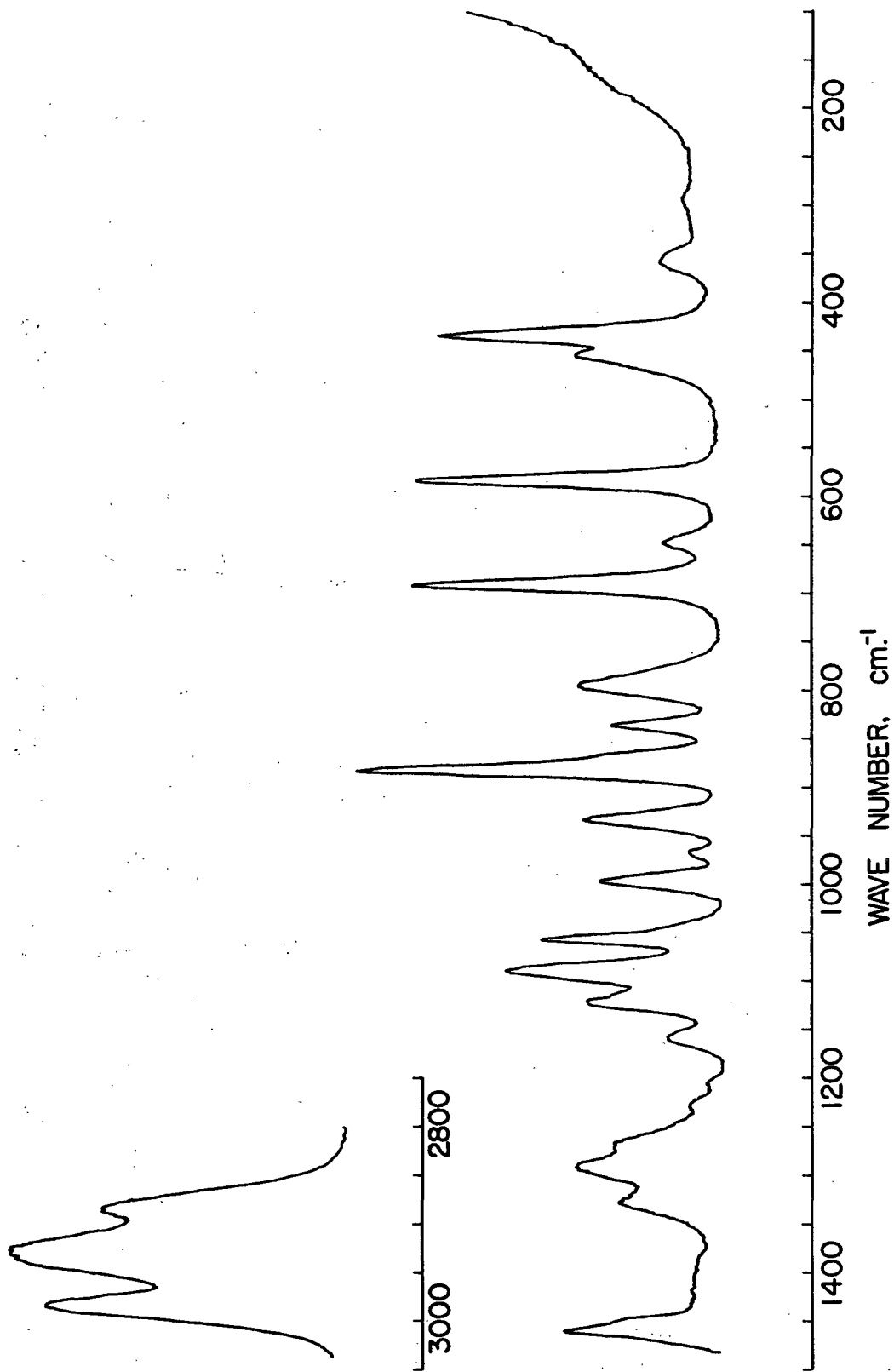


Figure 22. The Raman Spectrum of the Water Solution of 1,5-Anhydroribitol

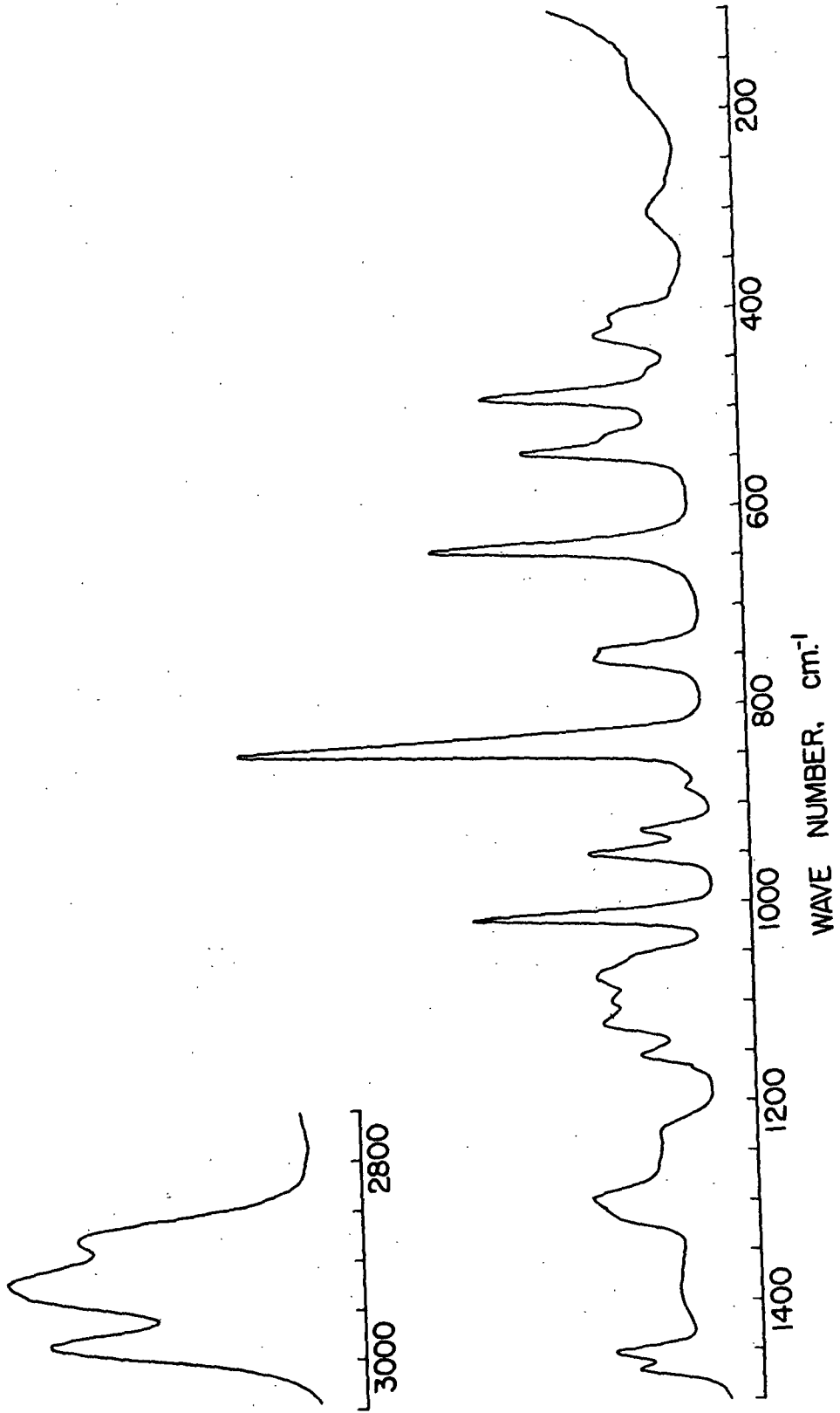


Figure 23. The Raman Spectrum of the Water Solution of 1,5-Anhydro-L-arabinitol



TABLE IX

TABULATED FREQUENCIES FOR THE RAMAN SPECTRA OF THE WATER AND DMSO-d<sub>6</sub> SOLUTIONS OF 1,5-ANHYDROXYLITOL

$\Delta\nu$ , H <sub>2</sub> O, cm. <sup>-1</sup> <sup>a</sup>	Relative Intensity	$\Delta\nu$ , DMSO-d <sub>6</sub> , cm. <sup>-1</sup> <sup>b</sup>	Relative Intensity
2985	34	2972	34
2912 <sup>c</sup>	27	2908 <sup>c</sup>	23
2875	45	2861	44
1469 <sup>c</sup>	12	1470 <sup>c</sup>	11
1462	19	1460	16
		1439	4
		1410	3
		1395 <sup>c</sup>	4
1385	10	1380	6
1368 <sup>c</sup>	6	1370 <sup>c</sup>	4
1340 <sup>c</sup>	6	1337 <sup>c</sup>	4
1325	16	1319	10
1313 <sup>c</sup>	9	1312 <sup>c</sup>	6
		1296 <sup>c</sup>	4
1285	5		
1232	2	1227	2
1202	6	1196	6
1140 <sup>c</sup>	20	1142 <sup>c</sup>	15
1123	28	1123	20
1098 <sup>c</sup>	21	1101 <sup>c</sup>	19
1092	26	1097	21
1062	7	solvent band	
1023	8	solvent band	
941	17	946	17
		913 <sup>c</sup>	3
896	32	899	20
812	4	812	9
630	5	solvent band	
535	100	536	100
456 <sup>c</sup>	9	457 <sup>c</sup>	5
437	22	439	18
416	24	413	20
376	3	solvent band	
290	5	solvent band	

<sup>a</sup>Raman spectrometer  
operating conditions:  
Sample arr.: quartz cell  
Laser wavelength: 5145 Å.  
Laser power: 800 mw.  
Slit width: 250 μm.  
Slit height: 10 mm.  
Scan speed: 50 cm.<sup>-1</sup>/min.

DC: 0.03 x 10<sup>-6</sup>  
RT: 0.3 sec.  
Neutral density filter used

<sup>b</sup>Raman spectrometer  
operating conditions:  
Sample arr.: quartz cell  
Laser wavelength: 5145 Å.

Laser power: 800 mw.  
Slit width: 250 μm.  
Slit height: 10 mm.  
Scan speed: 50 cm.<sup>-1</sup>/  
min.

DC: 10 x 10<sup>-9</sup>  
RT: 3 sec.  
Neutral density filter

<sup>c</sup>Shoulder.

TABLE X

TABULATED FREQUENCIES FOR THE RAMAN SPECTRA OF THE WATER  
AND DMSO-d<sub>6</sub> SOLUTIONS OF 1,5-ANHYDRORIBITOL

$\Delta\nu$ , H <sub>2</sub> O, cm. <sup>-1</sup> <sup>a</sup>	Relative Intensity	$\Delta\nu$ , DMSO-d <sub>6</sub> , cm. <sup>-1</sup> <sup>b</sup>	Relative Intensity
2983	82	2969	94
2928	92	2913	88
2885	67	2869	98
1471 <sup>c</sup>	19	1463 <sup>c</sup>	30
1461	44	1456	55
1452 <sup>c</sup>	32	1446 <sup>c</sup>	28
1408	9		
1329	29	1321	39
1291	40	1286	38
1270 <sup>c</sup>	30	1258	40
1229	10	1225	15
1206	5	1200	15
1160	15	1158	26
1121	37	1124	55
1090	60	1091	97
1054	50	solvent band	
1048 <sup>c</sup>	20	solvent band	
997	34	solvent band	
967	10	solvent band	
934	39	937	84
884	100	881	96
869 <sup>c</sup>	47	869 <sup>c</sup>	45
837	31	solvent band	
795	40	792 <sup>c</sup>	60
692	85	688	100
648	17	solvent band	
584	84	577	99
456	41	451	55
434	78	431	99
358	13	solvent band	
293	5	solvent band	
175	3		

<sup>a</sup>Raman spectrometer

operating conditions:

Sample arr.: cap. tube  
Laser wavelength: 5145 A.  
Laser power: 950 mw.  
Slit width: 250  $\mu$ m.  
Slit height: 2 mm.  
Scan speed: 50 cm.<sup>-1</sup>/min.  
DC:  $0.3 \times 10^{-6}$   
RT: 1 sec.  
PM voltage: 1900  
PM temp.: -20°C.

<sup>b</sup>Raman spectrometer

operating conditions:

Sample arr.: quartz cell  
Laser wavelength: 5145 A.  
Laser power: 800 mw.  
Slit width: 250  $\mu$ m.  
Slit height: 10 mm.  
Scan speed: 50 cm.<sup>-1</sup>/min.  
DC:  $10 \times 10^{-9}$   
RT: 3 sec.  
PM voltage: 1900  
PM temp.: -20°C.

Neutral density  
filter used

<sup>c</sup>Shoulder.

TABLE XI

TABULATED FREQUENCIES FOR THE RAMAN SPECTRA OF THE WATER  
AND DMSO-d<sub>6</sub> SOLUTIONS OF 1,5-ANHYDRO-L-ARABINITOL

$\Delta\nu$ , H <sub>2</sub> O, cm. <sup>-1</sup> <sup>a</sup>	Relative Intensity	$\Delta\nu$ , DMSO-d <sub>6</sub> , cm. <sup>-1</sup> <sup>b</sup>	Relative Intensity
2979	56	2968	55
2916	65	2902	52
2872	50	2863	49
1468	20	1463	13
1452	23	1446	16
1388	9	1375	6
1303 <sup>c</sup>	24	1308 <sup>c</sup>	17
1296	27	1292	20
1229	12	1225	10
1153	16	1156	12
1120	24	1121	22
1095	22	1110	22
1072 <sup>c</sup>	25	solvent band	
1060 <sup>c</sup>	19	solvent band	
1013	51	solvent band	
949	26	949	39
926	15	925	11
883	5	881	3
865	6	867	5
840	100	834	100
754	24	solvent band	
744	22	742 <sup>c</sup>	38
640	58	solvent band	
544	38	539	22
532 <sup>c</sup>	21	522	19
		510 <sup>c</sup>	8
487	46	483	26
465 <sup>c</sup>	12	464 <sup>c</sup>	6
425	22	420	13
407	19	409	12
301	8	solvent band	
270	3	solvent band	
165	6		

<sup>a</sup>Raman spectrometer  
operating conditions:  
Sample arr.: cap. tube  
Laser wavelength: 5145 Å.  
Laser power: 950 mw.  
Slit width: 130 μm.  
Slit height: 5 mm.  
Scan speed: 50 cm.<sup>-1</sup>/min.  
DC: 0.1 x 10<sup>-6</sup>  
RT: 1 sec.

PM voltage: 1900  
PM temp.: -20°C.  
Neutral density filter

<sup>b</sup>Raman spectrometer  
operating conditions:  
Sample arr.: quartz cell  
Laser wavelength: 5145 Å.  
Laser power: 800 mw.  
Slit width: 250 μm.

Slit height: 10 mm.  
Scan speed: 50 cm.<sup>-1</sup>/  
min.  
DC: 10 x 10<sup>-9</sup>  
RT: 3 sec.  
PM voltage: 1900  
PM temp.: -20°C.  
Neutral density  
filter

<sup>c</sup>Shoulder.

TABLE XII  
 MEASURED DEPOLARIZATION RATIOS FOR WATER AND DIMETHYL  
 SULFOXIDE- $d_6$  SOLUTIONS OF 1,5-ANHYDROXYLITOL

$\Delta\nu$ , $\text{cm.}^{-1}$	$\rho^a$ , $\text{H}_2\text{O}$	$\rho^a$ , $\text{DMSO-}d_6$	Symmetry <sup>b</sup>
1469 <sup>e</sup>	0.59	0.59	A'
1460 <sup>e</sup>	0.65	0.74	A'
1385 <sup>e</sup>	0.64	0.69	A'
1325 <sup>e</sup>	0.67	0.74	A'
1285 <sup>e</sup>	0.63	0.72	A'
1232 <sup>e</sup>	0.46	solvent <sup>c</sup>	A'
1202	0.68	0.74	A'
1140 <sup>e</sup>	0.67	0.72	A'
1123 <sup>e</sup>	0.62	0.61	A'
1092 <sup>e</sup>	0.21	0.29	A'
1062 <sup>e</sup>	0.19	solvent	A'
1023	0.70	solvent	A'
942	0.25	0.25	A'
896	0.16	0.19	A'
812	0.00	0.00	A'
630	0.44	solvent	A'
535	0.08	N.D. <sup>d</sup>	A'
456 <sup>e</sup>	N.D.	0.75	A''
437 <sup>e</sup>	0.71	0.75	A''
416 <sup>e</sup>	0.44	0.45	A'
369 <sup>e</sup>	0.29	N.D.	A'

<sup>a</sup> $\rho$  Designates the depolarization ratio.

<sup>b</sup>A' (symmetric symm. species).

A'' (antisymmetric species).

<sup>c</sup>Indicates that ratio could not be measured because of solvent band masking.

<sup>d</sup>N.D. = not determined.

<sup>e</sup>Measured depolarization ratio is questionable because band is overlapped with neighboring bands.

TABLE XIII

MEASURED DEPOLARIZATION RATIOS FOR WATER AND DIMETHYL  
SULFOXIDE-d<sub>6</sub> SOLUTIONS OF 1,5-ANHYDRORIBITOL

$\Delta\nu$ , cm. <sup>-1</sup>	$\rho^a$ , H <sub>2</sub> O	$\rho^a$ , DMSO-d <sub>6</sub>	Symmetry <sup>b</sup>
1471 <sup>d</sup>	0.55	0.59	A'
1461 <sup>d</sup>	0.56	0.64	A'
1329 <sup>d</sup>	0.73	0.58	A'
1291 <sup>d</sup>	0.61	0.60	A'
1270 <sup>d</sup>	0.71	0.58	A'
1229 <sup>d</sup>	0.68	0.60	A'
1160 <sup>d</sup>	0.25	0.28	A'
1121 <sup>d</sup>	0.78	0.80	A''
1090 <sup>d</sup>	0.46	0.56	A'
1054 <sup>d</sup>	0.64	solvent <sup>c</sup>	A'
1048 <sup>d</sup>	0.72	solvent	A'
997	0.67	solvent	A'
967	0.50	solvent	A'
934	0.07	0.13	A'
884	0.14	0.13	A'
837	0.23	solvent	A'
795	0.00	0.00	A'
692	0.06	0.15	A'
648	0.14	solvent	A'
584	0.06	0.06	A'
456 <sup>d</sup>	0.56	0.60	A'
434 <sup>d</sup>	0.16	0.09	A'
358 <sup>d</sup>	0.40	solvent	A'

<sup>a</sup> $\rho$  Designates the depolarization ratio.

<sup>b</sup>A' (symmetric species).

A'' (antisymmetric species).

<sup>c</sup>Indicates that the ratio could not be determined because the solvent band(s) masked the solute bands.

<sup>d</sup>Measured depolarization ratio is questionable because band is overlapped with neighboring bands.

INFRARED AND RAMAN SPECTRA OF 1,5-ANHYDRO-DL-ARABINITOL  
AND DEUTERATED 1,5-ANHYDRO-DL-ARABINITOL

The Raman (pellet) and infrared (KBr pellet) spectra of 1,5-ADLA appear in Fig. 24 and 25, respectively. The measured frequencies and their relative intensities are tabulated in Table XIV.

The Raman spectrum of deuterated 1,5-ADLA (pellet) is included in Fig. 26. The infrared spectrum of deuterated 1,5-ADLA is exhibited in Fig. 27, and the frequencies and relative intensities are tabulated in Table XV.

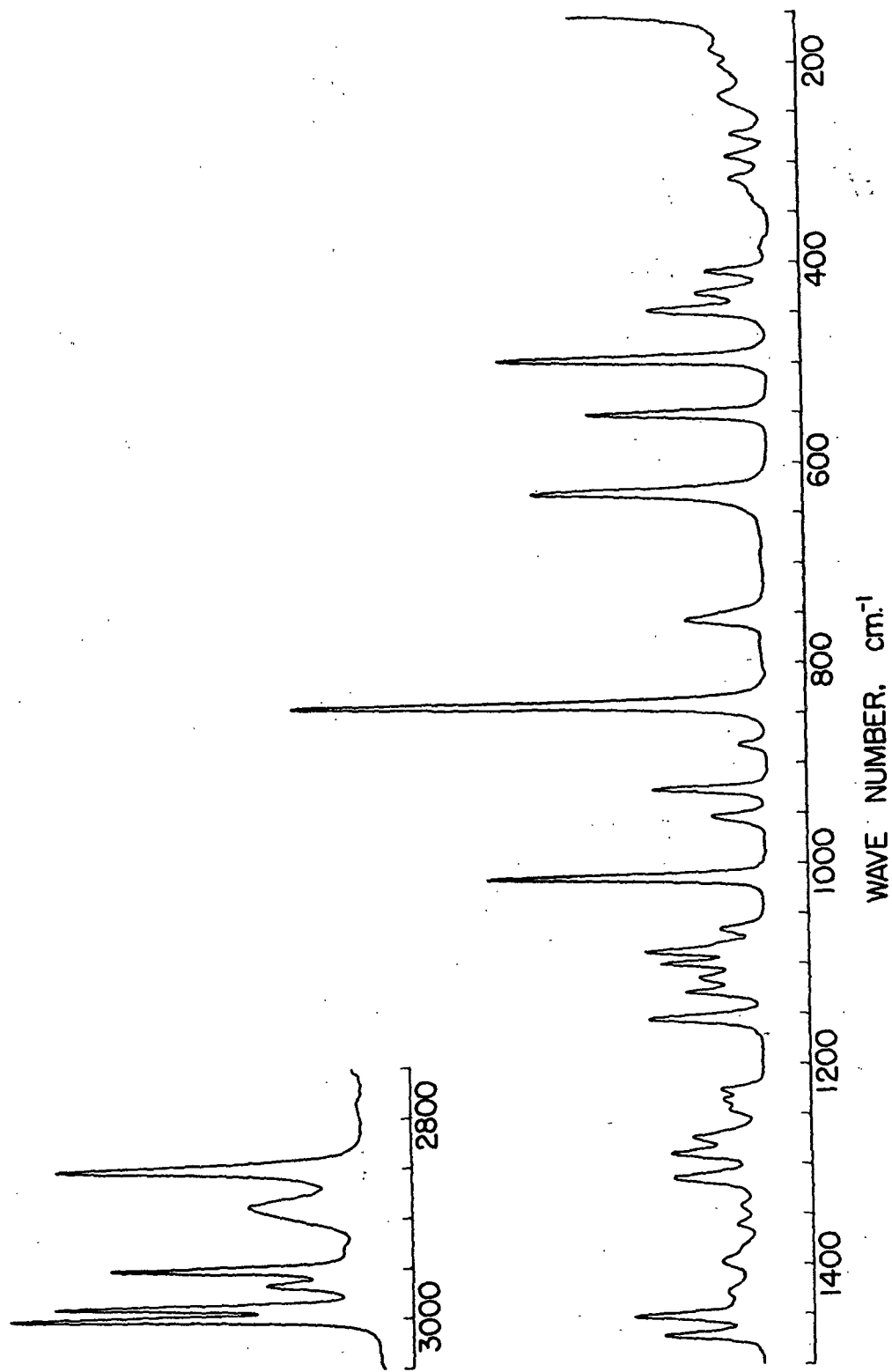


Figure 24. The Raman Spectrum of Crystalline 1,5-Anhydro-DL-arabinitol

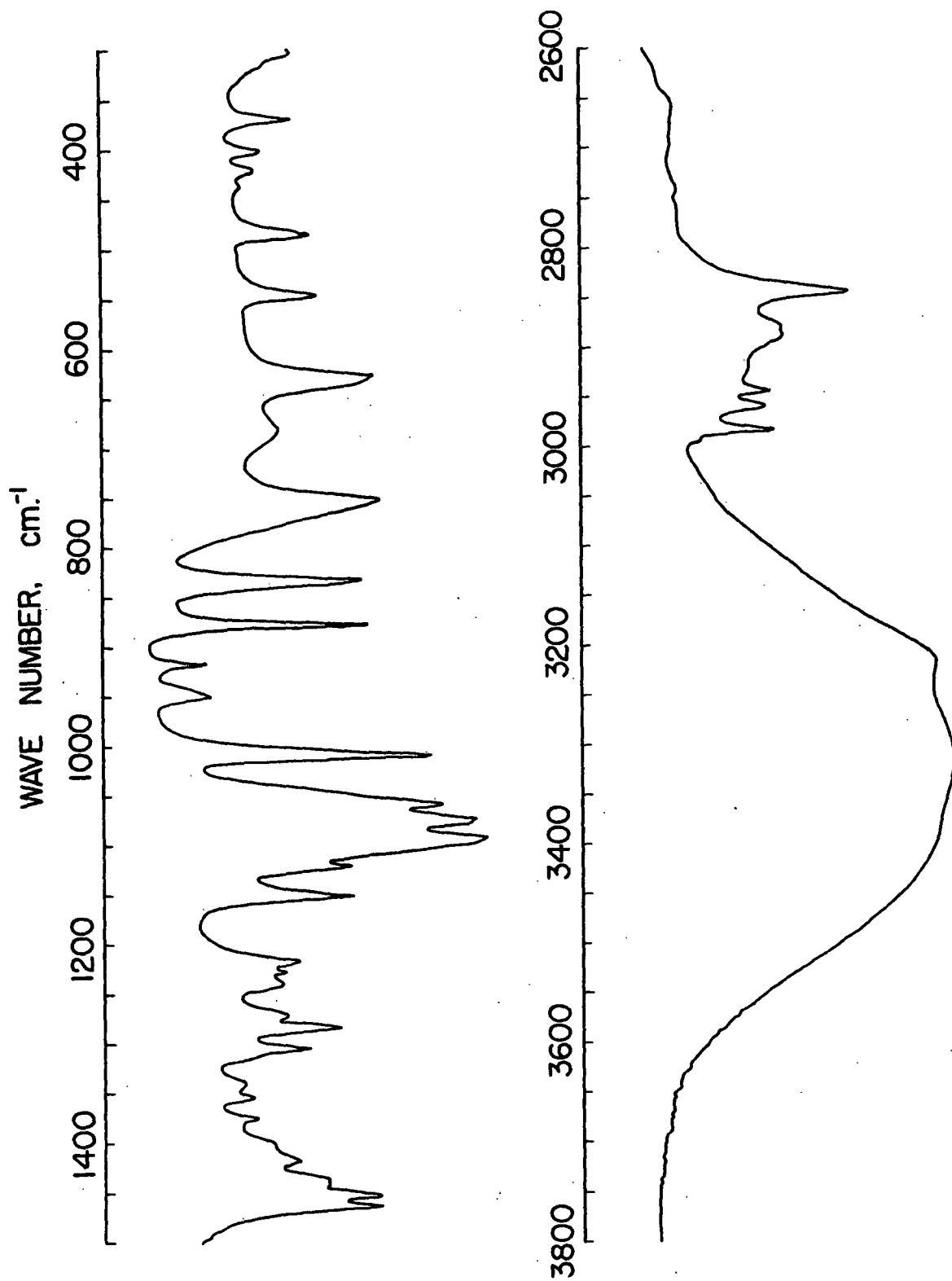


Figure 25. The Infrared Spectrum of Crystalline 1,5-Anhydro-DL-arabinitol



TABLE XIV

TABULATED FREQUENCIES FOR THE RAMAN AND INFRARED SPECTRA OF 1,5--ANHYDRO-DL--ARABINITOL

$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity	$\Delta\nu$ , R, cm. <sup>-1</sup>	Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity
		3400	78	1097	22	1096 <sup>c</sup>	98
3324	1	3317	84			1093	100
3214	6	3223	79	1085	25		
3000	75	2994 <sup>c</sup>	11	1079 <sup>c</sup>	13	1077 <sup>c</sup>	95
2989	65	2983	32			1074	97
2966	21	2960	29	1064	9	1059	87
2951	54	2945	30	1012	59	1009	84
2929	5	2925	27	951	12	950	19
2890 <sup>c</sup>	23	2889	34			944 <sup>c</sup>	16
2887	25	2881	34	923	24	916	18
2852	65	2845	53	880	6	877	65
2787	1					835 <sup>c</sup>	59
1469	21	1463	68	840	100	832	64
1450	28	1452	68	756	17	752	69
1443 <sup>c</sup>	7	1441	53	750 <sup>c</sup>	11		
		1437	53			678	14
1423	8					635 <sup>c</sup>	39
		1416	45	629	50	627	43
1396	9	1398 <sup>c</sup>	37	550	38	546	26
1381 <sup>c</sup>	5	1379	39	493	57	486	24
		1373	32			482 <sup>c</sup>	20
1359	6	1354	32	445	26	437	4
1340	5	1338	39	429	16	421	8
1312	19	1310 <sup>c</sup>	34	407	14	402	10
		1304	48	383	3		
1287	19	1283	57	375	1	369	19
1271	15	1270	42	338 <sup>c</sup>	3		
1243	7	1240	40	326 <sup>c</sup>	4		
1235	8	1237	41	313	9		
1224	9	1227	45			304	5
1154	25	1151	60	291	9		
1127	17	1125 <sup>c</sup>	48			283	3
		1121	60	269	8		
1113	14			231	6		
		1102 <sup>c</sup>	84	197	3		
				185	3		

<sup>a</sup>Raman spectrometer  
operating conditions:  
Sample arr.: pellet  
Laser wavelength: 5145 A.  
Laser power: 900 mw.  
Slit width: 250  $\mu$ m.  
Slit height: 2 mm.  
Scan speed: 50 cm.<sup>-1</sup>/min.  
DC: 0.1 x 10<sup>-6</sup>

RT: 1 sec.  
Zero suppression: 10<sup>-7</sup>  
PM voltage: 1900  
PM temp.: -20°C.  
Spike filter used

<sup>b</sup>Infrared spectrometer  
operating conditions:  
Sample arr.: KBr pellet

Slit program: 1000 x 1  
Gain: 4.6  
Atten. speed: 1100  
Scan time: 10 x 8  
Suppression: 6  
Scale expansion: 1X  
Source current: 0.8  
<sup>c</sup>Shoulder.

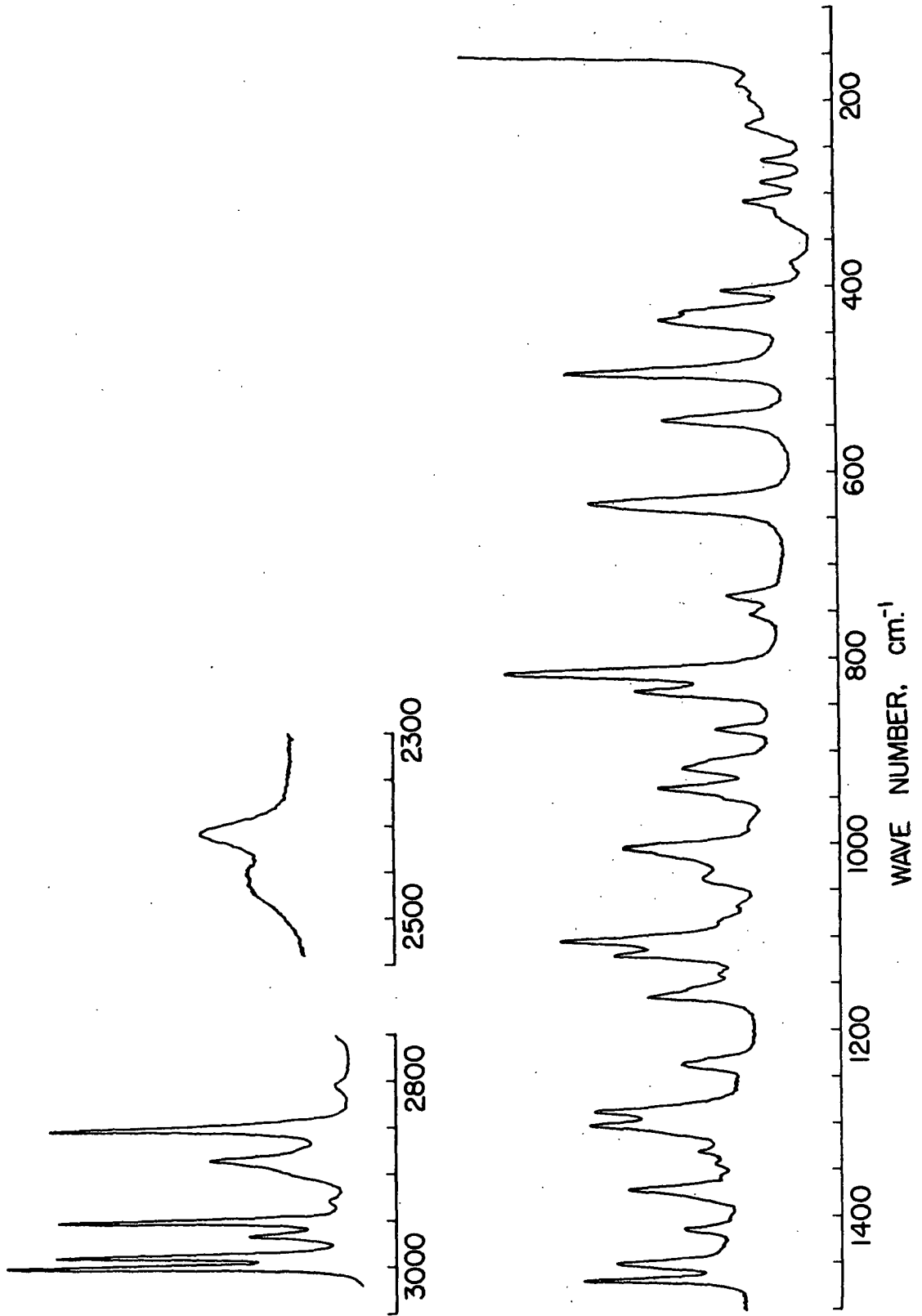


Figure 26. The Raman Spectrum of Crystalline Deuterated 1,5-Anhydro-DL-arabinitol

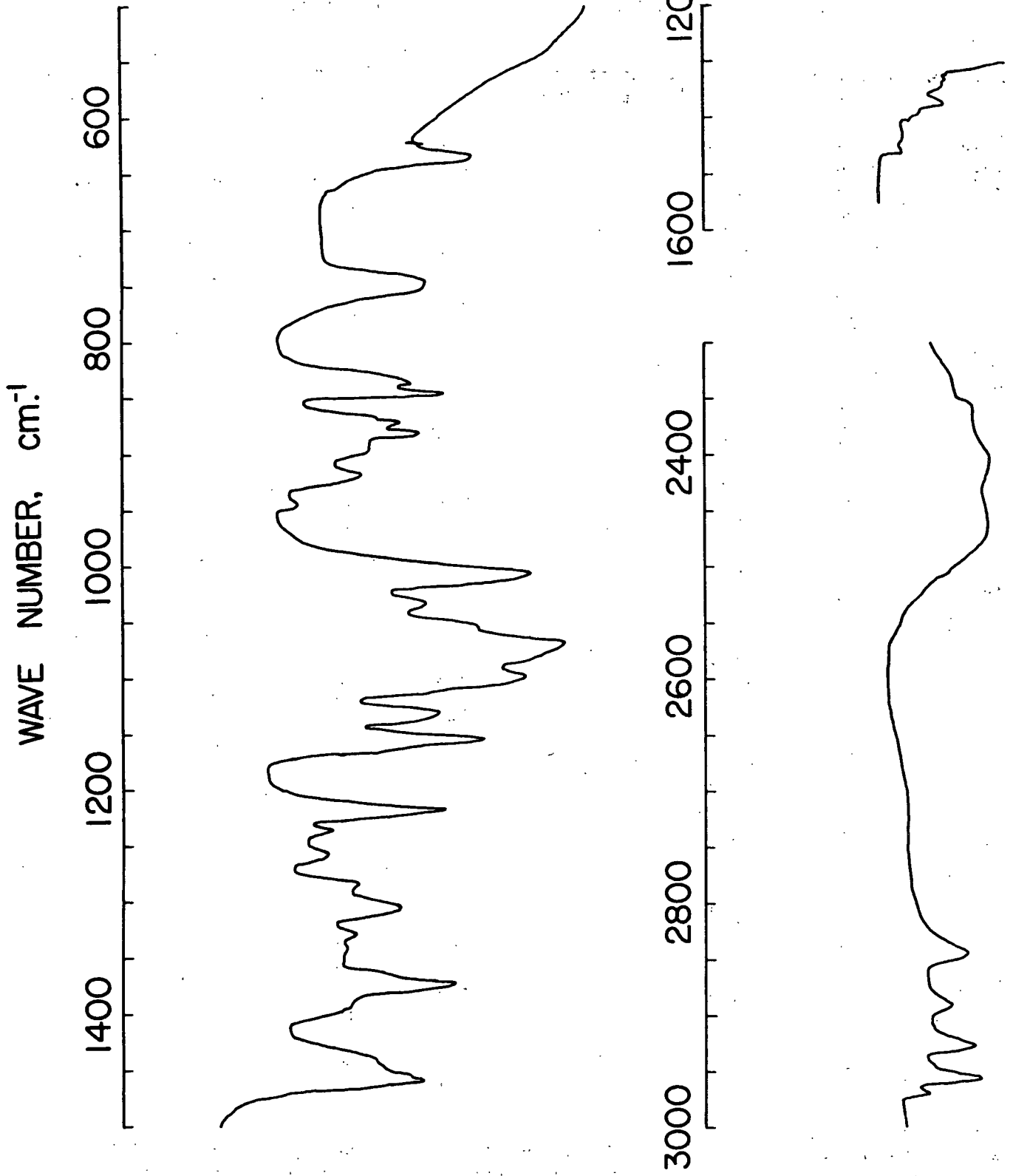


Figure 27. The Infrared Spectrum of Crystalline Deuterated 1,5-Anhydro-DL-arabinitol

TABLE XV

TABULATED FREQUENCIES FOR THE RAMAN AND INFRARED  
SPECTRA OF DEUTERATED 1,5-ANHYDRO-DL-ARABINTIOL

$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity	$\Delta\nu$ , R, cm. <sup>-1</sup>	<sup>a</sup> Relative Intensity	$\nu$ , IR, cm. <sup>-1</sup>	<sup>b</sup> Relative Intensity
2999	100			1137	10	1130	64
2988	86			1118	42		
2965	29	2970	27	1102 <sup>d</sup>	57	1097	89
2950	85	2956 <sup>d</sup>	79	1083 <sup>d</sup>	12		
		2943 <sup>d</sup>	31			1075 <sup>d</sup>	95
2929 <sup>d</sup>	6	2927	74	1069	7	1068 <sup>d</sup>	100
2894 <sup>d</sup>	20	2891	50			1052 <sup>d</sup>	76
2885 <sup>d</sup>	40			1036 <sup>d</sup>	16	1032	60
2875 <sup>d</sup>	16			1013 <sup>d</sup>	24		
2850	87	2845	67	1004	40	1005	90
						999 <sup>d</sup>	65
2804	4			980 <sup>d</sup>	3		
2458	13	2460	98	950 <sup>d</sup>	11		
2408	27	2405	100	939	30	944	25
		2356	83	917 <sup>d</sup>	24	916	43
1468	47	1462	24	912 <sup>d</sup>	20		
1450 <sup>d</sup>	38	1455 <sup>d</sup>	21	895 <sup>d</sup>	16	898 <sup>d</sup>	45
1441 <sup>d</sup>	9	1440 <sup>d</sup>	24	875	15	880	59
		1434 <sup>d</sup>	26			871	54
		1425 <sup>d</sup>	24			866 <sup>d</sup>	48
1414	19						
1401 <sup>d</sup>	6	1405 <sup>d</sup>	30			844	66
		1398 <sup>d</sup>	38	833	40	835	56
		1395 <sup>d</sup>	29	814	78		
1377 <sup>d</sup>	21			753	8	745	60
1370	35			733	15		
		1375 <sup>d</sup>	61	631	58	633	29
		1370 <sup>d</sup>	60	542	38		
1358	8	1358 <sup>c</sup>	61	491	67		
1342	10	1341	39	435	41		
1331	15	1329	41	427	35		
1308 <sup>d</sup>	28			402 <sup>d</sup>	24		
1301	47	1303	54	389 <sup>d</sup>	2		
1286	46	1283	42	374 <sup>d</sup>	4		
1275 <sup>d</sup>	13			329 <sup>d</sup>	9		
		1257	39	309	18		
1237 <sup>d</sup>	20	1235	35	287	12		
1224 <sup>d</sup>	2	1216 <sup>d</sup>	66	263	11		
1164 <sup>d</sup>	31	1162 <sup>d</sup>	52	227	11		
1156 <sup>d</sup>	20	1153	77	195	4		
1141	11			181	5		

<sup>a</sup>Raman spectrometer  
operating conditions:  
Sample arr.: pellet  
Laser power: 970 mw.  
Slit height: 5 mm.  
Rest of data same as  
in Table XIV.

<sup>b</sup>Infrared spectrometer  
operating conditions:  
Sample arr.: Nujol and  
Fluorolube mulls  
Rest of data same as in  
Table XIV.

<sup>c</sup>The regions above and below  
this point correspond to  
different spectra, so  
relative intensities are  
different.  
<sup>d</sup>Shoulder.

## NORMAL COORDINATE ANALYSES

The vibrational spectra of the saccharides and their derivatives are quite complex in that several of the bands arise from the coupling of two or more atomic group vibrations in the molecule. It would be almost, if not entirely, impossible to adequately interpret these spectra by the traditional group frequency approach. Normal coordinate calculations, supplemented with group frequency data, provide a means to interpret and understand the vibrational spectra.

Although these mathematical methods may not be considered rigorously quantitative, the qualitative results should provide an extremely valuable tool to the vibrational spectroscopist and physical chemist. With this tool, vibrational spectroscopy may play a more important role in future physical chemical research in the area of carbohydrates and also other complex molecules.

Therefore, an important aspect of this dissertation is the demonstration that the mathematical methods used by Schachtschneider and Snyder (54) and Snyder and Zerbi (56), to facilitate the interpretation of the vibrational spectra of the n-paraffins and aliphatic ethers, may be successfully extended to larger and more complex molecules, such as the 1,5-anhydropentitol compounds.

## THEORY

In attempting to account for the observed infrared and Raman spectra of real molecules, a certain simplified model for such molecules is adopted, and then the spectra which this model would exhibit are calculated. The model is specified to consist of particles held together by certain forces. The particles represent the atoms of the molecule and are to be treated as if all the mass were concentrated at a point. The definition of the model geometry is usually based on the

bond lengths and angles for the real molecule. This information may be obtained from x-ray and neutron diffraction studies. An important part of the model specification is that the model obeys the laws of quantum mechanics. The Born-Oppenheimer approximation, as cited by Pauling and Wilson (71), is made which permits the separation of the problems of electronic and nuclear motion.

The forces between the particles may be crudely thought of as weightless springs which only approximately obey Hooke's law and which hold the "atoms" in the neighborhood of certain configurations relative to one another. This picture of the forces as springs is useful for visualization, but is not sufficiently general for all cases. The search for a potential function which involves a small number of parameters and which at the same time permits good agreement with experiment is far from ended and poses the largest barrier in a normal coordinate analysis.

The mathematical treatment of the vibrational dynamics of the model is initiated by setting up the classical mechanical expressions for the kinetic and potential energies in terms of the coordinates of the "atoms." These expressions in conjunction with the steady state Schrodinger equation are used to write the quantum mechanical wave equation for the model. If the kinetic energy is expressed in suitable coordinates, the wave equation for the model can be approximately separated into three equations, one for translation, one for rotation, and one for vibration<sup>7,8</sup>.

---

<sup>7</sup> This fact is proved in a number of texts treating vibrational dynamics, for example, Wilson, et al. (68).

<sup>8</sup> The proper coordinates are the three cartesian coordinates for the center of mass of the model; the three Eulerian angles for a rotating system of cartesian coordinates, the axes of which coincide with the principal axes of inertia for the undistorted model; and a set of coordinates giving the displacements of the particles from their equilibrium positions.

If for example, the cartesian displacement of the  $N$  "atoms" are chosen or a set of  $3N$  equivalent coordinates, there will be six coordinates too many which describe the translational and rotational motion of the molecule. The six conditions relating these coordinates assure that the vibrations do not cause motion of the center of mass and that the coordinate system rotates with the model. The resulting vibrational wave equation is a partial differential equation in  $3N$  variables. This equation cannot be solved in most cases. By transforming to a new set of coordinates called normal coordinates, the partial differential wave equation may be separated into  $3N$  total differential equations in one variable, which are usually solvable. The condition for the existence of the transformation to normal coordinates is called the vibrational secular equation. The solution of this equation is the heart of a normal coordinate analysis.

#### KINETIC AND POTENTIAL ENERGY IN CLASSICAL MECHANICS

The potential energy of the model,  $V$ , may be expressed as a Taylor series in the  $3N$  generalized displacement coordinates,  $q_i$ , as shown in Equation (1).

$$\begin{aligned}
 2V &= 2V_0 + 2 \sum_{i=1}^{3N} \left( \frac{\partial V}{\partial q_i} \right)_0 q_i + \sum_{i,j=1}^{3N} \left( \frac{\partial^2 V}{\partial q_i \partial q_j} \right) q_i q_j + \dots \text{higher terms} \\
 &= 2V_0 + 2 \sum_{i=1}^{3N} f_i q_i + \sum_{i,j=1}^{3N} f_{ij} q_i q_j + \dots \text{higher terms.} \quad (1)
 \end{aligned}$$

If the energy is chosen to be zero at the equilibrium configuration, then

$V_0 = 0$ . Furthermore, when all the  $q_i$ 's are zero, the atoms are at their equilibrium positions so that the energy must be a minimum for  $q_i = 0$ ,  $i = 1, 2, 3, \dots, 3N$ .

Therefore,<sup>9</sup>

<sup>9</sup> This treatment ignores the fact that the coordinates,  $q_i$ , are not all independent. For redundant coordinates, the energy should be minimized with respect to an undetermined multiplier giving rise to one additional force constant for each redundancy. This point is discussed by Crawford and Overend (72).

$$(\partial V / \partial q_i)_0 = f_i = 0 \quad (2)$$

for  $i = 1, 2, \dots, 3N$ . For small amplitudes of vibration, the higher order terms can be neglected and

$$2V = \sum_{i,j=1}^{3N} f_{ij} q_i q_j \quad (3)$$

where the  $f_{ij}$ 's are constants, called force constants, given by  $f_{ij} = (\partial^2 V / \partial q_i \partial q_j)$ .

In matrix notation,  $2V = \underline{q}' \underline{f} \underline{q}$ , where  $\underline{q}$  is a column matrix of the  $q_i$ 's, and  $\underline{f}$  is a symmetric matrix<sup>10</sup> with elements  $f_{ij}$ . (The prime symbol shall denote the matrix transpose throughout this manuscript.)

The kinetic energy of the model is given by

$$2T = \sum_{i,j=1}^{3N} t_{ij} \dot{q}_i \dot{q}_j \quad (4)$$

where the  $t_{ij}$ 's are the kinetic energy coefficients and the  $\dot{q}_i$ 's are the velocities in generalized coordinates<sup>11</sup>. This expression may be written in matrix notation as  $2T = \underline{\dot{q}}' \underline{t} \underline{\dot{q}}$ . In general, the coefficients,  $t_{ij}$ , may be functions of the coordinates,  $q_i$ . The proper procedure in that event is to expand them as a power series in the coordinates.

$$t_{ij} = t_{ij}^0 + \sum_{k=1}^{3N} t_{ij}^k q_k + \dots \quad (5)$$

For infinitesimal vibrations, all but the first term,  $t_{ij}^0$ , are neglected. Thus, in the approximation of small vibrations, the kinetic and potential energies are homogeneous quadratic forms in the velocities and coordinates, respectively.

<sup>10</sup> This is easily verified by referring to Equation (3).

<sup>11</sup> The generalized coordinates do not involve time explicitly.



The Lagrangian function,  $L$ , may then be written as

$$L = T - V = \frac{1}{2} \sum_{i,j=1}^{3N} (t_{ij} \dot{q}_i \dot{q}_j - f_{ij} q_i q_j). \quad (5a)$$

Lagrange's equations of motion are defined in the following equation

$$d(\partial L / \partial \dot{q}_j) / dt - (\partial L / \partial q_j) = 0 \quad (5b)$$

where  $j = 1, 2, 3, \dots, 3N$ . Substitution of Equation (5a) into Equation (5b) results in the following expression for the equations of motion

$$\sum_{i=1}^{3N} (t_{ij} \ddot{q}_i + f_{ij} q_i) = 0 \quad (5c)$$

where  $j = 1, 2, 3, \dots, 3N$ . This expression is a form of the vibrational secular equation. These equations of motion are satisfied by an oscillatory solution not only for one frequency, but for a set of  $3N$  frequencies. Therefore, the complete solution of these equations involves a superposition of oscillations with all the allowed frequencies. The solutions of the secular equation are often designated as the frequencies of free vibration or as resonant frequencies. Unless the resonant frequencies are commensurable,  $q_i$  will never repeat its initial value. Hence, the coordinates  $q_i$  are not, in general, the separation coordinates of the problem, each of which is simply periodic. Such a set of periodic coordinates is obtained by a point transformation from the  $q_i$ 's to a new set of coordinates called normal coordinates,  $Q_i$ .

#### VIBRATIONAL WAVE EQUATION

From a quantum mechanical viewpoint, the classical kinetic and potential energy expressions may be used in conjunction with the steady state Schrodinger equation to derive the quantum mechanical wave equation for the model. By the

proper choice of coordinates (see footnote page 74), we can approximately separate the vibrational wave equation from the translational and rotational wave equations. The result is a partial differential equation in  $3N$  variables. In most cases, this equation is too complex to solve. However, by transforming to normal coordinates,  $Q_i$ , where the kinetic and potential energy expressions contain no cross terms, the wave equation for vibrational motion is immediately separable into  $3N$  one-dimensional equations. The wave function,  $\Psi_v$ , may be written as a product of wave functions

$$\Psi_v = \psi_1(Q_1)\psi_2(Q_2)\cdots\psi_{3N}(Q_{3N}) \quad (6)$$

where the wave equations for  $\psi_k$  are

$$(\partial^2 \psi_k / \partial Q_k^2) + (8\pi^2/h^2)(E_k - \frac{1}{2} \lambda_k Q_k^2) \psi_k = 0 \quad (7)$$

for  $k = 1, 2, 3, \dots, 3N$ . These are also the wave equations for the one-dimensional harmonic oscillators. The vibrational energy of the state described by the wave function (6) is the sum of the energies  $E_k$  belonging to the various  $\psi_k(Q_k)$  of (7).

$$E = \sum_{k=1}^{3N} E_k \quad (8)$$

The solutions of these equations are the well-known Hermite polynomials (71) and the energy levels are given by  $(v_k + \frac{1}{2})h\nu_k$  where  $v_k$  is the vibrational quantum number and  $\nu_k$  is the classical frequency of the oscillator given by

$$\nu_k = (\lambda_k)^{1/2} / 2\pi \quad (9)$$

#### VIBRATIONAL SECULAR EQUATION IN MATRIX NOTATION

The vibrational wave equation can be separated into a series of total differential equations by determining the transformation,  $L_{ij}$ , to normal

coordinates,  $Q_j$ , in which all the cross terms in the kinetic and potential energy expressions are eliminated. In matrix notation, the normal coordinate transformation,  $L_{ij}$ , is sought which simultaneously diagonalizes the kinetic energy matrix,  $t$ , [see Equation (4)] and the potential energy matrix,  $f$  [see Equation (3)]. The transformation matrix,  $L$ , is defined as

$$q_i = \sum_j L_{ij} Q_j \quad (9a)$$

or in matrix notation where  $Q$  is defined as a column matrix of the  $Q_j$ 's

$$q = LQ \quad (10)$$

As a consequence of the condition of  $L$ , we have

$$2T = \dot{q}' t \dot{q} = \dot{Q}' (L' t L) \dot{Q} = \dot{Q}' E \dot{Q} \quad (11)$$

or explicitly

$$2T = \sum_k \dot{Q}_k^2 \quad (11a)$$

and

$$2V = q' f q = Q' (L' f L) Q = Q' \Lambda Q \quad (12)$$

or explicitly

$$2V = \sum_k \lambda_k Q_k^2 \quad (12a)$$

where  $E$  is the identity matrix and  $\Lambda$  is a diagonal eigenvalue matrix. From Equations (11) and (12) we have the conditions

$$L' t L = E \quad (13)$$

and

$$\underline{\underline{L}}' \underline{\underline{f}} \underline{\underline{L}} = \underline{\underline{\Lambda}} . \quad (14)$$

Equation (13) is then solved for  $\underline{\underline{L}}'$ ,

$$\underline{\underline{L}}' = \underline{\underline{L}}^{-1} \underline{\underline{t}}^{-1} . \quad (15)$$

Substituting this expression for  $\underline{\underline{L}}'$  into Equation (14) results in the following expression,

$$\underline{\underline{L}}^{-1} \underline{\underline{t}}^{-1} \underline{\underline{f}} \underline{\underline{L}} = \underline{\underline{\Lambda}} . \quad (16)$$

Multiplying on the left by  $\underline{\underline{L}}$  we have

$$\underline{\underline{t}}^{-1} \underline{\underline{f}} \underline{\underline{L}} = \underline{\underline{L}} \underline{\underline{\Lambda}} \quad (17)$$

or

$$\underline{\underline{t}}^{-1} \underline{\underline{f}} \underline{\underline{L}} - \underline{\underline{L}} \underline{\underline{\Lambda}} = 0 . \quad (18)$$

Consider a single column of the  $\underline{\underline{L}}$  matrix denoted by  $\underline{\underline{L}}_{\underline{\underline{k}}}$  and denote the corresponding eigenvalue by  $\lambda_{\underline{\underline{k}}}$ . (The  $\lambda_{\underline{\underline{k}}}$ 's are the elements of  $\underline{\underline{\Lambda}}$ .) Equation (18) can now be rewritten in the form

$$(\underline{\underline{t}}^{-1} \underline{\underline{f}} - \lambda_{\underline{\underline{k}}} \underline{\underline{E}}) \underline{\underline{L}}_{\underline{\underline{k}}} = 0 \quad (19)$$

for  $\underline{\underline{k}} = 1, 2, 3, \dots, 3N$  which is a form of the vibrational secular equation. For this equation to have a nontrivial solution, that is,  $\underline{\underline{L}}_{\underline{\underline{k}}} \neq 0$ , the determinant of the coefficient matrix must be zero (73). Thus,

$$\det(\underline{\underline{t}}^{-1} \underline{\underline{f}} - \lambda_{\underline{\underline{k}}} \underline{\underline{E}}) = 0 \quad (20)$$

where  $\det ||$  indicates the determinant. The solution of this determinantal equation results in the determination of the frequency parameters,  $\lambda_{\underline{\underline{k}}}$ , for the

mathematical model. The frequency parameters are related to the calculated frequencies,  $\nu_{\underline{k}}$ , by the relationship,  $\lambda_{\underline{k}} = 4\pi^2\nu_{\underline{k}}^2$ . Substitution of the calculated frequency parameters,  $\lambda_{\underline{k}}$ , into the vibrational secular equation (19) results in sets of homogeneous linear equations, one for each column of  $\underline{L}$ , from which the  $\underline{L}_{\underline{k}}$ 's may be determined. (The  $\underline{L}_{\underline{k}}$ 's contain the information regarding the "atomic" vibrational motion of the model for each frequency,  $\nu_{\underline{k}}$ .) Stated another way, the transformation which diagonalizes the product  $\underline{t}^{-1}\underline{f}$  is sought, resulting in a diagonal matrix,  $\underline{\Lambda}$ , of the  $\lambda_{\underline{k}}$

$$\underline{L}^{-1}(\underline{t}^{-1}\underline{f})\underline{L} = \underline{\Lambda} \quad (21)$$

which is obtained by multiplying Equation (17) on the left by  $\underline{L}^{-1}$ . With this form of the secular equation, the inverse kinetic energy matrix,  $\underline{t}^{-1}$ , must be computed.

#### INTERNAL COORDINATES

As previously stated, the choice of  $3N$  generalized displacement coordinates,  $\underline{q}$ , leads to a vibrational secular equation of degree  $3N$  which has six zero roots corresponding to the translations and rotations. It is desirable to choose a set of coordinates which describe the internal configuration of the molecule only, that is, which satisfy the conditions that the center of mass remains fixed and assure that there is no rotation of its coordinate system, and satisfy the conditions set down by Eckart (74) and Sayvetz (75). A set of coordinates satisfying these conditions are known as internal coordinates.

A convenient set of internal coordinates has been defined by Wilson (76) and Decius (77). The internal coordinates in this set are bond stretching, valence angle bending, out-of-plane bending, and torsion. This particular set of internal coordinates is useful because the potential energy in terms of

these coordinates is chemically meaningful. Decius (78) has shown that this set of four types of internal coordinates is sufficient to describe the most general vibrational displacement of any molecule. Further, he has given a prescription for defining a kinematically complete set of valence coordinates for both cyclic and acyclic molecules.

In some cases, it is advantageous to choose more than  $3N-6$  internal valence coordinates, either to make use of symmetry or to put the force constants on an equivalent basis, thereby overdefining the problem and introducing redundant coordinates. For example, only five of the six HCH angles in methane are independent. However, if we leave one of the angles out, the force constants lose their simple chemical meaning, and it is not possible to use symmetry to factor the secular equation.

#### VIBRATIONAL SECULAR EQUATION IN INTERNAL COORDINATES

For internal coordinates,  $\underline{R}$ , it is easier to compute the inverse kinetic energy matrix; thus, the kinetic and potential energies are usually written in the form

$$2T = \dot{\underline{R}}' \underline{G}^{-1} \dot{\underline{R}} \quad (22)$$

and

$$2V = \underline{R}' \underline{F} \underline{R} \quad (23)$$

which is obtained when  $\underline{t} = \underline{G}^{-1}$ ,  $\underline{f} = \underline{F}$ , and  $\underline{q} = \underline{R}$  in Equations (3) and (4).

The vibrational secular equation is seen to be

$$\underline{GFL} = \underline{IA} \quad (24)$$

from Equation (17). We then seek the transformation,  $\underline{L}$ , from normal coordinates,  $\underline{Q}$ , to internal coordinates,  $\underline{R}$ ,

$$\underline{R} = \underline{LQ} \quad (25)$$

by solving the determinantal equation

$$\det (\underline{GF} - \lambda \underline{E}) = 0 . \quad (26)$$

The bulk of the normal coordinate computations to be described in this text is concerned with the solution of this determinantal equation (26) and the vibrational secular equation (24).

### COMPUTATIONS

In this section, the computational methods employed in the normal coordinate analyses of the 1,5-AP compounds will be presented. The data generated in the computations can be found in the appropriate appendices.

#### DEFINITION OF MODEL GEOMETRY

The positions of the "atoms" in the model are usually defined from the bond length and bond angle data for the real molecule. This information can be obtained from x-ray or neutron diffraction studies. If these data are not available, the model geometry must be approximated.

#### Molecular Structure of the 1,5-Anhydropentitol Compounds

Unfortunately, x-ray crystallographic data are not available to date for the 1,5-AP compounds. The geometry of these compounds must be inferred from structure data available for similar compounds, such as the pentoses. However, small differences in bond lengths and angles (in this case, deviations of the order of magnitude of a few hundredths of an angstrom in the bond lengths and a few degrees in the bond angles) should not affect the results significantly because such deviations from the real structure are overshadowed by other approximations incorporated into the mathematical methods. Snyder and Zerbi (56) were able to

perform a successful normal coordinate analysis for tetrahydropyran assuming tetrahedral bond angles and equivalent CC, CH, and CO bond lengths for their model.

#### Conformation

The first matter to consider when defining the model geometry for the 1,5-AP compounds is the molecular conformation. In his review of crystal structure data for simple carbohydrates and their derivatives, Straus (12) states that all of the crystalline pyranose-type compounds, thus far examined, adopt a chair conformation. In fact, a boat conformation has not yet been found for crystalline monocyclic compounds of sugars. Thus, it seems reasonable to assume that all of the 1,5-AP compounds adopt the chair conformation in the crystalline state. There are, however, two possible chair conformations for each structure. In solution there is an equilibrium existing between these two conformations. The position of the equilibrium is determined by the difference between the free energies of the components. When the components differ only in geometric configuration, the differences in free energy are due to steric factors, namely, to the energies of interaction between nonbonded atoms. In a comparatively rigid system, like that of the six-membered pyranose ring, the interaction energies can be evaluated and totaled. The comparison of these interaction energies have led to usually accurate predictions of the most stable conformer and the predominant conformer in solution. Eliel has provided a guide (79) for the calculation of the conformational free energies. More recently, Angyal (80) has reported a set of interaction energies derived specifically for pyranose compounds. The details of the conformational analysis method can be found in Eliel, *et al.* (81). The conformational free energies have been evaluated in this thesis investigation for each of the chair conformers of the 1,5-AP models by



employing the interaction energy values derived by Angyal (80). The results of this evaluation are listed in Table XVI. These conformational free energy calculations suggest that the 1,5-AP compounds most probably exist in the chair conformations drawn in Fig. 28 in the crystalline state.

TABLE XVI  
CALCULATED CONFORMATIONAL FREE ENERGIES ( $E_{-conf}$ ; kcal./mole)  
FOR THE 1,5-ANHYDRO-PENTITOL MODELS

	$E_{-conf}$	$E_{-conf}$	Difference	Ratio <sup>a</sup>
1,5-AX	2.40 <sub>b</sub> a-a-a	0.70 <sup>c</sup> <sub>b</sub> e-e-e	1.70	95:5
1,5-AR	2.20 a-e-a	1.60 <sup>c</sup> e-a-e	0.60	74:26
1,5-ALA	1.70 a-a-e	1.15 <sup>c</sup> e-e-a	0.55	72:28

<sup>a</sup>The proportion of each conformer existing in solution at equilibrium for the Angyal analysis is calculated from the expression  $G_1^0 - G_2^0 = RT \ln(N_1/N_2)$ , relating the difference in conformational free energy to the natural logarithm of the ratio of the mole fractions, for  $T = 298.16^\circ\text{K}$  or  $25^\circ\text{C}$ .

<sup>b</sup>The conformation is identified by designating the orientation of the hydroxyl group on C2, C3, and C4, respectively. An a denotes an axial hydroxyl group and an e denotes an equatorial hydroxyl group.

<sup>c</sup>This is the most stable conformer of the pair.

#### Bond Angles and Bond Lengths

As stated earlier, crystal structure data from x-ray and neutron diffraction studies were not available for the 1,5-AP compounds at the time of this investigation. One method of specifying the model geometry approximating a 1,5-AP molecule is to adapt as much of the available crystal structure data as possible from a related compound which in this case would be one of the pentoses. However, an equally valid approximation is to assume a tetrahedral model geometry. In

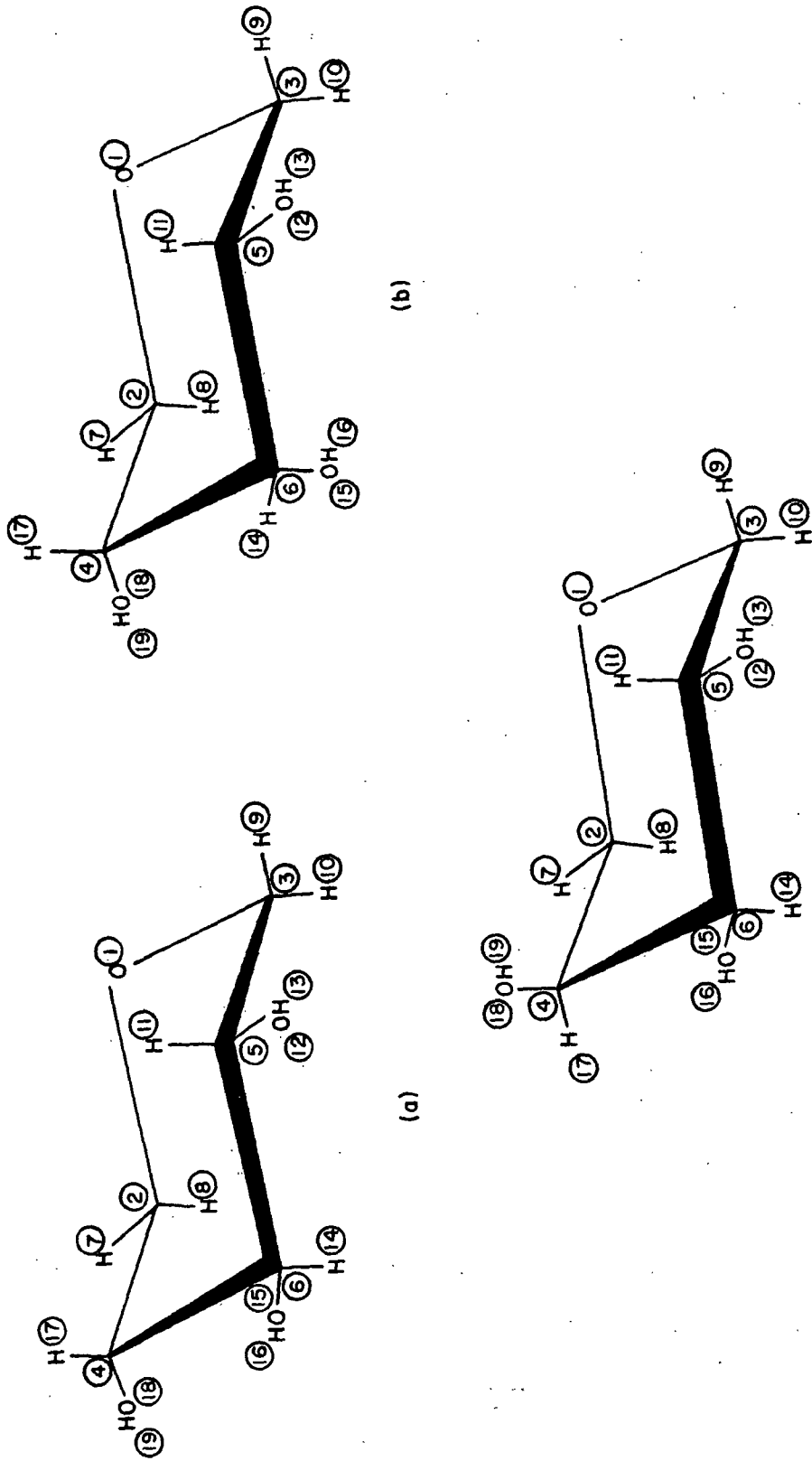


Figure 28. The Most Stable Conformations for the 1,5-Anhydropentitol Models as Predicted from Conformational Free Energy Calculations. The Sketches Depict (a) 1,5-Anhydroxylitol, (b) 1,5-Anhydroribitol, and (c) 1,5-Anhydro-L-arabinitol. The Atoms of Each Molecule are Numbered to Identify Them in the Normal Coordinate Computations

this model, all bond angles are assumed to be tetrahedral ( $109^{\circ}28'$ ) except the COC angle ( $112^{\circ}27'$ ) and the torsional (dihedral) angles are set equal to  $60^{\circ}$ . Further, all common bond types are assigned an equivalent bond length. In specifying the geometry for the 1,5-AP models, the COC bond angle and the corresponding CO bond length were adapted from the data resulting from an electron diffraction study of p-dioxane reported by Davis and Hassel (82). The remaining common bond lengths were estimated by averaging the appropriate crystal structure data reported for  $\alpha$ -D-glucose (83),  $\beta$ -D-glucose (84),  $\beta$ -DL-arabinose (85),  $\beta$ -lyxose (86),  $\alpha$ -xylose (87), and methyl  $\alpha$ -D-mannopyranoside (88). The estimated values for the bond lengths and COC bond angle are tabulated in Table XVII. One should note that the only structural difference existing between the three<sup>12</sup> 1,5-AP models is the orientation of the hydroxyl groups, i.e., axial versus equatorial.

#### Calculation of Cartesian Coordinates for the Model Atoms

The cartesian coordinates of the "atoms" in 1,5-AP models were computed from the bond lengths and bond angles specified in Table XVII by the computer program CART written by J. H. Schachtschneider (89). The atoms in the models were numbered in the manner depicted in Fig. 28.

The computational method employed in CART is discussed in Appendix I. The data input to CART and the resulting cartesian coordinates for the 1,5-AP models are also included in this appendix. A program written by Cole and Adamson (90) called PAMOLE which draws a three-dimensional stereographic

<sup>12</sup> The compounds 1,5-ALA and 1,5-ADA are mirror images of one another and exhibit identical vibrational spectra. Therefore, only one of these compounds (1,5-ALA) need be included in the normal coordinate calculations.

projection of a "ball and stick" representation of the model from the calculated cartesian coordinates may be used to check the cartesian coordinate calculations for errors. Drawings generated by PAMOLE for the 1,5-AP models based on the cartesian coordinates calculated by CART are included in Appendix I also.

TABLE XVII

BOND LENGTHS SPECIFIED FOR THE 1,5-ANHYDRO-PENTITOL MODELS<sup>a</sup>

Bond Length	Av. Value, A.	Bond Angle	Assigned Value
CO( <u>r</u> ) <sup>b</sup>	1.423	COC	112.45°
CC	1.523		
CH' <sup>c</sup>	1.096		
CH	1.093		
CO	1.415		
OH	0.970		

<sup>a</sup>The bond angles were assumed to be tetrahedral (109°28') and the dihedral angles set equal to 60°.

<sup>b</sup>(r) Designates the pyranose ring oxygen atom.

<sup>c</sup>The CH' refers to the C1 and C5 atoms of the ring.

The FORTRAN listing, flow diagram, and program instructions for CART and the program instructions for PAMOLE may be found in Appendix V.

TRANSFORMATION TO INTERNAL COORDINATES AND CALCULATION OF THE INVERSE KINETIC ENERGY MATRIX (G MATRIX)

Internal Coordinates

The vibrational problem is to be set up by the Wilson GF method (68,76,91). This method requires that the vibrational displacements be expressed in internal valence coordinates, R, which satisfy the Eckart (74)-Sayvetz (75) conditions, thereby separating the vibrational problem from translation and rotation. A

convenient set of internal valence coordinates has been defined by Wilson (76) and Decius (77). Decius has shown that a set of four types of internal valence coordinates, namely, bond stretching, valence angle bending, out-of-plane wagging, and torsion, is sufficient to describe the most general vibrational displacement of any molecule. He has also given a prescription for defining a kinematically complete set for both cyclic and acyclic molecules.

Definition of Internal Coordinates for the 1,5-Anhydropentitol Models

According to the prescription set down by Decius, there will be one bond stretching coordinate for each bond in the molecule. That is,

$$n_r = b \quad (27)$$

where  $b$  is the number of bonds in the molecule and  $n_r$  is the number of bond stretching internal coordinates. For the 1,5-AP models, there are 19 bonds; i.e.,  $n_r = b = 19$ . The minimum number of valence angle bending internal coordinates,  $n_\phi$ , is expressed as

$$n_\phi = 4b - 3a + a_1 \quad (28)$$

where  $a$  is the number of atoms in the molecule, and  $a_1$  is the number of terminal bonds (the number of atoms bonded to only one other atom). For the 1,5-AP models,  $a = 19$  and  $a_1 = 10$ ; thus,  $n_\phi = 76 - 57 + 10 = 29$ . The number of torsional internal coordinates,  $n_\tau$ , corresponds to the number of nonterminal bonds which is determined from the expression

$$n_\tau = b - a_1 \quad (29)$$

Therefore,  $n_\tau = 19 - 10 = 9$ . The result is a total of 57 internal coordinates. The minimum number of internal coordinates required to completely describe the

vibrational motion of the 1,5-AP models is equal to the number of vibrational degrees of freedom,  $f$ , where

$$f = 3a - 6. \quad (30)$$

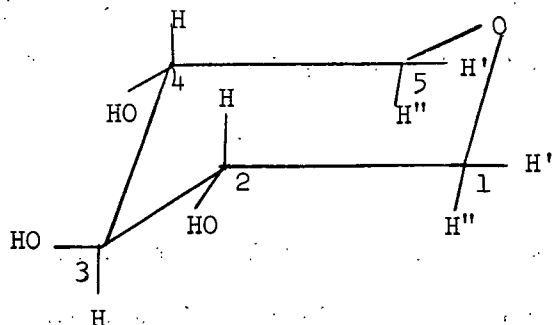
For the 1,5-AP models,  $f = 3(19) - 6 = 51$  degrees of freedom; so the set of internal coordinates derived from the Decius prescription is noted to contain six additional or redundant coordinates. These redundancies are due to the cyclic nature of the molecule and cannot be removed. There are six bond angles about each of the five carbon atoms in the ring. In the 29 valence angle bending coordinates specified above, only five of these angles have been included in each case because the sixth angle is not independent. To include this sixth angle would generate a locally redundant coordinate. However, to make use of symmetry and to put the force constants on an equivalent basis, the five redundant coordinates must be included, one for each carbon atom of the ring. This means that there are now 34 angle bending coordinates.

In summary, a total of 62 internal valence coordinates have been generated to describe the vibrational motion of the 1,5-AP models; namely, 19 bond stretching coordinates, 34 valence angle bending coordinates, and 9 torsional coordinates. Of these 62 coordinates, 11 are redundant. Five of these redundancies are local and removable, while the remaining six redundancies result from the cyclic nature of the molecule and are not removable.

The 62 internal coordinates for 1,5-AX are listed in Table XVIII. The internal coordinates for 1,5-AR and 1,5-ALA involve the same atoms, except for a few of the torsional coordinates, and are numbered in a similar manner as those for 1,5-AX.

TABLE XVIII

DESCRIPTION OF THE 62 INTERNAL COORDINATES  
FOR 1,5-ANHYDROXYLITOL



Bond Stretch

1. C1O	6. C5O	11. O2H2	16. C4O4
2. C1C2	7. C1H'	12. C3H3	17. O4H4
3. C2C3	8. C1H''	13. C3O3	18. C5H'
4. C3C4	9. C2H2	14. O3H3	19. C5H''
5. C4C5	10. C2O2	15. C4H4	

Valence Angle Bend

20. H'C1O	29. C1C2C3	38. C4C3O3	47. H'C5O4
21. H''C1O	30. H2C2C3	39. H3C3O3	48. H''C5O4
22. C2C1O	31. C3C2O2	40. C3C4H4	49. C4C5O
23. H'C1C2	32. H2C2O2	41. C3C4O4	50. H'C5O
24. H''C1C2	33. C2C3H3	42. C4O4H4	51. H''C5O
25. H'C1H''	34. C2C3O3	43. C3C4C5	52. H'C5H''
26. C1C2H2	35. C3O3H3	44. C5C4H4	53. C1O5
27. C1C2O2	36. C2C3C4	45. C5C4O4	
28. C2O2H2	37. C4C3H3	46. H4C4O4	

Torsion<sup>a</sup>

54. C3C4C5H' } <sup>b</sup>	56. H'C1C2C3 } <sup>b</sup>	58. H4C4O4H4
H4C4C5H'' } <sup>b</sup>	H''C1C2H2 } <sup>b</sup>	59. H3C3O3H3
O4C4C5O } <sup>b</sup>	OC1C2O2 } <sup>b</sup>	60. H2C2O2H2
55. H3C3C4H4 } <sup>b</sup>	57. H2C2C3H3 } <sup>b</sup>	61. H'C5O4C1
O3C3C4C5 } <sup>b</sup>	C1C2C3O3 } <sup>b</sup>	62. H'C1O5
C2C3C4O4 } <sup>b</sup>	O2C2C3O4 } <sup>b</sup>	

<sup>a</sup>The torsional coordinates were defined for those atoms in the trans position about each bond.

<sup>b</sup>The torsional coordinates in this group are summed together (linear combination) to avoid the introduction of further redundancies.

Inverse Kinetic Energy Matrix (G Matrix)

The expression for the kinetic energy in cartesian displacement coordinates may be written from Equation (11) by replacing  $\underline{q}$  with  $\underline{X}$  and  $\underline{t}$  with  $\underline{M}$  in the expression on the left-hand side where  $\underline{M}$  is defined to be a mass matrix. That is,

$$2T = \dot{\underline{X}}' \underline{M} \dot{\underline{X}} \quad (30a)$$

The transformation,  $\underline{B}$ , from cartesian displacement coordinates,  $\underline{X}$ , to internal coordinates,  $\underline{R}$ , may be computed from the set of internal coordinates specified in the last section.

$$\underline{R} = \underline{B} \underline{X} \quad (31)$$

$$\underline{X} = \underline{B}^{-1} \underline{R} \quad (31a)$$

The kinetic energy in internal coordinates may be written by substituting Equation (31a) into Equation (30a).

$$2T = (\underline{B}^{-1} \dot{\underline{R}})' \underline{M} (\underline{B}^{-1} \dot{\underline{R}}) = \dot{\underline{R}}' (\underline{B}^{-1})' \underline{M} \underline{B}^{-1} \dot{\underline{R}} \quad (32)$$

If we define  $\underline{G}^{-1} = [(\underline{B}^{-1})' \underline{M} \underline{B}^{-1}]$ , the expression defining the inverse kinetic energy matrix,  $\underline{G}$ , follows directly

$$\underline{G} = \underline{B} \underline{M}^{-1} \underline{B}' \quad (33)$$

and the kinetic energy is of the simple form  $2T = \dot{\underline{R}}' \underline{G}^{-1} \dot{\underline{R}}$ .

Computation of the G Matrix

The  $\underline{G}$  matrix elements were computed for the 1,5-AP models by the computer program GMAT which is based on Wilson's "S vector" technique (68). In the calculation of the  $\underline{G}$  matrix, the cartesian coordinates computed by CART for the "atoms" in the models were transformed into internal coordinates (see Table XVIII for a description of the internal coordinates for 1,5-AX).



The computational method employed in GMAT is discussed in Appendix II. The internal coordinate definitions for the 1,5-AP models and the resulting  $\underline{\underline{G}}$  matrices are also listed in this appendix.

### Symmetry Coordinates

Upon transforming from internal coordinates to symmetry coordinates, the  $\underline{\underline{G}}$  matrix factors into a number of smaller blocks, one for each symmetry species (irreducible representation) of the molecular point group. The symmetry coordinates are constructed from linear combinations of the internal coordinates by a method based on the molecular point group character table. The construction of symmetry coordinates will not be discussed here, but the interested reader may wish to refer to one of the many texts that treat this topic, for example (68,92,93).

The compounds 1,5-AX and 1,5-AR possess a plane of symmetry and, therefore, belong to the  $\underline{\underline{C}}_{\underline{\underline{s}}}$  point group. The symmetry coordinates for these two models were developed with the relationships derived by Wilson (68) and are defined in Table XIX. The internal coordinate numbers specified in the table refer to the coordinates defined in Tables XXXVII and XXXVIII in Appendix II. The  $\underline{\underline{C}}_{\underline{\underline{s}}}$  point group has two symmetry species (irreducible representations), symmetric, A', and antisymmetric, A''. The symmetry coordinates in Table XIX are classified into their respective symmetry species.

### Factoring the $\underline{\underline{G}}$ Matrix

In GMAT, to transform from internal coordinates,  $\underline{\underline{R}}$ , to symmetry coordinates,  $\underline{\underline{S}}$ , an orthogonal transformation matrix,  $\underline{\underline{U}}$ , must be included with the input data, since

$$\underline{\underline{S}} = \underline{\underline{U}} \underline{\underline{R}} . \quad (34)$$

TABLE XIX

DEFINITION OF SYMMETRY COORDINATES FOR 1,5-ANHYDROXYLITOL  
AND 1,5-ANHYDRORIBITOL

Sym. Coord. <sup>a</sup>	Comb.	In. Coord. <sup>b</sup>	Sym. Coord. <sup>a</sup>	Comb.	In. Coord. <sup>b</sup>		
A' {	=	1 + 6	A'' {	=	55 - 57		
	=	2 + 5		=	58 - 60		
	=	3 + 4		=	61 - 62		
	S4	=		7 + 18	S35	=	1 - 6
	S5	=		8 + 19	S36	=	2 - 5
	S6	=		9 + 15	S37	=	3 - 4
	S7	=		10 + 16	S38	=	7 - 18
	S8	=		11 + 17	S39	=	8 - 19
	S9	=		12	S40	=	9 - 15
	S10	=		13	S41	=	10 - 16
	S11	=		14	S42	=	11 - 17
	S12	=		20 + 50	S43	=	20 - 50
	S13	=		21 + 51	S44	=	21 - 51
	S14	=		22 + 49	S45	=	22 - 59
	S15	=		23 + 47	S46	=	23 - 47
	S16	=		24 + 48	S47	=	24 - 48
	S17	=		25 + 52	S48	=	25 - 52
	S18	=		26 + 44	S49	=	26 - 44
	S19	=		27 + 45	S50	=	27 - 45
	S20	=		28 + 42	S51	=	28 - 42
	S21	=		29 + 43	S52	=	29 - 43
	S22	=		30 + 40	S53	=	30 - 40
	S23	=		31 + 41	S54	=	31 - 41
	S24	=		32 + 46	S55	=	32 - 46
	S25	=		33 + 37	S56	=	33 - 37
	S26	=		34 + 38	S57	=	34 - 38
	S27	=		35	S58	=	54 - 56
	S28	=		36	S59	=	55 + 57
	S29	=		39	S60	=	58 + 60
	S30	=		53	S61	=	59
	S31	=		54 - 56	S62	=	61 + 62

<sup>a</sup> Normalization of the symmetry coordinates requires that each coordinate be multiplied by  $1/\sqrt{2}$ , except for the symmetry coordinates S9, S10, S11, S27, S28, S29, S30, and S61 where the factor is unity. The normalization is accomplished by GMAT.

<sup>b</sup> The internal coordinate numbers are defined in Tables XXXVII and XXXVIII in Appendix II.

The  $\underline{U}$  matrices are identical for 1,5-AX and 1,5-AR and are simply a matrix representation of Table XIX. The elements of  $\underline{U}$ , included with the input data, need not be normalized, since normalization is accomplished in the program.

The  $\underline{G}$  matrix in the new coordinate system,  $\underline{S}$ , is given by Equation (35),

$$\underline{G} = \underline{U} \underline{G}' \underline{U}' \quad (35)$$

#### Computation of the Factored $\underline{G}$ Matrices for the 1,5-Anhydropentitol Models

In the case of 1,5-AX and 1,5-AR, the transformation from internal coordinates to symmetry coordinates reduces the  $\underline{G}$  matrix from 62 x 62 to two smaller matrices, 34 x 34 and 28 x 28, which belong to the irreducible representations A' and A'', respectively. Listings of the factored  $\underline{G}$  matrices are not included in this manuscript because of space limitations.

#### SELECTION OF A FORCE FIELD FOR THE 1,5-ANHYDRO-PENTITOL MODELS

Before the vibrational secular equation can be solved, an explicit form must be given to the force constant matrix, that is, the  $\underline{F}$  matrix in Equation (26). Unlike the  $\underline{G}$  matrix, the  $\underline{F}$  matrix is not easily derivable from experimental data, and certainly not from nonspectroscopic data. The only convenient source of information is the vibrational spectrum itself. For anything larger than a diatomic molecule, this is insufficient, except in rare cases, to allow the determination of the field, even in the quadratic approximation. This indeterminacy in the force field of molecules is one of the most vexing problems in spectroscopy today. Since the force field can only be determined from the spectrum itself, one might question the feasibility of solving the vibrational secular equation. The following comments are offered as support for the procedure to be adopted. First, it is well known that the chemical and

thermodynamic properties of bonds with similar environments are very much the same. It is reasonable, therefore, to expect that the forces resisting deformation of these bonds will be similar. The same is true for bond angles. This implies that the force constants should be transferable between similar molecules or between similar groupings in different molecules. As a result, the force constants derived from simple systems can be employed to construct the field of more complex systems. Second, errors in a force field, which reproduces to an acceptable accuracy the vibrational frequencies of a grouping in one molecule, will be relatively unimportant in frequency calculations in related systems containing the grouping, provided that both the assumed field and true field place the bulk of potential energy within the common grouping in both situations. This is because most of the vibrational motion is within the common grouping, so that the model form varies little in the different systems. Third, further improvements in the field of complicated systems can only arise from perturbation treatment of existing calculations, in which efforts are made to minimize discrepancies between actual and calculated observations.

The use of internal coordinates as a basis for potential field expressions has been justified in an earlier section. A general quadratic field will have the form

$$2V = \sum_i \sum_j f_{ij} R_i R_j \quad (36)$$

where  $R_i$  and  $R_j$  are internal coordinates and  $f_{ij}$  are the appropriate force constants

$$f_{ij} = (\partial^2 V / \partial R_i \partial R_j)_0 \quad (37)$$

For a diatomic molecule, only one quadratic force constant can be defined and no problem exists to its evaluation. For a polyatomic molecule, the number of

quadratic force constants greatly exceeds the number of vibrational frequencies. Although other sources of information exist about the vibrational modes and force constants, this information has still not allowed a unique quadratic force field to be established for any molecule with more than five atoms.

Approximations within the quadratic approximation itself are clearly unavoidable, and many have been tried. As might be expected, no single approximation emerges triumphant in all cases, but experience has shown that some types of fields have reasonable validity in certain structural situations. Therefore, the selection of an appropriate force field for the normal coordinate analyses of the 1,5-AP compounds is an important aspect of this investigation. Many of the major force field approximations are described in a text by Steele (94). Several of these approximations are briefly discussed below, and are evaluated for use in the normal coordinate computations of the 1,5-AP compounds.

#### 1. The Valence Force Field (VFF)

This approximation treats the potential energy as arising from stretching of chemical bonds and deformation of bond angles. The potential energy expression, Equation (36), only involves the diagonal elements in the force constant matrix, with the other elements being set equal to zero, that is,

$$2V = \sum_i f_{ii} R_i^2 . \quad (38)$$

Although the VFF force field has only a few force constant parameters and can be easily interpreted in a chemical sense, it is too simplified to adequately describe the vibrational dynamics of the 1,5-AP compounds.

## 2. The General Quadratic Force Field (GQFF)

In this approximation, all possible  $f_{ij}$  terms are included. As has already been pointed out, this approximation usually introduces more parameters than can be determined with the available data, and therefore, in its complete form, it is indeterminate.

Since the GQFF is rarely derivable, many fields intermediate between the VFF and GQFF have been used. In the vast majority of force field studies, the GQFF has been simplified by arbitrarily fixing many interaction terms to zero and minimizing other interaction elements at their lowest possible values. Even though the assumptions have usually been made with some physical reasoning, such as that potential interactions between nonconjugated bonds with no common nucleus may be expected to be very small, the arbitrary character of the assumptions has rendered comparative studies of the different fields extremely difficult.

A small number of clearly defined fields have been used and their validity explored. The two fields which have evoked the most interest are Mills' Hybrid Orbital Force Field (HOFF) (95) and the older and controversial Urey Bradley Force Field (UBFF) (96). Also of considerable interest, though it has been little used except by its original exponent, is Linnett's Orbital Valency Force Field (OVFF) (97).

### A. OVFF

This approximation seeks to explain differences in the deformation force constants, as derived from different symmetry classes in the valence force approximation, in terms of electronic rehybridization phenomena. However, even this modification of the VFF is far too simplified to be successful in the

mathematical treatment of the 1,5-AP compounds. On the other hand, the OVFF may be useful as a basis for logically introducing interaction constants connecting angular deformations about a central nucleus in other types of force fields.

#### B. HOFF

This force field is founded on the idea that interaction force constants are related to electronic charge movements, accompanying the nuclear distortions. The HOFF appears to be a reasonable approximation; however, it has only been used in conjunction with relatively small molecules.

#### C. UBFF

The basic Urey Bradley field treats the force field as arising from the VFF supplemented by forces between nonbonded nuclei. In the general case, the linear potential energy terms for the interbond angles and the bonds are linearly related by geometric factors to the nonbonded interaction terms. The direct consequence of this is that the independent parameters in the field reduce to those of the VFF plus the quadratic and the linear nonbonded interaction terms. If a redundancy relationship exists among the set of internal coordinates,  $R_j$ , the condition for a potential minimum now takes the form

$$\partial V / \partial R_j + k_j = 0 \quad (39)$$

where  $k_j$  is usually known as the intramolecular tension and is an additional parameter in the force field. The UBFF in its simplest form is completely inadequate for the normal coordinate analyses of the 1,5-AP compounds. In order to improve the performance, additional quadratic valence-type interaction terms must be introduced, but this detracts from the original simplicity of the model.

In addition, the UBBF elements are difficult to perceive in a chemical sense. Also, for the 1,5-AP models, this type of force field contains a large number of nonzero elements which exceeds the limit of the computer program (based on the storage capacity of the computer facility) which solves the vibrational secular equation.

#### D. Inverse Force Constants

Inverse force constants are the elements of the reciprocal force constant matrix,  $\underline{\underline{F}}^{-1}$ , sometimes referred to as the compliance matrix,  $\underline{\underline{C}}$ . Several advantages of such fields exist, the main advantage arises from the independence of a given element,  $f_{ij}^{-1}$ , to the definitions of coordinates  $\underline{k}, \underline{l} \neq \underline{i}, \underline{j}$ . Since the potential energy must be invariant to coordinate transformations, it follows that the inverse force constant elements,  $f_{ij}^{-1}$ , transform as  $R_{\underline{i}}$  and  $R_{\underline{j}}$  (for  $f_{ij}^{-1} R_{\underline{i}} R_{\underline{j}}$  to be invariant). This requires that if a new set of internal coordinates is chosen leaving a given coordinate,  $R_{\underline{k}}$ , unaltered, then  $f_{kk}^{-1}$  will be identical in the two systems. This invariance means that the transference of inverse force constants may be done with less concern for the compatibility of coordinate systems assumed in the two molecular models. The inverse force matrix and its advantages are described in more detail by Decius (98).

The concept of inverse force constants is attractive because the elements of the compliance matrix are unique, which is not the case for the  $\underline{\underline{F}}$  matrix elements. However, the secular determinant, analogous to Equation (26), is now

$$\det (\underline{\underline{F}}^{-1} - \lambda^{-1} \underline{\underline{G}}) = 0 \quad (40)$$

for the case in which there are redundant internal coordinates, since  $\underline{\underline{G}}^{-1}$  cannot be determined. This means that new computer programs and computational methods must be developed to construct and solve this new secular determinant.



Furthermore, a least squares perturbation technique must be developed to refine the compliance parameters to minimize the differences existing between the calculated and observed frequencies. In addition, it is very difficult to secure the necessary initial compliance parameter data from the literature because workers in vibrational spectroscopy have been slow to adopt the inverse  $\underline{F}$  matrix method. For these reasons primarily, the  $\underline{F}^{-1}$  method was not selected for the investigation of the 1,5-AP vibrational spectra.

#### E. Simplified Valence Quadratic Force Field (SVQFF)

The force field finally selected for this study shall be referred to as a "Simplified Valence Quadratic Force Field" (SVQFF) throughout the remainder of this text. This empirical force field is an extension of the fields developed by Schachtschneider and Snyder (54), Snyder and Zerbi (56), Pickett and Strauss (57), and Vasko (99) in their normal coordinate calculations. The SVQFF is derived from the GQFF by assigning negligible interaction force constants a zero value and grouping similar force constants by assigning one common numerical value. Such assumptions greatly reduce the number of independent force constant parameters necessary to describe the force field of large, complex molecules. One should note that these force constant assignments are not completely arbitrary, but are based on past experimental data and experience.

For small molecules, especially those with a high order of symmetry, the diagonal and many of the interaction force constants can be determined from the vibrational spectrum. Assuming the validity of force constant transferability, many of these force constants are employed in the normal coordinate calculations for slightly larger, more complex molecules to determine additional force constant values, otherwise indeterminable, from the spectral data. When the diagonal and interaction force constants corresponding to particular atomic

groupings are compared for a series of related compounds, it is often observed that the numerical values are very close to one another if the chemical environments of the atomic groupings are similar, i.e., the force constants are indeed transferable. This fact is especially true for the diagonal force constants. Such comparisons also permit one to determine which force constants may be equated and which may be set equal to zero without significantly altering the calculated frequencies. Thus, one assembles the SVQFF from small to more complicated molecules, building on previous data. The result, although quite empirical, is a generally descriptive force field that satisfactorily predicts the observed vibrational frequencies and corresponding vibrational motion of the molecule. Generally, the number of independent force constant parameters required to specify adequately the SVQFF for large, complex molecules is approximately equal to the number of vibrational degrees of freedom. In addition, Schachtschneider and Snyder (54) have developed a method whereby the same set of force constant parameters may be refined for several similar molecules simultaneously. This greatly increases the ratio of experimental data points (measured spectral band frequencies) to variables (force constant parameters).

Schachtschneider and Snyder (54,55) have developed a SVQFF to describe the vibrational dynamics of a number of n-paraffins and saturated hydrocarbons. Snyder and Zerbi (56) started with this force field and from it developed a descriptive SVQFF for tetrahydropyran and the aliphatic ethers. Vasko (99) has demonstrated the generality and applicability of the SVQFF. He employed the SVQFF developed by Snyder and Zerbi for the aliphatic ethers and tetrahydropyran in the normal coordinate analysis of  $\alpha$ -D-glucose and estimated the values of the new diagonal force constants resulting from the addition of hydroxyl groups to the pyranose ring. However, he neglected the new interaction terms introduced by the hydroxyl groups, for the most part, and did not attempt to refine the

force field to minimize the differences between the calculated and observed frequencies. (Furthermore, the validity of the results of the normal coordinate analysis of  $\alpha$ -D-glucose also suffers from the fact that Vasko did not assign all the observed infrared and Raman spectral bands, only those in agreement with the calculations.) Yet, under the circumstances, he was able to predict the experimental frequencies for  $\alpha$ -D-glucose remarkably well.

### Computation of the $\underline{F}$ Matrix

For reasons of convenience, which will become apparent when the programs that solve the secular equation are discussed, the  $\underline{F}$  matrix is not evaluated directly. Rather, the constraint matrix,  $\underline{Z}$ , [which is the transformation from an independent set of force constant parameters to the force field in Equation (26)] is computed. The transformation,  $\underline{Z}$ , is defined by the expression

$$F_{ij} = \sum_k Z_{ijk} \phi_k \quad (41)$$

where the  $\phi_k$  are a set of independent force constants (to be called force constant parameters in this text), and the  $F_{ij}$  are the elements of the  $\underline{F}$  matrix. The computer program UBZM will construct the  $\underline{Z}$  matrix for a UBFF or a SVQFF. The computer program UBZM is discussed in Appendix III. Also included in this appendix are the tables of the  $\underline{Z}$  matrices for the 1,5-AP models. A program listing, user instructions, and flow diagram for UBZM may be found in Appendix V.

### Factoring the $\underline{F}$ Matrix

The  $\underline{Z}$  matrix and, therefore, the  $\underline{F}$  matrix may be factored into a number of smaller matrices by transforming from internal coordinates to symmetry coordinates in a manner similar to the factoring of the  $\underline{G}$  matrix discussed earlier in this text. Again, the number of smaller matrices is equal to the number of irreducible representations in the molecular point group character table.

146 (A') and 116 (A'') elements. The factored  $\underline{Z}$  matrices are not included in this text because of space limitations.

SVQFF Force Constant Parameters for the 1,5-Anhydropentitol Models

The force constant parameters specified in the  $\underline{Z}$  matrices are the elements which comprise the 1,5-AP SVQFF discussed earlier. The initial values for many of these parameters were taken from the papers by Snyder and Zerbi (56) and Vasko (99). A total of 56 parameters (actually, only 55 parameters because one of the parameters is a dummy) were required to specify the  $\underline{F}$  matrices for the 1,5-AP models. The constraint matrices,  $\underline{Z}$ , are presented in Tables XLIII, XLIV, and XLV in Appendix III. The force constant parameters are listed in Table XX along with the initial values, values after nonlinear least squares refinement, and the standard errors.

SOLUTION OF THE VIBRATIONAL SECULAR EQUATION AND LEAST SQUARES REFINEMENT OF THE FORCE CONSTANTS

Solution of the Secular Equation by the Method of Successive Orthogonalization of  $\underline{GF}$  Followed by Jacobi Diagonalization

The  $\underline{F}$  and  $\underline{G}$  matrices for the 1,5-AP models have now been computed. The next step is to solve the vibrational secular determinantal equation (26). There are several methods which are applicable to computers for solving the secular equation [for example, see Wilson, et al. (68)]. The method adopted for all such computer programs employed in this investigation is that of successive orthogonalization of the product  $\underline{GF}$  followed by Jacobi diagonalization.

In this method, the transformation to a new set of coordinates in which  $\underline{G}$  is a unit matrix is computed

$$\underline{\bar{G}} = \underline{A} \underline{G} \underline{A}' = (\underline{G}^{(m-1)}) \quad (46)$$

TABLE XX

SVQFF FORCE CONSTANT PARAMETERS FOR THE  
1,5-ANHYDRO-PENTITOL MODELS

Force Constant Parameter No.	Group	Coordinates Involved	Atoms Common to Interacting Coordinates	Initial Value, $\Phi_i$	Final Value, $\Phi_i$	Error <sup>a</sup> $\sigma(\Phi_i)$
Stretch						
1	C-O-C	C-O		5.090 <sup>b,c</sup>	5.067	0.071
2	C-OH	C-O		5.090 <sup>c</sup>	5.103	0.073
3	H-C-O-C	C-H		4.626 <sup>c</sup>	4.597	0.045
4	H-C-OH	C-H		4.688 <sup>c</sup>	4.589	0.062
5	C-C	C-C		4.261 <sup>c</sup>	4.247	0.071
6	O-H	O-H		6.440 <sup>d</sup>	6.283	0.034
Stretch-Stretch						
7	C-C-O-C	C-C, C-O	C	0.101 <sup>b,c</sup>	0.107	0.075
	C-C-OH	C-C, C-O	C			
	C-C-C	C-C, C-C	C			
8	C-O-C	C-O, C-O	O	0.288 <sup>c</sup>	0.324	0.072
9	H-C-O-C	C-O, C-H	C	0.000 <sup>e</sup>	0.016	0.071
	H-C-OH	C-O, C-H	C			
10	C-C(H)-O-C	C-C, C-H	C	0.000 <sup>e</sup>	-0.027	0.071
	C-C(H)-OH	C-C, C-H	C			
11	H-C(H)-O-C	C-H, C-H	C	-0.046 <sup>c</sup>	-0.010	0.034
12	C-O-H	C-O, O-H	O	0.000 <sup>e</sup>	0.005	0.071
Bend						
13	H-C-O-C	<HCO		0.901 <sup>c,f</sup>	0.926	0.066
14	C-C-O-C	<CCO		1.182 <sup>c</sup>	1.169	0.071
15	C-C(H)-O-C	<HCC		0.752 <sup>c</sup>	0.792	0.066
16	H-C(H)-O-C	<HCH		0.471 <sup>c</sup>	0.452	0.062
17	C-C(H)-OH	<HCC		0.718 <sup>c</sup>	0.725	0.064
18	C-C-OH	<CCO		1.182 <sup>c</sup>	1.180	0.071
19	C-O-H	<COH		0.760 <sup>d</sup>	0.734	0.069
20	C-C-C	<CCC		1.071 <sup>c</sup>	1.056	0.071
21	H-C-OH	<HCO		0.961 <sup>c</sup>	0.963	0.067
22	C-O-C	<COC		1.313 <sup>c</sup>	1.318	0.071

See end of table for footnote.

TABLE XX (Continued)

SVQFF FORCE CONSTANT PARAMETERS FOR THE  
1,5-ANHYDRO-PENTITOL MODELS

Force Constant Parameter No.	Group	Coordinates Involved	Atoms Common to Interacting Coordinates	Initial	Final	Error <sup>a</sup>
				Value, $\Phi_i$	Value, $\Phi_i$	$\sigma(\Phi_i)$
Stretch-Bend						
23	H-C-O-C	C-O, <HCO	CO	0.387 <sup>c, g</sup>	0.388	0.072
	H-C-OH	C-O, <HCO	CO			
24	C-C-O-C	C-O, <CCO	CO	0.618 <sup>c</sup>	0.664	0.070
	C-C-OH	C-O, <CCO	CO			
25	Dummy parameter, not specified in $Z$ matrices.					
26	C-O-C	C-O, <COC	CO	0.483 <sup>c</sup>	0.487	0.071
27	C-C-O-C	C-C, <CCO	CC	0.403 <sup>c</sup>	0.381	0.074
	C-C-OH	C-C, <CCO	CC			
28	C-C(H)-O-C	C-C, <HCC	CC	0.478 <sup>c</sup>	0.481	0.064
	C-C(H)-OH	C-C, <HCC	CC			
29	C-C-C	C-C, <CCC	CC	0.417 <sup>c</sup>	0.485	0.071
30	H-C-O-C	C-H, <HCO	CH	0.000 <sup>e</sup>	-0.167	0.063
	H-C(H)-O-C	C-H, <HCH	CH			
	C-C(H)-OH	C-H, <HCC	CH			
	C-C(H)-OH	C-H, <HCO	CH			
31	C-O-H	C-O, <COH	CO	0.387 <sup>d</sup>	0.357	0.070
32	C-O-H	O-H, <COH	OH	0.000 <sup>e</sup>	0.006	0.071
Bend-Bend						
33	C-C(H)-O-C	<HCO, <HCC	CH	0.115 <sup>c, f</sup>	0.135	0.042
	C-C(H)-OH	<HCO, <HCC	CH			
34	C-C(H)-O-C	<HCO, <CCO	CO	-0.031 <sup>c</sup>	-0.094	0.070
	C-C(H)-O-C	<CCO, <HCC	CC			
	C-C(H)-OH	<HCC, <CCO	CC			
	C-C(H)-C	<HCC, <CCC	CC			
	C-C-C-H	<HCC, <CCC	CC			
	C-C(H)-OH	<CCO, <HCO	CO			
35	H-C(H)-O-C	<HCO, <HCO	CO	-0.005 <sup>c</sup>	-0.027	0.063

See end of table for footnote.

TABLE XX (Continued)

SVQFF FORCE CONSTANT PARAMETERS FOR THE  
1,5-ANHYDRO-PENTITOL MODELS

Force Constant Parameter No.	Group	Coordinates Involved	Atoms Common to Interacting Coordinates	Initial Value, $\phi_i$	Final Value, $\phi_i$	Error <sup>a</sup> $\sigma(\phi_i)$
Bend-Bend (Continued)						
36	H-C(H)-C	<HCC,<HCC	CC	0.105 <sup>c</sup>	0.066	0.068
37	C-C(H)-C	<HCC,<HCC	CH	0.012 <sup>c</sup>	-0.001	0.062
38	C-C(OH)-C	<CCO,<CCO	CO	-0.041 <sup>c</sup>	0.052	0.071
	C-C(OH)-C	<CCO,<CCC	CC			
39	H-C-O-C	<HCO,<COC	(H)C-O(C) trans	-0.112 <sup>c</sup>	-0.096	0.071
40	H-C-O-C	<HCO,<COC	(H)C-O(C) gauche	0.004 <sup>c</sup>	-0.037	0.072
41	C-C-O-C	<CCO,<COC	(C)C-O(C) gauche	0.011 <sup>c</sup>	-0.024	0.073
	HO-C-C-O-C	<CCO,<CCO	(O)C-C(O) gauche			
	C-C-C-O-C	<CCO,<CCC	(C)C-C(O) gauche			
	C-C-C-OH	<CCC,<CCO	(C)C-C(O) gauche			
	HO-C-C-OH	<CCO,<CCO	(O)C-C(O) gauche			
	C-C-C-C	<CCC,<CCC	(C)C-C(C) gauche			
42	HO-C-C-O-C	<CCO,<CCO	(O)C-C(O) trans	-0.011 <sup>c</sup>	-0.014	0.072
	C-C-O-C	<CCO,<COC	(C)C-O(C) trans			
	HO-C-C-OH	<CCO,<CCO	(O)C-C(O) trans			
	C-C-C-C	<CCC,<CCC	(C)C-C(C) trans			
	C-C-C-OH	<CCC,<CCO	(C)C-C(O) trans			
43	H-C-C-O-C	<CCO,<HCC	(H)C-C(O) gauche	-0.113 <sup>c</sup>	-0.238	0.070
	H-C-C-OH	<CCO,<HCC	(H)C-C(O) gauche			
44	H-C-C-O-C	<CCO,<HCC	(H)C-C(O) trans	0.028 <sup>c</sup>	0.037	0.071
	H-C-C-OH	<CCO,<HCC	(H)C-C(O) trans			

See end of table for footnote.

TABLE XX (Continued)

SVQFF FORCE CONSTANT PARAMETERS FOR THE  
1,5-ANHYDRO-PENTITOL MODELS

Force Constant Parameter No.	Group	Coordinates Involved	Atoms Common to Interacting Coordinates	Initial Value, $\Phi_i$	Final Value, $\Phi_i$	Error <sup>a</sup> $\sigma(\Phi_i)$
Bend-Bend (Continued)						
45	H-C-O-H	<COH, <HCO	(H)O-C(H) gauche	0.000 <sup>e</sup>	0.000 <sup>h</sup>	0.000
46	H-C-C-H	<HCC, <CCH	(H <sub>a</sub> )C-C(H <sub>b</sub> ) gauche	0.004 <sup>c</sup>	-0.002	0.064
47	H-C-C-H	<HCC, <CCH	(H <sub>a</sub> )C-C(H <sub>b</sub> ) gauche	0.121 <sup>c</sup>	0.049	0.071
48	H-C-C-C	<CCC, <CCH	(C)C-C(H) trans	0.049 <sup>c</sup>	-0.047	0.074
49	H-C-C-C	<CCC, <CCH	(C)C-C(H) trans	-0.052	-0.106	0.071
50	C-C-O-H	<CCO, <COH	(C)C-O(H) gauche	0.000 <sup>e</sup>	0.010	0.070
51	H-C-O-H	<HOC, <OCH	(H)O-C(H) gauche trans	0.000 <sup>e</sup>	0.016	0.070
Torsion						
52	C-C	C-C		0.024 <sup>c, g</sup>	0.027	0.047
53	C-OH	C-O		0.026 <sup>c</sup>	0.028	0.055
54	C-O-C	C-O		0.026 <sup>c</sup>	0.012	0.073
Additional Bend-Bend						
55	H-C(H)-O-C	<HCO, <HCH	CH	0.000 <sup>e</sup>	-0.026	0.036
56	H-C(H)-C	<HCC, <HCH	CH	0.000 <sup>e</sup>	0.025	0.061

<sup>a</sup> $\sigma(\Phi_i)$  is the standard error in  $\Phi_i$  estimated from the standard error in the frequency parameters and the  $\bar{H}$  matrix in the nonlinear refinement.

<sup>b</sup>The units for the force constants in this group are m dyn./A.

<sup>c</sup>The initial force constant values were taken from Snyder and Zerbi (56).

<sup>d</sup>The initial force constant values were taken from Vasko (99).

<sup>e</sup>The force constant was assigned an initial value of zero because a value was not reported in the literature.

<sup>f</sup>The units for the force constants in this group are m dyn./A./rad<sup>2</sup>.

<sup>g</sup>The units for the force constants in this group are m dyn./rad.

<sup>h</sup>The force constant was not included in the refinement because it was not specified in any of the constraint matrices since all the H-C-O-H torsional coordinates were assumed to be trans in the definition of the 1,5-anhydropentitol models.



where  $(\underline{G}^{(m-1)})$  is a diagonal matrix

$$\underline{E} = (\underline{G}^{(m-1)})^{-\frac{1}{2}} (\underline{G}^{(m-1)}) (\underline{G}^{(m-1)})^{-\frac{1}{2}} = (\underline{G}^{(m-1)})^{-\frac{1}{2}} \underline{AGA}' (\underline{G}^{(m-1)})^{-\frac{1}{2}} \quad (47)^{13}$$

and then applied to the  $\underline{F}$  matrix.

$$\underline{H} = (\underline{G}^{(m-1)})^{\frac{1}{2}} (\underline{A}^{-1})' \underline{FA}^{-1} (\underline{G}^{(m-1)})^{\frac{1}{2}} \quad (48)$$

The new  $\underline{F}$  matrix,  $\underline{H}$ , is symmetric and may be diagonalized by the Jacobi method as cited by Acton (100).

$$\underline{HW} = \underline{W}\underline{\Lambda} \quad (49)$$

where  $\underline{\Lambda}$  is a diagonal matrix of the eigenvalues,  $\lambda$ . Although the transformation,  $\underline{A}$ , was first applied to  $\underline{G}$  and then to  $\underline{F}$ , the result is the same as applying the transformation to the product  $\underline{GF}$  which appears in Equation (26). That is,

$$\begin{aligned} (\underline{G}^{(m-1)})^{-\frac{1}{2}} \underline{AGFA}' (\underline{G}^{(m-1)})^{\frac{1}{2}} &= \{ (\underline{G}^{(m-1)})^{-\frac{1}{2}} \underline{AGA}' (\underline{G}^{(m-1)})^{-\frac{1}{2}} (\underline{G}^{(m-1)})^{\frac{1}{2}} \\ (\underline{A}^{-1})' \underline{FA}' (\underline{G}^{(m-1)})^{\frac{1}{2}} \} &= (\underline{G}^{(m-1)})^{\frac{1}{2}} (\underline{A}^{-1})' \underline{FA}^{-1} (\underline{G}^{(m-1)})^{\frac{1}{2}} = \underline{H} \end{aligned} \quad (50)$$

using Equation (47) and the fact that  $\underline{A}$  is orthogonal. The details of the computational method follow.

The elements of  $\underline{G}$  may be written as

$$G_{ij} = \sum_{k=1}^{3N} m_k^{-\frac{1}{2}} B_{ik} m_k^{-\frac{1}{2}} B_{jk} \quad (51)$$

<sup>13</sup> In this equation  $(\underline{G}^{(m-1)})^{-\frac{1}{2}}$  is defined to be  $[(\underline{G}^{(m-1)})^{\frac{1}{2}}]^{-1}$ .

which corresponds to the matrix expression for  $G$  given in Equation (32). A row vector,  $\underline{D}_i$ , may be defined with  $3N$  elements,  $m_k^{-1} B_{ik}$ , and Equation (51) may then be written as

$$G_{ij} = D_i D_j' \quad (52)$$

A new set of vectors,  $\bar{D}_i$ , are then defined as linear combinations of the  $\underline{D}_i$  such that the new vectors are mutually orthogonal, that is,

$$\bar{D}_i \bar{D}_j' = 0 \quad (53)$$

for  $i \neq j$ . The  $\underline{G}$  matrix in the new coordinates is diagonal, since

$$\bar{G}_{ij} = \bar{D}_i \bar{D}_j' = \begin{cases} 0 & i \neq j \\ \bar{D}_i \bar{D}_i' & i = j \end{cases} \quad (54)$$

The new vectors are obtained by the Schmidt orthogonalization procedure and are defined by the equations

$$\begin{aligned} \bar{D}_1 &= a_{11} D_1 \\ \bar{D}_2 &= a_{22} D_2 + a_{21} \bar{D}_1 \\ \bar{D}_3 &= a_{33} D_3 + a_{32} \bar{D}_2 + a_{31} \bar{D}_1 \\ &\text{etc.} \end{aligned} \quad (55)$$

where  $a_{ii} = 1$  for  $i = j$  and  $a_{ij} = -\bar{D}_j D_i' / (\bar{D}_j \bar{D}_j')$  for  $i \neq j$ .

The coordinate transformation can be written as

$$\bar{R} = \underline{A} R \quad (56)$$

where the matrix  $\underline{A}$  is triangular and the elements given by

$$A_{ij} = a_{ik} A_{kj} \quad (57)$$

for  $\underline{i} > \underline{j}$ . The coefficients  $a_{\underline{i}\underline{k}}$  may be computed by the following procedure. First,  $G_{\underline{i}\underline{i}}G_{\underline{1}\underline{j}}/G_{\underline{1}\underline{1}}$  is subtracted from each element of  $\underline{G}$  except  $G_{\underline{1}\underline{1}}$ , and the resulting matrix is designated as  $\underline{G}^{(1)}$ . The matrix  $\underline{G}^{(1)}$  is symmetric and the first row vanishes, so the operation need only be carried out for the rows two through  $\underline{N}$  and for  $G_{\underline{i}\underline{j}}^{(1)}$ ,  $\underline{i} \leq \underline{j}$ .

It will now be shown that

$$\bar{D}_2 \bar{D}'_2 = G_{22}^{(1)} \quad (58)$$

and that

$$\bar{D}_2 D'_j = G_{2j}^{(1)} \quad (59)$$

for  $\underline{j} > 2$ . By Equation (55), one may see that

$$\begin{aligned} \bar{D}_2 \bar{D}'_2 &= \bar{D}_2 (D'_2 + a_{21} \bar{D}'_1) = \bar{D}_2 D'_2 \\ &= (D_2 + a_{21} D_1) D'_2 = G_{22} + a_{21} G_{12} \\ &= G_{22} - G_{12} G_{12} / G_{11} = G_{22}^{(1)}. \end{aligned} \quad (60)$$

Similarly, we have

$$\bar{D}_2 D'_j = (D_2 + a_{21} D_1) D'_j = G_{2j} - G_{12} G_{1j} / G_{11} = G_{2j}^{(1)}. \quad (61)$$

A similar process may be carried out on  $\underline{G}^{(1)}$ , defining

$$G_{ij}^{(2)} = G_{ij}^{(1)} - G_{21}^{(1)} G_{2j}^{(1)} / G_{22}^{(1)} \quad (62)$$

for  $\underline{i} > 2$  and  $\underline{j} > \underline{i}$ , and it can be shown that

$$\bar{D}_3 \bar{D}'_3 = G_{33}^{(2)}$$

and

$$\bar{D}_3 D'_j = G_{3j}^{(2)}$$

for  $\underline{j} > 3$ .

Successive applications of this process will lead to a diagonal matrix,  $\underline{G}^{(m-1)}$ , whose elements are  $\underline{G}_{11}^{(0)}$ ,  $\underline{G}_{22}^{(1)}$ ,  $\dots$ , where  $\underline{G}^{(0)}$  is the original  $\underline{G}$  matrix. In general,

$$G_{ij}^{(k)} = G_{ij}^{(k-1)} - G_{ki}^{(k-1)}G_{kj}^{(k-1)}/G_{kk}^{(k-1)} \quad (64)$$

for  $\underline{k} = 1$  to  $\underline{m}-1$  and  $\underline{i} > \underline{k}$ ;  $\underline{j} \geq \underline{i}$ . Since

$$\bar{D}_i D'_j = G_{ij}^{(i-1)}$$

and

$$\bar{D}_i \bar{D}'_i = G_{ii}^{(i-1)}. \quad (65)$$

The coefficients,  $\underline{a}_{ji}$ , are given by

$$a_{ji} = -\bar{D}_i D'_j / (\bar{D}_i \bar{D}'_i) = G_{ij}^{(i-1)} / G_{ii}^{(i-1)}. \quad (66)$$

The corresponding  $\underline{F}$  matrix transformation is given by

$$\underline{F} = (\underline{A}^{-1})' \underline{F} \underline{A}^{-1}. \quad (67)$$

So, one needs to compute  $\underline{A}^{-1}$ . From Equation (55), one may see that, since

$\underline{a}_{ii} = 1$ , the inverse transformation is

$$\begin{aligned} D_1 &= \bar{D}_1 \\ D_2 &= \bar{D}_2 - a_{21} \bar{D}_1 \\ D_3 &= \bar{D}_3 - a_{32} \bar{D}_2 - a_{31} \bar{D}_1 \\ &\dots \\ &\text{etc.} \end{aligned} \quad (68)$$

Therefore, the matrix  $\underline{A}^{-1}$  has the form

$$\underline{\underline{A}}^{-1} = \begin{bmatrix} 1 & 0 & 0 & 0 & \dots\dots \\ G_{12}/G_{11} & 1 & 0 & 0 & \dots\dots \\ G_{13}/G_{11} & G_{23}^{(1)}/G_{22}^{(1)} & 1 & 0 & \dots\dots \\ G_{14}/G_{11} & G_{24}^{(1)}/G_{22}^{(1)} & G_{34}^{(2)}/G_{33}^{(2)} & 1 & \dots\dots \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & 1 \end{bmatrix} \quad (69)$$

The matrix  $\underline{\underline{G}}^{(m-1)}$  is diagonal, but not a unit matrix. It is made a unit matrix by normalizing the vectors  $\underline{\underline{D}}_t$  to unity.

$$E_i = \underline{\underline{D}}_i / (\underline{\underline{D}}_i \underline{\underline{D}}_i')^{1/2}. \quad (70)$$

This is equivalent to a coordinate transformation  $(\underline{\underline{G}}^{(m-1)})^{-1/2}$ , that is,

$$\underline{\underline{E}} = (\underline{\underline{G}}^{(m-1)})^{-1/2} (\underline{\underline{G}}^{(m-1)}) (\underline{\underline{G}}^{(m-1)})^{-1/2}. \quad (71)$$

The corresponding  $\underline{\underline{F}}$  matrix transformation is

$$\underline{\underline{H}} = (\underline{\underline{G}}^{(m-1)})^{1/2} \underline{\underline{F}} (\underline{\underline{G}}^{(m-1)})^{1/2}. \quad (72)$$

The matrix  $\underline{\underline{H}}$  is symmetric and can be diagonalized by an orthogonal matrix  $\underline{\underline{W}}$ , that is,

$$\underline{\underline{H}} \underline{\underline{W}} = \underline{\underline{W}} \underline{\underline{\Lambda}}. \quad (73)$$

Therefore, the transformations which diagonalize the kinetic and potential energy matrices are

$$\underline{\underline{W}}' (\underline{\underline{G}}^{(m-1)})^{-1/2} \underline{\underline{A}} \underline{\underline{G}} (\underline{\underline{G}}^{(m-1)})^{-1/2} \underline{\underline{W}} = \underline{\underline{E}} \quad (74)$$

and

$$\underline{\underline{W}}' (\underline{\underline{G}}^{(m-1)})^{1/2} (\underline{\underline{A}}^{-1})' \underline{\underline{F}} \underline{\underline{A}}^{-1} (\underline{\underline{G}}^{(m-1)})^{1/2} \underline{\underline{W}} = \underline{\underline{\Lambda}} \quad (75)$$

and 
$$\underline{L} = \underline{A}^{-1} (\underline{G}^{(m-1)})^{\frac{1}{2}} \underline{W} \quad (76)$$

$$\underline{L}^{-1} = \underline{W}' (\underline{G}^{(m-1)})^{-\frac{1}{2}} \underline{A} \quad (77)$$

If redundant coordinates are used, the same procedure applies. If, for example, the  $\underline{i}$ th coordinate is a member of a redundant set and the other members of the set have lower numbers, the  $\underline{i}$ th row of the  $\underline{G}^{(i-1)}$  matrix vanishes,

$$G_{ii}^{(i-1)} = 0 \quad (78)$$

and 
$$G_{ij}^{(i-1)} = 0 \quad (79)$$

for  $j > i$ . This would seem to lead to difficulties in computing

$$a_{ij} = G_{ij}^{(i-1)} / G_{ii}^{(i-1)} \quad (80)$$

and 
$$G_{kj}^{(i)} = G_{kj}^{(i)} - G_{ik}^{(i-1)} G_{ij}^{(i-1)} / G_{ii}^{(i-1)}. \quad (81)$$

However, in the computer programs the  $\underline{G}$  matrix is entered with an accuracy of about six decimal places and one finds that

$$G_{ij}^{(i-1)} \sim 10^{-6}$$

$$G_{ik}^{(i-1)} \sim 10^{-6} \quad (82)$$

and 
$$G_{ii}^{(i-1)} \sim 10^{-6}$$

and one can compute  $\underline{A}^{-1}$  even for redundant coordinates. Actually, the  $\underline{i}$ th row of  $\underline{A}$  gives the redundancy accurate to about six significant figures.

The inverse normal coordinate transformation is defined by setting

$$(G_{ii}^{(m-1)})^{-\frac{1}{2}} = 0 \quad (83)$$

for  $G_{ii}^{(m-1)} < 0.00001$ . This is possible because the momenta,  $\bar{P}_i$ , corresponds to a null coordinate,  $\bar{R}_i$ , and does not contribute to the kinetic or potential energy. The matrices  $\underline{L}$  and  $\underline{L}^{-1}$  are then rectangular and

$$\underline{L}^{-1} \underline{L} = \underline{E}_{3N-6} \quad (84)$$

$$\underline{L}' (\underline{L}^{-1})' = \underline{E}_{3N-6}$$

but

$$\underline{L} \underline{L}^{-1} \neq \underline{E}$$

and

$$(\underline{L}^{-1})' \underline{L}' \neq \underline{E}.$$

The matrix  $\underline{H}$  is diagonalized by the Jacobi method (100) to yield the eigenvalue matrix,  $\underline{\Lambda}$ , and the transformation matrix,  $\underline{W}$ . The transformation,  $\underline{L}$ , from internal coordinates to normal coordinates is then computed from the matrix  $\underline{W}$  by Equation (76).

#### Jacobi Diagonalization

Schachtschneider (89) considered three methods of computing the eigenvalues and eigenvectors of the real symmetric matrix,  $\underline{H}$ , by diagonalization; namely, the Jacobi method, the Givens method, and the Householder method. Although the Jacobi method is considered to be inefficient and slower than the other two methods, the eigenvectors resulting from this method have been shown to be more accurate (104). Also, the Jacobi method is less subject to catastrophic errors for degenerate and zero roots which are common in the vibrational problem. The Jacobi method of matrix diagonalization is discussed in several texts, for example, Schachtschneider (89), Greenstadt (102), and Froberg (103).

The Jacobi method is based on the following theorem. If  $\underline{H}$  is symmetric, there exists an orthogonal matrix,  $\underline{S}$ , such that  $\underline{S}' \underline{H} \underline{S}$  is a diagonal matrix whose diagonal elements are the characteristic roots of  $\underline{H}$ , that is,  $\underline{S}' \underline{H} \underline{S} = \underline{\Lambda}$ .





Furthermore,  $\underline{S}$  satisfies the orthogonality requirement as

$$\underline{S}'\underline{S} = \underline{E} = \underline{S}\underline{S}' \quad (89)$$

and the columns of  $\underline{S}$  turn out to be the eigenvectors,  $\underline{W}_i$ , corresponding to the eigenvalues,  $\lambda_i$ .

### Force Constant Refinement

The method of successive orthogonalization followed by diagonalization just discussed in the last sections provides the procedure for solving the following problem: given the force constants and the  $\underline{G}$  matrix, find the vibrational frequencies and normal coordinates. However, the problem posed in the normal coordinate calculations in this investigation is: given the observed vibrational frequencies and  $\underline{G}$  matrix, calculate the force constants and normal coordinates. The solution of this problem results in several difficulties. First, the number of observed frequencies is almost always smaller than the number of force constants in the general harmonic force field (GQFF). Second, the observed frequencies are anharmonic. Finally, the expansion and solution of the secular equation for the force constants is an extremely difficult procedure even with a digital computer. The first two problems are fundamental and require additional data or some approximations. The last difficulty is computational and can be overcome by using an iterative method in which approximate force constants are refined to give the "best" fit to the observed data.

For certain small molecules or molecules with a high degree of symmetry, the first difficulty can be overcome by using frequencies from isotopically substituted molecules, and by augmenting the frequency data with Coriolis coefficients, centrifugal stretching constants, mean amplitudes of vibration, or

vibrational intensities. In some cases, it is also possible to measure or estimate the anharmonic corrections to the observed frequencies. For most molecules, however, the data are far short of the number of force constants in the general harmonic force field, and in order to proceed with the calculation of force constants, we must make some approximations. That is, we must assume that certain force constants can be neglected; assume some model such as the UBFF, VFF, or SVQFF; and assume that the force constants can be transferred between related molecules. It is essential that the number of force constants be restricted so that it is less than or equal to the number of observed data. In most cases, we ignore the anharmonicity problem.

Because of the computational difficulties, it is desirable to have some iterative procedure by which a set of approximate force constants can be refined to give the "best" fit to the observed frequencies. Following are the discussions of two iterative refinement techniques that were employed in this investigation; one, a linear least squares perturbation method and the other, a nonlinear least squares method. The linear least squares technique failed to converge in the normal coordinate analyses of the 1,5-AP compounds and was replaced by the nonlinear technique in this investigation.

#### Linear Least Squares Refinement Method

The linear least squares refinement technique is based on a method by King (101). The relationship between the eigenvalues,  $\lambda_i$ , and the force constants,  $F_{jk}$ , is expanded in a Taylor series.

$$\Delta\lambda_i = \sum_j (\partial\lambda_i/\partial F_{jk})\Delta F_{jk} + \frac{1}{2} \sum_{jk} (\partial^2\lambda_i/\partial F_{jk}\partial F_{lm})\Delta F_{jk}\Delta F_{lm} + \dots \quad (90)$$

Only the first term in the expansion will be considered (i.e., linear refinement). Suppose one is given an initial  $\underline{F}$  matrix, and one solves the secular equation,

$$\underline{G} \underline{F} \underline{L} = \underline{L} \underline{\Lambda} \quad (91)$$

If one assumes  $\underline{L}_o^i$  to be the  $i$ th column of the  $\underline{L}$  matrix, one can write

$$\underline{G} \underline{F} \underline{L}_o^i = \underline{\Lambda}_o^i \underline{L}_o^i \quad (92)$$

Let  $\underline{\Delta F}$  be a change in the  $\underline{F}$  matrix, and let  $\underline{L}^i$  be the  $i$ th column of the new  $\underline{L}$  matrix. One can write

$$\underline{L}^i = \underline{L}_o^i + \sum_j \delta_{ij} \underline{L}_o^j \quad (93)$$

and the secular equation for the new  $\underline{F}$  matrix is

$$\underline{G}(\underline{F}_o + \underline{\Delta F})(\underline{L}_o^i + \sum_j \delta_{ij} \underline{L}_o^j) = (\lambda_o^i + \Delta \lambda_i)(\underline{L}_o^i + \sum_j \delta_{ij} \underline{L}_o^j) \quad (94)$$

Expanding the above expression, one obtains

$$\begin{aligned} \underline{G} \underline{F}_o \underline{L}_o^i + \underline{G} \underline{\Delta F} \underline{L}_o^i + \sum_j \delta_{ij} \underline{G} \underline{F}_o \underline{L}_o^j + \sum_j \delta_{ij} \underline{G} \underline{\Delta F} \underline{L}_o^j \\ \lambda_o^i \underline{L}_o^i + \Delta \lambda_i \underline{L}_o^i + \lambda_o^i \sum_j \delta_{ij} \underline{L}_o^j + \Delta \lambda_i \sum_j \delta_{ij} \underline{L}_o^j \end{aligned} \quad (95)$$

Using Equation (92) and rearranging, one has

$$\begin{aligned} \underline{G} \underline{\Delta F} \underline{L}_o^i + \sum_j \delta_{ij} \underline{G} \underline{\Delta F} \underline{L}_o^j = \sum_j \delta_{ij} (\lambda_o^i - \lambda_o^j) \underline{L}_o^j + \Delta \lambda_i \underline{L}_o^i \\ + \Delta \lambda_i \sum_j \delta_{ij} \underline{L}_o^j \end{aligned} \quad (96)$$

From the relation

$$\underline{L} \underline{L}' = \underline{G} \quad (97)$$

it follows that

$$(L_o^i)' = (L_o^{-1})_i G \quad (98)$$

where  $(L_o^{-1})_i$  is the  $i$ th row of  $L_o^{-1}$ . Equation (96) is now multiplied on the left by  $(L_o^{-1})_i$  to obtain

$$(L_o^i)' \Delta F L_o^i + \sum_j \delta_{ij} (L_o^i)' \Delta F (L_o^j) = \Delta \lambda_i + \delta_{ii} \Delta \lambda_i \quad (99)$$

This equation is exact, but not very useful since the new coefficients  $\delta_{ij}$  are functions of  $\Delta F$ . One may note, however, that if  $\Delta F$  is small, then the  $\delta_{ij}$  and  $\Delta \lambda_i$  are also small. If one neglects the terms involving the products of two small quantities, Equation (99) is approximated by

$$(L_o^i)' \Delta F (L_o^i) \approx \Delta \lambda_i \quad (100)$$

The linear refinement method is only as good as this approximation. Expanding Equation (100), one obtains

$$\Delta \lambda_i \approx \sum_j [(L_o)_{ji}^2 \Delta F_{jj}] + 2 \sum_{j < k} [(L_o)_{ji} (L_o)_{ki} \Delta F_{jk}] \quad (101)$$

which upon comparison with Equation (90) is seen to provide an approximation to the first derivatives of the Taylor expansion. This gives one a linear relation between the force constants and the frequency parameters,  $\lambda$ , which one can write in matrix notation as

$$\overline{\Delta \lambda} = J \overline{\Delta F} \quad (102)$$

where  $\overline{\Delta \lambda}$  is a column matrix of  $\Delta \lambda_i$ ,  $\overline{\Delta F}$  is a column matrix of the elements  $\Delta F_{ij}$ , and  $J$ , the Jacobian, is a rectangular matrix of the products  $(L_o)_{ji}^2$  and  $2(L_o)_{ji} (L_o)_{jk}$  which approximate  $(\partial \lambda_i / \partial F_{jk})$ . This relation forms the basis for the iterative linear least squares procedure for refining a set of force constants

to give the "best" fit to the observed frequencies. Suppose one is given an approximate  $\underline{F}$  matrix,  $\underline{F}_0$ , and the observed frequencies,  $\lambda_{obs}$ . One solves the secular equation

$$\underline{G} \underline{F} \underline{L} = \underline{L} \underline{\Lambda} \quad (103)$$

and letting  $\Delta \lambda_{\underline{i}} = \lambda_{\underline{i},obs} - \lambda_{\underline{i},0}$  in Equation (102) where  $\underline{J}$  is computed from the  $\underline{L}$ . One applies the least squares theory [for example, Draper and Smith (105)] to calculate Equation (104) by multiplying Equation (102) on the left by  $\underline{J}' \underline{P}$ , where  $\underline{P}$  is a weighting matrix (diagonal).

$$\underline{J}' \underline{P} \underline{\Delta \lambda} = (\underline{J}' \underline{P} \underline{J}) \underline{\Delta F} \quad (104)$$

The solution of this equation is obtained by inverting  $(\underline{J}' \underline{P} \underline{J})$  to give

$$\underline{\Delta F} = (\underline{J}' \underline{P} \underline{J})^{-1} \underline{J}' \underline{P} \underline{\Delta \lambda} \quad (105)$$

Now, if the number of frequencies is greater than the number of  $\underline{F}$  matrix elements, the matrix  $\underline{J}' \underline{P} \underline{J}$  should be nonsingular, and one obtains the corrections,  $\underline{\Delta F}$ , which will minimize,  $\underline{r}' \underline{P} \underline{r}$ , the sum of the weighted squares of the residuals, where  $\underline{r} = \underline{\Lambda}^{obs} - \underline{\Lambda}^{calc}$ . If the corrections,  $\underline{\Delta F}$ , are fairly large, Equation (101) is approximate and the higher order terms in the Taylor expansion are important. One, therefore, uses the corrections to form a new  $\underline{F} = \underline{F}_0 + \underline{\Delta F}$  and repeats the process. If the calculation is well behaved,  $\underline{\Delta F}$  will decrease on each cycle. The process is repeated until  $\underline{\Delta F}$  becomes very small. (See the following section on termination of the force constant refinement.)

As was mentioned earlier, in most cases, the number of data are not sufficient to determine all of the force constants in the GQFF, and it is necessary to introduce some constraints. Even when the data exceed the number

of force constants, it is usually not possible to determine all of the force constants. Mathematically, the determinant of  $\underset{\sim}{J}'\underset{\sim}{P}\underset{\sim}{J}$  is zero or very small, and the solution to Equation (105) is ill-defined, so that it becomes necessary to introduce some constraints. This is done by means of the constraint matrix,  $\underset{\sim}{Z}$ , discussed in an earlier section. The  $\underset{\sim}{Z}$  matrix is the transformation matrix between the force constant parameters,  $\underset{\sim}{\Phi}$ , and the  $\underset{\sim}{F}$  matrix. One has

$$F_{j_k} = \sum_l Z_{j_k l} \Phi_l \quad (106)$$

or in matrix notation

$$\underset{\sim}{F} = \underset{\sim}{Z}\underset{\sim}{\Phi} \quad (107)$$

where  $\underset{\sim}{Z}$  is a rectangular matrix of dimension  $\underline{n} \times \underline{m}$  ( $\underline{n}$  is the number of force constants in  $\underset{\sim}{F}$  and  $\underline{m}$  is the number of parameters in  $\underset{\sim}{\Phi}$ ),  $\underset{\sim}{\Phi}$  is a column matrix of elements  $\Phi_k$ , and  $\underset{\sim}{F}$  is a column matrix of the elements  $F_{j_k}$ . The elements of  $\underset{\sim}{Z}$  are determined by the force field model. Differentiating Equation (107), one obtains

$$\underset{\sim}{\Delta F} = \underset{\sim}{Z}\underset{\sim}{\Delta\Phi} \quad (108)$$

One substitutes this expression into Equation (104) to obtain

$$\underset{\sim}{J}'\underset{\sim}{P}\underset{\sim}{\Delta\lambda} = (\underset{\sim}{J}'\underset{\sim}{P}\underset{\sim}{J})\underset{\sim}{Z}\underset{\sim}{\Delta\Phi} \quad (109)$$

and multiplies on the left by  $\underset{\sim}{Z}'$  to obtain the "normal equations" of linear least squares theory.

$$\underset{\sim}{Z}'\underset{\sim}{J}'\underset{\sim}{P}\underset{\sim}{\Delta\lambda} = (\underset{\sim}{Z}'\underset{\sim}{J}'\underset{\sim}{P}\underset{\sim}{J}\underset{\sim}{Z})\underset{\sim}{\Delta\Phi} \quad (110)$$

Solving this equation for  $\underset{\sim}{\Delta\Phi}$ , one has

$$\underset{\sim}{\Delta\Phi} = (\underset{\sim}{Z}'\underset{\sim}{J}'\underset{\sim}{P}\underset{\sim}{J}\underset{\sim}{Z})^{-1}\underset{\sim}{Z}'\underset{\sim}{J}'\underset{\sim}{P}\underset{\sim}{\Delta\lambda} \quad (111)$$

The above expression is the one that is used to compute the corrections to the force constant parameters which minimize the differences between the calculated and observed frequencies. The  $\underline{F}$  matrix is then updated by Equation (108) to account for the perturbations in the force constant parameters,  $\Delta\phi_{\underline{i}}$ . Next, the secular equation (103) is solved with the corrected  $\underline{F}$  matrix, and the least squares corrections to the force constant parameters are computed by Equation (111). The iterative process is continued until the condition for termination is met.

The condition for termination of the force constant refinement is discussed in Appendix IV. The topics of evaluation of transferable force constants, potential energy distribution, error analysis, multiple solutions, multiple regression analysis, nonconvergence, scaling, and damped least squares are also discussed in Appendix IV in connection with the least squares refinement technique.

Computer program for linear least squares. A computer program, FADJ, has been written by J. H. Schachtschneider (89) and modified for use in this investigation which will solve the vibrational secular determinant, refine the force constant parameters by the method of linear least squares, and will perform a multiple regression analysis at the option of the user. A program listing, flow diagram, and instructions for use of the program, FADJ, are provided in Appendix V. In addition to the computations listed above, FADJ will also calculate the potential energy distribution in  $\phi_{\underline{i}}$ , the variance-covariance matrix, the correlation matrix, and the frequency error distribution.

Solution of the secular equation and linear least squares refinement for the 1,5-anhydropentitol models. FADJ was employed to solve the secular equation and refine the initial set of force constants (see Table XX) for the 1,5-AP models. Unfortunately, the linear refinement technique embodied in FADJ failed in all attempts to refine the force constants. The force constant perturbations, computed by Equation (111), resulted in the differences between the calculated and observed frequencies increasing upon each iteration, that is, the refinement diverged. The most probable cause of the divergence was that the problem was extremely ill-conditioned resulting from several of the force constants being strongly correlated. This, in turn, had the effect of making the normal matrix,  $(Z'J'PJZ)$ , nearly singular. Scaling and damped least squares were employed in an attempt to force convergence of the refinement without success. The force constants were refined successfully later in the investigation after the linear least squares technique was abandoned for a nonlinear method, which will be discussed next.

#### Nonlinear Least Squares Refinement Method

The nonlinear least squares refinement technique to be described was suggested by Gans (120) and is based on the method of Fletcher and Powell (121).

In the Fletcher-Powell method (FP), the normal matrix,  $(Z'J'PJZ)^{-1}$ , is not computed directly as in the linear Gauss-Newton-Raphson method (GNR) just discussed. Rather, the matrix is approximated on each iteration, beginning with a unit matrix and becoming a very good approximation to  $(Z'J'PJZ)^{-1}$  near the minimum. This approach avoids the generation of errors that occur in the GNR method upon inverting a nearly singular matrix resulting from highly correlated force constants. In addition, the FP method considers the second-order derivatives in the Taylor expansion of the eigenvalues, whereas the GNR technique



terminates the series after the first term. The FP method has been reported (120) to converge to a minimum even though the initial set of force constants may be a poor approximation.

To derive the expressions comprising the nonlinear refinement technique, one again starts with an expansion of the eigenvalues in a Taylor series, say at the  $r$ th iteration.

$$\Delta\lambda_i^r = (\lambda_i - \lambda_i^r) = \sum_j (\partial\lambda_i/\partial F_{jk})^r \Delta F_{jk}^r + \frac{1}{2} \sum_{j\ell} (\partial^2\lambda_i/\partial F_{jk}\partial F_{\ell m})^r \Delta F_{jk}^r \Delta F_{\ell m}^r + \dots \quad (112)$$

In the GNR method, one truncates the series after the linear term (Gauss linear approximation), excluding the second and higher order terms. Based on this approximation and linear least squares theory, one then derives the following expression for the corrections to the force constant parameters

$$\overline{\Delta\Phi}^r = [(\underline{J}^r \underline{Z})' \underline{P} (\underline{J}^r \underline{Z})]^{-1} (\underline{J}^r \underline{Z})' \underline{P} \overline{\Delta\lambda}^r \quad (113)^{14}$$

where the  $r$  indicates the  $r$ th iteration. In the method of least squares, one attempts to minimize the difference between the calculated frequency parameters,  $\lambda_{\underline{i}}^r$ , and the experimental frequency parameters,  $\lambda_{\underline{i}}$ , such that the parameter  $R$ , in Equation (114), is a minimum.

$$R^r = \sum_k P_k (\lambda_k - \lambda_k^r)^2 = (\overline{\Delta\lambda}^r)' \underline{P} \overline{\Delta\lambda}^r \quad (114)$$

In the above expression,  $P_{\underline{k}}$  are the elements of the weighting matrix,  $\underline{P}$ . Now, if the expression in Equation (114) is differentiated with respect to the force constant parameters,  $\phi_{\underline{i}}$ , the result is

<sup>14</sup>  $\overline{\Delta\lambda}^r$  is defined to be a matrix of the elements  $\Delta\lambda_{\underline{i}}^r$ .

$$\begin{aligned}
 g_i^r &= (\partial R / \partial \Phi_i)^r = (\partial R / \partial F_{lm})^r (\partial F_{lm} / \partial \Phi_i)^r \\
 &= -2 \sum_k P_k \Delta \lambda_k^r (\partial \lambda_k / \partial F_{lm})^r Z_{lm}
 \end{aligned}
 \tag{115}$$

where  $\underline{g}_i^r$  is the  $i$ th element of the gradient vector,  $\underline{g}_i^r$ ;  $\underline{F}_{lm}$  is an element of the  $\underline{F}$  matrix; and  $\Delta \lambda_k^r = (\lambda_{\underline{k}} - \lambda_{\underline{k}}^r)$ . [The above result was obtained by employing the chain rule for differentiation and the relation between  $\underline{F}$  and  $\underline{\Phi}$  which appears in Equation (107).] Equation (115) may be written in matrix notation as

$$\underline{g}^r = -2 (\underline{J}^r \underline{Z})' \underline{P} \underline{\Delta \lambda}^r \tag{116}$$

where the Jacobian matrix,  $\underline{J}^r$ , contains the elements  $(\partial \lambda_{\underline{k}} / \partial F_{lm})^r$ . When  $\underline{R}$  is a minimum, the gradient vector is zero. From Equation (116), it is seen that when  $\underline{g}^r$  is zero, either  $\underline{\Delta \lambda}^r$  is zero, and the experimental frequencies are fitted exactly, or  $(\underline{J}^r \underline{Z})$  is singular, and the minimum value of  $\underline{R}$  is not and cannot be zero. [In general, the counterpart of Equation (116) requires that  $[(\underline{J}^r \underline{Z})' \underline{P} - (\underline{J}^r \underline{Z})]$  is singular if  $\underline{\Delta \lambda}^r \neq 0$ .] If Equation (114) is differentiated once again with respect to  $\Phi_i$ , one obtains Equation (117) [again employing the chain rule for differentiation and the relation expressed in Equation (107)].

$$\begin{aligned}
 D_{ij}^r &= (\partial^2 R / \partial \Phi_i \partial \Phi_j)^r = 2 \sum_k P_k \{ (\partial \lambda_k / \partial \Phi_i)^r (\partial \lambda_k / \partial \Phi_j)^r \\
 &\quad - (\partial^2 \lambda_k / \partial \Phi_i \partial \Phi_j)^r \Delta \lambda_k^r \}.
 \end{aligned}
 \tag{117}$$

Applying the linear hypothesis, one has

$$\begin{aligned}
 D_{ij}^r &\cong 2 \sum_k P_k \{ (\partial \lambda_k / \partial \Phi_i)^r (\partial \lambda_k / \partial \Phi_j)^r \} \\
 &= 2 \sum_k P_k \{ (\partial \lambda_k / \partial F_{mn})^r (\partial F_{mn} / \partial \Phi_i) (\partial \lambda_k / \partial F_{rs})^r (\partial F_{rs} / \partial \Phi_j) \} \\
 &= 2 \sum_k (\underline{J}^r \underline{Z})_{ki} P_k (\underline{J}^r \underline{Z})_{kj}
 \end{aligned}
 \tag{118}$$

This expression is written in matrix form in Equation (119).

$$\underline{D}^r = 2(\underline{J}^r \underline{Z})' \underline{P}(\underline{J}^r \underline{Z}). \quad (119)$$

By comparing Equations (116) and (119) with Equation (113), one notes that the latter expression can be rewritten as

$$\Delta \underline{\Phi}^r = -(\underline{D}^r)^{-1} \underline{g}^r. \quad (120)$$

In the FP method, the second derivative terms in Equation (117) are reintroduced indirectly through Equation (120) in the following manner. A positive definite matrix,  $\underline{H}^r$ , where  $\underline{H}$  is to be distinguished from  $\underline{H}$  in Equation (72), is updated at each iteration from being, initially, a unit matrix to eventually becoming a good approximation to  $(\underline{D}^r)^{-1}$ . The increment added to the force constants,  $\Delta \underline{\Phi}^r$ , is calculated for each iteration by the following expression,

$$\Delta \underline{\Phi}^r = -\underline{H}^r \underline{g}^r. \quad (121)$$

For linear problems, the FP and the GNR methods are ultimately identical because the linear hypothesis made in Equation (118) is valid. For nonlinear problems, the FP method ultimately becomes identical with Newton's method for nonlinear equations. The latter method converges slowly when not near the minimum. The FP technique attempts to overcome this by setting  $\underline{H}^1 = \underline{E}$  (unit matrix) and, therefore,  $\Delta \underline{\Phi}^1 = -\underline{g}^1$ ; that is, the first iteration follows the path of steepest descent. However, Gans (120) suggests that a more effective choice might be  $\underline{H}^1 = \frac{1}{2} \{(\underline{J}^1 \underline{Z})' \underline{P}(\underline{J}^1 \underline{Z})\}^{-1}$ . This choice for  $\underline{H}^1$  is not practical, however, in those problems where the force constants are highly correlated because then the matrix  $[(\underline{JZ})' \underline{P}(\underline{JZ})]$  is singular or nearly singular and cannot be inverted.

To approach  $(D^r)^{-1}$ , a method of successive linear searches in  $\bar{H}$ -conjugate directions is used. At the  $(r+1)$ st iteration step, a linear search is made in the direction  $\underline{h}^r = -\bar{H}^r \underline{g}^r$ . By means of the linear search, the minimum of  $R^{(r)}(\underline{t}) = \text{Func}(\bar{\Phi}^r + \underline{t} \cdot \underline{h}^r)$  is determined, giving the argument  $\bar{\Phi}^{r+1} = \bar{\Phi}^r + \underline{t}_r \cdot \underline{h}^r = \bar{\Phi}^r + \Delta\bar{\Phi}^r$ , where  $\Delta\bar{\Phi}^r$  is now equal to  $\underline{t}_r \cdot \underline{h}^r$  and  $\underline{t}_r$  is an adjustable scalar. The argument of the minimum,  $\bar{\Phi}^{r+1}$ , on the line through  $\bar{\Phi}^r$  in the direction  $\underline{h}^r$  is determined by the relation that the scalar product  $(\underline{g}^{r+1}, \underline{h}^r) = 0$ . Now, one has

$$\bar{\Phi}^n = \bar{\Phi}^j + \sum_{i=j}^{n-1} t_i \underline{h}^i \quad \text{for } j < n-1 \quad (122)$$

and

$$\underline{g}^n = \underline{g}^j + \sum_{i=j}^{n-1} t_i \bar{H}^i \underline{h}^i \quad \text{for } j < n-1 \quad (123)$$

and therefore,

$$(\underline{g}^n, \underline{h}^j) = \sum_{i=j+1}^{n-1} t_i (\bar{H}^i \underline{h}^i, \underline{h}^j). \quad (124)$$

For the generation of  $\bar{H}$ -conjugate directions, one starts with  $\underline{h}^1 = -\underline{g}^1$  and calculates successive directions,  $\underline{h}^r$ , by means of  $\underline{h}^r = -\bar{H}^r \underline{g}^r$ , where  $\bar{H}^r$  is modified to  $\bar{H}^{r+1}$ , so that  $\underline{h}^r$  is an eigenvector of the matrix  $\bar{H}^{r+1} \bar{H}^r$  with eigenvalue 1. This ensures that  $\bar{H}^r$  approaches  $(D^r)^{-1}$  as  $\bar{\Phi}^r$  approaches  $\bar{\Phi}_{\min}$ . The  $\bar{H}^r$  matrix is modified on each iteration by the following expression

$$\begin{aligned} \bar{H}^{r+1} = \bar{H}^r &+ \frac{(d\bar{\Phi})(d\bar{\Phi})'}{[(d\bar{\Phi})'(dg)]} \\ &- \frac{\bar{H}^r (dg)(dg)' \bar{H}^r}{[(dg)' \bar{H}^r (dg)]} \end{aligned} \quad (125)$$

where  $(dg) = \underline{g}^{r+1} - \underline{g}^r = \Delta \underline{g}^r$  and  $(d\bar{\Phi}) = \bar{\Phi}^{r+1} - \bar{\Phi}^r = \Delta \bar{\Phi}^r$ . The refinement is terminated after  $|\Delta \bar{\Phi}_i^r|$  become smaller than some arbitrary constant, set by the user, for one or more perturbations, also determined by the user. The linear search technique mentioned above is as follows. For a given argument vector,

$\bar{\Phi}$ , a direction vector,  $\underline{h}$ , defining a direction through  $\bar{\Phi}$ , a local minimum of the function  $R(\underline{t}) = \text{Func}(\bar{\Phi}^r + \underline{t} \cdot \underline{h}^r)$  must be found. This means that a value,  $\underline{t}_m$ , must be determined for which  $R^r(\underline{t}_m) = (\partial R / \partial \bar{\Phi})_{\underline{t}_m}^r = \text{scalar product}$

$[\underline{g}(\bar{\Phi} + \underline{t}_m \cdot \underline{h}), \underline{h}] = 0$ . From  $R^r(0) = [\underline{g}(\bar{\Phi}), \underline{h}] < 0$  it is evident that a minimum  $R^r(\underline{t}_m) < R^r(0)$  should be found for positive values of  $\underline{t}$ .

The calculation of the minimum is in three stages. The first estimates the magnitude of  $\underline{t}_m$ , the second determines an interval containing  $\underline{t}_m$ , and the third interpolates cubically the value of  $\underline{t}_m$ . [The interested reader can find the details of the cubic interpolation scheme in the IBM manual (122).]

For each new argument vector,  $\bar{\Phi}$ , the secular equation must be solved to determine  $\lambda_k$ ,  $R^r(\bar{\Phi})$  must be evaluated by Equation (114), and  $\underline{g}^r$  determined by Equation (116). For each iteration,  $\underline{r}$ , the process above may be repeated several times in search of a local minimum. Therefore, the time to complete a refinement is oftentimes longer with the FP method as compared to the GNR method because of the more numerous solutions of the secular determinant required by the FP method. Thus, the computer time needed to diagonalize the transformed  $\underline{F}$  matrix,  $\underline{H}$ , in Equation (73) becomes very important for large molecules or for a series of molecules. The inefficiency of the Jacobi method of diagonalizing a symmetric matrix has already been stated. However, at the present, computer time must be sacrificed because the Jacobi method results in more accurate eigenvalues and is less subject to errors due to redundancies in the coordinates than the two leading possible replacement methods (Givens and Householder methods) even though these methods are faster and more efficient.

Termination of the force constant refinement. The force constant refinement is terminated and said to have "converged" if either of the following two conditions are satisfied. The first condition requires that all the corrections to the force constants,  $|\Delta\bar{\Phi}_{\underline{i}}|$ , for a particular perturbation, be less than or equal to an arbitrary constant supplied by the program user. The second condition requires that the ratio of successive weighted sums of squares of the residuals be greater than a fractional constant supplied by the user (usually very close to 1.0). The user may require that this condition be met several times before actual termination is initiated, so as to provide a check against premature termination.

Error analysis. The standard error in the force constant parameters,  $\sigma(\bar{\Phi}_{\underline{i}})$ , may also be estimated for the FP method. The reader may recall that the standard error was computed from the diagonal elements of the normal matrix in the GNR method, that is,

$$\sigma(\bar{\Phi}_{\underline{i}}) = \{[(JZ)'P(JZ)]_{ii}^{-1}\}^{\frac{1}{2}}\sigma_{\lambda} \quad (126)$$

where  $\sigma_{\lambda} = (\sum_{\underline{i}} \Delta\lambda_{\underline{i}}^2 P_{\underline{i}} / n)^{\frac{1}{2}}$  is the standard error in  $\lambda$  ( $n$  is the number of nonzero experimental frequencies entered in the refinement). In the previous section, the following expressions were derived for linear problems.

$$\underline{g}^r = -2 \frac{(JZ)' P \Delta \lambda^r}{\lambda \lambda \lambda}, \quad (127)$$

$$\underline{H}^r = \frac{1}{2} \frac{[(JZ)' P (JZ)]^{-1}}{\lambda \lambda \lambda} \quad (128)$$

For nonlinear problems, the above equations become approximations. Thus,  $\underline{H}^r$  may be used to compute the standard error in the force constant parameters, since

Potential energy distribution, cartesian displacement coordinates, and mean square amplitudes. The potential energy distributions in terms of the force constant parameters,  $\overline{\Phi}$ , and the internal coordinates,  $\underline{R}$ ; the cartesian displacement coordinates; the transformation matrix,  $\underline{L}$ , from normal coordinates to internal coordinates; and the mean square amplitudes of vibration all aid one in the interpretation of the vibrational dynamics of the molecular model in terms of the atomic group vibrations for each of the normal modes.

The  $\underline{L}$  matrix may be computed by Equation (76) and  $\underline{L}^{-1}$  by Equation (77) after the secular determinant has been solved by the method of successive orthogonalization followed by diagonalization. The  $\underline{B}$  matrix, which is the transformation from cartesian coordinates to internal coordinates, is computed by the Wilson "S vector" technique discussed in the section on  $\underline{G}$  matrix computation. The transformation,  $\underline{T}$ , from normal coordinates,  $\underline{Q}$ , to cartesian coordinates,  $\underline{X}$ , where

$$\underline{X} = \underline{T}\underline{Q} \quad (133)$$

is then computed from the relation

$$\underline{T} = \underline{M}^{-1}\underline{B}'(\underline{L}^{-1})' \quad (134)$$

where  $\underline{M}^{-1}$  is the inverse of the atomic mass matrix. The  $\underline{T}$  matrix gives the cartesian displacements for each atom in the molecule for each normal mode. If, for example, one gives the normal coordinate,  $Q_i$ , a unit displacement, the cartesian displacements are given by

$$\underline{X}^{(i)} = \underline{T}^{(i)} \quad (135)$$

where  $\underline{T}^{(i)}$  is the  $i$ th column of the matrix  $\underline{T}$ . Let  $\underline{X}_0$  be the column matrix of the equilibrium cartesian coordinates used to compute the  $\underline{B}$  matrix; then the

cartesian coordinates of the atoms for the molecule displaced by one unit of

$Q_i$  are

$$\underline{X}^{(i)} = \underline{X}_0 + \underline{T}^{(i)}. \quad (136)$$

If one plots the points  $\underline{X}^{(i)}$  and  $\underline{X}_0$ , one obtains a representation of the molecule displaced in the normal mode  $Q_i$ . The elements of  $\underline{T}^{(i)}$  taken three at a time, giving the  $x$ ,  $y$ , and  $z$  coordinates of an atom, may be considered to be elements of a vector,  $\underline{a}^{(i)}$ , with its origin at atom  $a$ . These vectors give the direction of the straight-line motions of the  $n$  atoms vibrating in normal mode  $i$ , and the lengths show the relative amplitudes of vibration for each atom.

The expression for the potential energy in terms of the normal coordinates is given in the next equation.

$$2V = \sum_i \lambda_i Q_i^2. \quad (137)$$

One can see from this expression that  $\lambda_i$  is the potential energy for a unit displacement of normal mode  $Q_i$ . The following relation for  $\lambda_i$  may be derived from one of the conditions on the matrix  $\underline{L}$ .

$$\lambda_i = \sum_{j,k} L_{ji} L_{ki} F_{jk}. \quad (138)$$

The fractional contribution to  $\lambda_i$  from the various  $\underline{F}$  matrix elements, in terms of the internal coordinates, is given by

$$2L_{ji} L_{ki} F_{jk} / \lambda_i \quad (139)$$

for  $i < j$  for the off-diagonal elements of  $\underline{F}$  and by

$$L_{ji}^2 F_{jj} / \lambda_i \quad (140)$$

for the diagonal elements of  $F$ . The sum of these terms is seen to be unity.



In the harmonic oscillator approximation, the mean square amplitude of the normal mode  $Q_{\underline{i}}$  is given by

$$\overline{Q_{\underline{i}}^2} = (h/8\pi^2\nu_{\underline{i}}) \text{Coth}(h\nu_{\underline{i}}/2kT) \quad (141)$$

where  $\nu_{\underline{i}}$  is the vibrational frequency in  $\text{sec.}^{-1}$ ,  $h$  is Planck's constant,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. Also, one has  $\overline{Q_{\underline{i}}Q_{\underline{j}}} = 0$  for  $\underline{i} \neq \underline{j}$ . The mean square amplitude matrix for normal coordinates is defined as

$$\underline{\Sigma}^Q = \underline{\overline{QQ'}} \quad (142)$$

and is a diagonal matrix with elements

$$\Sigma_{kk}^Q = \overline{Q_k^2} = (h/8\pi^2\nu_{\underline{i}}) \text{Coth}(h\nu_{\underline{i}}/2kT). \quad (143)$$

The mean square amplitude matrices for other coordinates, such as internal coordinates or cartesian coordinates, can be obtained from the normal coordinate transformations

$$\underline{R} = \underline{LQ} \quad (144)$$

and

$$\underline{X} = \underline{TQ}. \quad (145)$$

The matrices are defined as

$$\underline{\Sigma}^R = \underline{\overline{RR'}} = \underline{L\underline{\overline{QQ'}}L'} = \underline{L\underline{\Sigma}^QL'} \quad (146)$$

and

$$\underline{\Sigma}^X = \underline{\overline{XX'}} = \underline{T\underline{\overline{QQ'}}T'} = \underline{T\underline{\Sigma}^QT'} \quad (147)$$

The diagonal elements of the  $\underline{\Sigma}$  matrices are the mean square amplitudes of vibration, and the off-diagonal elements are called the interaction mean square amplitudes. The mean amplitude of vibration for a given coordinate,  $\underline{i}$ , is the root

mean square deviation of the coordinate and is given by the square root of the appropriate diagonal element of  $\underline{\Sigma}$ .

In this investigation, the computer program which calculates the mean square amplitude matrix was modified to include the computation of what shall be referred to in this text as the "squared amplitudes," in terms of the internal coordinates, for each normal mode. The program already calculated a similar quantity for the cartesian coordinates. For any particular normal mode,  $Q_i$ , the "squared amplitudes" for the displaced molecule in terms of internal and cartesian coordinates are defined by the following equations.

$$\underline{\Sigma}^R(i) = \underline{L}^{(i)^2} (h/8\pi^2\nu_i) \text{Coth}(h\nu_k/2kT) \quad (148)$$

and

$$\underline{\Sigma}^X(i) = \underline{T}^{(i)^2} (h/8\pi^2\nu_i) \text{Coth}(h\nu_k/2kT) \quad (149)$$

where  $\underline{L}^{(i)}$  and  $\underline{T}^{(i)}$  are the  $i$ th columns of the  $\underline{L}$  and  $\underline{T}$  matrices. A comparison of the "squared amplitudes" for the various internal coordinates of any  $Q_i$  gives the relative magnitudes of the displacements of the coordinates from their equilibrium positions for that particular normal mode.

Computer program to compute the potential energy distribution, cartesian displacement coordinates, mean square amplitudes, and "squared amplitudes." The potential energy distribution in terms of internal coordinates, the cartesian displacement coordinates, the mean square amplitude matrix, and the "squared amplitudes" are all calculated by the computer program, EIGV, written by J. H. Schachtschneider (89) and modified for use in this investigation. The Coriolis coupling constants may also be computed with this program if desired [see Schachtschneider (89) for a discussion of the computation]. At the option of the user, the potential energy distribution and "squared amplitudes" are written on tape. The computer program, SASORT, written by the author of this text,

uses the tape as input, orders the numerical arrays in descending order, and identifies each value using an internal coordinate coding system. The computer program, NFAD, which is an abbreviated version of FADJ, writes the potential energy distribution in terms of the force constants on tape. The computer program, PESORT, also written by the author, then orders the data in descending order and labels the elements of the arrays with the appropriate internal coordinate code. The programs EIGV, SASORT, and PESORT are listed in Appendix V along with instructions for their use. A flow diagram accompanies the listing of EIGV.

Solution of the secular equation and nonlinear least squares refinement of the force constants for the 1,5-anhydropentitol models. Using the  $\tilde{G}$  (Tables XL-XLII in Appendix II) and  $\tilde{Z}$  (Tables XLIII-XLV in Appendix III) matrices previously described for the 1,5-AP models, the computer program FLPO was employed to solve the secular equation by the method of successive orthogonalization of  $\tilde{GF}$  followed by Jacobi diagonalization to yield the eigenvalues,  $\lambda$ , for the initial set of force constant parameters listed in Table XX. The calculated frequencies were then computed from the eigenvalues,  $\lambda$ , using the expression  $\lambda_{\underline{k}} = 4\pi^2\nu_{\underline{k}}^2$ . Theoretically, there should be  $3N-6$  calculated frequencies for the vibrational model where  $N$  corresponds to the number of "atoms." For the 1,5-AP models, there are 19 "atoms" and thus, 51 nonzero calculated fundamental frequencies. The calculated frequencies for the tetrahedral 1,5-AP models, based on this initial set of frequencies, are shown in Table XXI. The initial frequency agreement of the calculated frequencies (Table XXI) with the crystalline infrared and Raman spectra (Tables III-V) is noted to be in the "ballpark" which supports the validity of the initial force field. The experimental frequencies from both the Raman and infrared spectra of the crystalline compounds were then correlated with these calculated frequencies with the Raman frequency being the value correlated if a choice between Raman and infrared existed. The correlation of

TABLE XXI

CALCULATED FREQUENCIES FOR THE 1,5-ANHYDRO-PENTITOL  
 MODELS BASED ON THE INITIAL SET OF FORCE CONSTANTS  
 LISTED IN TABLE XXXII

$\nu$ 1,5-AX (cm. <sup>-1</sup> )		$\nu$ 1,5-AR (cm. <sup>-1</sup> )		$\nu$ 1,5-ALA (cm. <sup>-1</sup> )	
3398	1149	3398	1144	3398	1139
3398	1139	3398	1119	3398	1132
3398	1113	3398	1119	3398	1106
2970	1086	2971	1040	2970	1078
2968	1059	2968	1039	2968	1071
2945	1023	2939	995	2943	989
2938	976	2937	989	2937	959
2932	943	2937	948	2934	928
2863	905	2863	872	2862	885
2862	876	2862	871	2861	839
1463	638	1462	651	1463	723
1459	561	1459	632	1460	622
1415	521	1412	588	1412	545
1405	462	1405	454	1401	484
1391	433	1397	449	1375	435
1356	421	1364	439	1373	409
1355	366	1340	362	1342	397
1330	327	1326	325	1331	315
1323	310	1316	293	1306	309
1316	299	1280	251	1301	260
1288	231	1273	231	1279	228
1256	223	1268	219	1263	227
1252	220	1256	215	1258	217
1234	196	1254	199	1242	180
1213	131	1248	136	1220	131
1155		1174		1176	

frequencies was based on band position and distribution. That is, bands in the spectra were correlated with calculated bands having approximately the same numerical frequency in wave numbers and/or with calculated bands distributed in a like manner throughout an approximately equivalent region of the experimental spectra. For an example of this last technique for band correlation, consider the calculated bands 462, 433, and 421 cm.<sup>-1</sup> for 1,5-AX in Table XXI. These

three bands are grouped together, locally "isolated" from other bands on either side. The closest band to  $462\text{ cm.}^{-1}$  is  $521\text{ cm.}^{-1}$ , and the closest band to  $421\text{ cm.}^{-1}$  is  $366\text{ cm.}^{-1}$ . The Raman and infrared spectra are next examined for three bands in this region, essentially "isolated" from their neighbors. Examination of the tabulated frequencies for the Raman and infrared spectra of crystalline 1,5-AX in Table III reveals that there are three bands in this region, namely  $455$ ,  $437$ , and  $418\text{ cm.}^{-1}$ . These experimental bands are locally "isolated" from neighboring bands. The nearest band to  $455\text{ cm.}^{-1}$  is  $533\text{ cm.}^{-1}$ , and the nearest band to  $418\text{ cm.}^{-1}$  appears at  $369\text{ cm.}^{-1}$ . These three spectral bands are then assigned to the calculated bands with frequencies  $462$ ,  $433$ , and  $421\text{ cm.}^{-1}$ . In addition, the information provided by the water and DMSO- $d_6$  solution spectra, deuterated 1,5-AP spectra, and depolarization ratio measurements assists in the frequency assignments.

The 56 initial force constant parameters (Table XX) were then refined for all three models simultaneously to minimize the differences between the observed and calculated frequencies. The nonlinear least squares technique based on the Fletcher-Powell method, available in the computer program FLPO, was employed in this refinement. Actually, only 54 of the listed 56 parameters were included in the refinement. One of these parameters is a dummy and the other is a gauche bend-bend interaction term which does not appear in the  $\underline{F}$  matrices for the 1,5-AP compounds, but was included for completeness. Therefore, the refinement involved 54 variables (force constant parameters in the SVQFF) and 144 data points (experimental frequencies for the three 1,5-AP compounds) to result in 90 statistical degrees of freedom. The refinement converged after 24 iterations (i.e., the ratio of successive weighted sum of squares exceeded 0.995 a total of twelve times). The final set of force constants resulting from the refinement is listed in Table XX. The calculated frequencies and the assigned experimental frequencies

for the final set of refined force constants are tabulated in Tables XXII-XXIV for 1,5-AX, 1,5-AR, and 1,5-ALA, respectively. The corresponding average errors (mean deviations) between the observed and calculated frequencies after force constant refinement were 5.91, 7.60, and 5.16  $\text{cm.}^{-1}$  for 1,5-AX, 1,5-AR, and 1,5-ALA, respectively, for an overall average error of 6.22  $\text{cm.}^{-1}$  (This average error does not include the OH stretch bands because an attempt was not made to improve the frequency "fit" in this region by allowing separate OH stretch force constant parameters for the individual OH groups.)

The factored  $\underline{G}$  and  $\underline{Z}$  matrices resulting from the transformation to symmetry coordinates were employed along with the final set of force constant parameters to calculate the frequencies belonging to each of the two irreducible representations, A' and A'', for the  $\underline{C}_s$  point group for 1,5-AX and 1,5-AR. The results of the symmetry classification are listed in Tables XXII and XXIII and also the results of the depolarization ratio measurements (see Tables XII and XIII). The depolarization ratios proved to be valuable in several cases where the assignment was questionable by providing additional data with which to evaluate the assignment and permitted a check on the assignment in other cases.

EIGV was employed to compute the potential energy distribution,  $\underline{L}$  matrix, internal coordinates, "squared amplitudes," and cartesian displacement coordinates for each of the 1,5-AP models based on the final set of refined force constant parameters. These data provided the basis for classifying the vibrational motion of each normal mode in terms of the vibrations of the substituent atomic groups for each of the 1,5-AP models. The potential energy distribution, in terms of the internal coordinates, provides the relative contribution of each internal coordinate to the molecular vibration for each normal mode. The potential energy distributions are presented for 1,5-AX, 1,5-AR, and 1,5-ALA in

TABLE XXII

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDROXYLITOL

Exper. Freq., cm. <sub>1</sub>		Calc. Freq., cm. <sub>1</sub>	Sym. Class.		Approx. PE Dist., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR		Calc.	Exp.		
3383	3387	3356	A'		OH(99.9)	OH stretch (str.)
3343	3350	3356	A''		OH(99.9)	OH str.
3290	3300	3356	A'		OH(99.9)	OH str.
2985	2990	2982	A'		ACH(90)	Asymmetric (asym.) methylene str.
2970	2973	2979	A''		ACH(92)	Asym. methylene str.
	2941	2946	A'		CH(90)	Methine str.
2928	2933	2926	A''		CH(92)	Methine str.
2896		2911	A'		CH(96)	Methine str.
2885	2900	2882	A'		ACH(95)	Symmetric (sym.) methylene str.
2871	2873	2880	A''		ACH(97)	Sym. methylene str.
1472	1470	1468	A'	A'	HCOR(49)HCH(47)	Methylene wag(49) coupled with methylene scissor(47)
1459	1464	1460	A''	A'	HCOR(50)HCH(48)	Methylene wag(50) coupled with methylene scissor(48)
1439	1440	1437	A'		HCC(38)AHCC(21) HCOR(12)	Methine op bend(38) coupled with methylene wag(33)
1427		1410	A''		AHCC(35)HCC(20) HCOR(11)COH(10)	Methylene wag(46) coupled with methine op bend and OH ip bend
1385	1391	1388	A'	A'	HCC(42)AHCC(23) HCO(12)	Methine deformation (both ip and op bend)(54) coupled with methylene wag(28)
1370	1372	1363	A''		HCC(41)AHCC(27) HCOR(10)HCO(10)	Methine deformation (both ip and op bend)(51) coupled with methylene wag(37)
1349	1356	1347	A'		HCO(56)HCC(32) AHCC(10)	Methine deformation (both ip and op bend)(88) coupled with methylene wag(12)
1340	1340	1345	A''		HCC(71)HCO(11)	Methine deformation (both ip and op bend)(82)

See end of table for footnotes.

TABLE XXII (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDROXYLITOL

Exper. Freq., cm.		Calc. Freq., cm.	Sym. Class.		Approx. PE Dist., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR		Calc.	Exp.		
1320	1321	1329	A'	A'	HCO(59)HCC(19) HCOR(19)COH(10) AHCC(8)	Methine deformation (both ip and op bend)(78) coupled with methylene twist(27)
1306		1298	A''		HCO(38)HCC(32) HCOR(30)	Methine deformation (both ip and op bend)(70) coupled with methylene twist(33)
1296	1301	1292	A'		HCOR(64)HCO(19) AHCC(15)	Methylene twist(79) coupled with methine ip bend(19)
1285	1279	1272	A''	A'	HCOR(46)HCO(25) HCC(17)AHCC(14)	Methylene twist(60) coupled with methine deformation (both ip and op bend)(42)
1268	1267	1257	A'	A'	COH(56)HCC(16) HCO(14)HCOR(8) AHCC(6)	OH ip bend(56) coupled with methine deformation and CO ip bend(30) and methylene twist coupled with rock(14)
1239	1235	1207	A''		COH(80)HCC(17)	OH ip bend(80) coupled with methine op bend(17)
1199	1198	1201	A'	A'	COH(77)HCO(11) HCC(10)	OH ip bend(77) coupled with methine deformation (both ip and op bend)(21)
1143	1145	1141	A'	A'	CO(49)AHCC(18) CC(15)HCOR(2)	CO str.(49) coupled with methylene twist and rock (20) and ring CC str.(15)
		1131	A''		COR(60)AHCC(19) CC(19)CO(10) HCOR(2)	Asym. CORC str.(60) coupled with methylene twist(21), ring CC str.(19) and CO str.(10)
1120	1125	1110	A'	A'	CO(81)CC(16) CCC(13)	CO str.(81) coupled with ring vibration
1100	1100	1096	A''		CC(41)CO(33) COR(20)	CO str.(33) coupled with ring CC(41) and COR str. (20)
1092	1095	1095	A'	A'	CO(28)AHCC(26) CC(26)COH(18) HCOR(2)	CO str.(28) coupled with methylene twist and rock (28), ring CC str.(26), and OH ip bend(18)

See end of table for footnotes.



TABLE XXII (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDROXYLITOL

Exper. Freq., cm. <sub>i</sub>		Calc. Freq., cm. <sub>i</sub>	Sym. Class.		Approx. PE Dist., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR		Calc.	Exp.		
1056	1060	1049	A''	A'	CO(47)CC(34) AHCC(26)	CO str.(47) coupled with ring CC str.(34) and methylene twist and rock (28)
1017	1018	1014	A'	A'	CC(52)COR(34)	Ring CC(52) and COR(34) str.
		950	A''		CC(72)AHCC(30) HCC(18)	Primarily ring CC str.(72) coupled with methylene twist and rock(38)
933	936	927	A'	A'	COR(22)AHCC(19) CC(13)CCO(11) CO(9)CCOR(7) HCOR(6)COH(6)	Sym. ring str.(35) coupled with methylene twist and rock(25) and CO str.(9)
905	904	901	A''		CC(70)CCO(21) AHCC(15)CO(12)	Asym. ring str.(70) coupled with methylene twist and rock(18) and CO str.(12)
896	899	882	A'	A'	CC(61)COR(23) AHCC(20)CCO(19) HCC(19)	Sym. ring str.(61) coupled with methylene twist and rock(23), CO op bend(19), and methine op bend (19)
635	637	655	A'	A'	CCOR(25)CORC(24)	Sym. ring bend
	565	563	A''		CCO(60)HCC(26)	CO op bend(60) coupled with methine op bend(26)
544 538 (av.)	542 537 (av.)	533	A'	A'	CC(35)CCO(14) CO(14)	Ring CC str.(35) coupled with CO op bend(14) and CO str.(14)
455	456	467	A''	A''	CCO(43)HCC(14) CC(11)	CO op bend(43) coupled with methine op bend(14) and ring CCC bend(11)
437	440	429	A''	A''	CCC(29)CCO(24) CCOR(23)	Asym. ring bend
418	420	420	A'	A'	CCC(37)CORC(24) CCO(19)	Sym. ring bend

See end of table for footnotes.

TABLE XXII (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDROXYLITOL

Exper. Freq., cm. <sub>1</sub>		Calc. Freq., cm. <sub>1</sub>	Sym. Class.		Approx. PE Dist., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR		Calc.	Exp.		
369	366	368	A'	A'	HCC(24)CCC(23) CCO(15)CORC(13) CCOR(12)	Sym. ring bend(48) coupled with methine op bend(24) and CO op bend(15)
315	317	318	A'		CCO(66)HCC(18) CCOR(15)AHCC(12)	CO op bend(66) coupled with methine op bend(18), ring CCOR bend(15), and methylene rock(15)
299	295	297	A'		CCO(48)TCC(12) TCO(10)CCOR(9) HCC(9)CCC(8)	CO op bend(48) coupled with ring twist(21), OH op bend(10), and methine op bend(9)
280	285	278	A''		CCO(102)	CO op bend
234		241	A''		TCO(88)	OH op bend
225		230	A''		TCO(73)	OH op bend
220		228	A'		TCO(81)	OH op bend
202		200	A''		TCC(52)CCOR(13) CCO(12)CCC(10) TCO(10)	Ring twist coupled with CO op bend(12) and OH op bend(10)
		131	A'		TCC(52)CCC(27) CCO(11)CORC(8)	Ring twist

Average error = 5.91 cm.<sup>-1g</sup>

<sup>a</sup>Just the most significant contributions to the potential energy are listed. The sum of the components of the potential energy distribution may total more than 100% due to the presence of negative contributions resulting from negative interaction force constants.

<sup>b</sup>AC...denotes the "anomeric" carbon atom (i.e., the carbon atom adjacent to the ring oxygen atom).

<sup>c</sup>...OR denotes the ring oxygen atom.

<sup>d</sup>TCC, TCO, and TCOR denote torsion about the CC, CO, and COR bonds, respectively.

<sup>e</sup>In this column the molecular vibration for each normal mode is classified in terms of the particular group vibrations accounting for most of the molecular vibration.

<sup>f</sup>ip denotes "in-plane" bending and op denotes "out-of-plane" bending.

<sup>g</sup>The average error (mean deviation) is computed from the difference between the calculated and corresponding experimental frequencies, either infrared or Raman, whichever is closest, and excludes the OH stretching bands. The maximum deviation in Table XXII is 26.8 cm.<sup>-1</sup> and the minimum deviation in this table is -0.5 cm.<sup>-1</sup>

TABLE XXIII

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDRORIBITOL

Exper. Freq., cm. <sub>i</sub>		Calc. Freq., cm. <sub>i</sub>	Sym. Class.		Approx. PE Dist., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR		Calc.	Exp.		
3406	3409	3356	A'		OH(99.9)	OH stretch (str.)
3350	3345	3356	A''		OH(99.9)	OH str.
3250	3279	3356	A'		OH(99.9)	OH str.
2997	3000	2982	A'		ACH(92)	Asymmetric (asym.) methylene str.
2972	2970	2979	A''		ACH(92)	Asym. methylene str.
2943	2945	2931	A'		CH(94)	Methine str.
2932	2934	2925	A''		CH(92)	Methine str.
	2929	2921	A'		CH(95)	Methine str.
2918		2882	A'		ACH(96)	Symmetric (sym.) methylene str.
2875	2880	2880	A''		ACH(97)	Sym. methylene str.
1468	1466	1468	A'	A'	HCOR(53)HCH(45)	Methylene wag(53) coupled with methylene scissor(45)
1458		1460	A''	A'	HCOR(49)HCH(48)	Methylene wag(49) coupled with methylene scissor(48)
1419		1418	A''		AHCC(36)HCC(27) HCOR(14)	Methylene wag(50) coupled with methine op bend(27)
1403	1400	1412	A'		AHCC(42)HCC(21) HCOR(14)	Methylene wag(56) coupled with methine op bend(21)
1385	1388	1393	A'		HCC(51)HCO(18) AHCC(9)CO(7)	Methine deformation (mostly op but some ip bend)(69)
	1365	1367	A''		HCC(56)AHCC(17)	Methine op bend(56) coupled with methylene wag(17)
1350	1354	1344	A'		HCO(59)HCC(29)	Methine deformation (mostly ip, but some op bend)
		1320	A''		HCO(68)HCC(25) HCOR(12)	Methine deformation (mostly ip with some op bend) coupled with methylene twist(12)

See end of table for footnotes.

TABLE XXIII (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDRORIBITOL

Exper. Freq., cm. <sup>-1</sup>		Calc. Freq., cm. <sup>-1</sup>	Sym. Class.		Approx. PE Dist., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR		Calc.	Exp.		
1315	1310	1317	A'	A'	HCO(59)HCC(28) HCO(10)	Methine deformation (mostly ip with some op bend) coupled with methylene twist(10)
	1290	1295	A'	A'	HCO(69)AHCC(20) HCO(13)	Methylene twist(89) coupled with methine ip bend(13)
1281		1289	A''		HCC(45)HCO(32) AHCC(12)	Methine op bend(45) coupled with methylene twist(44)
1265	1264	1265	A''	A'	HCC(39)HCO(37) HCO(16)AHCC(10)	Methine deformation (mostly op with some ip bend)(55) coupled with methylene twist and rock(47)
1244	1245	1255	A'		COH(77)CC(8)	OH ip bend(77)
	1226	1233	A'	A'	COH(64)AHCC(13) HCC(12)HCO(9)	OH ip bend(64) coupled with methylene twist and rock(17)
1202	1202	1220	A''		COH(69)HCC(13) AHCC(11)HCO(7)	OH ip bend(69) coupled with methylene twist and rock(14)
1156	1156	1155	A'	A'	CO(42)AHCC(22) CC(16)	CO str.(42) coupled with methylene twist and rock(25) and ring CC str.(16)
1124	1126	1131	A''	A''	COR(56)AHCC(27) CC(11)	Asym. COR str.(56) coupled with methylene twist(28) and ring CC str.(11)
1104	1103	1106	A''		CC(52)CO(25) COR(22)	Asym. ring str.(74) coupled with CO str.(25)
1082	1083	1096	A'	A'	CO(37)CC(26) HCO(16)COH(16) AHCC(15)	CO str.(37) coupled with ring CC str.(26), methine ip bend(16), OH ip bend(16), and methylene twist and rock(16)
1043 (av.)	1045	1042	A''	A'	CO(60)AHCC(23) CC(12)	CO str.(60) coupled with methylene twist and rock(26) and ring CC str.(12)

See end of table for footnotes.

TABLE XXIII (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDRORIBITOL

Exper. Freq., cm. <sub>i</sub>		Calc. Freq., cm. <sub>i</sub>	Sym. Class.		Approx. PE Dist., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR		Calc.	Exp.		
		1024	A'		CC(40)COR(25) AHCC(21)	Sym. ring str.(65) coupled with methylene twist and rock(25)
1005	1000	1010	A'	A'	CO(62)AHCC(19) CC(15)	CO str.(62) coupled with methylene twist and rock(21) and ring CC str.(15)
993	989	981	A''		CC(63)AHCC(22) HCC(19)CCO(15) COR(11)	Asym. ring str.(74) coupled with methylene twist and rock(27), methine op bend (19), and CO op bend(15)
925	928	926	A'	A'	COR(41)CC(25) CCO(17)	Sym. COR str.(41) coupled with ring CC str.(25) and CO op bend(17)
878	879	876	A'	A'	CC(45)CO(16) CCOR(15)COR(10)	Sym. ring str.(70) coupled with CO str.(16)
	832	850	A''		CC(88)AHCC(12) CCOR(10)	Asym. ring CC str.(88) coupled with methylene rock(12)
669	668	676	A'		HCC(21)CCO(18) CC(18)CCC(17) AHCC(13)	Methine op bend(21) coupled with CO op bend(18), ring vib.(35) and methylene twist and rock(13)
647	649	641	A''	A'	CCO(53)HCC(24) CC(15)AHCC(9)	CO op bend(53) coupled with methine op bend(24)
581	582	599	A'	A'	COR(25)CC(21) CCOR(20)CO(11)	Sym. ring bend(66) coupled with CO str.(11)
448	451	463	A'	A'	CCOR(20)CCO(15) CCC(14)CC(10)	Ring bend(44) coupled with CO op bend(15)
437	433	446	A''	A'	CCOR(29)CCC(25) CCO(19)	Ring bend(54) coupled with CO op bend(19)
406	406	413	A''		CCO(88)AHCC(13) HCC(11)	CO op bend(88) coupled with methylene rock(17) and methine op bend(11)
345	342	342	A'	A'	CCO(39)CCOR(28) COR(16)TCC(11)	CO op bend(39) coupled with ring bend and twist

See end of table for footnotes.

TABLE XXIII (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDRORIBITOL

Exper. Freq., cm. <sup>-1</sup>		Calc. Freq., cm. <sup>-1</sup>	Sym. Class.		Approx. PE Dist., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR		Calc.	Exp.		
319		308	A'		CCO(70)CCC(8) CCOR(7)HCC(7) TCC(7)	CO op bend(70) coupled with ring bend and twist
306	305	283	A''		CCO(69)TCO(19) HCC(16)	CO op bend(69) coupled with OH op bend(19) and methine op bend(16)
271		255	A'		TCO(31)CCO(30) CCC(21)HCC(13)	OH op bend(31) coupled with CO op bend, ring CCC bend(21), and methine op bend(13)
238		240	A''		TCO(89)	OH op bend(89)
		227	A''		TCO(77)CCO(15)	OH op bend(77) coupled with CO op bend(15)
		220	A'		TCO(56)CCO(18) CCC(13)	OH op bend(56) coupled with CO op bend(18) and ring CC bend(13)
208		202	A''		TCC(56)CCOR(14) CCC(12)CCO(12)	Ring twist coupled with CO op bend(12)
(169) <sup>g</sup>		137	A'		TCC(51)CCC(26) CORC(10)CCO(8)	Ring twist

Average error = 7.60 cm.<sup>-1h</sup>

<sup>a</sup>Just the most significant contributions to the potential energy are listed. The sum of the components of the potential energy distribution may total more than 100% due to the presence of negative contributions resulting from negative interaction force constants.

<sup>b</sup>AC...denotes the "anomeric" carbon atom (i.e., the carbon atom adjacent to the ring oxygen atom).

<sup>c</sup>...OR denotes the ring oxygen atom.

<sup>d</sup>TCC, TCO, and TCOR denote torsion about the CC, CO, and COR bonds, respectively.

<sup>e</sup>In this column the molecular vibration for each normal mode is classified in terms of the particular group vibrations accounting for most of the molecular vibration.

<sup>f</sup>ip denotes "in-plane" bending and op denotes "out-of-plane" bending.

<sup>g</sup>This band was not included in the force constant refinement.

<sup>h</sup>The average error (mean deviation) is computed from the difference between the calculated and corresponding experimental frequencies, either infrared or Raman, whichever is closest, and excludes the OH stretching bands and the band at 169 cm.<sup>-1</sup> denoted by footnote g. In Table XXIII the maximum deviation is 36.5 cm.<sup>-1</sup> and the minimum deviation is 0.2 cm.<sup>-1</sup>

TABLE XXIV

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDRO-L-ARABINITOL

Exper. Freq., cm. <sup>-1</sup>		Calc. Freq., cm. <sup>-1</sup>	Approx. PE Distr., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR			
3425	3428	3356	OH(99.9)	OH stretch (str.)
	3385	3356	OH(99.9)	OH str.
3310	3320	3356	OH(99.9)	OH str.
2983	2985	2981	ACH(92)	Asymmetric (asym.) methylene str.
2973	2976	2978	ACH(95)	Asym. methylene str.
2932	2932	2940	CH(92)	Methine str.
	2925	2926	CH(96)	Methine str.
2916	2917	2915	CH(96)	Methine str.
2879	2879	2882	ACH(96)	Symmetric (sym.) methylene str.
2860	2863	2880	ACH(97)	Sym. methylene str.
1467	1463	1469	HCOR(50)HCH(46)	Methylene wag(50) coupled with methylene scissor(46)
1454	1460	1461	HCOR(48)HCH(48)	Methylene wag(48) coupled with methylene scissor(48)
1410	1410	1419	AHCC(32)HCC(26) HCOR(11)COH(8)	Methylene wag(43) coupled with methine op bend(26)
		1395	HCC(54)AHCC(21)	Methine op bend(54) coupled with methylene wag(21)
1381	1379	1378	HCC(50)AHCC(14) HCO(10)COH(8)	Methine op bend(50) coupled with methylene wag(18)
1369	1371	1372	HCC(47)HCO(28) AHCC(17)	Methine deformation (both op and ip bend)(75) coupled with methylene wag(22)
1343	1349	1341	HCO(45)HCC(35) AHCC(11)	Methine deformation (both op and ip bend)(80) coupled with methylene wag(14)
1325	1329	1326	HCO(61)HCC(26) HCOR(13)	Methine deformation (mostly ip with some op bend)(87) coupled with methylene twist(18)

See end of table for footnotes.

TABLE XXIV (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDRO-L-ARABINITOL

Exper. Freq., cm. <sup>-1</sup>		Calc. Freq., cm. <sup>-1</sup>	Approx. PE Distr., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR			
1309	1313	1313	HCOR(39)HCO(20) AHCC(19)HCC(11)	Methylene twist and rock (58) coupled with methine deformation (both ip and op bend)(31)
1302	1300	1304	HCOR(39)AHCC(22) HCO(12)HCC(11)	Methylene twist(61) coupled with methine deformation (both ip and op bend)(23)
1281	1279	1284	HCO(39)HCOR(30) HCC(21)COH(12) AHCC(8)	Methine deformation (both ip and op bend)(60) coupled with methylene twist(38) and OH ip bend(12)
1269	1262	1263	HCOR(44)AHCC(21) COH(16)HCC(15)	Methylene twist(65) coupled with OH ip bend(16) and methine op bend(15)
	1248	1251	COH(54)HCC(13) HCOR(11)HCO(10)	OH ip bend(54) coupled with methine deformation (both ip and op bend)(23) and methylene twist and rock(15)
1233	1233	1234	COH(57)HCC(15) HCO(12)	OH ip bend(57) coupled with methine deformation (both ip and op bend)(27)
1216	1217	1199	COH(77)HCC(14) HCO(8)	OH ip bend(77) coupled with methine deformation (both ip and op bend)(22)
1150	1151	1163	AHCC(25)CC(21)CO(18) HCC(17)COH(11)COR(11) HCO(8)	Methylene rock(31) coupled with ring str.(32), CO str.(18), methine deformation (25), and OH ip bend(11)
1136	1145	1130	CO(34)AHCC(24) COR(19)CC(17) CCC(9)	Asym. ring str.(45) coupled with methylene twist and rock(27) and CO str.(34)
1108 (av.)	1108 (av.)	1108	CO(73)CC(12) AHCC(8)CCC(8)	CO str.(73) coupled with ring vib.(20) and methylene rock(9)
1092	1093	1097	COR(41)CC(30)CO(26)	Asym. COR str.(41) coupled with ring CC str.(30) and CO str.(26)

See end of table for footnotes.



TABLE XXIV (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDRO-L-ARABINITOL

Exper. Freq., cm. <sup>-1</sup>		Calc. Freq., cm. <sup>-1</sup>	Approx. PE Distr., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR			
1067	1074	1074	CC(35)CO(27) AHCC(27)COH(10) HCC(10)	Asym. ring str.(35) coupled with CO str.(27), methylene twist and rock (30), OH ip bend(10), and methine op bend(10)
1057	1056	1061	CC(56)COR(28) CO(22)AHCC(11)	Sym. ring str.(84) coupled with CO str.(22) and methylene rock(17)
1005	1008	988	CC(44)AHCC(19) COR(13)CO(10)	Asym. ring str.(57) coupled with methylene twist and rock(23) and CO str.(10)
948	947	941	CC(61)CCO(18) AHCC(14)CCOR(12)	Asym. ring str.(87) coupled with methylene rock(22)
926	927	931	CO(40)AHCC(26) CC(26)COR(14) HCC(12)	CO str.(40) coupled with ring str.(40), methylene twist and rock(27), and methine op bend(12)
876	880	873	CC(58)COR(23) HCC(17)AHCC(16) CCO(11)	Sym. ring str.(81) coupled with methine op bend(17), methylene twist and rock (17), and CO op bend(11)
837	840	851	CC(30)CO(27)COR(21) CCO(12)	Sym. ring str.(51) coupled with CO str.(27) and CO op bend(12)
758	755	743	CCOR(21)CC(16)CO(14) CCO(10)CORC(9)CCC(7) HCC(6)	Ring bend(53) coupled with CO str.(14) and methine op bend(6)
633	636	637	CCO(25)CC(21)HCC(12) CORC(11)CCOR(8)	Ring bend(40) coupled with CO op bend(25) and methine op bend(12)
546	546	540	CCO(34)CC(17)CCOR(17)	CO op bend(34) coupled with ring bend(34)
483	483	487	CCO(40)CC(13)CCC(11)	CO op bend(40) coupled with ring bend(24)
430	426	441	CCO(46)HCC(24) CORC(15)	CO op bend(46) coupled with methine op bend(24) and CORC bend(15)

See end of table for footnotes.

TABLE XXIV (Continued)

CALCULATED AND EXPERIMENTAL FREQUENCIES INCLUDING  
APPROXIMATE POTENTIAL ENERGY DISTRIBUTIONS FOR  
CRYSTALLINE 1,5-ANHYDRO-L-ARABINITOL

Exper. Freq., cm. <sup>-1</sup>		Calc. Freq., cm. <sup>-1</sup>	Approx. PE Distr., % <sup>a,b,c,d</sup>	Description <sup>e,f</sup>
Raman	IR			
408	408	403	CCC(31)CCO(27) COR(10)CCOR(7)	Ring bend(48) coupled with methine op bend(27)
	383	380	CCO(44)CCC(25) CCOR(15)AHCC(11) TCC(11)	Ring bend and twist(51) coupled with CO op bend (44) and methylene wag(11)
314		302	CCO(38)CCOR(19) TCC(15)CORC(12)	Ring bend and twist(46) coupled with CO op bend (38)
296	296	285	CCO(102)	CO op bend(102)
256		260	CCO(38)TCO(26) HCC(16)CCC(16)	CO op bend(38) coupled with OH op bend(26), methine op bend(16), and ring CCC bend(16)
233		237	TCO(90)	OH op bend(90)
		236	TCO(82)	OH op bend(82)
		222	TCO(62)CCO(24)	OH op bend(62) coupled with CO op bend(24)
176		185	TCC(49)CCOR(18) CCO(10)CCC(7)	Ring twist(74) coupled with CO op bend(10)
		132	TCC(50)CCC(28) CCO(9)	Ring twist(78) coupled with CO op bend(9)

Average error = 5.16 cm.<sup>-1g</sup>

<sup>a</sup>Just the most significant contributions to the potential energy are listed. The sum of the components of the potential energy distribution may total more than 100% due to the presence of negative contributions resulting from negative interaction force constants.

<sup>b</sup>AC...denotes the "anomeric" carbon atom (i.e., the carbon atom adjacent to the ring oxygen atom).

<sup>c</sup>...OR denotes the ring oxygen atom.

<sup>d</sup>TCC, TCO, and TCOR denote torsion about the CC, CO, and COR bonds, respectively.

<sup>e</sup>In this column the molecular vibration for each normal mode is classified in terms of the particular group vibrations accounting for most of the molecular vibration.

<sup>f</sup>ip denotes "in-plane" bending and op denotes "out-of-plane" bending.

<sup>g</sup>The average error (mean deviation) is computed from the difference between the calculated and corresponding experimental frequencies, either infrared or Raman, whichever is closer, and excludes the OH stretching bands. In Table XXIV the maximum deviation is -20.2 cm.<sup>-1</sup> and the minimum deviation is 0.3 cm.<sup>-1</sup>

Tables XXII, XXIII, and XXIV, respectively. This information is essentially the heart of the interpretation of the vibrational spectra. The molecular vibrational motion was then classified in terms of the particular atomic group vibrations making the greatest contributions to the potential energy for each frequency or normal mode from the data computed by the program EIGV. The results of this classification appear in the last column in Tables XXII-XXIV. The definitions of several of the atomic group vibrations listed in these tables are presented in Fig. 29.

DISCUSSION OF RESULTS

GENERAL COMMENTS CONCERNING THE NORMAL COORDINATE ANALYSES

In general, the normal coordinate analyses of the 1,5-AP models were a success. The computer methods of J. H. Schachtschneider (89) with appropriate modification coupled with nonlinear least squares refinement of the force constants appear to provide the means for successful analyses and interpretation of the vibrational spectra of large, complex<sup>15</sup> molecules, at least of the mono-saccharides. The successful application of the nonlinear least squares refinement technique based on the Fletcher-Powell method has been the key to the mathematical treatment of the molecular vibrations of the 1,5-AP compounds, since the commonly used linear refinement technique could not be made to converge for these compounds.

The quality of the normal coordinate computations for the 1,5-AP compounds can be estimated from a number of observations.

1. The average error between the calculated and experimental frequencies is noted to be numerically small ( $6.22 \text{ cm.}^{-1}$ ). This observation suggests that the 1,5-AP model geometry and the SVQFF are reasonable approximations to the real molecule.
2. The same SVQFF was used in the calculation of frequencies for all three models with the resulting average errors in the three cases being numerically small and of the same order of magnitude ( $5.91$ ,  $7.60$ , and  $5.16 \text{ cm.}^{-1}$  for 1,5-AX, 1,5-AR, and 1,5-ALA, respectively). This observation supports the validity of the force field employed in the calculations.
3. The calculated frequencies for the three models tend to reproduce the distribution of bands in the 1,5-AP vibrational spectra. The agreement between calculated and experimental band distribution is evident

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<sup>15</sup>The reader is reminded that in this text the term complex is used to describe those molecules with several different atomic groups.

in the bar graph representation of the 1,5-AP spectra shown in Fig. 30. This observation is probably a more important indicator of the validity of the normal coordinate calculations than is the small average error value.

4. The analysis of the contributing group vibrations for the 1,5-AP spectral bands, which is based on the potential energy distributions in Tables XXII-XXIV, is in agreement with the group frequency correlation charts for those regions of the spectrum where the charts may be applied. This analysis also agrees with Snyder and Zerbi's interpretation of the tetrahydropyran spectrum (56).
5. The elements of the final SVQFF matrix in this investigation are, in general, numerically similar to Snyder and Zerbi's force field elements with the differences occurring in the hundredths place.

Several of the "new" interaction force constants which result from the introduction of hydroxyl groups to the tetrahydropyran ring are noted to have negligible values. These constants are primarily bend-bend interactions. However, when all the interaction force constants are compared with respect to magnitude, the CO stretch-bend interaction force constants as a group are found to contain the most significant members of any other group. The contribution of the CO stretch-bend interactions to the 1,5-AP force field is a major difference between the force fields of tetrahydropyran and the 1,5-AP compounds (models).

The standard errors in the force constants resulting from the nonlinear refinement (see Table XX) are observed to be larger, by a factor of about 2 to 10, than the standard errors listed by Snyder and Zerbi (56) resulting from the linear force constant refinement in the case of the aliphatic ethers. This may be a direct consequence of the fact that the nonlinear refinement in the analyses of the 1,5-AP compounds was based on 90 statistical degrees of freedom, while the linear refinement in the analyses of the aliphatic ethers was based on 171 degrees of freedom. Another reason for the discrepancy may be that the force constant refinement in the investigation of the 1,5-AP compounds was based on a nonlinear least squares technique in which the estimation of standard error is not as

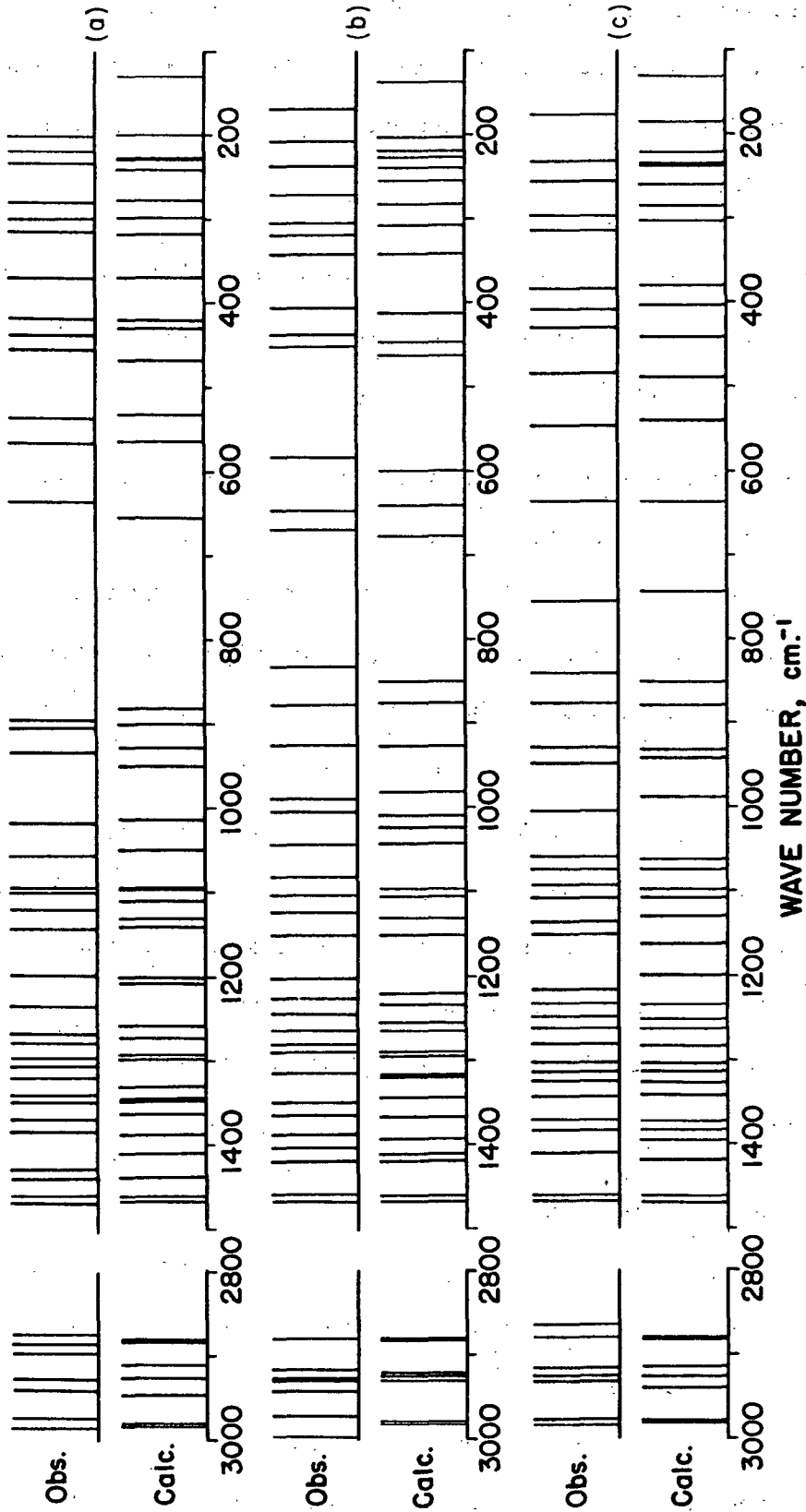


Figure 30. Comparative Bar Graphs for the 1,5-Anhydropentitol Compounds Showing the Agreement Between the Calculated and Experimental Spectra (a) 1,5-Anhydroxylylitol, (b) 1,5-Anhydroribitol, and (c) 1,5-Anhydro-L-arabinitol

straightforward as for the linear least squares technique employed by Snyder and Zerbi. [The reader may wish to compare the method of estimating the standard error in the linear refinement technique (Appendix IV) with the method for the nonlinear technique (page 131).]

A plot of eigenvalues vs. perturbation number reveals that the final set of eigenvalues for the 1,5-AP models were approached asymptotically, for the most part, in the nonlinear Fletcher-Powell refinement.

The average errors between the calculated and experimental frequencies are 5.91, 7.60, and 5.16  $\text{cm.}^{-1}$  for 1,5-AX, 1,5-AR, and 1,5-ALA, respectively, which excludes the three OH stretching bands. The overall average error is 6.22  $\text{cm.}^{-1}$ . This agreement is better than Snyder and Zerbi (56) obtained for tetrahydropyran (average error 12.5  $\text{cm.}^{-1}$ ) even though they did not attempt to assign the CH stretch region of the spectrum. In fact, the agreement is better than these workers obtained for the entire series of aliphatic ethers (average error 10.4  $\text{cm.}^{-1}$ ). The improved agreement between calculated and experimental frequencies resulting from the normal coordinate analyses of the 1,5-AP compounds is probably the result of including several additional interaction force constants that were excluded by Snyder and Zerbi. A few of these force constants were determined to have significant magnitude.

The close agreement between the calculated and experimental frequencies for the 1,5-AP compounds, as indicated by the low overall average error, suggests that the assumption of tetrahedral geometry for the models was reasonable. Indeed, the bond angles of the real molecules would not be expected to deviate from the ideal tetrahedral angle by more than a few degrees. Most of the averaged bond lengths used in the models should not vary more than a few hundredths of an

angstrom from those of the real molecules. However, the frequency agreement might have been even better had the exact molecular geometry been known."

The frequencies were calculated for the 1,5-AR model with the lower portion of the ring, i.e., C2-C3-C4, being made "flatter." That is, the angle of intersection between the planes passing through C2-C3-C4 and C1-C2, C4-C5 of the ring was reduced incrementally in a number of calculations keeping the force field constant. The average error was plotted vs. the CCCO(r) dihedral angle (initially 60°) which is related to the angle of intersection of the ring planes. The result was that the average error decreased until the dihedral angle reached 58° after which the average error began to increase as the dihedral angle decreased. This observation suggests that the real molecule may be slightly "flatter" than the assumed 1,5-AR model by a few degrees in the CCCO(r) dihedral angle which may account for the somewhat higher average error for this compound. This suggestion is partially supported by the x-ray diffraction data reported for methyl β-D-ribofuranoside (123) in which the lower portion of the ring is observed to be somewhat "flatter" by a few degrees in the CCCO(r) dihedral angle. However, a crystal structure study of 1,5-AR must be completed before the validity of this suggestion based on normal coordinate calculations can be established.

The potential energy distribution (Tables XXII-XXIV) was used to characterize the calculated frequencies (therefore, the assigned frequencies also) as to the dominant group vibrations. The potential energy contributions of each internal coordinate comprising a particular group vibration (see Fig. 29), e.g., methylene "wag" which involves the internal coordinates  $\angle\text{HCO}(\underline{r})$  and  $\angle\text{HCC}$ , are summed to estimate the contribution of that atomic group vibration to the potential energy of a calculated frequency. The characterization of each of the



calculated frequencies in terms of atomic group vibrations appears in the last column of Tables XXII-XXIV. This information simplifies the correlation with group frequency charts and interpretation of the 1,5-AP spectra.

Examination of the potential energy distributions for 1,5-AX, 1,5-AR, and 1,5-ALA in Tables XXII-XXIV reveals that the vibrational bands are highly coupled; that is, more than one group vibration contributes significantly to the molecular vibration. This extensive vibrational coupling is the primary reason for the failure of the traditional group frequency approach for interpreting complex vibrational spectra. A comparison of Tables XXII-XXIV shows that corresponding calculated frequencies for each of the three 1,5-AP models exhibit essentially equivalent potential energy distributions. Further examination of Tables XXII and XXIII, corresponding to 1,5-AX and 1,5-AR, provides the observation that several of the corresponding calculated frequencies for the two models that differ by more than  $10 \text{ cm.}^{-1}$  involve internal coordinates of the OH group at C3 in the potential energy distribution, as might be expected.

The assigned symmetry species for the calculated frequencies for 1,5-AX and 1,5-AR resulting from the solutions of the secular determinants using the factored  $\underline{G}$  and  $\underline{Z}$  matrices (factored by the introduction of symmetry coordinates) are in agreement, for the most part, with the symmetry species determined from the depolarization ratio measurements. In most of the cases where there is a conflict between the two symmetry classifications, the depolarization ratio is questionable because the spectral band is overlapped with another. In this situation, an accurate depolarization ratio cannot be determined. The only exception to the above statements is provided by the 1,5-AR spectral band at  $648 \text{ cm.}^{-1}$ . The symmetry classification from the depolarization ratio measurement is in conflict with the calculated symmetry classification from the normal

coordinate computations. In this case, the band is not significantly overlapped with another. However, the band is quite weak which makes the depolarization ratio measurement questionable. In general, the depolarization ratio measurements agree with the calculated symmetry species.

The agreement between the experimental and calculated frequencies (i.e., average error) is approximately the same for the 1,5-AP models. In addition, the force fields for the 1,5-AP models are identical, with the exception of one or two numerically small interaction constants. Therefore, the differences in the spectral band positions (frequencies) between compounds (see Fig. 31 for a comparison of the Raman spectra and also Fig. 32 for a comparative bar graph of the Raman spectra for the 1,5-AP compounds), which tend to be reproduced by the calculated frequencies (see Fig. 30), must be the result of differences in the  $\underline{G}$  matrix, primarily. The  $\underline{G}$  matrices contain 862 nonzero elements each for the 1,5-AP models. There are 160 elements that differ between the  $\underline{G}$  matrices of 1,5-AX and 1,5-AR and 150 elements that differ between the  $\underline{G}$  matrices of 1,5-AX and 1,5-ALA. These discrepancies are the result of the differences in the orientation of the hydroxyl groups, that is, axial vs. equatorial, between models. Since the bond angles and bond lengths remain the same, the orientation of the hydroxyl groups is the dominant source of frequency differences between the vibrational spectra of the 1,5-AP compounds. The frequency variations may then be attributed primarily to a kinetic energy effect rather than a potential energy effect.

The NMR spectra of the 1,5-AP compounds were measured in this investigation in anticipation that they would provide conformational information regarding the 1,5-AP solutions. Unfortunately, the NMR spectra of the 1,5-AP compounds in D<sub>2</sub>O

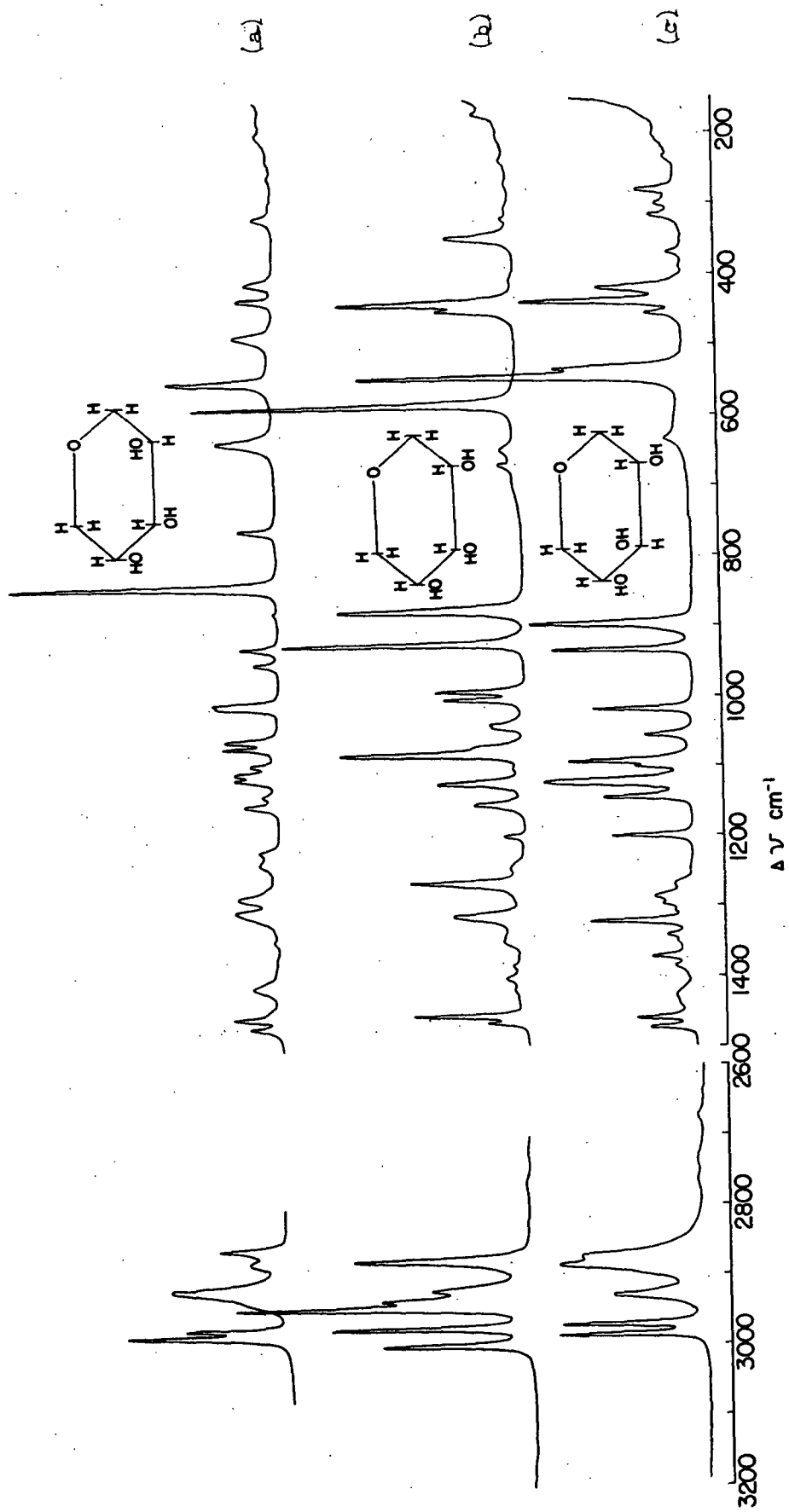


Figure 31. A Comparison of the Raman Spectra of Crystalline (a) 1,5-Anhydro-xylitol, (b) 1,5-Anhydro-arabinitol, and (c) 1,5-Anhydro-ribitol

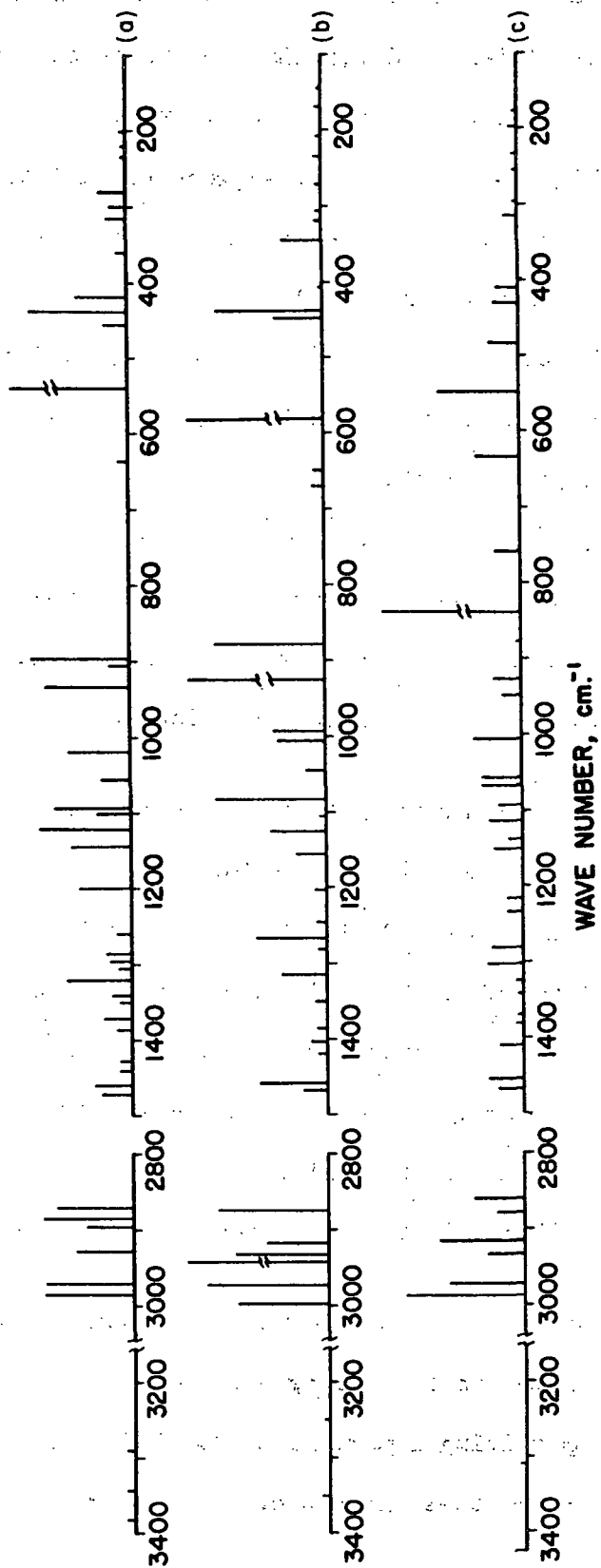


Figure 32. Comparative Bar Graphs Representing the Raman Spectra of the 1,5-Anhydropentitol Compounds. The Differences in the Spectra are Clearly Visible: (a) 1,5-Anhydroxylytol, (b) 1,5-Anhydroribitol, and (c) 1,5-Anhydro-L-arabinitol

and DMSO-d<sub>6</sub> do not offer much conformational information. The NMR spectra are much too complex to analyze. The series of spectral bands in the region from  $\delta$  4.2 to  $\delta$  2.7 p.p.m. in the 1,5-AX and 1,5-ALA D<sub>2</sub>O NMR spectra appears as a much condensed set of bands in the region from  $\delta$  4.0 to  $\delta$  3.6 p.p.m. in the 1,5-AR D<sub>2</sub>O spectrum (see Fig. 3-5). This may suggest rapid interconversion between conformations for 1,5-AR. (The strong band at approximately  $\delta$  4.6 p.p.m. is due to the OH impurity in the D<sub>2</sub>O.) The DMSO-d<sub>6</sub> NMR spectrum for 1,5-AR displays OH bands between  $\delta$  4.0 and  $\delta$  5.0 p.p.m. (see Fig. 7). That these are OH bands is demonstrated by the fact that these bands disappear when D<sub>2</sub>O is added to the system [for example, compare Fig. 8a with Fig. 8b]. In summary, it is difficult to gain any evidence for the most stable conformer existing in solution for the 1,5-AP compounds from the NMR spectra because of their complexity. However, later in this text it is shown that some conformational information is obtained from the Raman solution spectra.

The SVQFF developed in this investigation of the 1,5-AP compounds is expected to provide a reasonable initial force field for normal coordinate analyses of the pentoses. This force field should result in the simplification of the task of initially correlating the calculated frequencies with the experimental data. The additional interaction force constants which result from the introduction of a Cl hydroxyl group in going from the 1,5-AP compounds to the pentoses may be set equal to zero in the initial force field and evaluated later in the force field refinement after the frequency correlation is accomplished.

The vibrational spectra of the 1,5-AP compounds (both crystalline and aqueous solution) have been interpreted in this study based on the normal coordinate analyses. In addition to providing important spectral data for a class of compounds previously unstudied, these interpretations should serve as a guide in

the assignment of other carbohydrate spectra. The previous interpretations of carbohydrate spectra which were based on the normal coordinate analysis of tetrahydropyran may be reevaluated with the results of this study, since the 1,5-AP compounds provide a more closely related saccharide model compound than does tetrahydropyran.

The results of the spectra analyses for the 1,5-AP compounds will now be discussed for each of the compounds individually.

#### DISCUSSION OF THE INDIVIDUAL 1,5-ANHYDRO-PENTITOL VIBRATIONAL SPECTRA

##### 1,5-ANHYDROXYLITOL

##### Interpretation of the Solid State Spectra

In general, the Raman and infrared spectra for 1,5-AX in the solid state are complementary. Most of the spectral bands appear in both spectra, which should be the case, since the fundamental bands for the 1,5-AP compounds are both Raman and infrared active. A few additional bands appear in the infrared. These bands are suspected to be overtone or combination bands. It is a well-known fact that combination and overtone bands are more likely to be observed in the infrared spectrum than in the Raman spectrum.

The possibility of spectral aberrations in the infrared spectra of the 1,5-AP pellets which might result from interaction with the potassium bromide was investigated. The infrared spectra of the 1,5-AP compounds were recorded as Nujol and Fluorolube mulls. No spectral differences were observed when the mull spectra and pellet spectra were compared.

The interpretation of the crystalline 1,5-AX vibrational spectra (infrared and Raman) has essentially been accomplished by the normal coordinate analysis.

The resulting potential energy distributions and their characterization in terms of atomic group vibrations (see Table XXII and Fig. 29) are basically the spectral interpretation. Only a few comments concerning the interpretation of the 1,5-AX spectra are required regarding those points not evident from the table. In the following discussions, the spectral bands will be referred to by their frequencies in wave numbers ( $\text{cm.}^{-1}$ ). The Raman frequency will be reported first with the corresponding infrared frequency following in parentheses. Any exceptions to this convention will be noted when they occur. (The reader may wish to refer to the crystalline 1,5-AX spectra in Fig. 9 and 10 and the tabulated frequencies in Table III for the discussion to follow. The comparative bar graphs in Fig. 30 and 31 may also be helpful.)

There are three OH stretching bands observed in the solid state spectra at 3383(3387), 3343(3350), and 3290(3300)  $\text{cm.}^{-1}$ . However, the normal coordinate computations predict three bands in this region of the same frequency, 3356  $\text{cm.}^{-1}$ . The reason for this is that only one OH stretching force constant was used in the force field, which is equivalent to saying that the three OH groups have identical bond strengths. This assumption is invalid as the spectra demonstrate. One might use three independent OH force constants to rectify this situation. Nevertheless, the final results would not indicate a great improvement in the average error because the three OH stretching force constants would be averaged for the three molecules, and these bands differ widely in frequency for each compound because of the varying degrees of hydrogen bonding. The OH stretching bands are independent of the rest of the vibrational spectrum. Therefore, the OH stretching force constants could be set equal to zero without affecting the normal coordinate calculations. It is just as reasonable to employ only one force constant for OH stretching to make the analysis complete, but to disregard the contribution of the OH stretching bands to the average error. The differences between observed and

calculated frequencies in this region of the spectrum are not indicative of the frequency agreement for the rest of the vibrational spectrum, so to exclude these bands from the average error computation is justifiable.

The mathematical analysis predicts seven CH stretching bands. Only six bands are seen in the individual Raman and infrared spectra. However, when the two spectra are compared, one observes that the seventh band appears at  $2941\text{ cm.}^{-1}$  in the infrared spectrum and is not seen in the Raman spectrum. Correspondingly, the shoulder at  $2896\text{ cm.}^{-1}$  in the Raman spectrum is not observed in the infrared spectrum.

The spectral region from  $1472(1470)\text{ cm.}^{-1}$  through  $1340(1340)\text{ cm.}^{-1}$  is characterized primarily by methylene "wag" coupled with methine deformation. An interesting observation is that the bands at  $1472(1470)\text{ cm.}^{-1}$  and  $1459(1464)\text{ cm.}^{-1}$  are not pure methylene "scissoring" bands as might be expected, but are equally coupled with methylene "wag" resulting in a more complex group vibration. Two bands observed in the infrared, but not Raman spectrum at  $1402$  and  $1397\text{ cm.}^{-1}$ , have not been assigned to fundamental vibrations. These bands are weak shoulders which the author suspects might arise from a combination of fundamentals, i.e., combination bands. Possible combinations which might result in each of these bands are presented in Table XXV to suggest that such bands are possible in this region of the spectrum. Further support for the argument that these bands are combination bands comes from the fact, stated above, that such bands are more likely to appear in the infrared than Raman spectrum.

The next region, from  $1320(1321)\text{ cm.}^{-1}$  through  $1285(1279)\text{ cm.}^{-1}$ , is distinguished by primarily methylene "twist" coupled with methine deformation.



TABLE XXV

SUGGESTED COMBINATION BANDS IN THE VIBRATIONAL SPECTRA  
OF CRYSTALLINE 1,5-ANHYDROXYLITOL AND POSSIBLE  
COMBINATIONS WHICH MIGHT RESULT IN SUCH BANDS

Suspected Combination Band, <sup>a</sup> cm. <sup>-1</sup>	Possible Combination, <sup>b</sup> cm. <sup>-1</sup>
1402(IR)	2 x (1018) - (637) = 1399
1397(IR)	(1199) + (1095) - (899) = 1395
1168(IR)	(1095) + (1018) - (936) = 1177
1052(IR)	(1018) + (936) - (899) = 1055
928(IR)	2 x (1060) - (1198) = 922

<sup>a</sup>IR designates that the band is observed in the infrared spectrum.

<sup>b</sup>The numbers shown in parentheses are the fundamental band frequencies in wave numbers.

The spectral bands at 1268(1267), 1239(1235), and 1199(1198) cm.<sup>-1</sup> are interpreted as primarily COH bending bands (OH in-plane bending). This interpretation is supported by the fact that the corresponding bands in the spectra of deuterated 1,5-AX (see Fig. 15 and 16 along with Table VI) are reduced in relative intensity.

A very weak infrared band appearing at 1168 cm.<sup>-1</sup> is not assigned to a fundamental vibration. The author suspects that this band is a combination band. A possible combination which might result in a band in this region is presented in Table XXV.

From 1143(1145) cm.<sup>-1</sup> through 1120(1125) cm.<sup>-1</sup>, the spectral bands are attributed to CO(H) and CO(r) stretching vibrations, where (r) designates the pyranose ring oxygen atom. A calculated band in this region at 1131 cm.<sup>-1</sup> is not observed in either the Raman or infrared spectrum. However, it is possible

that this band is present, but hidden because of the overlapping band tails of the bands at 1143(1145) and 1120(1125)  $\text{cm.}^{-1}$

The bands in the region from 1100(1100)  $\text{cm.}^{-1}$  through 896(899)  $\text{cm.}^{-1}$  are assigned to CO stretching vibrations and ring stretching vibrations coupled with methylene "twist" and "rock." A shoulder appears in the infrared spectrum at 1052  $\text{cm.}^{-1}$ . This band could be a combination band. A possible combination is presented in Table XXV. Another shoulder, although much weaker, is noted in the infrared at 928  $\text{cm.}^{-1}$ . This band also does not correlate with the set of calculated frequencies. The author suggests that this band is a combination band (see Table XXV). The normal coordinate calculations predict a band at 950  $\text{cm.}^{-1}$  which is not observed in either the Raman or infrared spectrum. Perhaps, the intensity of this band is too weak for the band to be detected or the band may be masked by the strong band at 933(936)  $\text{cm.}^{-1}$

The spectral region from 635(637)  $\text{cm.}^{-1}$  through 315(317)  $\text{cm.}^{-1}$  is dominated by ring vibrations, bending, and stretching, coupled to a lesser extent with methine deformation or methylene "rock." In this region, a shoulder appears at 533(533)  $\text{cm.}^{-1}$  in both the Raman and infrared spectra which does not correlate with the calculated frequencies resulting from the mathematical analysis. The author suggests that this band is the result of band splitting, producing two bands at 544(542) and 533(533)  $\text{cm.}^{-1}$ , caused by vibrational coupling within the crystal lattice. In other words, the splitting of a fundamental vibrational band into two bands is the result of the crystalline state of the compound. The position of the unperturbed fundamental band might be estimated to appear at 538  $\text{cm.}^{-1}$  which is the average of 544 and 533  $\text{cm.}^{-1}$ . The solution spectra of 1,5-AX offer support for this argument (see Fig. 21 and Table IX). A single band is observed at 535  $\text{cm.}^{-1}$  in the water solution spectrum and at 536  $\text{cm.}^{-1}$  in the DMSO- $d_6$  solution

spectrum. Furthermore, an average value of  $538 \text{ cm.}^{-1}$  is in closer agreement with the calculated frequency corresponding to the fundamental band which is  $533 \text{ cm.}^{-1}$ .

Potassium bromide absorbs strongly in the infrared region below  $300 \text{ cm.}^{-1}$ , so the measured infrared spectrum is limited to the region above  $300 \text{ cm.}^{-1}$ . The Raman spectrum, on the other hand, can be recorded below  $300 \text{ cm.}^{-1}$ , but below  $150 \text{ cm.}^{-1}$  Rayleigh scattering and grating ghosts (with the Spex Raman spectrometer equipped with an Argon ion laser employed in this investigation) mask the spectral bands of crystalline compounds.

The spectral bands at  $299(295)$  and  $280(285) \text{ cm.}^{-1}$  are assigned to CO(H) deformation.

The weak Raman bands at  $234$ ,  $225$ , and  $220 \text{ cm.}^{-1}$  are assigned to CO(H) torsional vibrations (OH out-of-plane bending). The Raman spectrum of a magnesium oxide pellet displays two weak, broad bands at  $232$  and  $212 \text{ cm.}^{-1}$  with the wavelength of the laser beam at  $5145 \text{ \AA}$ . and the slit conditions similar to those employed for the 1,5-AX pellet spectra. These bands are grating ghosts as demonstrated by the fact that they shift in frequency when the wavelengths of the laser beam is changed to  $4880 \text{ \AA}$ . This observation suggests that the bands at  $234$  and  $220 \text{ cm.}^{-1}$  in the crystalline 1,5-AX Raman spectrum may be the result of grating ghosts. To investigate this possibility, the Raman spectrum of crystalline 1,5-AX was recorded with the wavelength of the laser beam set at  $4880 \text{ \AA}$ . The two bands at  $234$  and  $220 \text{ cm.}^{-1}$  remained unshifted which indicates that they are real vibrational bands.

The Raman band at  $202 \text{ cm.}^{-1}$  is attributed to a ring twisting vibration. The calculations predict a band at  $131 \text{ cm.}^{-1}$  due to a ring twisting vibration, but this band cannot be detected in the solid state Raman spectrum because of the

Rayleigh scattering and grating ghosts. Although the grating ghosts did not appear in the 1,5-AX solution spectrum, a band at approximately  $131 \text{ cm.}^{-1}$  could not be detected. If such a band does exist in the vibrational spectrum, it is probably extremely weak, too weak to be recorded in the solution spectrum.

#### Solution Spectra of 1,5-Anhydroxylitol

The concentrated water solution (more than 25%) spectrum of 1,5-AX appears in Fig. 21 and the frequencies for both the water and DMSO- $d_6$  solution spectra are tabulated in Table IX. (The spectra of the more concentrated solutions were observed to be quite similar to the less concentrated solutions except that the spectral bands were more intense in the former spectra.) The solution spectra provide a comparison of the vibrational dynamics of 1,5-AX in solution with that for the compound in the solid state. The concentrated water solution spectrum may be used as a substitute for the melt spectrum which could not be recorded in this investigation. In addition, the effect of solvent type on the vibrational spectrum can be estimated from a comparison of the solution spectrum of 1,5-AX in water, an amphiprotic solvent, with the solution spectrum of 1,5-AX in DMSO- $d_6$ , an aprotic solvent. Such an examination (see Table IX) suggests that the solvent type has very little effect on the spectrum, at least at concentrations greater than 30% by weight, because the two spectra are almost identical. Furthermore, the solvent itself does not appear to alter the spectrum to any large extent, since the solution spectral bands correlate well with the solid state spectral bands. (The correlation of the solution spectra with the solid state Raman spectrum is presented in Table XXVI.) Some of the solution spectral bands are shifted in frequency or are broadened from the corresponding bands appearing in the solid state spectrum, but these deviations are suggested to result from the rotation of the molecules rather than from the interaction with the solvent.

TABLE XXVI

CORRELATION OF THE 1,5-ANHYDROXYLITOL SOLUTION SPECTRA  
(WATER AND DMSO-d<sub>6</sub>) WITH THE SOLID STATE RAMAN SPECTRUM

Raman, cm. <sup>-1</sup>	H <sub>2</sub> O Solution, cm. <sup>-1</sup>	DMSO-d <sub>6</sub> Solution, cm. <sup>-1</sup>
2985	2985	2972
2970		
2928	2912	2908
2896		
2885		
2871	2875(broad)	2861(broad)
1472	1469	1470
1459	1462	1460
1439	broad band	1439
1427	broad band	broad band
1385	1385	1380
1370	1368	1370
1349	lost in background	lost in background
1340	lost in background	lost in background
1320	1325	1319
	1313	1312
1306	hidden in broad band	hidden in broad band
1296	hidden in broad band	hidden in broad band
1285	1285(broad)	broad bend
1268	hidden in broad band	hidden in broad band
1239	1232	1227
1199	1202	1196
1143	1140	1142
1120	1123	1123
1100	1098	1101
1092	1092	1097
1056	1062	solvent band
1017	1023	solvent band
933	941	946
905	not visible	not visible
896	896	899
	812(new)	812(new)
635	630	solvent band
544	535	536
533		
455	456	457
437	437	439
418	416	413
369	broad band	solvent band
315	broad band	solvent band
299		
280		

In Table XXVI, one notes that a "new" spectral band appears at  $812\text{ cm.}^{-1}$  in the solution spectra. This band does not appear in the solid state spectra and is not predicted by the mathematical analysis. This band is suspected to result from a small proportion of the 1,5-AX molecules existing in the alternate chair conformation in solution. The conformational free energy calculations, in Table XVI, suggest that only about 5% of the molecules exist in the alternate conformation in solution at equilibrium. Furthermore, based on other information this is a reasonable region of the spectrum to expect a band due to the alternate conformer. The band at  $812\text{ cm.}^{-1}$  may be the most intense band in the spectrum of the alternate conformer which would explain why it is seen and no other "new" bands are observed. Depolarization ratio measurements for this band classify it as belonging to the symmetric symmetry species,  $A'$ . These bands are usually more intense in the Raman spectrum than the antisymmetric bands,  $A''$ .

#### Spectra of Deuterated 1,5-Anhydroxylitol

The vibrational spectra of crystalline deuterated 1,5-AX were measured for the purpose of providing additional information to assist the assignment of the 1,5-AX solid state spectral bands, especially the assignment of the COH deformation bands.

In general, the spectra of deuterated 1,5-AX is characterized by the appearance of several (11) "new" bands, the decrease in relative intensity of several bands (10), and the increase in relative intensity of other bands (2). (The reader may wish to compare the spectra of deuterated 1,5-AX, Fig. 15 and 16 and summarized in Table VI, with the spectra for 1,5-AX, Fig. 9 and 10 and summarized in Table III.) The bands that were reduced in relative intensity were found to contain a significant contribution of COH bending. An examination of the

deuterated 1,5-AX spectra reveals that the compound was not completely deuterated, i.e., 100%, after pellet preparation.

### 1,5-ANHYDRORIBITOL

#### Interpretation of the Solid State Spectra

The interpretation of the 1,5-AR solid state spectra (Fig. 11 and 12 along with Table IV) is again based upon the potential energy distributions expressed in terms of the various group vibrations (see Table XXIII and Fig. 29) which result from the normal coordinate computations. In keeping with the discussion of the 1,5-AX vibrational spectra, only those points of the interpretation requiring further comment will be presented. In the following discussion, the frequency, in wave numbers, of the Raman band will be given first followed by the corresponding frequency for the infrared band in parentheses, unless otherwise indicated.

The three OH stretching bands at 3406(3409), 3350(3345), and 3250(3279)  $\text{cm.}^{-1}$  are assigned to the three calculated bands of the same frequency, 3356  $\text{cm.}^{-1}$ . As stated in the discussion of the 1,5-AX spectra, this is a result of using only one OH stretching force constant. These bands are not included in the computation of the average error because they are not representative of the frequency agreement for the rest of the spectrum. An interesting observation is that the middle OH stretching band which occurs at 3350(3345)  $\text{cm.}^{-1}$  is at approximately the same position as the middle OH stretching band for 1,5-AX which is at 3343(3350)  $\text{cm.}^{-1}$ . The other two bands are spread further apart for 1,5-AR, 3406(3409)  $\text{cm.}^{-1}$  for 1,5-AR versus 3383(3387)  $\text{cm.}^{-1}$  for 1,5-AX and 3290(3279)  $\text{cm.}^{-1}$  versus 3290(3300)  $\text{cm.}^{-1}$ . This observation suggests that there are differences in the hydrogen bonding in the two crystalline compounds.

Again, one notes that the calculations predict seven CH stretching bands and both the Raman and infrared spectra show only six bands each in this region. By comparing the Raman and infrared spectra, the seventh band is observed in the infrared spectrum at  $2929 \text{ cm.}^{-1}$ , since it is an additional band to what is seen in the Raman spectrum. The Raman band at  $2918 \text{ cm.}^{-1}$  is not seen in the infrared, so this accounts for the fact that only six bands appear in each of the spectra.

The spectral region from  $1468(1466) \text{ cm.}^{-1}$  through  $1350(1354) \text{ cm.}^{-1}$  is characterized by primarily methylene "wagging" vibrations coupled with methylene deformation. The bands at  $1468(1466)$  and  $1458 \text{ cm.}^{-1}$  are not pure methylene "scissor" vibrations as was noted for 1,5-AX, but are methylene "scissor" coupled with methylene "wag," approximately equally mixed, to produce a complex methylene vibration. The broad band appearing at  $1435 \text{ cm.}^{-1}$  in the infrared spectrum is suspected of originating from the overlap of two bands corresponding to the bands at  $1458$  and  $1419 \text{ cm.}^{-1}$  in the Raman spectrum. These individual bands do not appear in the infrared spectrum.

The calculated band with a frequency of  $1320 \text{ cm.}^{-1}$  is not observed in either the Raman or infrared spectrum. It is possible that this band may be hidden in the tail of the strong Raman band at  $1315 \text{ cm.}^{-1}$

The region from  $1315(1310) \text{ cm.}^{-1}$  through  $1265(1264) \text{ cm.}^{-1}$  is described by methine deformation coupled with methylene "twist."

The three bands at  $1244(1245)$ ,  $(1226)$ , and  $1202(1202) \text{ cm.}^{-1}$  are assigned to COH bending (OH in-plane bending). This assignment is supported by the fact that the corresponding spectral bands in the deuterated 1,5-AR spectra are decreased in relative intensity (see Fig. 17 and 18 along with Table VII).



The spectral band at 1167  $\text{cm.}^{-1}$  in the infrared does not correlate with the calculated frequencies. This band may be a combination band. A possible combination which might result in a band in this region is presented in Table XXVII.

TABLE XXVII

SUGGESTED COMBINATION BANDS IN THE VIBRATIONAL SPECTRA  
OF CRYSTALLINE 1,5-ANHYDRORIBITOL AND POSSIBLE  
COMBINATIONS WHICH MIGHT RESULT IN SUCH BANDS

Suspected Combination Band, <sup>a</sup> $\text{cm.}^{-1}$	Possible Combination, <sup>b</sup> $\text{cm.}^{-1}$
1167(IR)	$(1045) + (1000) - (879) = 1166$
1093(IR)	$2 \times (1045) - (1000) = 1090$
1077(IR)	$2 \times (1103) - (1126) = 1080$
1073(R)(IR)	$2 \times (1000) - (928) = 1072$
963(IR)	$2 \times (1045) - (1126) = 964$
916(R)(IR)	$(1045) + (879) - (1000) = 924$
873(IR)	$(1045) + (928) - (1103) = 870$
776(IR)	$(1045) + (1000) - (1264) = 781$
683(IR)	$2 \times (342) = 684$
	$(1045) + (989) - (1354) = 680$
396(R)(IR)	$(1400) - (1000) = 400$

<sup>a</sup>IR designates that the band is observed in the infrared spectrum; while R designates that the band is observed in the Raman spectrum.

<sup>b</sup>The numbers shown in parentheses are the fundamental band frequencies in wave numbers.

The spectral region from 1156(1156)  $\text{cm.}^{-1}$  through (832)  $\text{cm.}^{-1}$  is characterized by CO stretching and ring stretching vibrations coupled with methylene "twist" and "rock." There are two shoulders at 1093 and 1077  $\text{cm.}^{-1}$  in the infrared which do not correlate with the calculated frequencies. These bands

may be explained as combination bands (see Table XXVII). The band at 1073(1070)  $\text{cm}^{-1}$  in both the Raman and infrared spectra may also be attributed to a combination band (see Table XXVII). The Raman bands at 1045 and 1040  $\text{cm}^{-1}$  may result from band splitting due to vibrational coupling within the crystal lattice. Support for this argument comes from the fact that the calculations predict only one band in this region and that the infrared solid state, solution, and deuterated 1,5-AR spectra display only one band in this region. In further support, the average of the two Raman band frequencies is 1043  $\text{cm}^{-1}$  which is in close agreement with the calculated band in this region at 1042  $\text{cm}^{-1}$ . The normal coordinate calculations predict a band at 1024  $\text{cm}^{-1}$  which is not observed in the Raman spectrum. However, a weak shoulder in the infrared spectrum at 1018  $\text{cm}^{-1}$  might be assigned to the calculated band. This assignment is questionable and was not made in the normal coordinate calculations. A weak band at 963  $\text{cm}^{-1}$  in the infrared spectrum, which is not evident in the 1,5-AR mull spectra, is suspected of being a combination band (see Table XXVII). The weak shoulder at 916(916)  $\text{cm}^{-1}$  appears in both the Raman and infrared spectra, but does not correlate with the calculated frequencies for the 1,5-AR model. This band is also suspected of being a combination band (see Table XXVII). In addition, the three infrared bands occurring at 873, 776, and 683  $\text{cm}^{-1}$  are possibly combination bands with the exception that the last band might be an overtone band. (This band is not evident in the mull spectra.)

From 669(668)  $\text{cm}^{-1}$  through 306(305)  $\text{cm}^{-1}$ , the vibrational bands consist of mostly ring bending or twisting vibrations coupled with methylene "rocking" and "twisting" or CO deformation. The very weak band at 396(395)  $\text{cm}^{-1}$  which is observed in both Raman and infrared spectra is suspected of being a combination band (Table XXVII), since it does not correlate with the calculated frequencies. What appears to be a shoulder at 353  $\text{cm}^{-1}$  in the infrared spectrum is

interpreted to be an artifact of the infrared spectrometer resulting from a slit width change occurring in this region.

The Raman bands in the region from 306(305)  $\text{cm}^{-1}$  through 208  $\text{cm}^{-1}$  (the infrared spectral bands in this region being masked by the absorption of potassium bromide) are assigned to COH torsional vibrations (OH out-of-plane bending) except the band at 306(305)  $\text{cm}^{-1}$  which is a CO deformation. The Raman bands at 238 and 208  $\text{cm}^{-1}$  do not appear to be grating ghosts because they remain unshifted when the wavelength of the laser beam is changed to 4880 Å. Two calculated bands at 227 and 220  $\text{cm}^{-1}$  are not visible in the Raman spectrum; however, since torsional vibrations are generally quite weak in intensity, it is possible that they are not detected by the spectrometer.

The calculated bands at 202 and 137  $\text{cm}^{-1}$  are characterized by ring twisting vibrations. The spectral band at 208  $\text{cm}^{-1}$  was assigned to the calculated frequency 202  $\text{cm}^{-1}$ . Because of the Rayleigh scattering and the grating ghosts in the Raman spectrum of crystalline 1,5-AR, the predicted band at 137  $\text{cm}^{-1}$  could not be detected. However, a band is observed at 169  $\text{cm}^{-1}$  in the Raman spectrum of the solid and at 175  $\text{cm}^{-1}$  in the solution spectrum. It is conceivable to assign this band to the calculated frequency 137  $\text{cm}^{-1}$ , but such an assignment was not made for the normal coordinate calculations.

#### Solution Spectra of 1,5-Anhydroribitol

The solution spectra, both water and DMSO- $d_6$  (see Fig. 22 and Table X), correlate quite well with the solid state spectra for 1,5-AR (see Fig. 11 and 12 along with Table IV) as was noted for the 1,5-AX spectra. The correlation between the solution and solid state Raman spectra for 1,5-AR is presented in Table XXVIII. An examination of this table indicates that several "new" bands exist in the solution spectra. These bands may result from the vibrational

TABLE XXVIII

CORRELATION OF THE 1,5-ANHYDRORIBITOL SOLUTION SPECTRA  
(WATER AND DMSO-d<sub>6</sub>) WITH THE SOLID STATE RAMAN SPECTRUM

Raman, cm. <sup>-1</sup>	H <sub>2</sub> O Solution, cm. <sup>-1</sup>	DMSO-d <sub>6</sub> Solution, cm. <sup>-1</sup>
2997		
2972	2983	2969
2943		
2932	2928(broad)	2913(broad)
2918		
2875	2885	2869
1468	1471	1463
1458	1461	1456
	1452	1446
1419	broad band	broad band
1403	broad band	broad band
1385	broad band	broad band
1350	broad band	broad band
1315	1329	1321
	1291(IR of solid)	1286(IR of solid)
1265	1270	1258
1244	not visible	not visible
	1229(IR of solid)	1225(IR of solid)
1202	1206	1200
1156	1160	1158
1124	1121	1124
1104	hidden in overlap	hidden in overlap
1082	1090	1091
1073	hidden in overlap	hidden in overlap
	1054(new band)	solvent band
1045	1048	solvent band
1040		
1005	997	solvent band
993		
	967(new band)	solvent band
925	934	937
916		
878	884	881
	869(new band)	869(new band)
	837(new band)	solvent band
	795(new band)	solvent band
	692(new band)	688(new band)
669	hidden by above band	solvent band
647	648	solvent band
581	584	577
448	456	451
437	434	431
406	hidden in overlap	solvent band
396	hidden in overlap	solvent band
345	358(broad)	solvent band

motion of a significant amount of the molecules existing in the alternate conformation in solution (i.e., molecules in the alternative conformation to the more stable crystalline conformation). The free energy calculations for conformational differences reported in Table XVI imply that approximately 26% of the molecules may exist in the alternate conformation at equilibrium in solution. As discussed earlier in this section, the NMR spectra are too complicated to provide support for this argument. However, normal coordinate calculations, for which the ring of the 1,5-AR model is "inverted" to form the alternate chair conformation, do provide some support for the above argument. Solution of the secular determinant for 1,5-AR in the alternate conformation (i.e., a new  $\tilde{G}$  matrix, but with the same  $\tilde{F}$  matrix used in the calculations presented in Table XXIV) results in several calculated frequencies which are significantly "shifted" in frequency from the corresponding calculated frequencies for the more stable conformer. These "shifted" frequencies are in fair agreement with the "new" spectral bands appearing in the solution spectra as may be judged from Table XXIX. The results of these calculations support the alternate conformation argument and support the validity of the normal coordinate computations for the 1,5-AP compounds. (A complete listing of the calculated frequencies for both conformations for each of the 1,5-AP models may be found in Appendix VI.)

TABLE XXIX

CORRELATION BETWEEN THE CALCULATED BANDS FOR THE  
ALTERNATE 1,5-ANHYDRORIBITOL CONFORMER AND THE  
"NEW" BANDS APPEARING IN THE SOLUTION SPECTRA

H <sub>2</sub> O, cm. <sup>-1</sup>	"New" Band DMSO-d <sub>6</sub> , cm. <sup>-1</sup>	Calculated Band, cm. <sup>-1</sup>
1054		1059
967		963
869	869	865
837		809
795		786
692	688	

### Spectra of Deuterated 1,5-Anhydroribitol

The spectra of crystalline deuterated 1,5-AR have provided additional information which has assisted the assignment of spectral bands in the crystalline 1,5-AR spectra, especially the COH deformation (OH in-plane bending) bands. A comparison of Fig. 17 and 18 along with Table VII for deuterated 1,5-AR with Fig. 11 and 12 accompanied by Table IV for 1,5-AR reveal that several additional bands appear upon deuteration (14), some bands were reduced in relative intensity (16), and others increased in relative intensity (4). From Table XXIII, it is found that most of the bands reduced in intensity involve COH vibrations. In general, the correlation between the spectra of 1,5-AR and its deuterated analog is quite good. Examination of the infrared spectra of deuterated 1,5-AR suggests that the degree of deuteration is below 100%. However, the degree of deuteration was undoubtedly reduced during sample preparation. Therefore, there is really no information regarding the extent of deuteration after preparation of the deuterated derivative.

### 1,5-ANHYDRO-L-ARABINITOL

#### Interpretation of the Solid State Spectra

The 1,5-ALA solid state spectra have been presented in Fig. 13 and 14 with the frequencies tabulated in Table V. Since the spectra of the isomers 1,5-ALA and 1,5-ADA are identical, the following comments concerning 1,5-ALA shall also pertain to 1,5-ADA.

The interpretation of the solid state 1,5-ALA spectra is based on the potential energy distributions in terms of the various atomic group vibrations which are listed in Table XXIV. The definitions for several of the group vibrations are given in Fig. 29. As for 1,5-AX and 1,5-AR, only those comments concerning the interpretation not immediately realized from Table XXIV shall be

presented in this section. The same convention regarding the listing of spectral band frequencies will be followed; that is, the frequency of the Raman band, in wave numbers, will be given first followed by the corresponding infrared band frequency in parentheses.

Again, the three OH stretching bands at 3425(3428), (3385), and 3310(3320)  $\text{cm.}^{-1}$  are matched by three calculated bands, all of the same frequency, 3356  $\text{cm.}^{-1}$ . As before, the OH stretching frequencies are not included in the computation of the average error. An interesting observation is that these three bands are spread out over an even wider spectral area than the corresponding bands for 1,5-AX and 1,5-AR. This suggests that there are differences in the hydrogen bonding for the crystalline 1,5-AP compounds.

All seven of the CH stretching bands are observed in the infrared spectrum of 1,5-ALA. The only band not seen in the Raman spectrum is the one occurring at 2925  $\text{cm.}^{-1}$ .

The spectral region from 1467(1463)  $\text{cm.}^{-1}$  through 1343(1349)  $\text{cm.}^{-1}$  is characterized primarily by methylene "wag" vibrations coupled with methine deformation. The two bands at 1467(1463) and 1454(1460)  $\text{cm.}^{-1}$  are again noted to be equal mixtures of methylene "scissoring" and methylene "wagging." The result is a complex methylene vibration. The weak shoulder appearing at 1446(1442)  $\text{cm.}^{-1}$  in both the infrared and Raman spectra does not correlate with the calculated frequencies. This band is suspected of being a combination band. A possible combination resulting in a band in this region is suggested in Table XXX. The normal coordinate calculations predict a band at 1395  $\text{cm.}^{-1}$  which is not seen in the Raman or infrared spectrum. However, a band in this region is almost evident as a shoulder to the band at 1410  $\text{cm.}^{-1}$  in the Raman spectrum.

TABLE XXX.

SUGGESTED COMBINATION BANDS IN THE VIBRATIONAL SPECTRA  
OF CRYSTALLINE 1,5-ANHYDRO-L-ARABINITOL AND POSSIBLE  
COMBINATIONS WHICH MIGHT RESULT IN SUCH BANDS

Suspected Combination Band, <sup>a</sup> cm. <sup>-1</sup>	Possible Combination, <sup>b</sup> cm. <sup>-1</sup>
1446(R)(IR)	(1281) + (1005) - (837) = 1449
406(R)	(1410) - (1005) = 405
371(R)(IR)	(1467) - (1092) = 375

<sup>a</sup>IR (R) designates that the band is observed in the infrared (Raman) spectrum.

<sup>b</sup>The fundamental band frequencies, in wave numbers, appear in parentheses.

From 1325(1329) cm.<sup>-1</sup> through 1269(1262) cm.<sup>-1</sup>, the spectral bands are described by methylene "twisting" vibrations coupled with methine deformation.

The bands at (1248), 1233(1233), and 1216(1217) cm.<sup>-1</sup> are assigned to COH bending vibrations (OH in-plane bending). The corresponding spectral bands in the spectra of deuterated 1,5-ALA are only slightly reduced in relative intensity or not reduced at all. However, examination of the deuterated 1,5-ALA spectra (Fig. 19 and 20 along with Table VIII) suggests that the degree of deuteration was well below 100% which may account for the above observation.

The region from 1150(1151) cm.<sup>-1</sup> through 758(755) cm.<sup>-1</sup> is distinguished by CO stretching vibrations and ring stretching vibrations coupled with methylene "twisting" and "rocking" vibrations. The two bands at 1112(1112) and 1104(1103) cm.<sup>-1</sup> are suspected of resulting from the splitting of a fundamental band due to vibrational coupling within the crystalline lattice. The calculations predict only one band in this region at 1108 cm.<sup>-1</sup> The argument for band splitting is supported by the fact that only one band is noted in



this region in the solution spectra. In addition, the average of these two bands,  $1108 \text{ cm.}^{-1}$ , agrees exactly with the frequency of the calculated band in this region for the 1,5-ALA model.

The spectral region from  $633(636) \text{ cm.}^{-1}$  through  $256 \text{ cm.}^{-1}$  is characterized by primarily CO(H) deformation with some ring vibrations. The Raman shoulder band at  $406 \text{ cm.}^{-1}$  and the shoulder band at  $371(375) \text{ cm.}^{-1}$  in both the Raman and infrared spectra are suspected of being combination bands, since they do not correlate with the calculated frequencies (see Table XXX).

The normal coordinate calculations predict three bands resulting from OH torsional vibrations (OH out-of-plane bending) at  $237$ ,  $236$ , and  $222 \text{ cm.}^{-1}$ . The Raman band at  $233 \text{ cm.}^{-1}$  may be assigned to either of the calculated bands at  $237$  or  $236 \text{ cm.}^{-1}$  since it is impossible to evaluate the validity of one of the assignments over the other. In the normal coordinate calculations, this band was assigned to the calculated frequency  $237 \text{ cm.}^{-1}$ . The calculated band at  $222 \text{ cm.}^{-1}$  is not observed in the Raman spectrum of 1,5-ALA. However, torsional vibrational bands are generally quite weak, and it is possible that such a band may not be detected by the instrument.

There are two ring twisting bands predicted by the computations at  $185$  and  $132 \text{ cm.}^{-1}$ . There are two Raman bands in this region in the Raman crystalline 1,5-ALA spectrum at  $197$  and  $176 \text{ cm.}^{-1}$ . The assignment listed in Table XXIV, which was assumed in the normal coordinate calculations, is based on the assumption that the band at  $197 \text{ cm.}^{-1}$  is a grating ghost. Grating ghosts have been observed in this region in several solid state spectra. Then the band at  $176 \text{ cm.}^{-1}$  is correlated with the calculated band  $185 \text{ cm.}^{-1}$ . It is not possible to detect a band in the region of  $132 \text{ cm.}^{-1}$  because of the Rayleigh scattering and grating ghosts. Further, the band is probably too weak to be observed in

the solution spectra. In an alternate assignment, one might assume that the band at  $197\text{ cm.}^{-1}$  is not a grating ghost and correlate this with the calculated band at  $185\text{ cm.}^{-1}$ . The observed band at  $176\text{ cm.}^{-1}$  ( $165\text{ cm.}^{-1}$  in the water solution spectrum) might then be correlated with the calculated band at  $132\text{ cm.}^{-1}$ . In the case of 1,5-AR, a band was observed at  $169\text{ cm.}^{-1}$  ( $175\text{ cm.}^{-1}$  in the water solution spectrum), and the suggestion was made that this band might be correlated to a calculated band at  $137\text{ cm.}^{-1}$ . In this respect, the above assignment is in agreement with the assignment for 1,5-AR. However, the first assignment was favored in the normal coordinate computations, based entirely on preference.

#### Solution Spectra of 1,5-Anhydro-L-arabinitol

The solution spectra of 1,5-ALA, both water and DMSO- $d_6$  (see Fig. 23 and Table XI), agree quite well with the solid state spectra. Because of the rotation of the molecules, some of the solution spectral bands appear shifted in frequency and several of the bands are broadened. The water and DMSO- $d_6$  solution spectral bands are correlated with the solid state spectral bands for 1,5-ALA in Table XXXI. (The reader should note the frequency agreement between the water and the DMSO- $d_6$  solution spectra.)

The most noticeable feature of the solution spectra is the appearance of a few "new" bands not observed in the solid state spectra. As with 1,5-AR, these "new" bands are suggested to result from the presence of a significant amount of the 1,5-ALA molecules in the alternate conformation in solution. The conformational free energy calculations in Table XVI imply that approximately 28% of the molecules will exist in the alternate conformation in solution at equilibrium. The NMR spectra of 1,5-ALA in  $D_2O$  (Fig. 5) and DMSO- $d_6$  (Fig. 8a) cannot be used to support this argument because of the difficulty in interpreting the complex spectra. However, the normal coordinate calculations do support this

TABLE XXXI

CORRELATION OF THE 1,5-ANHYDRO-L-ARABINITOL SOLUTION SPECTRA  
(WATER AND DMSO-d<sub>6</sub>) WITH THE SOLID STATE RAMAN SPECTRUM

Raman, cm. <sup>-1</sup>	H <sub>2</sub> O Solution, cm. <sup>-1</sup>	DMSO-d <sub>6</sub> Solution, cm. <sup>-1</sup>
2983		
2973	2979	2968
2932		
2916	2916	2902
2879		
2860	2872	2863
1467	1468	1463
1454	1452	1446
1442	slightly evident	slightly evident
1410	broad band	broad band
1381	broad band	broad band
1369	broad band	broad band
1343	broad band	broad band
1325	broad band	broad band
1309	1303	1308
1302	1296	1292
1281		
1233	1229	1225
1216		
1150	1153	1156
1136	hidden in overlap	hidden in overlap
1112	1120	1121
1104		
1092	1095	1110
1067	1072	solvent band
1057	1060	solvent band
1008	1013	solvent band
1005		solvent band
948	949	949
926	926	925
876	883	881
	865(new band)	867(new band)
837	840	834
758	754	solvent band
	744(new band)	742(new band)
633	640	solvent band
546	544	539
	532(new band)	522(new band)
430	425	420
408	407	409
314		solvent band

argument as they did in the discussion of the 1,5-AR solution spectra. That is, the frequencies were calculated for the 1,5-ALA model with the ring "inverted" (i.e., in the alternate conformation) using the same  $\underline{F}$  matrix employed for the calculations reported in Table XXIV. The solution of the secular determinant for the "inverted" 1,5-ALA model resulted in a few calculated frequencies which deviated significantly from those calculated frequencies for the stable conformer. These calculated frequencies were found to be in fair agreement with the "new" spectral bands observed in the 1,5-ALA solution spectra. The results are tabulated in Table XXXII. (The complete calculated frequency list for both conformers appears in Appendix VI for each of the 1,5-AP models.)

TABLE XXXII

CORRELATION BETWEEN THE CALCULATED BANDS FOR THE ALTERNATE 1,5-ANHYDRO-L-ARABINITOL CONFORMER AND THE "NEW" BANDS APPEARING IN THE SOLUTION SPECTRA

<u>"New" Band</u>		Calculated Band, cm. <sup>-1</sup>
H <sub>2</sub> O, cm. <sup>-1</sup>	DMSO-d <sub>6</sub> , cm. <sup>-1</sup>	
865	867	831
744	742	720
532	522	518

#### Spectra of Deuterated 1,5-Anhydro-L-arabinitol

The deuterated 1,5-ALA spectra appear in Fig. 19 and 20 and the frequencies are tabulated in Table VIII. Examination of these spectra reveals that the degree of deuteration after pellet preparation is well below 100%. The spectra of the deuterated derivative of 1,5-ALA is in close agreement with the 1,5-ALA spectra. Some bands are observed to be shifted slightly in frequency and others differ in relative intensity (15). In addition, several additional bands are apparent in the deuterated 1,5-ALA spectra (5).

1,5-ANHYDRO-DL-ARABINITOL

Comparison of the 1,5-Anhydro-DL-arabinitol Spectra  
With that of the L Isomer

As a matter of interest, the preparation of 1,5-ADLA, measurement of the vibrational spectra, and comparison of the spectra with that of the L isomer were completed in this investigation. To the author's knowledge, such a comparison has not been made in the literature. The 1,5-ADLA spectra is found to correlate fairly well with the 1,5-ALA spectra, but a number of the 1,5-ADLA spectral bands are noted to be shifted significantly in frequency from the corresponding 1,5-ALA bands, and the relative intensity of several bands differ. A correlation of the Raman 1,5-ADLA spectral bands with the Raman 1,5-ALA spectral bands is presented in Table XXXIII.

Kim and Jeffrey (85) have noted that the structure of the unit cell of  $\beta$ -DL-arabinose has a center of symmetry while that of the isomers does not. Perhaps, the same is true for the 1,5-anhydroalditol derivatives. The geometry of the unit cell may affect the resulting vibrational spectrum of a compound and, thus, explain the differences observed in the 1,5-ADLA spectra from the 1,5-ALA spectrum. In addition, the melting point of 1,5-ADLA is 23 degrees lower than 1,5-ALA (see Table II). Thus, the intermolecular bonding, which is primarily hydrogen bonding, must differ for the two forms. The intermolecular bonding may very well affect the vibrational spectra and account for the differences between the 1,5-ADLA and 1,5-ALA spectra.

The 1,5-ADLA spectra and also the deuterated 1,5-ADLA spectra for completeness (see Fig. 26 and 27 along with Table XV) have been presented in this thesis as a stimulus for research into the aspects of the effects of unit cell geometry and intermolecular bonding upon the vibrational spectra of saccharide and saccharide-type compounds.

TABLE XXXIII

CORRELATION BETWEEN THE SOLID STATE RAMAN SPECTRA  
OF 1,5-ANHYDRO-DL-ARABINITOL AND  
1,5-ANHYDRO-L-ARABINITOL

1,5-ADLA, cm. <sup>-1</sup>	1,5-ALA, cm. <sup>-1</sup>	1,5-ADLA, cm. <sup>-1</sup>	1,5-ALA, cm. <sup>-1</sup>
3324	3425	1085	1092
3214	3310	1064	1067
3000	2983		1057
2989	2973	1012	1005
2966	2932	951	948
	2951	923	926
2916		880	876
	2890	840	837
2879	2887	756	758
2860	2852	750	
1469	1467	629	633
1450	1454	550	546
	1446	493	483
1423		445	
1396	1410	429	430
1381	1381	407	408
1359	1369		406
1340	1343	383	
	1325	375	371
	1309	338	
1312	1302	326	
1287	1281	313	314
1271	1269	291	296
1243		269	
1235	1233		256
1224	1216	231	233
1154	1150	197	197
1127	1136	185	176
1113	1112		
1097	1104		

## CONCLUSIONS

The successful normal coordinate analyses of the 1,5-AP compounds has demonstrated the feasibility of extending such calculations to large, complex molecules. It now appears quite reasonable to attempt a complete normal coordinate analysis for, at least, the monosaccharides and their derivatives. The successful application of these methods to even larger molecules will depend upon the availability of a computer with the necessary core storage and computational speed. An important element in determining the success of the normal coordinate analyses was the introduction of the nonlinear force field perturbation technique which is based on the Fletcher-Powell method (121). Such a refinement method is very necessary for problems involving extensive vibrational coupling as is present in the case of large, complex molecules such as the 1,5-AP compounds and the monosaccharides.

The normal coordinate analyses have provided reasonable interpretations of the 1,5-AP solid state vibrational spectra. The mathematical methods employed in these analyses are admittedly qualitative. However, it is the qualitative aspects of the methods that make them so valuable to the physical chemist and vibrational spectroscopist. Although the numerical percentage contribution of  $\underline{F}$  matrix elements to the potential energy distribution cannot be assumed rigorously accurate, the numbers do indicate the relative contribution of each element to the potential energy which is extremely valuable in interpreting the spectra. The fact that such a close agreement was reached between the calculated and experimental frequencies for the three 1,5-AP compounds (average error of  $6.2 \text{ cm.}^{-1}$ ) and that the interpretation agrees with the experimental vibrational information available for similar compounds, including the group frequency correlation charts, add support to the results of the normal coordinate computations.

The SVQFF derived in this investigation is specific for pyranose ring compounds with hydroxyl groups. It should simplify the normal coordinate analyses of the pentoses (which should be considered the next logical set of compounds to be analyzed in the physical chemical investigation of the vibrational spectra of the saccharides) by reducing the difficulty involved in the initial correlation of the experimental and calculated frequencies. The spectral interpretation for the 1,5-AP compounds should, by itself, assist in the assignment of the saccharide spectra. The assignment of these spectra in the past has been based on the normal coordinate analysis of tetrahydropyran, but the 1,5-AP compounds are more closely related, structurally, to the saccharides.

The assumption of tetrahedral geometry for the 1,5-AP models in this investigation appears to be quite reasonable and provides acceptable results. This approximation in the model geometry seems to be appropriate for those situations where the exact geometry is not available from crystal structure data. However, a better agreement (perhaps, 1-2  $\text{cm}^{-1}$ ) between experimental and calculated frequencies is expected when the exact molecular geometry is used. The normal coordinate computations suggest that the lower portion of the ring for the 1,5-AR compound is "flatter" in the real molecule than in the tetrahedral approximation. This variation between the real structure and the tetrahedral approximation is suggested as the source of the slightly larger average error for 1,5-AR.

The normal coordinate computations have further demonstrated that the main source of the differences in the band positions between the 1,5-AP spectra is a kinetic energy effect rather than a potential energy effect. More specifically, the shifts in frequencies between spectra are a result of the variation in orientation of the hydroxyl groups, i.e., axial versus equatorial, between 1,5-AP compounds. However, no spectral differences could be detected which could be



attributed to loss of symmetry in going from 1,5-AX and 1,5-AR to 1,5-ALA or 1,5-ADA.

In general, the solution spectra were quite similar to the solid state spectra, with some shifting of bands and considerable band broadening. Band broadening is a typical phenomenon of solution spectra resulting from rotation-vibration coupling. There appears to be little band splitting in the solid state spectra since the solution spectra correlate so well with the solid state spectra. The type of solvent, i.e., amphiprotic versus aprotic, does not appear to affect the solution vibrational spectra, since the spectra of the 1,5-AP solutions in water and DMSO-d<sub>6</sub> are identical. Several additional bands were observed in the solution spectra of 1,5-AR and 1,5-ALA. These bands are suspected of resulting from a significant amount of each species existing in the alternate conformation in solution. This argument is supported by normal coordinate computations for the alternate conformers and conformational free energy calculations.

The vibrational spectra of 1,5-ADLA were presented in this text so that they might be compared with the corresponding spectra of 1,5-ALA. Several differences in the spectra of the two compounds were noted, both in band position and relative intensity. The crystal structure and hydrogen bonding are suspected of differing in the two compounds. An investigation of this observation might result in the explanation of the effect of crystal structure and hydrogen bonding on the solid state vibrational spectra.

### SUGGESTIONS FOR FUTURE WORK

This investigation immediately suggests three areas for future work in the investigation of the saccharide vibrational spectra and normal coordinate computations.

1. The most immediate extension of this work is the normal coordinate analyses of the pentoses. The SVQFF developed in this study should simplify the computations for the pentoses. The normal coordinate computations for the pentoses should then permit the SVQFF developed for the 1,5-AP compounds in this study to be extended to include the C1 hydroxyl group interactions. This should make the force field more specific for the monosaccharides. The pentoses would provide an even better model system upon which to base the interpretation of the saccharide spectra.

At the time this dissertation is being written, the normal coordinate analyses of the pentitols is in progress at the Institute. The study is being conducted by Gary Watson and includes an investigation of the effect of conformation on the vibrational spectrum. The results of this investigation should complement the work done on the pyranose ring compounds and provide the basis for future analyses of the vibrational spectra of open-chain polyalcohols.

2. The inverse  $\tilde{F}$  matrix technique should be investigated and compared with the conventional computational methods that were used in this investigation. The uniqueness of the  $\tilde{F}^{-1}$  elements is very attractive. In addition, the HOFF and OVFF should be examined for the possibility of generating additional force field data from application of quantum mechanical principles. This would reduce the totally empirical character of the present SVQFF used in this study.

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APPENDIX I

COMPUTER PROGRAM FOR THE CALCULATION OF CARTESIAN  
COORDINATES FOR THE ATOMS

A computer program, CART, written by J. H. Schachtschneider (89) of Shell Development Co., Emeryville, California, was employed to compute the cartesian coordinates of the "atoms" (mass points) for the 1,5-AP models. The program was originally written for an IBM-7040 computer and coded in FORTRAN IV. (All computer programs to be discussed in this dissertation are coded in FORTRAN IV.) It was necessary to modify this program for use on the Institute's IBM-360/44 computer. CART calculates the cartesian coordinates of the atoms in a molecule from the bond distances and bond angles. If desired, the program will also compute the moments of inertia.

In the first part of the program, the coordinates of each atom of the molecule are calculated in a fixed coordinate system,  $O(\underline{x}, \underline{y}, \underline{z})$ , from the bond angles and bond lengths. The atoms are numbered in the order in which they are given in the data. (The atom numbering scheme used for the 1,5-AP models is specified in Fig. 28 in the main text.) The first three atoms are used to define the coordinate system,  $O(\underline{x}, \underline{y}, \underline{z})$ . The origin is located at the first atom. The positive  $\underline{x}$ -axis points in the direction of atom number two, and the triad 1-2-3 defines the  $\underline{x}$ - $\underline{y}$  plane. For each additional atom, a new coordinate system,  $O'(\underline{x}', \underline{y}', \underline{z}')$ , is used. The atom is located by the spherical coordinates  $\underline{R}$ ,  $\theta$ , and  $\phi$  in terms of its bond distances and bond angles.  $O'(\underline{x}', \underline{y}', \underline{z}')$  is located by giving the numbers of three previously defined atoms. The program calculates the transformation,  $\underline{T}$ , from  $O'(\underline{x}', \underline{y}', \underline{z}')$  to  $O(\underline{x}, \underline{y}, \underline{z})$ ; determines the cartesian coordinates  $\underline{x}'$ ,  $\underline{y}'$ , and  $\underline{z}'$  from the spherical coordinates  $\underline{R}$ ,  $\theta$ , and  $\phi$ ; and transforms  $\underline{x}'$ ,  $\underline{y}'$ , and  $\underline{z}'$  to  $\underline{x}$ ,  $\underline{y}$ , and  $\underline{z}$ . At the user's option, the center of mass and moments of inertia are computed by conventional methods.

The input to CART includes a control card giving the number of atoms, the number of isotopic molecules, and specifying if the moments of inertia are to be computed. The following data are read in for each atom in the molecule:

1. The atom number, NO. (The atoms are numbered consecutively.)
2. The numbers of the atoms determining the coordinate system,  $O'_{NO}(x', y', z')$ , used to locate atom NO.
  - a. NA: the number of atom A. (This atom determines the origin of the coordinate system.)
  - b. NB: the number of atom B defining the positive x' directions running along the bond from A to B.
  - c. NC: the number of atom C which together with atoms A and B define the x'-y' plane such that the positive half plane is on the same side of the x'-axis as atom C.
3. The spherical coordinates of the atom N in the coordinate system  $O'_{NO}(x', y', z')$ .
  - a. R: the length of the bond from atom A to atom N.
  - b.  $\theta$ : the angle between the x-axis and the bond between atom A and N, i.e., angle NAB.
  - c.  $\phi$ : the azimuthal angle between R and the x-y plane, i.e., the dihedral angle between the plane C-B-A and the plane N-A-B.<sup>16</sup>
  - d. WT: the mass of atom N. (Masses need not be entered if the moment of inertia is not desired.)

Since the first three atoms define the coordinate system,  $O(x, y, z)$ , some of these data are not required for these atoms. Thus, for atom number one, the cartesian coordinates are all zero by definition. For atom number two, the x-coordinate is equal to R by definition, and only NA and R are needed. For

<sup>16</sup> For a right-handed coordinate system the angle is defined as follows: Observe the configuration from the direction of atom C along the bond B-A or A-B depending on whether C is bonded to B or A. Now rotate about B-A or A-B to move atom C into the plane N-A-B. A clockwise rotation is defined as positive. However, if the angle of rotation is less than 90°, a clockwise rotation is defined as negative.

atom number three, the z-coordinate is zero and only NA, NB, R, and  $\theta$  are needed.

The x-coordinate of atom C is

$$x_C = x_A \pm R \cos \theta \quad (150)$$

where + is used if A = 1 and - is used if A = 2. The y-coordinate is

$$y_C = R \sin \theta. \quad (151)$$

For each additional atom, the transformation matrix, T, from  $O'(x', y', z')$  is determined and used to transform x', y', and z' to x, y, and z. The coordinates for atom N in  $O'(x', y', z')$  are given by

$$\begin{aligned} x'_N &= R \cos \theta \\ y'_N &= R \sin \theta \cos \phi \\ z'_N &= R \sin \theta \sin \phi \end{aligned} \quad (152)$$

and

$$x_N = x_A + T_{xx} x'_N + T_{xy} y'_N + T_{xz} z'_N. \quad (153)$$

The coordinates of the center of mass C<sub>x</sub>, C<sub>y</sub>, and C<sub>z</sub> are given by

$$\begin{aligned} C_x &= (-1/M) \sum_i m_i x_i \\ C_y &= (-1/M) \sum_i m_i y_i \\ C_z &= (-1/M) \sum_i m_i z_i \end{aligned} \quad (154)$$

where  $\underline{M} = \sum_i \underline{m}_i$ . The elements of the moment of inertia tensor are

$$I_{xx} = \sum_i m_i [r_i - (x_i + C_x)]^2 \quad (155)$$

where r<sub>i</sub> is the distance from the center of mass to atom i and

$$r_i^2 = (x_i + C_x)^2 + (y_i + C_y)^2 + (z_i + C_z)^2 \quad (156)$$

$$I_{xy} = -\sum_i m_i (x_i + C_x)(y_i + C_y). \quad (157)$$

The moment of inertia tensor is diagonalized to give the principal moments and the transformation to principal coordinates. Provision has been made for reading in a new set of masses for the calculation of the moments of inertia of isotropically substituted molecules.

The calculated cartesian coordinates are punched onto cards in a form suitable for input to the  $\underline{G}$  matrix program described later in this manuscript.

A listing of CART along with a flow diagram and instructions for use of the program may be found in Appendix V.

#### COMPUTATION OF THE CARTESIAN COORDINATES FOR THE 1,5-ANHYDRO-PENTITOL MODELS

The input data to CART for the 1,5-AX, 1,5-AR, and 1,5-ALA models, based on the geometry specified in an earlier section and summarized in Table XVII, are presented in Tables XXXIV, XXXV, and XXXVI, respectively. In addition, each table lists the cartesian coordinates computed in CART for each model.

#### ERROR CHECKS IN SPECIFICATION OF MODEL GEOMETRY

The cartesian coordinates computed in CART may be examined for errors in two ways. First, CART contains an atom distance check. The distances between every "atom" of the model and every other "atom" are calculated. These distances may be inspected to see if they are reasonable. The second check is provided by the computer program, PAMOLE, written by Cole and Adamson (90), which employs the Calcomp 110 Digital Plotter to draw "ball and stick"

TABLE XXXIV

COMPUTER PROGRAM INPUT AND CALCULATED CARTESIAN  
COORDINATES FOR 1,5-ANHYDROXYLITOL

CARTESIAN COORDINATES  
1,5-ANHYDROXYLITOL. ALL BOND ANGLES ARE TETRAHEDRAL EXCEPT FOR  
THE C-O-C ANGLE. ONE BOND LENGTH VALUE EACH FOR CO,CC,CH,OH,AND CO(R).

1	0	0	0	0.0	0.0	0.0	15.994906
2	1	0	0	1.422999	0.0	0.0	12.000000
3	1	2	0	1.422999	112.449997	0.0	12.000000
4	2	1	3	1.523000	0.0	-60.000000	12.000000
5	3	1	2	1.523000	0.0	60.000000	12.000000
6	5	3	1	1.523000	0.0	-61.103989	12.000000
7	2	1	4	1.096000	0.0	-120.000000	1.007825
8	2	4	1	1.096000	0.0	-120.000000	1.007825
9	3	1	5	1.096000	0.0	120.000000	1.007825
10	3	5	1	1.096000	0.0	120.000000	1.007825
11	5	3	6	1.092999	0.0	120.000000	1.007825
12	5	3	6	1.415000	0.0	-120.000000	15.994906
13	12	5	11	0.970000	0.0	180.000000	1.007825
14	6	4	5	1.092999	0.0	117.265396	1.007825
15	6	5	4	1.415000	0.0	117.265091	15.994906
16	15	6	14	0.970000	0.0	180.000000	1.007825
17	4	2	6	1.092999	0.0	-120.000000	1.007825
18	4	2	6	1.415000	0.0	120.000000	15.994906
19	18	4	17	0.970000	0.0	180.000000	1.007825

ATOM NO.	X	Y	Z	MASS
1	0.0	0.0	0.0	15.994906
2	1.422999	0.0	0.0	12.000000
3	-0.543409	1.315155	0.0	12.000000
4	1.930665	0.717949	1.243524	12.000000
5	-0.073737	2.058514	1.243524	12.000000
6	1.445708	2.161613	1.229767	12.000000
7	1.788332	-1.033318	0.000001	1.007825
8	1.788332	0.516660	-0.894880	1.007825
9	-1.637928	1.258201	0.000001	1.007825
10	-0.205418	1.850101	-0.894880	1.007825
11	-0.393934	1.514558	2.135842	1.007825
12	-0.634535	3.357575	1.256446	15.994906
13	-0.350369	3.840312	0.464541	1.007825
14	1.769657	2.645977	0.305053	1.007825
15	1.884583	2.817815	2.404078	15.994906
16	1.562932	2.336884	3.182631	1.007825
17	1.550211	0.214294	2.135842	1.007825
18	3.345430	0.695734	1.256444	15.994906
19	3.683066	1.142712	0.464539	1.007825

TABLE XXXV

COMPUTER PROGRAM INPUT AND CALCULATED CARTESIAN  
COORDINATES FOR 1,5-ANHYDRORIBITOL

CARTESIAN COORDINATES  
1,5-ANHYDRORIBITOL. ALL BOND ANGLES ARE TETRAHEDRAL EXCEPT FOR  
THE C-O-C ANGLE. ONE BOND LENGTH VALUE EACH FOR CO,CC,CH,OH,AND COIR).

1	0	0	0	0.0	0.0	0.0	15.994906
2	1	0	0	1.422999	0.0	0.0	12.000000
3	1	2	0	1.422999	112.449997	0.0	12.000000
4	2	1	3	1.523000	0.0	-60.000000	12.000000
5	3	1	2	1.523000	0.0	60.000000	12.000000
6	5	3	1	1.523000	0.0	-61.103989	12.000000
7	2	1	4	1.096000	0.0	-120.000000	1.007825
8	2	4	1	1.096000	0.0	-120.000000	1.007825
9	3	1	5	1.096000	0.0	120.000000	1.007825
10	3	5	1	1.096000	0.0	120.000000	1.007825
11	5	3	6	1.092999	0.0	120.000000	1.007825
12	5	3	6	1.415000	0.0	-120.000000	15.994906
13	12	5	11	0.970000	0.0	180.000000	1.007825
14	6	4	5	1.092999	0.0	-117.265396	1.007825
15	6	5	4	1.415000	0.0	-117.265198	15.994906
16	15	6	14	0.970000	0.0	180.000000	1.007825
17	4	2	6	1.092999	0.0	-120.000000	1.007825
18	4	2	6	1.415000	0.0	120.000000	15.994906
19	18	4	17	0.970000	0.0	180.000000	1.007825

ATOM NO.	X	Y	Z	MASS
1	0.0	0.0	0.0	15.994906
2	1.422999	0.0	0.0	12.000000
3	-0.543409	1.315155	0.0	12.000000
4	1.930665	0.717949	1.243524	12.000000
5	-0.073737	2.058514	1.243524	12.000000
6	1.445708	2.161613	1.229767	12.000000
7	1.788332	-1.033318	0.000001	1.007825
8	1.788332	0.516660	-0.894880	1.007825
9	-1.637928	1.258201	0.000001	1.007825
10	-0.205418	1.850101	-0.894880	1.007825
11	-0.393934	1.514558	2.135842	1.007825
12	-0.634535	3.357575	1.256446	15.994906
13	-0.350369	3.840312	0.464541	1.007825
14	1.784715	2.668490	2.136847	1.007825
15	1.865091	2.788672	0.032629	15.994906
16	1.530784	2.288821	-0.728482	1.007825
17	1.550211	0.214294	2.135842	1.007825
18	3.345430	0.695734	1.256444	15.994906
19	3.683066	1.142712	0.464539	1.007825



TABLE XXXVI

COMPUTER PROGRAM INPUT AND CALCULATED CARTESIAN  
COORDINATES FOR 1,5-ANHYDRO-L-ARABINITOL

CARTESIAN COORDINATES  
1,5-ANHYDRO-L-ARABINITOL. ALL BOND ANGLES ARE TETRAHEDRAL EXCEPT FOR  
THE C-O-C ANGLE. ONE BOND LENGTH VALUE EACH FOR CO,CC,CH,OH,AND CO(R).

1	0	0	0	0.0	0.0	0.0	15.994906
2	1	0	0	1.422999	0.0	0.0	12.000000
3	1	2	0	1.422999	112.449997	0.0	12.000000
4	2	1	3	1.523000	0.0	-60.000000	12.000000
5	3	1	2	1.523000	0.0	60.000000	12.000000
6	5	3	1	1.523000	0.0	-61.103989	12.000000
7	2	1	4	1.096000	0.0	-120.000000	1.007825
8	2	4	1	1.096000	0.0	-120.000000	1.007825
9	3	1	5	1.096000	0.0	120.000000	1.007825
10	3	5	1	1.096000	0.0	120.000000	1.007825
11	5	3	6	1.092999	0.0	120.000000	1.007825
12	5	3	6	1.415000	0.0	-120.000000	15.994906
13	12	5	11	0.970000	0.0	180.000000	1.007825
14	6	4	5	1.092999	0.0	117.265396	1.007825
15	6	5	4	1.415000	0.0	117.265091	15.994906
16	15	6	14	0.970000	0.0	180.000000	1.007825
17	4	2	6	1.092999	0.0	120.000000	1.007825
18	4	2	6	1.415000	0.0	-120.000000	15.994906
19	18	4	17	0.970000	0.0	180.000000	1.007825

ATOM NO.	X	Y	Z	MASS
1	0.0	0.0	0.0	15.994906
2	1.422999	0.0	0.0	12.000000
3	-0.543409	1.315155	0.0	12.000000
4	1.930665	0.717949	1.243524	12.000000
5	-0.073737	2.058514	1.243524	12.000000
6	1.445708	2.161613	1.229767	12.000000
7	1.788332	-1.033318	0.000001	1.007825
8	1.788332	0.516660	-0.894880	1.007825
9	-1.637928	1.258201	0.000001	1.007825
10	-0.205418	1.850101	-0.894880	1.007825
11	-0.393934	1.514558	2.135842	1.007825
12	-0.634535	3.357575	1.256446	15.994906
13	-0.350369	3.840312	0.464541	1.007825
14	1.769657	2.645977	0.305053	1.007825
15	1.884583	2.817815	2.404078	15.994906
16	1.562932	2.336884	3.182631	1.007825
17	3.023482	0.700789	1.253504	1.007825
18	1.438128	0.065916	2.398722	15.994906
19	0.468288	0.081146	2.389860	1.007825

representations of the molecules from the cartesian coordinates of the atoms. (The program instructions for PAMOLE are presented in Appendix V.) Examination of these drawings based on the calculated cartesian coordinates may pinpoint any errors existing in the set of coordinates. The "ball and stick" drawings of the 1,5-AP models generated by PAMOLE from the cartesian coordinates listed in Tables XXXIV, XXXV, and XXXVI appear in Fig. 33, 34, and 35, respectively.

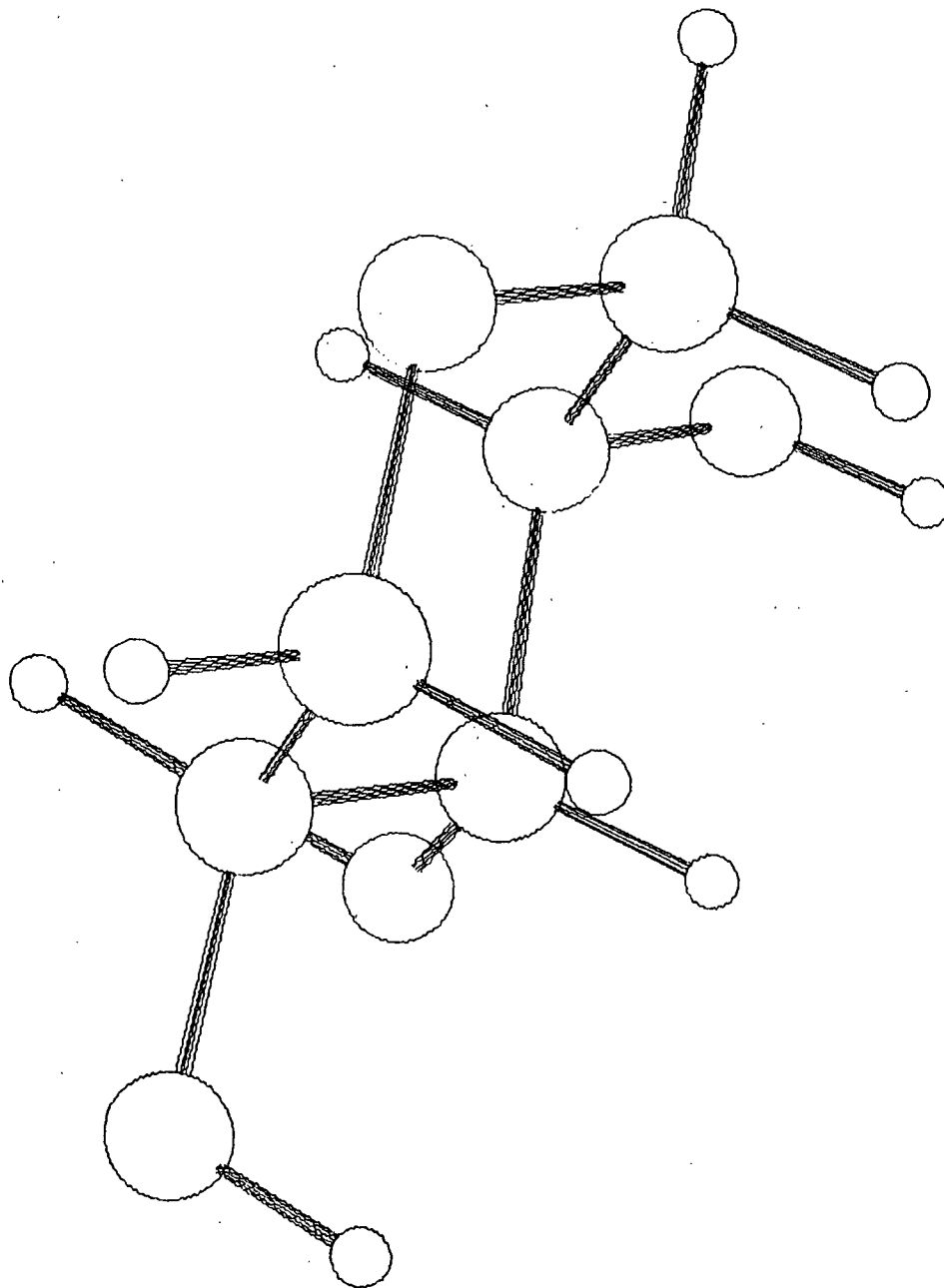


Figure 33. The "Ball and Stick" Representation of 1,5-Anhydroxylitol Generated by the Computer Program PAMOLE Based on the Set of Cartesian Coordinates of the Atoms Computed by CART

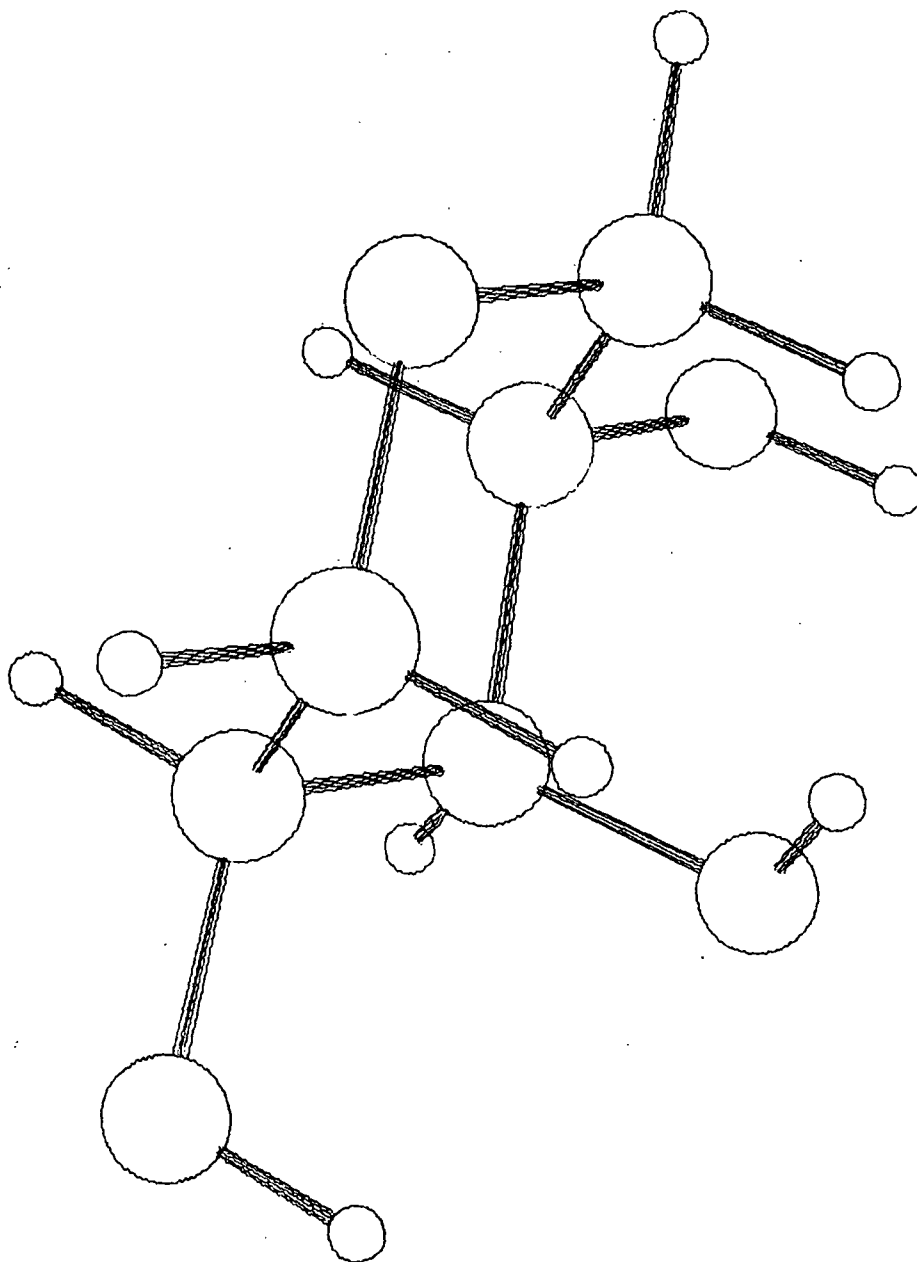


Figure 34. The "Ball and Stick" Representation of 1,5-Anhydroribitol Generated by the Computer Program PAMOLE Based on the Set of Cartesian Coordinates of the Atoms Computed by CART

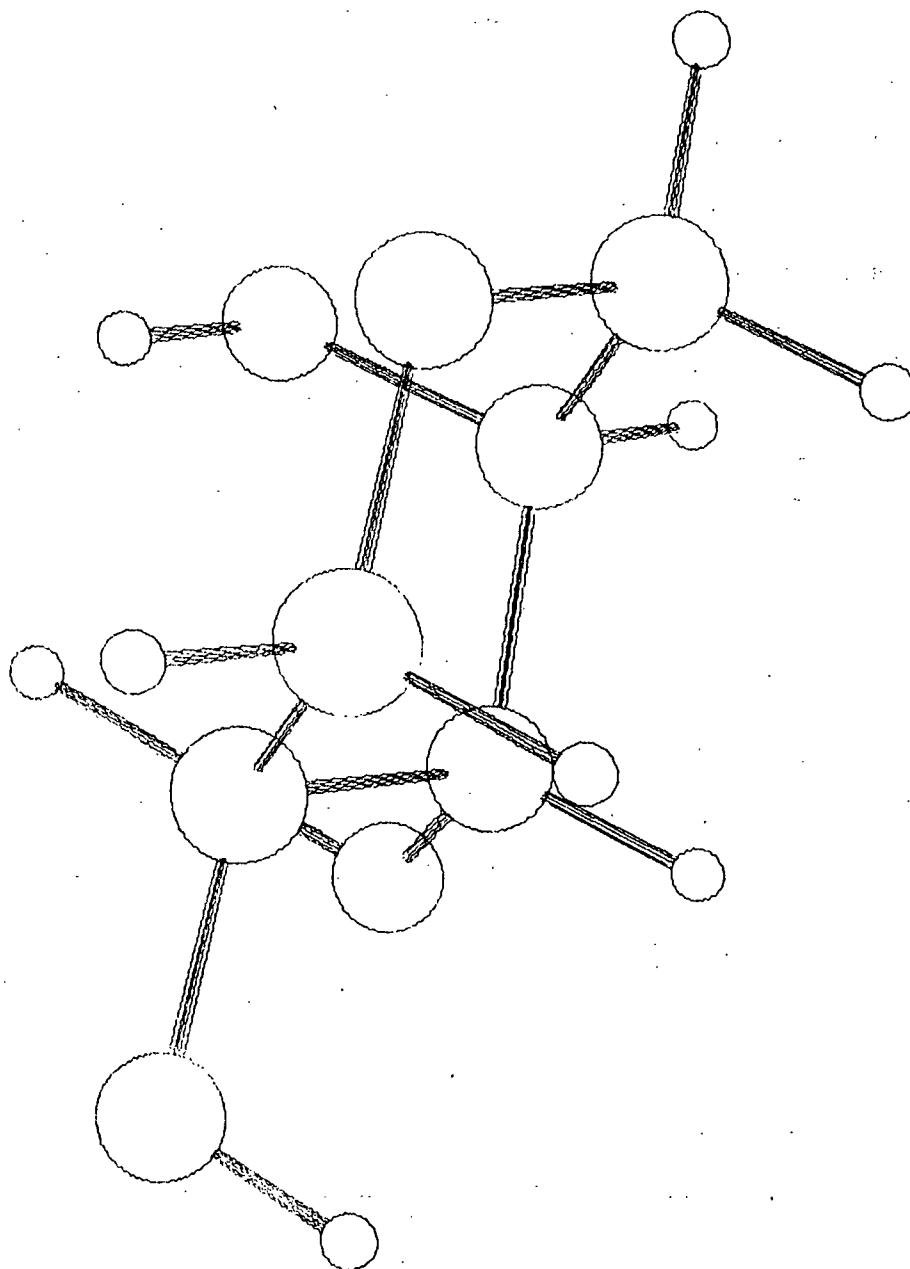


Figure 35. The "Ball and Stick" Representation of 1,5-Anhydro-L-arabinitol Generated by the Computer Program PAMOLE Based on the Set of Cartesian Coordinates of the Atoms Computed by CART

APPENDIX II

COMPUTER PROGRAM FOR COMPUTING THE  $\underline{\underline{G}}$  MATRIX

The  $\underline{\underline{B}}$  and  $\underline{\underline{G}}$  matrix elements are calculated by a computer program, GMAT, written by J. H. Schachtschneider (89) and modified for use in this investigation. GMAT punches the  $\underline{\underline{G}}$  matrix and factored  $\underline{\underline{G}}$  matrix (optional) onto cards in a form suitable for input into the computer programs which solve the vibrational secular equation that are discussed in the text. The listing, flow diagram, and user instructions for GMAT are presented in Appendix V.

In GMAT, the  $\underline{\underline{B}}$  matrix elements are computed by Wilson's "S vector" technique (68). If  $R_{\underline{t}}$  represents one of the  $3N-6$  internal coordinates and  $X_{\underline{i}}$  one of the  $3N$  cartesian displacement coordinates, the relations sought will be of the form

$$R_{\underline{t}} = \sum_{i=1}^{3N} B_{\underline{t}i} X_i \quad (158)$$

where  $\underline{t} = 1, 2, 3, \dots, 3N-6$ . Instead of using three cartesian coordinates to describe the displacement of an atom, it is convenient to introduce a vector  $\vec{\rho}_{\alpha}$  for each atom  $\alpha$  whose components along the three axis directions are the cartesian displacement coordinates  $X_{\underline{i}}, X'_{\underline{i}}, X''_{\underline{i}}$  for that atom. Likewise, it is useful to group the coefficients,  $B_{\underline{t}i}$ , for a given  $R_{\underline{t}}$  into sets of three, each set  $B_{\underline{t}i}, B'_{\underline{t}i}, B''_{\underline{t}i}$  being associated with a given atom  $\alpha$ . These quantities can be considered as components of a vector,  $\vec{s}_{\underline{t}\alpha}$ , associated with the atom  $\alpha$  and with the internal coordinate  $R_{\underline{t}}$ . Then, Equation (158) takes on the simple form

$$R_{\underline{t}} = \sum_{\alpha=1}^N \vec{s}_{\underline{t}\alpha} \cdot \vec{\rho}_{\alpha} \quad (159)$$

where the dot represents the scalar product of two vectors. The physical meaning of the vector  $\vec{s}_{\underline{t}\alpha}$  is as follows: Let all atoms except atom  $\alpha$  be in their

equilibrium positions. The direction of  $\vec{s}_{t\alpha}$  is the direction in which a given displacement of atom  $\alpha$  will produce the greatest increase of  $R_t$ . The magnitude,  $|\vec{s}_{t\alpha}|$ , is equal to the increase in  $R_t$  produced by unit displacement of the atom in this most effective direction.

Six types of internal coordinates are recognized by the program, namely, bond stretching, valence angle bending, torsion, out-of-plane wagging, perpendicular pair of linear valence angle bendings, and linear valence angle bending. The internal coordinates specified for the 1,5-AP models involve only the first three types in the list; therefore, only these internal coordinates will be discussed. The reader may wish to refer to Wilson (68) or Schachtschneider (89) for a description of the other coordinate types.

A "vector" describing the internal coordinate is made up of eight integers which are denoted by NI, NCOD, N1, N2, N3, N4, N5, and N6. NI gives the number assigned to the internal coordinate; NCOD is a code identifying the type of internal coordinate; and N1, N2, N3, N4, N5, and N6 give the numbers of the atoms defining the internal coordinates.

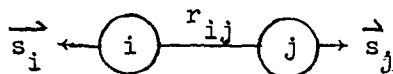
Following are the "S vector" expressions for the bond stretching, valence angle bending, and torsion internal coordinates. In these expressions, the unit vectors along the bonds,  $\vec{e}_{ij}$ , are represented in cartesian coordinates as

$$\vec{e}_{ij} = [(x_j - x_i)\vec{i} + (y_j - y_i)\vec{j} + (z_j - z_i)\vec{k}]/r_{ij} \quad (160)$$

where  $r_{ij}$  is the distance between atoms i and j.

1. Bond Stretching:  $\Delta r_{ij}$

NCOD	N1	N2	N3	N4	N5	N6
1	i	j				



The "S vectors" for atoms i and j are

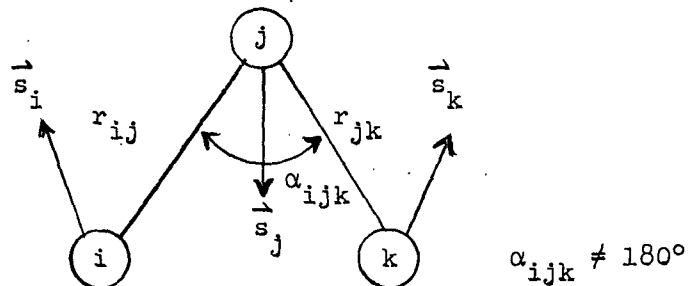
$$\vec{s}_i = -\vec{e}_{ij}$$

and

$$\vec{s}_j = \vec{e}_{ij}$$

2. Valence Angle Bend:  $r_{ix,jx} \Delta \alpha_{ijk}$

NCOD	N1	N2	N3	N4	N5	N6
2	i	j	k	0	ix	jx



The atom numbers ix and jx define a bond distance,  $R(\underline{ix}-\underline{jx})$ , by which the internal coordinate is weighted. The weighted bending force constants will then have the same dimensions as the stretching force constants. If ix = jx = 0, the angle is not weighted, that is,  $r_{\underline{ix},\underline{jx}} = 1.0$ . The "S vectors" for atoms i, j, and k are



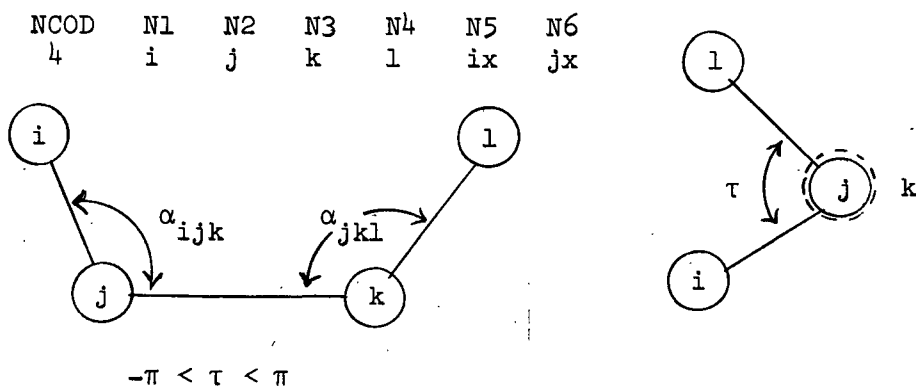
$$\vec{s}_i = r_{ix,jx} (\cos \alpha_{ijk} \vec{e}_{ji} - \vec{e}_{jk}) / r_{ij} \sin \alpha_{ijk}$$

$$\vec{s}_k = r_{ix,jx} (\cos \alpha_{ijk} \vec{e}_{jk} - \vec{e}_{ji}) / r_{jk} \sin \alpha_{ijk}$$

and

$$\vec{s}_j = -(\vec{s}_i + \vec{s}_k).$$

3. Torsion:  $\frac{r_{ix,jx} \Delta \tau_{ijkl}}$



The "S vectors" for atoms i, j, k, and l are

$$\vec{s}_i = -r_{ix,jx} (\vec{e}_{ij} \times \vec{e}_{jk}) / (r_{ij} \sin^2 \alpha_{ijk})$$

$$\begin{aligned} \vec{s}_j &= r_{ix,jx} (r_{jk} - r_{ij} \cos \alpha_{ijk}) (\vec{e}_{ij} \times \vec{e}_{jk}) / (r_{jk} r_{ij} \sin^2 \alpha_{ijk}) \\ &\quad - r_{ix,jx} \cos \alpha_{jkl} (\vec{e}_{jk} \times \vec{e}_{kl}) / (r_{ij} \sin^2 \alpha_{jkl}) \end{aligned}$$

$$\vec{s}_k = -(\vec{s}_i + \vec{s}_j + \vec{s}_l)$$

where x represents the vector product. In many cases, it is convenient to use the sum of several torsions to avoid the introduction of redundancies. A provision has been made in GMAT for defining a coordinate as the sum of several torsions. (This provision is discussed in the user instructions for GMAT in Appendix V.)

The 62 internal coordinate "vector" descriptions for the 1,5-AP models are listed in Tables XXXVII, XXXVIII, and XXXIX for 1,5-AX, 1,5-AR, and 1,5-ALA, respectively. The atom numbering scheme for these tables has been defined in Fig. 28 in the text. The internal coordinate definitions, along with the cartesian coordinates of the atoms, embody the input data to GMAT. The computer program then calculates the  $\underline{\underline{B}}$  and  $\underline{\underline{G}}$  matrices. The inverse kinetic energy matrix is computed by the expression

$$G_{tt'} = \sum_{i=1}^{3N} (1/m_i) B_{ti} B_{t'i} \quad (161)$$

where  $t, t' = 1, 2, 3, \dots, 3N-6$ . This relationship has been expressed in matrix notation in Equation (32) in the text. Employing Equations (158) and (159), we may write Equation (160) in terms of the "S vector," that is,

$$G_{tt'} = \sum_{\alpha=1}^N \mu_{\alpha} \vec{s}_{t\alpha} \cdot \vec{s}_{t'\alpha} \quad (162)$$

where  $\mu_{\alpha} = 1/m_{\alpha}$ , the reciprocal of the mass of atom  $\alpha$ . GMAT uses Equation (162) to compute the  $\underline{\underline{G}}$  matrix. The various formulae resulting from the scalar product of "S vectors" in Equation (162) defining the  $\underline{\underline{G}}$  matrix elements have been assembled, condensed, and tabulated by Decius (77) and summarized by Wilson, et al. (68).

#### CALCULATION OF THE $\underline{\underline{G}}$ MATRICES FOR THE 1,5-ANHYDRO-PENTITOL MODELS

The  $\underline{\underline{G}}$  matrices for the 1,5-AP models are listed in Tables XL, XLI, and XLII. The corresponding  $\underline{\underline{B}}$  matrices have not been included in this manuscript because of space considerations.

TABLE XXXVII

INTERNAL COORDINATE DEFINITIONS FOR 1,5-ANHYDROXYLITOL

NO.	CODE	I	J	K	L	IX	JX
1	1	1	3	0	0	0	0
2	1	3	5	0	0	0	0
3	1	5	6	0	0	0	0
4	1	4	6	0	0	0	0
5	1	2	4	0	0	0	0
6	1	1	2	0	0	0	0
7	1	3	9	0	0	0	0
8	1	3	10	0	0	0	0
9	1	5	11	0	0	0	0
10	1	5	12	0	0	0	0
11	1	12	13	0	0	0	0
12	1	6	14	0	0	0	0
13	1	6	15	0	0	0	0
14	1	15	16	0	0	0	0
15	1	4	17	0	0	0	0
16	1	4	18	0	0	0	0
17	1	18	19	0	0	0	0
18	1	2	7	0	0	0	0
19	1	2	8	0	0	0	0
20	2	1	3	9	0	0	0
21	2	1	3	10	0	0	0
22	2	1	3	5	0	0	0
23	2	9	3	5	0	0	0
24	2	10	3	5	0	0	0
25	2	9	3	10	0	0	0
26	2	3	5	11	0	0	0
27	2	3	5	12	0	0	0
28	2	5	12	13	0	0	0
29	2	3	5	6	0	0	0
30	2	11	5	6	0	0	0
31	2	12	5	6	0	0	0
32	2	11	5	12	0	0	0
33	2	5	6	14	0	0	0
34	2	5	6	15	0	0	0
35	2	6	15	16	0	0	0
36	2	4	6	5	0	0	0
37	2	4	6	14	0	0	0
38	2	4	6	15	0	0	0
39	2	14	6	15	0	0	0
40	2	17	4	6	0	0	0
41	2	18	4	6	0	0	0
42	2	4	18	19	0	0	0
43	2	2	4	6	0	0	0
44	2	2	4	17	0	0	0
45	2	2	4	18	0	0	0
46	2	17	4	18	0	0	0
47	2	7	2	4	0	0	0
48	2	8	2	4	0	0	0

TABLE XXXVII (Continued)

NO.	CODE	I	J	K	L	IX	JX
49	2	1	2	4	0	0	0
50	2	1	2	7	0	0	0
51	2	1	2	8	0	0	0
52	2	7	2	8	0	0	0
53	2	2	1	3	0	0	0
54	4	7	2	4	6	0	0
54	4	8	2	4	17	0	0
54	4	1	2	4	18	0	0
55	4	17	4	6	14	0	0
55	4	2	4	6	15	0	0
55	4	18	4	6	5	0	0
56	4	9	3	5	6	0	0
56	4	10	3	5	11	0	0
56	4	1	3	5	12	0	0
57	4	11	5	6	14	0	0
57	4	3	5	6	15	0	0
57	4	12	5	6	4	0	0
58	4	17	4	18	19	0	0
59	4	14	6	15	16	0	0
60	4	11	5	12	13	0	0
61	4	7	2	1	3	0	0
62	4	9	3	1	2	0	0

TABLE XXXVIII

INTERNAL COORDINATE DEFINITIONS FOR 1,5-ANHYDRORIBITOL

NO.	CODE	I	J	K	L	IX	JX
1	1	1	3	0	0	0	0
2	1	3	5	0	0	0	0
3	1	5	6	0	0	0	0
4	1	4	6	0	0	0	0
5	1	2	4	0	0	0	0
6	1	1	2	0	0	0	0
7	1	3	9	0	0	0	0
8	1	3	10	0	0	0	0
9	1	5	11	0	0	0	0
10	1	5	12	0	0	0	0
11	1	12	13	0	0	0	0
12	1	6	14	0	0	0	0
13	1	6	15	0	0	0	0
14	1	15	16	0	0	0	0
15	1	4	17	0	0	0	0
16	1	4	18	0	0	0	0
17	1	18	19	0	0	0	0
18	1	2	7	0	0	0	0
19	1	2	8	0	0	0	0

TABLE XXXVIII (Continued)

NO.	CODE	I	J	K	L	IX	JX
20	2	1	3	9	0	0	0
21	2	1	3	10	0	0	0
22	2	1	3	5	0	0	0
23	2	9	3	5	0	0	0
24	2	10	3	5	0	0	0
25	2	9	3	10	0	0	0
26	2	3	5	11	0	0	0
27	2	3	5	12	0	0	0
28	2	5	12	13	0	0	0
29	2	3	5	6	0	0	0
30	2	11	5	6	0	0	0
31	2	12	5	6	0	0	0
32	2	11	5	12	0	0	0
33	2	5	6	14	0	0	0
34	2	5	6	15	0	0	0
35	2	6	15	16	0	0	0
36	2	4	6	5	0	0	0
37	2	4	6	14	0	0	0
38	2	4	6	15	0	0	0
39	2	14	6	15	0	0	0
40	2	17	4	6	0	0	0
41	2	18	4	6	0	0	0
42	2	4	18	19	0	0	0
43	2	2	4	6	0	0	0
44	2	2	4	17	0	0	0
45	2	2	4	18	0	0	0
46	2	17	4	18	0	0	0
47	2	7	2	4	0	0	0
48	2	8	2	4	0	0	0
49	2	1	2	4	0	0	0
50	2	1	2	7	0	0	0
51	2	1	2	8	0	0	0
52	2	7	2	8	0	0	0
53	2	2	1	3	0	0	0
54	4	7	2	4	6	0	0
54	4	8	2	4	17	0	0
54	4	1	2	4	18	0	0
55	4	17	4	6	15	0	0
55	4	2	4	6	14	0	0
55	4	18	4	6	5	0	0
56	4	9	3	5	6	0	0
56	4	10	3	5	11	0	0
56	4	1	3	5	12	0	0
57	4	11	5	6	15	0	0
57	4	3	5	6	14	0	0
57	4	12	5	6	4	0	0
58	4	17	4	18	19	0	0
59	4	14	6	15	16	0	0
60	4	11	5	12	13	0	0
61	4	7	2	1	3	0	0
62	4	9	3	1	2	0	0

TABLE XXXIX

INTERNAL COORDINATE DEFINITIONS FOR 1,5-ANHYDRO-L-ARABINITOL

NO.	CODE	I	J	K	L	IX	JX
1	1	1	3	0	0	0	0
2	1	3	5	0	0	0	0
3	1	5	6	0	0	0	0
4	1	4	6	0	0	0	0
5	1	2	4	0	0	0	0
6	1	1	2	0	0	0	0
7	1	3	9	0	0	0	0
8	1	3	10	0	0	0	0
9	1	5	11	0	0	0	0
10	1	5	12	0	0	0	0
11	1	12	13	0	0	0	0
12	1	6	14	0	0	0	0
13	1	6	15	0	0	0	0
14	1	15	16	0	0	0	0
15	1	4	17	0	0	0	0
16	1	4	18	0	0	0	0
17	1	18	19	0	0	0	0
18	1	2	7	0	0	0	0
19	1	2	8	0	0	0	0
20	2	1	3	9	0	0	0
21	2	1	3	10	0	0	0
22	2	1	3	5	0	0	0
23	2	9	3	5	0	0	0
24	2	10	3	5	0	0	0
25	2	9	3	10	0	0	0
26	2	3	5	11	0	0	0
27	2	3	5	12	0	0	0
28	2	5	12	13	0	0	0
29	2	3	5	6	0	0	0
30	2	11	5	6	0	0	0
31	2	12	5	6	0	0	0
32	2	11	5	12	0	0	0
33	2	5	6	14	0	0	0
34	2	5	6	15	0	0	0
35	2	6	15	16	0	0	0
36	2	4	6	5	0	0	0
37	2	4	6	14	0	0	0
38	2	4	6	15	0	0	0
39	2	14	6	15	0	0	0
40	2	17	4	6	0	0	0
41	2	18	4	6	0	0	0
42	2	4	18	19	0	0	0
43	2	2	4	6	0	0	0
44	2	2	4	17	0	0	0
45	2	2	4	18	0	0	0
46	2	17	4	18	0	0	0
47	2	7	2	4	0	0	0
48	2	8	2	4	0	0	0

TABLE XXXIX (Continued)

NO.	CODE	I	J	K	L	IX	JX
49	2	1	2	4	0	0	0
50	2	1	2	7	0	0	0
51	2	1	2	8	0	0	0
52	2	7	2	8	0	0	0
53	2	2	1	3	0	0	0
54	4	7	2	4	6	0	0
54	4	8	2	4	18	0	0
54	4	1	2	4	17	0	0
55	4	17	4	6	5	0	0
55	4	2	4	6	15	0	0
55	4	18	4	6	14	0	0
56	4	9	3	5	6	0	0
56	4	10	3	5	11	0	0
56	4	1	3	5	12	0	0
57	4	11	5	6	14	0	0
57	4	3	5	6	15	0	0
57	4	12	5	6	4	0	0
58	4	17	4	18	19	0	0
59	4	14	6	15	16	0	0
60	4	11	5	12	13	0	0
61	4	7	2	1	3	0	0
62	4	9	3	1	2	0	0

TABLE XL

G MATRIX FOR 1,5-ANHYDROXYLITOL

1	1	0.145758	1	2	-0.027752	1	6	-0.023868	1	7	-0.027752
1	8	-0.027752	1	20	-0.071619	1	21	-0.071619	1	22	-0.051540
1	23	0.061579	1	24	0.061579	1	25	0.071619	1	26	0.026625
1	27	-0.051530	1	29	0.024905	1	49	0.020297	1	50	-0.040594
1	51	0.020297	1	53	-0.040594	1	54	-0.037288	1	57	-0.047860
2	2	0.166512	2	3	-0.027752	2	7	-0.027752	2	8	-0.027752
2	9	-0.027752	2	10	-0.027752	2	20	0.063390	2	21	0.063390
2	22	-0.055161	2	23	-0.071619	2	24	-0.071619	2	25	0.071619
2	26	-0.071816	2	27	-0.055473	2	28	0.027737	2	29	-0.051540
2	30	0.061677	2	31	0.053506	2	32	0.063645	2	33	0.028654
2	34	-0.051517	2	36	0.024953	2	53	0.027581	2	55	0.046618
2	57	-0.012218	2	60	0.065968	2	61	0.051688	2	62	0.062938
3	3	0.166512	3	4	-0.021099	3	9	-0.027752	3	10	-0.027752
3	12	-0.027752	3	13	-0.027752	3	22	0.024905	3	23	-0.051530
3	24	0.026625	3	26	0.061677	3	27	0.053506	3	28	0.027737
3	29	-0.051540	3	30	-0.071816	3	31	-0.055473	3	32	0.063645
3	33	-0.071816	3	34	-0.055473	3	35	0.030127	3	36	-0.052881
3	37	0.053677	3	38	0.046975	3	39	0.069130	3	40	0.027270
3	41	-0.052872	3	43	0.025603	3	54	-0.049077	3	55	0.015809
3	56	0.015012	3	59	-0.070088	3	60	-0.065967	4	4	0.166512
4	5	-0.027752	4	12	-0.027752	4	13	-0.027752	4	15	-0.027752
4	16	-0.027752	4	29	0.025603	4	30	0.027270	4	31	-0.052872
4	33	0.053677	4	34	0.046975	4	35	0.030127	4	36	-0.052881
4	37	-0.071816	4	38	-0.055473	4	39	0.069129	4	40	-0.071816
4	41	-0.055473	4	42	0.027737	4	43	-0.051540	4	44	0.061677
4	45	0.053506	4	46	0.063645	4	47	-0.051530	4	48	0.026625
4	49	0.024905	4	54	-0.015012	4	56	0.049077	4	57	-0.015809
4	58	0.065967	4	59	0.070089	5	5	0.166512	5	6	-0.027752
5	15	-0.027752	5	16	-0.027752	5	18	-0.027752	5	19	-0.027752
5	36	0.024953	5	37	0.028654	5	38	-0.051517	5	40	0.061678
5	41	0.053506	5	42	0.027737	5	43	-0.051539	5	44	-0.071816
5	45	-0.055473	5	46	0.063645	5	47	-0.071619	5	48	-0.071619
5	49	-0.055161	5	50	0.063390	5	51	0.063390	5	52	0.071619
5	53	0.027581	5	55	0.012218	5	57	-0.046618	5	58	-0.065968
5	61	-0.062938	5	62	-0.051688	6	6	0.145758	6	18	-0.027752
6	19	-0.027752	6	20	-0.040594	6	21	0.020297	6	22	0.020297
6	43	0.024905	6	44	0.026625	6	45	-0.051530	6	47	0.061579
6	48	0.061579	6	49	-0.051539	6	50	-0.071619	6	51	-0.071619
6	52	0.071619	6	53	-0.040594	6	55	0.047860	6	56	0.037288
7	7	1.075350	7	8	-0.027752	7	20	-0.055162	7	21	0.063390
7	22	0.053350	7	23	-0.051540	7	24	0.061579	7	25	-0.071619
7	26	0.024905	7	27	0.026625	7	29	-0.051530	7	53	-0.055161
7	56	-0.015117	7	57	0.001053	8	8	1.075349	8	20	0.063390
8	21	-0.055161	8	22	0.053350	8	23	0.061579	8	24	-0.051540
8	25	-0.071619	8	26	-0.051530	8	27	0.024905	8	29	0.026625
8	53	0.027581	8	56	0.015117	8	57	0.046807	8	61	-0.051688
8	62	-0.062938	9	9	1.075350	9	10	-0.027752	9	22	0.026625
9	23	0.024905	9	24	-0.051530	9	26	-0.051540	9	27	0.053507
9	28	-0.055473	9	29	0.051539	9	30	-0.051540	9	31	0.053507
9	32	-0.055473	9	33	-0.051427	9	34	0.027076	9	36	0.026578
9	55	-0.045648	9	56	0.003613	9	57	-0.006349	10	10	0.145758
10	11	-0.020834	10	22	-0.051530	10	23	0.026625	10	24	0.024905
10	26	0.061678	10	27	-0.051540	10	28	-0.060751	10	29	0.051539



TABLE XL (Continued)

10	30	0.061678	10	31	-0.051539	10	32	-0.071816	10	33	0.022773
10	34	0.024440	10	36	-0.051531	10	55	-0.000970	10	56	-0.018625
10	57	0.018567	11	11	1.054595	11	27	0.020823	11	28	-0.041645
11	31	0.020823	11	32	-0.041645	11	56	0.038254	11	57	-0.038254
12	12	1.075349	12	13	-0.033693	12	29	0.028654	12	30	-0.051427
12	31	0.022773	12	33	-0.051539	12	34	0.059128	12	35	-0.053805
12	36	0.047221	12	37	-0.051539	12	38	0.059128	12	39	-0.053805
12	40	-0.051427	12	41	0.022773	12	43	0.028654	12	54	0.045438
12	55	0.003398	12	56	-0.045438	12	57	-0.003398	13	13	0.145758
13	14	-0.020834	13	29	-0.051517	13	30	0.027076	13	31	0.024440
13	33	0.067737	13	34	-0.051539	13	35	-0.060750	13	36	0.047221
13	37	0.067736	13	38	-0.051539	13	39	-0.069656	13	40	0.027077
13	41	0.024440	13	43	-0.051517	13	54	-0.001614	13	55	-0.017515
13	56	0.001614	13	57	0.017515	14	14	1.054595	14	34	0.022617
14	35	-0.041645	14	38	0.022617	14	39	-0.041645	14	55	0.037090
14	57	-0.037090	15	15	1.075351	15	16	-0.027752	15	36	0.026578
15	37	-0.051427	15	38	0.027076	15	40	-0.051540	15	41	0.053507
15	42	-0.055473	15	43	0.051539	15	44	-0.051540	15	45	0.053506
15	46	-0.055474	15	47	0.024905	15	48	-0.051530	15	49	0.026625
15	54	-0.003613	15	55	0.006349	15	57	0.045648	16	16	0.145758
16	17	-0.020834	16	36	-0.051531	16	37	0.022773	16	38	0.024440
16	40	0.061678	16	41	-0.051539	16	42	-0.060750	16	43	0.051539
16	44	0.061678	16	45	-0.051542	16	46	-0.071816	16	47	0.026625
16	48	0.024905	16	49	-0.051530	16	54	0.018625	16	55	-0.018567
16	57	0.000969	17	17	1.054595	17	41	0.020823	17	42	-0.041645
17	45	0.020824	17	46	-0.041645	17	54	-0.038254	17	55	0.038254
18	18	1.075351	18	19	-0.027752	18	43	-0.051530	18	44	0.024905
18	45	0.026625	18	47	-0.051540	18	48	0.061579	18	49	0.053350
18	50	-0.055162	18	51	0.063390	18	52	-0.071620	18	53	-0.055161
18	54	0.015117	18	55	-0.001053	19	19	1.075349	19	43	0.026625
19	44	-0.051530	19	45	0.024905	19	47	0.061579	19	48	-0.051540
19	49	0.053350	19	50	0.063390	19	51	-0.055162	19	52	-0.071619
19	53	0.027581	19	54	-0.015117	19	55	-0.046807	19	61	0.062938
19	62	0.051688	20	20	1.002793	20	21	0.003973	20	22	-0.009726
20	23	-0.432808	20	24	-0.140658	20	25	-0.423575	20	26	-0.058979
20	27	0.034237	20	29	0.024742	20	49	-0.005894	20	50	0.011787
20	51	-0.005894	20	53	0.101564	20	54	0.010827	20	56	0.746442
20	57	0.057083	21	21	1.002789	21	22	-0.009726	21	23	-0.140658
21	24	-0.432807	21	25	-0.423573	21	26	0.022650	21	27	0.036074
21	29	-0.058724	21	49	-0.020203	21	50	-0.005894	21	51	0.026097
21	53	-0.050782	21	54	-0.019590	21	56	-0.746438	21	57	0.008220
21	61	0.085718	21	62	0.036697	22	22	0.169380	22	23	-0.006123
22	24	-0.006124	22	25	-0.137681	22	26	-0.052312	22	27	0.097452
22	28	-0.007082	22	29	-0.046659	22	30	-0.057105	22	31	0.024312
22	32	0.034311	22	33	-0.022906	22	34	-0.004851	22	36	0.030295
22	49	0.026097	22	50	-0.005894	22	51	-0.020203	22	53	-0.048287
22	54	0.008763	22	55	-0.010499	22	56	0.012880	22	57	0.035081
22	60	-0.014800	22	61	-0.081044	22	62	-0.031005	23	23	1.000262
23	24	0.005239	23	25	-0.425911	23	26	-0.050779	23	27	-0.052326
23	28	-0.025321	23	29	0.100359	23	30	0.036567	23	31	0.025394
23	32	-0.059214	23	33	-0.006076	23	34	0.011937	23	36	-0.006397
23	53	0.023116	23	55	-0.010474	23	56	0.004780	23	57	0.001956
23	60	0.030622	23	61	-0.062021	23	62	-0.834169	24	24	1.000258
24	25	-0.425909	24	26	0.105065	24	27	-0.048946	24	28	0.032403
24	29	-0.051854	24	30	0.020537	24	31	-0.049706	24	32	0.024904
24	33	0.028982	24	34	-0.007086	24	36	-0.023899	24	53	-0.061199
24	55	0.020972	24	56	-0.017660	24	57	-0.040584	24	60	-0.015822
24	61	-0.009350	24	62	-0.011385	25	25	1.836644	25	26	0.034355
25	27	-0.066491	25	29	0.032136	25	53	0.035588	25	57	-0.061756
25	61	0.066696	25	62	0.839860	26	26	1.005274	26	27	-0.005808

TABLE XL (Continued)

26	28	0.023222	26	29	-0.008532	26	30	-0.436830	26	31	-0.118916
26	32	-0.435187	26	33	0.017992	26	34	0.034337	26	36	-0.057114
26	53	-0.025179	26	55	-0.009504	26	56	-0.014095	26	57	0.751018
26	60	-0.842150	26	61	0.023994	26	62	0.029216	27	27	0.170341
27	28	-0.050428	27	29	-0.016120	27	30	-0.118916	27	31	-0.019366
27	32	-0.010131	27	33	-0.049681	27	34	0.027448	27	36	0.024266
27	53	-0.007042	27	55	-0.044849	27	56	0.017391	27	57	-0.001279
27	60	-0.022934	27	61	-0.011597	27	62	-0.014120	28	28	1.223996
28	29	-0.051511	28	30	0.023222	28	31	-0.050428	28	32	0.105922
28	33	0.032859	28	34	-0.026403	28	36	-0.007047	28	55	0.034460
28	56	-0.040672	28	57	0.042737	29	29	0.167503	29	30	-0.008532
29	31	-0.016120	29	32	-0.118197	29	33	-0.055832	29	34	0.096587
29	35	-0.006033	29	36	-0.044953	29	37	-0.060013	29	38	0.023615
29	39	0.033908	29	40	-0.024637	29	41	-0.004975	29	43	0.029612
29	53	0.032221	29	54	0.012041	29	55	-0.034803	29	56	-0.003296
29	57	-0.001018	29	59	0.017196	29	61	-0.012397	29	62	-0.015095
30	30	1.005272	30	31	-0.005809	30	32	-0.435187	30	33	0.104902
30	34	-0.053237	30	35	0.031276	30	36	-0.050307	30	37	0.019657
30	38	-0.052394	30	39	0.025009	30	40	0.028768	30	41	-0.004131
30	43	-0.024637	30	54	-0.020146	30	55	0.040940	30	56	-0.751588
30	57	0.007961	30	59	0.018315	30	60	0.842150	31	31	0.170341
31	32	-0.010132	31	33	-0.044776	31	34	-0.046255	31	35	-0.025244
31	36	0.093746	31	37	0.040356	31	38	0.028779	31	39	-0.058917
31	40	-0.004130	31	41	0.009105	31	43	-0.004975	31	54	0.008105
31	55	-0.001951	31	56	-0.001409	31	57	-0.006692	31	59	-0.035511
31	60	0.022933	32	32	1.008831	32	33	0.027395	32	34	-0.058879
32	36	0.034363	32	55	0.050166	32	56	0.752995	32	57	-0.749989
33	33	1.005272	33	34	-0.014423	33	35	0.018646	33	36	-0.001012
33	37	-0.352559	33	38	-0.116795	33	39	-0.479267	33	40	0.019658
33	41	0.040356	33	43	-0.060013	33	54	0.012675	33	55	-0.792841
33	56	0.040848	33	57	0.007062	33	59	0.846825	33	60	0.017028
34	34	0.170341	34	35	-0.054773	34	36	-0.009213	34	37	-0.116795
34	38	-0.010148	34	39	-0.018905	34	40	-0.052394	34	41	0.028779
34	43	0.023615	34	54	0.049708	34	55	-0.001731	34	56	-0.004747
34	57	-0.008365	34	59	0.030584	34	60	-0.030615	35	35	1.223994
35	36	-0.051263	35	37	0.018646	35	38	-0.054773	35	39	0.109763
35	40	0.031276	35	41	-0.025244	35	43	-0.006033	35	54	-0.034611
35	55	-0.038469	35	56	0.034611	35	57	0.038468	36	36	0.161767
36	37	-0.001011	36	38	-0.009213	36	39	-0.117627	36	40	-0.050307
36	41	0.093746	36	42	-0.007047	36	43	-0.044953	36	44	-0.057114
36	45	0.024266	36	46	0.034363	36	47	-0.006397	36	48	-0.023899
36	49	0.030295	36	54	0.032242	36	55	-0.000564	36	56	-0.032242
36	57	0.000565	36	58	-0.014829	36	60	0.014829	37	37	1.005272
37	38	-0.014423	37	39	-0.479265	37	40	0.104902	37	41	-0.044776
37	42	0.032859	37	43	-0.055832	37	44	0.017992	37	45	-0.049681
37	46	0.027395	37	47	-0.006076	37	48	0.028982	37	49	-0.022906
37	54	-0.040848	37	55	-0.007062	37	56	-0.012675	37	57	0.792842
37	58	-0.017028	37	59	-0.846827	38	38	0.170341	38	39	-0.018905
38	40	-0.053237	38	41	-0.046255	38	42	-0.026403	38	43	0.096587
38	44	0.034337	38	45	0.027448	38	46	-0.058879	38	47	0.011937
38	48	-0.007086	38	49	-0.004851	38	54	0.004747	38	55	0.008365
38	56	-0.049708	38	57	0.001731	38	58	0.030614	38	59	-0.030584
39	39	1.016509	39	40	0.025009	39	41	-0.058917	39	43	0.033908
39	54	-0.051394	39	55	0.730806	39	56	0.051394	39	57	-0.730805
40	40	1.005276	40	41	-0.005808	40	42	0.023222	40	43	-0.008532
40	44	-0.436831	40	45	-0.118916	40	46	-0.435188	40	47	0.036567
40	48	0.020537	40	49	-0.057105	40	54	0.751590	40	55	-0.007961
40	56	0.020146	40	57	-0.040940	40	58	-0.842151	40	59	-0.018315
41	41	0.170341	41	42	-0.050428	41	43	-0.016120	41	44	-0.118916
41	45	-0.019365	41	46	-0.010132	41	47	0.025394	41	48	-0.049706

TABLE XL (Continued)

41	49	0.024312	41	54	0.001409	41	55	0.006692	41	56	-0.008105
41	57	0.001951	41	58	-0.022933	41	59	0.035511	42	42	1.223993
42	43	-0.051511	42	44	0.023222	42	45	-0.050425	42	46	0.105922
42	47	-0.025321	42	48	0.032403	42	49	-0.007082	42	54	0.040672
42	55	-0.042737	42	57	-0.034460	43	43	0.167503	43	44	-0.008533
43	45	-0.016120	43	46	-0.118197	43	47	0.100359	43	48	-0.051854
43	49	-0.046659	43	50	0.024742	43	51	-0.058724	43	52	0.032136
43	53	0.032221	43	54	0.003296	43	55	0.001018	43	56	-0.012041
43	57	0.034803	43	59	-0.017196	43	61	0.015095	43	62	0.012397
44	44	1.005275	44	45	-0.005808	44	46	-0.435186	44	47	-0.050779
44	48	0.105065	44	49	-0.052312	44	50	-0.058979	44	51	0.022650
44	52	0.034355	44	53	-0.025179	44	54	0.014095	44	55	-0.751021
44	57	0.009504	44	58	0.842152	44	61	-0.029216	44	62	-0.023994
45	45	0.170341	45	46	-0.010131	45	47	-0.052326	45	48	-0.048946
45	49	0.097452	45	50	0.034237	45	51	0.036074	45	52	-0.066491
45	53	-0.007042	45	54	-0.017391	45	55	0.001279	45	57	0.044849
45	58	0.022933	45	61	0.014120	45	62	0.011597	46	46	1.008832
46	47	-0.059214	46	48	0.024903	46	49	0.034311	46	54	-0.752998
46	55	0.749991	46	57	-0.050166	47	47	1.000262	47	48	0.005239
47	49	-0.006124	47	50	-0.432808	47	51	-0.140658	47	52	-0.425911
47	53	0.023116	47	54	-0.004780	47	55	-0.001956	47	57	0.010474
47	58	-0.030622	47	61	0.834169	47	62	0.062021	48	48	1.000258
48	49	-0.006123	48	50	-0.140658	48	51	-0.432806	48	52	-0.425910
48	53	-0.061199	48	54	0.017661	48	55	0.040584	48	57	-0.020972
48	58	0.015822	48	61	0.011385	48	62	0.009350	49	49	0.169380
49	50	-0.009726	49	51	-0.009726	49	52	-0.137681	49	53	-0.048287
49	54	-0.012881	49	55	-0.035081	49	56	-0.008763	49	57	0.010499
49	58	0.014800	49	61	0.031005	49	62	0.081044	50	50	1.002792
50	51	0.003973	50	52	-0.423575	50	53	0.101564	50	54	-0.746442
50	55	-0.057083	50	56	-0.010827	51	51	1.002789	51	52	-0.423574
51	53	-0.050782	51	54	0.746439	51	55	-0.008220	51	56	0.019590
51	61	-0.036697	51	62	-0.085718	52	52	1.836649	52	53	0.035589
52	55	0.061756	52	61	-0.839861	52	62	-0.066696	53	53	0.167539
53	54	0.027912	53	55	-0.011106	53	56	-0.027912	53	57	0.011106
54	54	2.912177	54	55	-0.487531	54	56	-0.035927	54	57	-0.003006
54	58	-0.501667	54	59	0.032961	54	61	-0.491836	54	62	0.011649
55	55	2.027383	55	56	-0.003007	55	57	-0.405595	55	58	-0.500009
55	59	-0.559957	55	60	0.027703	55	61	-0.026538	55	62	-0.021795
56	56	2.912174	56	57	-0.487529	56	59	0.032962	56	60	-0.501668
56	61	0.011649	56	62	-0.491836	57	57	2.027379	57	58	0.027703
57	59	-0.559960	57	60	-0.500007	57	61	-0.021795	57	62	-0.026538
58	58	2.273606	59	59	2.339827	60	60	2.273607	61	61	1.088884
61	62	0.076993	62	62	1.088884	-1	0	0.0			

TABLE XLI

G MATRIX FOR 1,5-ANHYDRORIBITOL

1	1	0.145758	1	2	-0.027752	1	6	-0.023868	1	7	-0.027752
1	8	-0.027752	1	20	-0.071619	1	21	-0.071619	1	22	-0.051540
1	23	0.061579	1	24	0.061579	1	25	0.071619	1	26	0.026625
1	27	-0.051530	1	29	0.024905	1	49	0.020297	1	50	-0.040594
1	51	0.020297	1	53	-0.040594	1	54	-0.037288	1	57	-0.047860
2	2	0.166512	2	3	-0.027752	2	7	-0.027752	2	8	-0.027752
2	9	-0.027752	2	10	-0.027752	2	20	0.063390	2	21	0.063390
2	22	-0.055161	2	23	-0.071619	2	24	-0.071619	2	25	0.071619
2	26	-0.071816	2	27	-0.055473	2	28	0.027737	2	29	-0.051540
2	30	0.061677	2	31	0.053506	2	32	0.063645	2	33	-0.051517
2	34	0.028654	2	36	0.024953	2	53	0.027581	2	55	0.046618
2	57	-0.012218	2	60	0.065968	2	61	0.051688	2	62	0.062938
3	3	0.166512	3	4	-0.021099	3	9	-0.027752	3	10	-0.027752
3	12	-0.027752	3	13	-0.027752	3	22	0.024905	3	23	-0.051530
3	24	0.026625	3	26	0.061677	3	27	0.053506	3	28	0.027737
3	29	-0.051540	3	30	-0.071816	3	31	-0.055473	3	32	0.063645
3	33	-0.071816	3	34	-0.055473	3	35	0.030127	3	36	-0.052881
3	37	0.053678	3	38	0.046975	3	39	0.069130	3	40	0.027270
3	41	-0.052872	3	43	0.025603	3	54	-0.049077	3	55	-0.015809
3	56	0.015012	3	59	0.070088	3	60	-0.065967	4	4	0.166512
4	5	-0.027752	4	12	-0.027752	4	13	-0.027752	4	15	-0.027752
4	16	-0.027752	4	29	0.025603	4	30	0.027270	4	31	-0.052872
4	33	0.053678	4	34	0.046975	4	35	0.030127	4	36	-0.052881
4	37	-0.071816	4	38	-0.055473	4	39	0.069129	4	40	-0.071816
4	41	-0.055473	4	42	0.027737	4	43	-0.051540	4	44	0.061677
4	45	0.053506	4	46	0.063645	4	47	-0.051530	4	48	0.026625
4	49	0.024905	4	54	-0.015012	4	56	0.049077	4	57	0.015810
4	58	0.065967	4	59	-0.070088	5	5	0.166512	5	6	-0.027752
5	15	-0.027752	5	16	-0.027752	5	18	-0.027752	5	19	-0.027752
5	36	0.024953	5	37	-0.051517	5	38	0.028654	5	40	0.061678
5	41	0.053506	5	42	0.027737	5	43	-0.051539	5	44	-0.071816
5	45	-0.055473	5	46	0.063645	5	47	-0.071619	5	48	-0.071619
5	49	-0.055161	5	50	0.063390	5	51	0.063390	5	52	0.071619
5	53	0.027581	5	55	0.012218	5	57	-0.046618	5	58	-0.065968
5	61	-0.062938	5	62	-0.051688	6	6	0.145758	6	18	-0.027752
6	19	-0.027752	6	20	-0.040594	6	21	0.020297	6	22	0.020297
6	43	0.024905	6	44	0.026625	6	45	-0.051530	6	47	0.061579
6	48	0.061579	6	49	-0.051539	6	50	-0.071619	6	51	-0.071619
6	52	0.071619	6	53	-0.040594	6	55	0.047860	6	56	0.037288
7	7	1.075350	7	8	-0.027752	7	20	-0.055162	7	21	0.063390
7	22	0.053350	7	23	-0.051540	7	24	0.061579	7	25	-0.071619
7	26	0.024905	7	27	0.026625	7	29	-0.051530	7	53	-0.055161
7	56	-0.015117	7	57	0.001053	8	8	1.075349	8	20	0.063390
8	21	-0.055161	8	22	0.053350	8	23	0.061579	8	24	-0.051540
8	25	-0.071619	8	26	-0.051530	8	27	0.024905	8	29	0.026625
8	53	0.027581	8	56	0.015117	8	57	0.046807	8	61	-0.051688
8	62	-0.062938	9	9	1.075350	9	10	-0.027752	9	22	0.026625
9	23	0.024905	9	24	-0.051530	9	26	-0.051540	9	27	0.053507
9	28	-0.055473	9	29	0.051539	9	30	-0.051540	9	31	0.053507
9	32	-0.055473	9	33	0.027076	9	34	-0.051427	9	36	0.026578
9	55	-0.045648	9	56	0.003613	9	57	-0.006349	10	10	0.145758
10	11	-0.020834	10	22	-0.051530	10	23	0.026625	10	24	0.024905
10	26	0.061678	10	27	-0.051540	10	28	-0.060751	10	29	0.051539

TABLE XLI (Continued)

10	30	0.061678	10	31	-0.051539	10	32	-0.071816	10	33	0.024440
10	34	0.022773	10	36	-0.051531	10	55	-0.000970	10	56	-0.018625
10	57	0.018567	11	11	1.054595	11	27	0.020823	11	28	-0.041645
11	31	0.020823	11	32	-0.041645	11	56	0.038254	11	57	-0.038254
12	12	1.075351	12	13	-0.033693	12	29	-0.051517	12	30	0.027076
12	31	0.024440	12	33	-0.051540	12	34	0.059128	12	35	-0.053805
12	36	0.047221	12	37	-0.051540	12	38	0.059128	12	39	-0.053806
12	40	0.027076	12	41	0.024441	12	43	-0.051517	12	54	-0.001614
12	55	-0.003398	12	56	0.001614	12	57	0.003398	13	13	0.145758
13	14	-0.020834	13	29	0.028654	13	30	-0.051427	13	31	0.022773
13	33	0.067737	13	34	-0.051539	13	35	-0.060750	13	36	0.047221
13	37	0.067736	13	38	-0.051539	13	39	-0.069656	13	40	-0.051427
13	41	0.022773	13	43	0.028654	13	54	0.045438	13	55	0.017515
13	56	-0.045438	13	57	-0.017515	14	14	1.054595	14	34	0.022617
14	35	-0.041645	14	38	0.022617	14	39	-0.041645	14	55	-0.037090
14	57	0.037090	15	15	1.075351	15	16	-0.027752	15	36	0.026578
15	37	0.027076	15	38	-0.051427	15	40	-0.051540	15	41	0.053507
15	42	-0.055473	15	43	0.051539	15	44	-0.051540	15	45	0.053506
15	46	-0.055474	15	47	0.024905	15	48	-0.051530	15	49	0.026625
15	54	-0.003613	15	55	0.006349	15	57	0.045648	16	16	0.145758
16	17	-0.020834	16	36	-0.051531	16	37	0.024440	16	38	0.022773
16	40	0.061678	16	41	-0.051539	16	42	-0.060750	16	43	0.051539
16	44	0.061678	16	45	-0.051542	16	46	-0.071816	16	47	0.026625
16	48	0.024905	16	49	-0.051530	16	54	0.018625	16	55	-0.018567
16	57	0.000969	17	17	1.054595	17	41	0.020823	17	42	-0.041645
17	45	0.020824	17	46	-0.041645	17	54	-0.038254	17	55	0.038254
18	18	1.075351	18	19	-0.027752	18	43	-0.051530	18	44	0.024905
18	45	0.026625	18	47	-0.051540	18	48	0.061579	18	49	0.053350
18	50	-0.055162	18	51	0.063390	18	52	-0.071620	18	53	-0.055161
18	54	0.015117	18	55	-0.001053	19	19	1.075349	19	43	0.026625
19	44	-0.051530	19	45	0.024905	19	47	0.061579	19	48	-0.051540
19	49	0.053350	19	50	0.063390	19	51	-0.055162	19	52	-0.071619
19	53	0.027581	19	54	-0.015117	19	55	-0.046807	19	61	0.062938
19	62	0.051688	20	20	1.002793	20	21	0.003973	20	22	-0.009726
20	23	-0.432808	20	24	-0.140658	20	25	-0.423575	20	26	-0.058979
20	27	0.034237	20	29	0.024742	20	49	-0.005894	20	50	0.011787
20	51	-0.005894	20	53	0.101564	20	54	0.010827	20	56	0.746442
20	57	0.057083	21	21	1.002789	21	22	-0.009726	21	23	-0.140658
21	24	-0.432807	21	25	-0.423573	21	26	0.022650	21	27	0.036074
21	29	-0.058724	21	49	-0.020203	21	50	-0.005894	21	51	0.026097
21	53	-0.050782	21	54	-0.019590	21	56	-0.746438	21	57	0.008220
21	61	0.085718	21	62	0.036697	22	22	0.169380	22	23	-0.006123
22	24	-0.006124	22	25	-0.137681	22	26	-0.052312	22	27	0.097452
22	28	-0.007082	22	29	-0.046659	22	30	-0.057105	22	31	0.024312
22	32	0.034311	22	33	-0.004851	22	34	-0.022906	22	36	0.030295
22	49	0.026097	22	50	-0.005894	22	51	-0.020203	22	53	-0.048287
22	54	0.008763	22	55	-0.010499	22	56	0.012880	22	57	0.035081
22	60	-0.014800	22	61	-0.081044	22	62	-0.031005	23	23	1.000262
23	24	0.005239	23	25	-0.425911	23	26	-0.050779	23	27	-0.052326
23	28	-0.025321	23	29	0.100359	23	30	0.036567	23	31	0.025394
23	32	-0.059214	23	33	0.011937	23	34	-0.006076	23	36	-0.006397
23	53	0.023116	23	55	-0.010474	23	56	0.004780	23	57	0.001956
23	60	0.030622	23	61	-0.062021	23	62	-0.834169	24	24	1.000258
24	25	-0.425909	24	26	0.105065	24	27	-0.048946	24	28	0.032403
24	29	-0.051854	24	30	0.020537	24	31	-0.049706	24	32	0.024904
24	33	-0.007086	24	34	0.028982	24	36	-0.023899	24	53	-0.061199
24	55	0.020972	24	56	-0.017660	24	57	-0.040584	24	60	-0.015822
24	61	-0.009350	24	62	-0.011385	25	25	1.836644	25	26	0.034355
25	27	-0.066491	25	29	0.032136	25	53	0.035588	25	57	-0.061756
25	61	0.066696	25	62	0.839860	26	26	1.005274	26	27	-0.005808

TABLE XLI (Continued)

26	28	0.023222	26	29	-0.008532	26	30	-0.436830	26	31	-0.118916
26	32	-0.435187	26	33	0.034337	26	34	0.017992	26	36	-0.057114
26	53	-0.025179	26	55	-0.009504	26	56	-0.014095	26	57	0.751018
26	60	-0.842150	26	61	0.023994	26	62	0.029216	27	27	0.170341
27	28	-0.050428	27	29	-0.016120	27	30	-0.118916	27	31	-0.019366
27	32	-0.010131	27	33	0.027448	27	34	-0.049681	27	36	0.024266
27	53	-0.007042	27	55	-0.044849	27	56	0.017391	27	57	-0.001279
27	60	-0.022934	27	61	-0.011597	27	62	-0.014120	28	28	1.223996
28	29	-0.051511	28	30	0.023222	28	31	-0.050428	28	32	0.105922
28	33	-0.026403	28	34	0.032859	28	36	-0.007047	28	55	0.034460
28	56	-0.040672	28	57	0.042737	29	29	0.167503	29	30	-0.008532
29	31	-0.016120	29	32	-0.118197	29	33	0.100380	29	34	-0.053723
29	35	0.030852	29	36	-0.044953	29	37	0.021753	29	38	-0.052250
29	39	0.023042	29	40	-0.024637	29	41	-0.004975	29	43	0.029612
29	53	0.032221	29	54	0.012041	29	55	-0.037436	29	56	-0.003296
29	57	0.009372	29	59	-0.017196	29	61	-0.012397	29	62	-0.015095
30	30	1.005272	30	31	-0.005809	30	32	-0.435187	30	33	-0.055230
30	34	0.101116	30	35	-0.004841	30	36	-0.050307	30	37	-0.060409
30	38	0.021894	30	39	0.035649	30	40	0.028768	30	41	-0.004131
30	43	-0.024637	30	54	-0.020146	30	55	0.038135	30	56	-0.751588
30	57	0.019028	30	59	-0.018315	30	60	0.842150	31	31	0.170341
31	32	-0.010132	31	33	-0.048055	31	34	-0.043100	31	35	-0.026011
31	36	0.093746	31	37	0.038655	31	38	0.030356	31	39	-0.058691
31	40	-0.004130	31	41	0.009105	31	43	-0.004975	31	54	0.008105
31	55	0.003487	31	56	-0.001409	31	57	-0.028150	31	59	0.035511
31	60	0.022933	32	32	1.008831	32	33	-0.058879	32	34	0.027395
32	36	0.034363	32	55	0.050166	32	56	0.752995	32	57	-0.749989
33	33	1.005276	33	34	-0.014423	33	35	0.018646	33	36	-0.001012
33	37	-0.352561	33	38	-0.116795	33	39	-0.479268	33	40	-0.060409
33	41	0.038655	33	43	0.021753	33	54	0.060664	33	55	-0.792845
33	56	-0.004866	33	57	0.004744	33	59	-0.846828	33	60	-0.030615
34	34	0.170341	34	35	-0.054773	34	36	-0.009213	34	37	-0.116795
34	38	-0.010148	34	39	-0.018905	34	40	0.021894	34	41	0.030356
34	43	-0.052250	34	54	0.005182	34	55	0.001730	34	56	0.037503
34	57	0.020171	34	59	-0.030584	34	60	0.017028	35	35	1.223991
35	36	-0.051262	35	37	0.018646	35	38	-0.054773	35	39	0.109762
35	40	-0.004841	35	41	-0.026011	35	43	0.030852	35	54	-0.012963
35	55	0.038469	35	56	0.012963	35	57	-0.038468	36	36	0.161767
36	37	-0.001012	36	38	-0.009213	36	39	-0.117627	36	40	-0.050307
36	41	0.093746	36	42	-0.007047	36	43	-0.044953	36	44	-0.057114
36	45	0.024266	36	46	0.034363	36	47	-0.006397	36	48	-0.023899
36	49	0.030295	36	54	0.032242	36	55	0.026335	36	56	-0.032242
36	57	-0.026336	36	58	-0.014829	36	60	0.014829	37	37	1.005275
37	38	-0.014422	37	39	-0.479266	37	40	-0.055230	37	41	-0.048055
37	42	-0.026403	37	43	0.100379	37	44	0.034337	37	45	0.027448
37	46	-0.058879	37	47	0.011937	37	48	-0.007085	37	49	-0.004851
37	54	0.004866	37	55	-0.004744	37	56	-0.060664	37	57	-0.792846
37	58	0.030614	37	59	0.846830	38	38	0.170341	38	39	-0.018905
38	40	0.101116	38	41	-0.043100	38	42	0.032859	38	43	-0.053723
38	44	0.017992	38	45	-0.049681	38	46	0.027395	38	47	-0.006076
38	48	0.028982	38	49	-0.022906	38	54	-0.037503	38	55	-0.020171
38	56	-0.005182	38	57	-0.001731	38	58	-0.017028	38	59	0.030584
39	39	1.016513	39	40	0.035649	39	41	-0.058691	39	43	0.023042
39	54	-0.057771	39	55	-0.730810	39	56	0.057771	39	57	0.730810
40	40	1.005276	40	41	-0.005808	40	42	0.023222	40	43	-0.008532
40	44	-0.436831	40	45	-0.118916	40	46	-0.435188	40	47	0.036567
40	48	0.020537	40	49	-0.057105	40	54	0.751590	40	55	-0.019028
40	56	0.020146	40	57	-0.038135	40	58	-0.842151	40	59	0.018315
41	41	0.170341	41	42	-0.050428	41	43	-0.016120	41	44	-0.118916
41	45	-0.019365	41	46	-0.010132	41	47	0.025394	41	48	-0.049706

TABLE XLI (Continued)

41	49	0.024312	41	54	0.001409	41	55	0.028149	41	56	-0.008105
41	57	-0.003487	41	58	-0.022933	41	59	-0.035511	42	42	1.223993
42	43	-0.051511	42	44	0.023222	42	45	-0.050425	42	46	0.105922
42	47	-0.025321	42	48	0.032403	42	49	-0.007082	42	54	0.040672
42	55	-0.042737	42	57	-0.034460	43	43	0.167503	43	44	-0.008533
43	45	-0.016120	43	46	-0.118197	43	47	0.100359	43	48	-0.051854
43	49	-0.046659	43	50	0.024742	43	51	-0.058724	43	52	0.032136
43	53	0.032221	43	54	0.003296	43	55	-0.009372	43	56	-0.012041
43	57	0.037436	43	59	0.017196	43	61	0.015095	43	62	0.012397
44	44	1.005275	44	45	-0.005808	44	46	-0.435186	44	47	-0.050779
44	48	0.105065	44	49	-0.052312	44	50	-0.058979	44	51	0.022650
44	52	0.034355	44	53	-0.025179	44	54	0.014095	44	55	-0.751020
44	57	0.009504	44	58	0.842152	44	61	-0.029216	44	62	-0.023994
45	45	0.170341	45	46	-0.010131	45	47	-0.052326	45	48	-0.048946
45	49	0.097452	45	50	0.034237	45	51	0.036074	45	52	-0.066491
45	53	-0.007042	45	54	-0.017391	45	55	0.001279	45	57	0.044849
45	58	0.022933	45	61	0.014120	45	62	0.011597	46	46	1.008832
46	47	-0.059214	46	48	0.024903	46	49	0.034311	46	54	-0.752998
46	55	0.749991	46	57	-0.050166	47	47	1.000262	47	48	0.005239
47	49	-0.006124	47	50	-0.432808	47	51	-0.140658	47	52	-0.425911
47	53	0.023116	47	54	-0.004780	47	55	-0.001956	47	57	0.010474
47	58	-0.030622	47	61	0.834169	47	62	0.062021	48	48	1.000258
48	49	-0.006123	48	50	-0.140658	48	51	-0.432806	48	52	-0.425910
48	53	-0.061199	48	54	0.017661	48	55	0.040584	48	57	-0.020972
48	58	0.015822	48	61	0.011385	48	62	0.009350	49	49	0.169380
49	50	-0.009726	49	51	-0.009726	49	52	-0.137681	49	53	-0.048287
49	54	-0.012881	49	55	-0.035081	49	56	-0.008763	49	57	0.010499
49	58	0.014800	49	61	0.031005	49	62	0.081044	50	50	1.002792
50	51	0.003973	50	52	-0.423575	50	53	0.101564	50	54	-0.746442
50	55	-0.057083	50	56	-0.010827	51	51	1.002789	51	52	-0.423574
51	53	-0.050782	51	54	0.746439	51	55	-0.008220	51	56	0.019590
51	61	-0.036697	51	62	-0.085718	52	52	1.836649	52	53	0.035589
52	55	0.061756	52	61	-0.839861	52	62	-0.066696	53	53	0.167539
53	54	0.027912	53	55	-0.011106	53	56	-0.027912	53	57	0.011106
54	54	2.912177	54	55	-0.467614	54	56	-0.035927	54	57	-0.008054
54	58	-0.501667	54	59	-0.032961	54	61	-0.491836	54	62	0.011649
55	55	2.027388	55	56	-0.008054	55	57	-0.405599	55	58	-0.500009
55	59	-0.559958	55	60	0.027703	55	61	-0.026538	55	62	-0.021795
56	56	2.912174	56	57	-0.467611	56	59	-0.032962	56	60	-0.501668
56	61	0.011649	56	62	-0.491836	57	57	2.027386	57	58	0.027703
57	59	-0.559963	57	60	-0.500007	57	61	-0.021795	57	62	-0.026538
58	58	2.273606	59	59	2.339830	60	60	2.273607	61	61	1.088884
61	62	0.076993	62	62	1.088884	-1	0	0.0			

TABLE XLII

G MATRIX FOR 1,5-ANHYDRO-L-ARABINITOL

1	1	0.145758	1	2	-0.027752	1	6	-0.023868	1	7	-0.027752
1	8	-0.027752	1	20	-0.071619	1	21	-0.071619	1	22	-0.051540
1	23	0.061579	1	24	0.061579	1	25	0.071619	1	26	0.026625
1	27	-0.051530	1	29	0.024905	1	49	0.020297	1	50	-0.040594
1	51	0.020297	1	53	-0.040594	1	54	-0.037288	1	57	-0.047860
2	2	0.166512	2	3	-0.027752	2	7	-0.027752	2	8	-0.027752
2	9	-0.027752	2	10	-0.027752	2	20	0.063390	2	21	0.063390
2	22	-0.055161	2	23	-0.071619	2	24	-0.071619	2	25	0.071619
2	26	-0.071816	2	27	-0.055473	2	28	0.027737	2	29	-0.051540
2	30	0.061677	2	31	0.053506	2	32	0.063645	2	33	0.028654
2	34	-0.051517	2	36	0.024953	2	53	0.027581	2	55	0.046618
2	57	-0.012218	2	60	0.065968	2	61	0.051688	2	62	0.062938
3	3	0.166512	3	4	-0.021099	3	9	-0.027752	3	10	-0.027752
3	12	-0.027752	3	13	-0.027752	3	22	0.024905	3	23	-0.051530
3	24	0.026625	3	26	0.061677	3	27	0.053506	3	28	0.027737
3	29	-0.051540	3	30	-0.071816	3	31	-0.055473	3	32	0.063645
3	33	-0.071816	3	34	-0.055473	3	35	0.030127	3	36	-0.052881
3	37	0.053677	3	38	0.046975	3	39	0.069130	3	40	-0.052872
3	41	0.027270	3	43	0.025603	3	54	-0.049077	3	55	0.015809
3	56	0.015012	3	59	-0.070088	3	60	-0.065967	4	4	0.166512
4	5	-0.027752	4	12	-0.027752	4	13	-0.027752	4	15	-0.027752
4	16	-0.027752	4	29	0.025603	4	30	0.027270	4	31	-0.052872
4	33	0.053677	4	34	0.046975	4	35	0.030127	4	36	-0.052881
4	37	-0.071816	4	38	-0.055473	4	39	0.069129	4	40	-0.071816
4	41	-0.055473	4	42	0.027737	4	43	-0.051540	4	44	0.061678
4	45	0.053506	4	46	0.063645	4	47	-0.051530	4	48	0.026625
4	49	0.024905	4	54	0.015012	4	56	0.049077	4	57	-0.015809
4	58	-0.065967	4	59	0.070089	5	5	0.166512	5	6	-0.027752
5	15	-0.027752	5	16	-0.027752	5	18	-0.027752	5	19	-0.027752
5	36	0.024953	5	37	0.028654	5	38	-0.051517	5	40	0.061678
5	41	0.053506	5	42	0.027737	5	43	-0.051539	5	44	-0.071816
5	45	-0.055473	5	46	0.063645	5	47	-0.071619	5	48	-0.071619
5	49	-0.055161	5	50	0.063390	5	51	0.063390	5	52	0.071619
5	53	0.027581	5	55	-0.017805	5	57	-0.046618	5	58	0.065968
5	61	-0.062938	5	62	-0.051688	6	6	0.145758	6	18	-0.027752
6	19	-0.027752	6	20	-0.040594	6	21	0.020297	6	22	0.020297
6	43	0.024905	6	44	-0.051530	6	45	0.026625	6	47	0.061579
6	48	0.061579	6	49	-0.051539	6	50	-0.071619	6	51	-0.071619
6	52	0.071619	6	53	-0.040594	6	55	0.047860	6	56	0.037288
7	7	1.075350	7	8	-0.027752	7	20	-0.055162	7	21	0.063390
7	22	0.053350	7	23	-0.051540	7	24	0.061579	7	25	-0.071619
7	26	0.024905	7	27	0.026625	7	29	-0.051530	7	53	-0.055161
7	56	-0.015117	7	57	0.001053	8	8	1.075349	8	20	0.063390
8	21	-0.055161	8	22	0.053350	8	23	0.061579	8	24	-0.051540
8	25	-0.071619	8	26	-0.051530	8	27	0.024905	8	29	0.026625
8	53	0.027581	8	56	0.015117	8	57	0.046807	8	61	-0.051688
8	62	-0.062938	9	9	1.075350	9	10	-0.027752	9	22	0.026625
9	23	0.024905	9	24	-0.051530	9	26	-0.051540	9	27	0.053507
9	28	-0.055473	9	29	0.051539	9	30	-0.051540	9	31	0.053507
9	32	-0.055473	9	33	-0.051427	9	34	0.027076	9	36	0.026578
9	55	-0.045648	9	56	0.003613	9	57	-0.006349	10	10	0.145758
10	11	-0.020834	10	22	-0.051530	10	23	0.026625	10	24	0.024905
10	26	0.061678	10	27	-0.051540	10	28	-0.060751	10	29	0.051539



TABLE XLII (Continued)

10	30	0.061678	10	31	-0.051539	10	32	-0.071816	10	33	0.022773
10	34	0.024440	10	36	-0.051531	10	55	-0.000970	10	56	-0.018625
10	57	0.018567	11	11	1.054595	11	27	0.020823	11	28	-0.041645
11	31	0.020823	11	32	-0.041645	11	56	-0.038254	11	57	-0.038254
12	12	1.075349	12	13	-0.033693	12	29	0.028654	12	30	-0.051427
12	31	0.022773	12	33	-0.051539	12	34	0.059128	12	35	-0.053805
12	36	0.047221	12	37	-0.051539	12	38	0.059128	12	39	-0.053805
12	40	0.022773	12	41	-0.051427	12	43	0.028654	12	54	0.045438
12	55	0.003398	12	56	-0.045438	12	57	-0.003398	13	13	0.145758
13	14	-0.020834	13	29	-0.051517	13	30	0.027076	13	31	0.024440
13	33	0.067737	13	34	-0.051539	13	35	-0.060750	13	36	0.047221
13	37	0.067736	13	38	-0.051539	13	39	-0.069656	13	40	0.024440
13	41	0.027077	13	43	-0.051517	13	54	-0.001614	13	55	-0.017515
13	56	0.001614	13	57	0.017515	14	14	1.054595	14	34	0.022617
14	35	-0.041645	14	38	0.022617	14	39	-0.041645	14	55	0.037090
14	57	-0.037090	15	15	1.075349	15	16	-0.027752	15	36	-0.051531
15	37	0.022773	15	38	0.024440	15	40	-0.051540	15	41	0.053507
15	42	-0.055473	15	43	0.051539	15	44	-0.051540	15	45	0.053507
15	46	-0.055474	15	47	0.026625	15	48	0.024905	15	49	-0.051530
15	54	0.003613	15	55	-0.003555	15	57	0.000969	16	16	0.145758
16	17	-0.020834	16	36	0.026578	16	37	-0.051427	16	38	0.027076
16	40	0.061678	16	41	-0.051539	16	42	-0.060750	16	43	0.051539
16	44	0.061678	16	45	-0.051540	16	46	-0.071816	16	47	0.024905
16	48	-0.051530	16	49	0.026625	16	54	-0.018625	16	55	0.021360
16	57	0.045648	17	17	1.054594	17	41	0.020823	17	42	-0.041645
17	45	0.020823	17	46	-0.041645	17	54	0.038254	17	55	-0.038254
18	18	1.075351	18	19	-0.027752	18	43	-0.051530	18	44	0.026625
18	45	0.024905	18	47	-0.051540	18	48	0.061579	18	49	0.053350
18	50	-0.055162	18	51	0.063390	18	52	-0.071620	18	53	-0.055161
18	54	0.015117	18	55	-0.001053	19	19	1.075349	19	43	0.026625
19	44	0.024905	19	45	-0.051530	19	47	0.061579	19	48	-0.051540
19	49	0.053350	19	50	0.063390	19	51	-0.055162	19	52	-0.071619
19	53	0.027581	19	54	-0.015117	19	55	-0.046807	19	61	0.062938
19	62	0.051688	20	20	1.002793	20	21	0.003973	20	22	-0.009726
20	23	-0.432808	20	24	-0.140658	20	25	-0.423575	20	26	-0.058979
20	27	0.034237	20	29	0.024742	20	49	-0.005894	20	50	0.011787
20	51	-0.005894	20	53	0.101564	20	54	0.010827	20	56	0.746442
20	57	0.057083	21	21	1.002789	21	22	-0.009726	21	23	-0.140658
21	24	-0.432807	21	25	-0.423573	21	26	0.022650	21	27	0.036074
21	29	-0.058724	21	49	-0.020203	21	50	-0.005894	21	51	0.026097
21	53	-0.050782	21	54	-0.019590	21	56	-0.746438	21	57	0.008220
21	61	0.085718	21	62	0.036697	22	22	0.169380	22	23	-0.006123
22	24	-0.006124	22	25	-0.137681	22	26	-0.052312	22	27	0.097452
22	28	-0.007082	22	29	-0.046659	22	30	-0.057105	22	31	0.024312
22	32	0.034311	22	33	-0.022906	22	34	-0.004851	22	36	0.030295
22	49	0.026097	22	50	-0.005894	22	51	-0.020203	22	53	-0.048287
22	54	0.008763	22	55	-0.010499	22	56	0.012880	22	57	0.035081
22	60	-0.014800	22	61	-0.081044	22	62	-0.031005	23	23	1.000262
23	24	0.005239	23	25	-0.425911	23	26	-0.050779	23	27	-0.052326
23	28	-0.025321	23	29	0.100359	23	30	0.036567	23	31	0.025394
23	32	-0.059214	23	33	-0.006076	23	34	0.011937	23	36	-0.006397
23	53	0.023116	23	55	-0.010474	23	56	0.004780	23	57	0.001956
23	60	0.030622	23	61	-0.062021	23	62	-0.834169	24	24	1.000258
24	25	-0.425909	24	26	0.105065	24	27	-0.048946	24	28	0.032403
24	29	-0.051854	24	30	0.020537	24	31	-0.049706	24	32	0.024904
24	33	0.028982	24	34	-0.007086	24	36	-0.023899	24	53	-0.061199
24	55	0.020972	24	56	-0.017660	24	57	-0.040584	24	60	-0.015822
24	61	-0.009350	24	62	-0.011385	25	25	1.836644	25	26	0.034355
25	27	-0.066491	25	29	0.032136	25	53	0.035588	25	57	-0.061756
25	61	0.066696	25	62	0.839860	26	26	1.005274	26	27	-0.005808

TABLE XLII (Continued)

26	28	0.023222	26	29	-0.008532	26	30	-0.436830	26	31	-0.118916
26	32	-0.435187	26	33	0.017992	26	34	0.034337	26	36	-0.057114
26	53	-0.025179	26	55	-0.009504	26	56	-0.014095	26	57	0.751018
26	60	-0.842150	26	61	0.023994	26	62	0.029216	27	27	0.170341
27	28	-0.050428	27	29	-0.016120	27	30	-0.118916	27	31	-0.019366
27	32	-0.010131	27	33	-0.049681	27	34	0.027448	27	36	0.024266
27	53	-0.007042	27	55	-0.044849	27	56	0.017391	27	57	-0.001279
27	60	-0.022934	27	61	-0.011597	27	62	-0.014120	28	28	1.223996
28	29	-0.051511	28	30	0.023222	28	31	-0.050428	28	32	0.105922
28	33	0.032859	28	34	-0.026403	28	36	-0.007047	28	55	0.034460
28	56	-0.040672	28	57	0.042737	29	29	0.167503	29	30	-0.008532
29	31	-0.016120	29	32	-0.118197	29	33	-0.055832	29	34	0.096587
29	35	-0.006033	29	36	-0.044953	29	37	-0.060013	29	38	0.023615
29	39	0.033908	29	40	-0.004975	29	41	-0.024637	29	43	0.029612
29	53	0.032221	29	54	0.012041	29	55	-0.034803	29	56	-0.003296
29	57	-0.001018	29	59	0.017196	29	61	-0.012397	29	62	-0.015095
30	30	1.005272	30	31	-0.005809	30	32	-0.435187	30	33	0.104902
30	34	-0.053237	30	35	0.031276	30	36	-0.050307	30	37	0.019657
30	38	-0.052394	30	39	0.025009	30	40	-0.004131	30	41	0.028768
30	43	-0.024637	30	54	-0.020146	30	55	0.040940	30	56	-0.751588
30	57	0.007961	30	59	0.018315	30	60	0.842150	31	31	0.170341
31	32	-0.010132	31	33	-0.044776	31	34	-0.046255	31	35	-0.025244
31	36	0.093746	31	37	0.040356	31	38	0.028779	31	39	-0.058917
31	40	0.009105	31	41	-0.004130	31	43	-0.004975	31	54	0.008105
31	55	-0.001951	31	56	-0.001409	31	57	-0.006692	31	59	-0.035511
31	60	0.022933	32	32	1.008831	32	33	0.027395	32	34	-0.058879
32	36	0.034363	32	55	0.050166	32	56	0.752995	32	57	-0.749989
33	33	1.005272	33	34	-0.014423	33	35	0.018646	33	36	-0.001012
33	37	-0.352559	33	38	-0.116795	33	39	-0.479267	33	40	0.040356
33	41	0.019658	33	43	-0.060013	33	54	0.012675	33	55	-0.792841
33	56	0.040848	33	57	0.007062	33	59	0.846825	33	60	0.017028
34	34	0.170341	34	35	-0.054773	34	36	-0.009213	34	37	-0.116795
34	38	-0.010148	34	39	-0.018905	34	40	0.028779	34	41	-0.052394
34	43	0.023615	34	54	0.049708	34	55	-0.001730	34	56	-0.004747
34	57	-0.008365	34	59	0.030584	34	60	-0.030615	35	35	1.223994
35	36	-0.051263	35	37	0.018646	35	38	-0.054773	35	39	0.109763
35	40	-0.025244	35	41	0.031276	35	43	-0.006033	35	54	-0.034611
35	55	-0.038469	35	56	0.034611	35	57	0.038468	36	36	0.161767
36	37	-0.001011	36	38	-0.009213	36	39	-0.117627	36	40	0.097539
36	41	-0.048351	36	42	0.031986	36	43	-0.044953	36	44	0.022549
36	45	-0.049648	36	46	0.022863	36	47	-0.006397	36	48	-0.023899
36	49	0.030295	36	54	0.035617	36	55	-0.010688	36	56	-0.032242
36	57	0.000565	36	58	0.014829	36	60	0.014829	37	37	1.005272
37	38	-0.014423	37	39	-0.479265	37	40	-0.046453	37	41	0.101116
37	42	-0.004221	37	43	-0.055832	37	44	-0.057685	37	45	0.020535
37	46	0.038319	37	47	-0.006076	37	48	0.028982	37	49	-0.022906
37	54	-0.036973	37	55	-0.018687	37	56	-0.012675	37	57	0.792842
37	58	0.017028	37	59	-0.846827	38	38	0.170341	38	39	-0.018905
38	40	-0.048054	38	41	-0.051244	38	42	-0.025086	38	43	0.096587
38	44	0.037025	38	45	0.024953	38	46	-0.059267	38	47	0.011937
38	48	-0.007086	38	49	-0.004851	38	54	-0.002220	38	55	0.029265
38	56	-0.049708	38	57	0.001731	38	58	-0.030615	38	59	-0.030584
39	39	1.016509	39	40	-0.058917	39	41	0.025009	39	43	0.033908
39	54	-0.051394	39	55	0.730806	39	56	0.051394	39	57	-0.730805
40	40	1.005276	40	41	-0.005808	40	42	0.023222	40	43	-0.008532
40	44	-0.436831	40	45	-0.118916	40	46	-0.435188	40	47	0.034813
40	48	-0.057419	40	49	0.022606	40	54	-0.751590	40	55	-0.007252
40	56	-0.008105	40	57	0.001879	40	58	0.842152	40	59	0.035511
41	41	0.170341	41	42	-0.050428	41	43	-0.016120	41	44	-0.118916
41	45	-0.019365	41	46	-0.010132	41	47	0.027021	41	48	0.022624

TABLE XLII (Continued)

41	49	-0.049645	41	54	-0.001409	41	55	-0.021699	41	56	0.020146
41	57	-0.037580	41	58	0.022933	41	59	-0.018315	42	42	1.223995
42	43	-0.051511	42	44	0.023222	42	45	-0.050428	42	46	0.105922
42	47	-0.026180	42	48	-0.005793	42	49	0.031973	42	54	-0.040672
42	55	0.039945	42	57	-0.012133	43	43	0.167503	43	44	-0.008533
43	45	-0.016120	43	46	-0.118197	43	47	0.100359	43	48	-0.051854
43	49	-0.046659	43	50	0.024742	43	51	-0.058724	43	52	0.032136
43	53	0.032221	43	54	-0.024583	43	55	0.028897	43	56	-0.012041
43	57	0.034803	43	59	-0.017196	43	61	0.015095	43	62	0.012397
44	44	1.005276	44	45	-0.005808	44	46	-0.435187	44	47	-0.054286
44	48	-0.050779	44	49	0.101245	44	50	0.034237	44	51	0.036074
44	52	-0.066491	44	53	-0.007042	44	54	-0.003451	44	55	0.754891
44	57	0.055072	44	58	-0.842152	44	61	0.014120	44	62	0.011597
45	45	0.170341	45	46	-0.010131	45	47	-0.048946	45	48	0.101272
45	49	-0.050352	45	50	-0.058979	45	51	0.022650	45	52	0.034355
45	53	-0.025179	45	54	0.028034	45	55	0.001563	45	57	0.002570
45	58	-0.022933	45	61	-0.029216	45	62	-0.023994	46	46	1.008832
46	47	-0.058961	46	48	0.036156	46	49	0.022805	46	54	0.752997
46	55	-0.756398	46	57	-0.056744	47	47	1.000262	47	48	0.005239
47	49	-0.006124	47	50	-0.432808	47	51	-0.140658	47	52	-0.425911
47	53	0.023116	47	54	-0.025685	47	55	0.005013	47	57	0.010474
47	58	0.030622	47	61	0.834169	47	62	0.062021	48	48	1.000258
48	49	-0.006123	48	50	-0.140658	48	51	-0.432806	48	52	-0.425910
48	53	-0.061199	48	54	0.028462	48	55	0.036984	48	57	-0.020972
48	58	-0.015822	48	61	0.011385	48	62	0.009350	49	49	0.169380
49	50	-0.009726	49	51	-0.009726	49	52	-0.137681	49	53	-0.048287
49	54	-0.002777	49	55	-0.038449	49	56	-0.008763	49	57	0.010499
49	58	-0.014800	49	61	0.031005	49	62	0.081044	50	50	1.002792
50	51	0.003973	50	52	-0.423575	50	53	0.101564	50	54	-0.746442
50	55	-0.057083	50	56	-0.010827	51	51	1.002789	51	52	-0.423574
51	53	-0.050782	51	54	0.746439	51	55	-0.008220	51	56	0.019590
51	61	-0.036697	51	62	-0.085718	52	52	1.836649	52	53	0.035589
52	55	0.061756	52	61	-0.839861	52	62	-0.066696	53	53	0.167539
53	54	0.027912	53	55	-0.011106	53	56	-0.027912	53	57	0.011106
54	54	2.912177	54	55	-0.487909	54	56	-0.035927	54	57	-0.009311
54	58	-0.501668	54	59	0.032961	54	61	-0.491836	54	62	0.011649
55	55	2.029649	55	56	-0.003007	55	57	-0.386683	55	58	-0.503330
55	59	-0.559957	55	60	0.027703	55	61	-0.026538	55	62	-0.021795
56	56	2.912174	56	57	-0.487529	56	59	0.032962	56	60	-0.501668
56	61	0.011649	56	62	-0.491836	57	57	2.027379	57	58	-0.027703
57	59	-0.559960	57	60	-0.500007	57	61	-0.021795	57	62	-0.026538
58	58	2.273607	59	59	2.339827	60	60	2.273607	61	61	1.088884
61	62	0.076993	62	62	1.088884	-1	0	0.0			

up of 1,326 elements (independent elements), which may be reduced to 682 elements for 1,5-AX and 1,5-AR by introducing symmetry coordinates. The SVQFF for the 1,5-AP models is seen to be greatly reduced in size from the GQFF.

TABLE XLIII

Z MATRIX FOR 1,5-ANHYDROXYLITOL

1	1	1	1.000000	1	2	7	1.000000	1	6	8	1.000000	1	7	9	1.000000
1	8	9	1.000000	1	20	23	1.000000	1	21	23	1.000000	1	22	24	1.000000
1	53	26	1.000000	2	2	5	1.000000	2	3	7	1.000000	2	7	10	1.000000
2	8	10	1.000000	2	9	10	1.000000	2	10	7	1.000000	2	22	27	1.000000
2	23	28	1.000000	2	24	28	1.000000	2	26	28	1.000000	2	27	27	1.000000
2	29	29	1.000000	3	3	5	1.000000	3	4	7	1.000000	3	9	10	1.000000
3	10	7	1.000000	3	12	10	1.000000	3	13	7	1.000000	3	29	29	1.000000
3	30	28	1.000000	3	31	27	1.000000	3	33	28	1.000000	3	34	27	1.000000
3	36	29	1.000000	4	4	5	1.000000	4	5	7	1.000000	4	12	10	1.000000
4	13	7	1.000000	4	15	10	1.000000	4	16	7	1.000000	4	36	29	1.000000
4	37	28	1.000000	4	38	27	1.000000	4	40	28	1.000000	4	41	27	1.000000
4	43	29	1.000000	5	5	5	1.000000	5	6	7	1.000000	5	15	10	1.000000
5	16	7	1.000000	5	18	10	1.000000	5	19	10	1.000000	5	43	29	1.000000
5	44	28	1.000000	5	45	27	1.000000	5	47	28	1.000000	5	48	28	1.000000
5	49	27	1.000000	6	6	1	1.000000	6	18	9	1.000000	6	19	9	1.000000
6	49	24	1.000000	6	50	23	1.000000	6	51	23	1.000000	6	53	26	1.000000
7	7	3	1.000000	7	8	11	1.000000	7	20	30	1.000000	7	23	30	1.000000
7	25	30	1.000000	8	8	3	1.000000	8	21	30	1.000000	8	24	30	1.000000
8	25	30	1.000000	9	9	4	1.000000	9	10	9	1.000000	9	26	30	1.000000
9	30	30	1.000000	9	32	30	1.000000	10	10	2	1.000000	10	11	12	1.000000
10	27	24	1.000000	10	28	31	1.000000	10	31	24	1.000000	10	32	23	1.000000
11	11	6	1.000000	11	28	32	1.000000	12	12	4	1.000000	12	13	9	1.000000
12	33	30	1.000000	12	37	30	1.000000	12	39	30	1.000000	13	13	2	1.000000
13	14	12	1.000000	13	34	24	1.000000	13	35	31	1.000000	13	38	24	1.000000
13	39	23	1.000000	14	14	6	1.000000	14	35	32	1.000000	15	15	4	1.000000
15	16	9	1.000000	15	40	30	1.000000	15	44	30	1.000000	15	46	30	1.000000
16	16	2	1.000000	16	17	12	1.000000	16	41	24	1.000000	16	42	31	1.000000
16	45	24	1.000000	16	46	23	1.000000	17	17	6	1.000000	17	42	32	1.000000
18	18	3	1.000000	18	19	11	1.000000	18	47	30	1.000000	18	50	30	1.000000
18	52	30	1.000000	19	19	3	1.000000	19	48	30	1.000000	19	51	30	1.000000
19	52	30	1.000000	20	20	13	1.000000	20	21	35	1.000000	20	22	34	1.000000
20	23	33	1.000000	20	25	55	1.000000	20	53	39	1.000000	21	21	13	1.000000
21	22	34	1.000000	21	24	33	1.000000	21	25	55	1.000000	21	53	40	1.000000
22	22	14	1.000000	22	23	34	1.000000	22	24	34	1.000000	22	26	43	1.000000
22	27	42	1.000000	22	29	41	1.000000	22	53	41	1.000000	23	23	15	1.000000
23	24	36	1.000000	23	25	56	1.000000	23	26	46	1.000000	23	27	43	1.000000
23	29	48	1.000000	24	24	15	1.000000	24	25	56	1.000000	24	26	47	1.000000
24	27	43	1.000000	24	29	49	1.000000	25	25	16	1.000000	26	26	17	1.000000
26	27	34	1.000000	26	29	34	1.000000	26	30	37	1.000000	26	32	33	1.000000
27	27	18	1.000000	27	28	50	1.000000	27	29	38	1.000000	27	31	38	1.000000
27	32	34	1.000000	28	28	19	1.000000	28	31	50	1.000000	28	32	51	1.000000
29	29	20	1.000000	29	30	34	1.000000	29	31	38	1.000000	29	33	49	1.000000
29	34	42	1.000000	29	36	41	1.000000	30	30	17	1.000000	30	31	34	1.000000
30	32	33	1.000000	30	33	47	1.000000	30	34	43	1.000000	30	36	49	1.000000
31	31	18	1.000000	31	32	34	1.000000	31	33	43	1.000000	31	34	41	1.000000
31	36	42	1.000000	32	32	21	1.000000	33	33	17	1.000000	33	34	34	1.000000
33	36	34	1.000000	33	37	37	1.000000	33	39	33	1.000000	34	34	18	1.000000
34	35	50	1.000000	34	36	38	1.000000	34	38	38	1.000000	34	39	34	1.000000
35	35	19	1.000000	35	38	50	1.000000	35	39	51	1.000000	36	36	20	1.000000
36	37	34	1.000000	36	38	38	1.000000	36	40	49	1.000000	36	41	42	1.000000

TABLE XLIII (Continued)

36	43	41	1.000000	37	37	17	1.000000	37	38	34	1.000000	37	39	33	1.000000
37	40	47	1.000000	37	41	43	1.000000	37	43	49	1.000000	38	38	18	1.000000
38	39	34	1.000000	38	40	43	1.000000	38	41	41	1.000000	38	43	42	1.000000
39	39	21	1.000000	40	40	17	1.000000	40	41	34	1.000000	40	43	34	1.000000
40	44	37	1.000000	40	46	33	1.000000	41	41	18	1.000000	41	42	50	1.000000
41	43	38	1.000000	41	45	38	1.000000	41	46	34	1.000000	42	42	19	1.000000
42	45	50	1.000000	42	46	51	1.000000	43	43	20	1.000000	43	44	34	1.000000
43	45	38	1.000000	43	47	48	1.000000	43	48	49	1.000000	43	49	41	1.000000
44	44	17	1.000000	44	45	34	1.000000	44	46	33	1.000000	44	47	46	1.000000
44	48	47	1.000000	44	49	43	1.000000	45	45	18	1.000000	45	46	34	1.000000
45	47	43	1.000000	45	48	43	1.000000	45	49	42	1.000000	46	46	21	1.000000
47	47	15	1.000000	47	48	36	1.000000	47	49	34	1.000000	47	50	33	1.000000
47	52	56	1.000000	48	48	15	1.000000	48	49	34	1.000000	48	51	33	1.000000
48	52	56	1.000000	49	49	14	1.000000	49	50	34	1.000000	49	51	34	1.000000
49	53	41	1.000000	50	50	13	1.000000	50	51	35	1.000000	50	52	55	1.000000
50	53	39	1.000000	51	51	13	1.000000	51	52	55	1.000000	51	53	40	1.000000
52	52	16	1.000000	53	53	22	1.000000	54	54	52	1.000000	55	55	52	1.000000
56	56	52	1.000000	57	57	52	1.000000	58	58	53	1.000000	59	59	53	1.000000
60	60	53	1.000000	61	61	54	1.000000	62	62	54	1.000000				

TABLE XLIV

Z MATRIX FOR 1,5-ANHYDRORIBITOL

1	1	1	1.000000	1	2	7	1.000000	1	6	8	1.000000	1	7	9	1.000000
1	8	9	1.000000	1	20	23	1.000000	1	21	23	1.000000	1	22	24	1.000000
1	53	26	1.000000	2	2	5	1.000000	2	3	7	1.000000	2	7	10	1.000000
2	8	10	1.000000	2	9	10	1.000000	2	10	7	1.000000	2	22	27	1.000000
2	23	28	1.000000	2	24	28	1.000000	2	26	28	1.000000	2	27	27	1.000000
2	29	29	1.000000	3	3	5	1.000000	3	4	7	1.000000	3	9	10	1.000000
3	10	7	1.000000	3	12	10	1.000000	3	13	7	1.000000	3	29	29	1.000000
3	30	28	1.000000	3	31	27	1.000000	3	33	28	1.000000	3	34	27	1.000000
3	36	29	1.000000	4	4	5	1.000000	4	5	7	1.000000	4	12	10	1.000000
4	13	7	1.000000	4	15	10	1.000000	4	16	7	1.000000	4	36	29	1.000000
4	37	28	1.000000	4	38	27	1.000000	4	40	28	1.000000	4	41	27	1.000000
4	43	29	1.000000	5	5	5	1.000000	5	6	7	1.000000	5	15	10	1.000000
5	16	7	1.000000	5	18	10	1.000000	5	19	10	1.000000	5	43	29	1.000000
5	44	28	1.000000	5	45	27	1.000000	5	47	28	1.000000	5	48	28	1.000000
5	49	27	1.000000	6	6	1	1.000000	6	18	9	1.000000	6	19	9	1.000000
6	49	24	1.000000	6	50	23	1.000000	6	51	23	1.000000	6	53	26	1.000000
7	7	3	1.000000	7	8	11	1.000000	7	20	30	1.000000	7	23	30	1.000000
7	25	30	1.000000	8	8	3	1.000000	8	21	30	1.000000	8	24	30	1.000000
8	25	30	1.000000	9	9	4	1.000000	9	10	9	1.000000	9	26	30	1.000000
9	30	30	1.000000	9	32	30	1.000000	10	10	2	1.000000	10	11	12	1.000000
10	27	24	1.000000	10	28	31	1.000000	10	31	24	1.000000	10	32	23	1.000000
11	11	6	1.000000	11	28	32	1.000000	12	12	4	1.000000	12	13	9	1.000000
12	33	30	1.000000	12	37	30	1.000000	12	39	30	1.000000	13	13	2	1.000000
13	14	12	1.000000	13	34	24	1.000000	13	35	31	1.000000	13	38	24	1.000000
13	39	23	1.000000	14	14	6	1.000000	14	35	32	1.000000	15	15	4	1.000000
15	16	9	1.000000	15	40	30	1.000000	15	44	30	1.000000	15	46	30	1.000000
16	16	2	1.000000	16	17	12	1.000000	16	41	24	1.000000	16	42	31	1.000000

TABLE XLIV (Continued)

16	45	24	1.000000	16	46	23	1.000000	17	17	6	1.000000	17	42	32	1.000000
18	18	3	1.000000	18	19	11	1.000000	18	47	30	1.000000	18	50	30	1.000000
18	52	30	1.000000	19	19	3	1.000000	19	48	30	1.000000	19	51	30	1.000000
19	52	30	1.000000	20	20	13	1.000000	20	21	35	1.000000	20	22	34	1.000000
20	23	33	1.000000	20	25	55	1.000000	20	53	39	1.000000	21	21	13	1.000000
21	22	34	1.000000	21	24	33	1.000000	21	25	55	1.000000	21	53	40	1.000000
22	22	14	1.000000	22	23	34	1.000000	22	24	34	1.000000	22	26	43	1.000000
22	27	42	1.000000	22	29	41	1.000000	22	53	41	1.000000	23	23	15	1.000000
23	24	36	1.000000	23	25	56	1.000000	23	26	46	1.000000	23	27	43	1.000000
23	29	48	1.000000	24	24	15	1.000000	24	25	56	1.000000	24	26	47	1.000000
24	27	43	1.000000	24	29	49	1.000000	25	25	16	1.000000	26	26	17	1.000000
26	27	34	1.000000	26	29	34	1.000000	26	30	37	1.000000	26	32	33	1.000000
27	27	18	1.000000	27	28	50	1.000000	27	29	38	1.000000	27	31	38	1.000000
27	32	34	1.000000	28	28	19	1.000000	28	31	50	1.000000	28	32	51	1.000000
29	29	20	1.000000	29	30	34	1.000000	29	31	38	1.000000	29	33	48	1.000000
29	34	41	1.000000	29	36	41	1.000000	30	30	17	1.000000	30	31	34	1.000000
30	32	33	1.000000	30	33	46	1.000000	30	34	44	1.000000	30	36	49	1.000000
31	31	18	1.000000	31	32	34	1.000000	31	33	43	1.000000	31	34	41	1.000000
31	36	42	1.000000	32	32	21	1.000000	33	33	17	1.000000	33	34	34	1.000000
33	36	34	1.000000	33	37	37	1.000000	33	39	33	1.000000	34	34	18	1.000000
34	35	50	1.000000	34	36	38	1.000000	34	38	38	1.000000	34	39	34	1.000000
35	35	19	1.000000	35	38	50	1.000000	35	39	51	1.000000	36	36	20	1.000000
36	37	34	1.000000	36	38	38	1.000000	36	40	49	1.000000	36	41	42	1.000000
36	43	41	1.000000	37	37	17	1.000000	37	38	34	1.000000	37	39	33	1.000000
37	40	46	1.000000	37	41	43	1.000000	37	43	48	1.000000	38	38	18	1.000000
38	39	34	1.000000	38	40	44	1.000000	38	41	41	1.000000	38	43	41	1.000000
39	39	21	1.000000	40	40	17	1.000000	40	41	34	1.000000	40	43	34	1.000000
40	44	37	1.000000	40	46	33	1.000000	41	41	18	1.000000	41	42	50	1.000000
41	43	38	1.000000	41	45	38	1.000000	41	46	34	1.000000	42	42	19	1.000000
42	45	50	1.000000	42	46	51	1.000000	43	43	20	1.000000	43	44	34	1.000000
43	45	38	1.000000	43	47	48	1.000000	43	48	49	1.000000	43	49	41	1.000000
44	44	17	1.000000	44	45	34	1.000000	44	46	33	1.000000	44	47	46	1.000000
44	48	47	1.000000	44	49	43	1.000000	45	45	18	1.000000	45	46	34	1.000000
45	47	43	1.000000	45	48	43	1.000000	45	49	42	1.000000	46	46	21	1.000000
47	47	15	1.000000	47	48	36	1.000000	47	49	34	1.000000	47	50	33	1.000000
47	52	56	1.000000	48	48	15	1.000000	48	49	34	1.000000	48	51	33	1.000000
48	52	56	1.000000	49	49	14	1.000000	49	50	34	1.000000	49	51	34	1.000000
49	53	41	1.000000	50	50	13	1.000000	50	51	35	1.000000	50	52	55	1.000000
50	53	39	1.000000	51	51	13	1.000000	51	52	55	1.000000	51	53	40	1.000000
52	52	16	1.000000	53	53	22	1.000000	54	54	52	1.000000	55	55	52	1.000000
56	56	52	1.000000	57	57	52	1.000000	58	58	53	1.000000	59	59	53	1.000000
60	60	53	1.000000	61	61	54	1.000000	62	62	54	1.000000				

TABLE XLV

Z MATRIX FOR 1,5-ANHYDRO-L-ARABINITOL

1	1	1	1.000000	1	2	7	1.000000	1	6	8	1.000000	1	7	9	1.000000
1	8	9	1.000000	1	20	23	1.000000	1	21	23	1.000000	1	22	24	1.000000
1	53	26	1.000000	2	2	5	1.000000	2	3	7	1.000000	2	7	10	1.000000
2	8	10	1.000000	2	9	10	1.000000	2	10	7	1.000000	2	22	27	1.000000
2	23	28	1.000000	2	24	28	1.000000	2	26	28	1.000000	2	27	27	1.000000
2	29	29	1.000000	3	3	5	1.000000	3	4	7	1.000000	3	9	10	1.000000
3	10	7	1.000000	3	12	10	1.000000	3	13	7	1.000000	3	29	29	1.000000
3	30	28	1.000000	3	31	27	1.000000	3	33	28	1.000000	3	34	27	1.000000
3	36	29	1.000000	4	4	5	1.000000	4	5	7	1.000000	4	12	10	1.000000
4	13	7	1.000000	4	15	10	1.000000	4	16	7	1.000000	4	36	29	1.000000
4	37	28	1.000000	4	38	27	1.000000	4	40	28	1.000000	4	41	27	1.000000
4	43	29	1.000000	5	5	5	1.000000	5	6	7	1.000000	5	15	10	1.000000
5	16	7	1.000000	5	18	10	1.000000	5	19	10	1.000000	5	43	29	1.000000
5	44	28	1.000000	5	45	27	1.000000	5	47	28	1.000000	5	48	28	1.000000
5	49	27	1.000000	6	6	1	1.000000	6	18	9	1.000000	6	19	9	1.000000
6	49	24	1.000000	6	50	23	1.000000	6	51	23	1.000000	6	53	26	1.000000
7	7	3	1.000000	7	8	11	1.000000	7	20	30	1.000000	7	23	30	1.000000
7	25	30	1.000000	8	8	3	1.000000	8	21	30	1.000000	8	24	30	1.000000
8	25	30	1.000000	9	9	4	1.000000	9	10	9	1.000000	9	26	30	1.000000
9	30	30	1.000000	9	32	30	1.000000	10	10	2	1.000000	10	11	12	1.000000
10	27	24	1.000000	10	28	31	1.000000	10	31	24	1.000000	10	32	23	1.000000
11	11	6	1.000000	11	28	32	1.000000	12	12	4	1.000000	12	13	9	1.000000
12	33	30	1.000000	12	37	30	1.000000	12	39	30	1.000000	13	13	2	1.000000
13	14	12	1.000000	13	34	24	1.000000	13	35	31	1.000000	13	38	24	1.000000
13	39	23	1.000000	14	14	6	1.000000	14	35	32	1.000000	15	15	4	1.000000
15	16	9	1.000000	15	40	30	1.000000	15	44	30	1.000000	15	46	30	1.000000
16	16	2	1.000000	16	17	12	1.000000	16	41	24	1.000000	16	42	31	1.000000
16	45	24	1.000000	16	46	23	1.000000	17	17	6	1.000000	17	42	32	1.000000
18	18	3	1.000000	18	19	11	1.000000	18	47	30	1.000000	18	50	30	1.000000
18	52	30	1.000000	19	19	3	1.000000	19	48	30	1.000000	19	51	30	1.000000
19	52	30	1.000000	20	20	13	1.000000	20	21	35	1.000000	20	22	34	1.000000
20	23	33	1.000000	20	25	55	1.000000	20	53	39	1.000000	21	21	13	1.000000
21	22	34	1.000000	21	24	33	1.000000	21	25	55	1.000000	21	53	40	1.000000
22	22	14	1.000000	22	23	34	1.000000	22	24	34	1.000000	22	26	43	1.000000
22	27	42	1.000000	22	29	41	1.000000	22	53	41	1.000000	23	23	15	1.000000
23	24	36	1.000000	23	25	56	1.000000	23	26	46	1.000000	23	27	43	1.000000
23	29	48	1.000000	24	24	15	1.000000	24	25	56	1.000000	24	26	47	1.000000
24	27	43	1.000000	24	29	49	1.000000	25	25	16	1.000000	26	26	17	1.000000
26	27	34	1.000000	26	29	34	1.000000	26	30	37	1.000000	26	32	33	1.000000
27	27	18	1.000000	27	28	50	1.000000	27	29	38	1.000000	27	31	38	1.000000
27	32	34	1.000000	28	28	19	1.000000	28	31	50	1.000000	28	32	51	1.000000
29	29	20	1.000000	29	30	34	1.000000	29	31	38	1.000000	29	33	49	1.000000
29	34	42	1.000000	29	36	41	1.000000	30	30	17	1.000000	30	31	34	1.000000
30	32	33	1.000000	30	33	47	1.000000	30	34	43	1.000000	30	36	49	1.000000
31	31	18	1.000000	31	32	34	1.000000	31	33	43	1.000000	31	34	41	1.000000
31	36	42	1.000000	32	32	21	1.000000	33	33	17	1.000000	33	34	34	1.000000
33	36	34	1.000000	33	37	37	1.000000	33	39	33	1.000000	34	34	18	1.000000
34	35	50	1.000000	34	36	38	1.000000	34	38	38	1.000000	34	39	34	1.000000
35	35	19	1.000000	35	38	50	1.000000	35	39	51	1.000000	36	36	20	1.000000
36	37	34	1.000000	36	38	38	1.000000	36	40	48	1.000000	36	41	41	1.000000



TABLE XLV (Continued)

36	43	41	1.000000	37	37	17	1.000000	37	38	34	1.000000	37	39	33	1.000000
37	40	46	1.000000	37	41	44	1.000000	37	43	49	1.000000	38	38	18	1.000000
38	39	34	1.000000	38	40	43	1.000000	38	41	41	1.000000	38	43	42	1.000000
39	39	21	1.000000	40	40	17	1.000000	40	41	34	1.000000	40	43	34	1.000000
40	44	37	1.000000	40	46	33	1.000000	41	41	18	1.000000	41	42	50	1.000000
41	43	38	1.000000	41	45	38	1.000000	41	46	34	1.000000	42	42	19	1.000000
42	45	50	1.000000	42	46	51	1.000000	43	43	20	1.000000	43	44	34	1.000000
43	45	38	1.000000	43	47	48	1.000000	43	48	49	1.000000	43	49	41	1.000000
44	44	17	1.000000	44	45	34	1.000000	44	46	33	1.000000	44	47	46	1.000000
44	48	46	1.000000	44	49	44	1.000000	45	45	18	1.000000	45	46	34	1.000000
45	47	43	1.000000	45	48	44	1.000000	45	49	41	1.000000	46	46	21	1.000000
47	47	15	1.000000	47	48	36	1.000000	47	49	34	1.000000	47	50	33	1.000000
47	52	56	1.000000	48	48	15	1.000000	48	49	34	1.000000	48	51	33	1.000000
48	52	56	1.000000	49	49	14	1.000000	49	50	34	1.000000	49	51	34	1.000000
49	53	41	1.000000	50	50	13	1.000000	50	51	35	1.000000	50	52	55	1.000000
50	53	39	1.000000	51	51	13	1.000000	51	52	55	1.000000	51	53	40	1.000000
52	52	16	1.000000	53	53	22	1.000000	54	54	52	1.000000	55	55	52	1.000000
56	56	52	1.000000	57	57	52	1.000000	58	58	53	1.000000	59	59	53	1.000000
60	60	53	1.000000	61	61	54	1.000000	62	62	54	1.000000				

APPENDIX IV

TERMINATION OF THE LINEAR LEAST SQUARES REFINEMENT

The criterion normally employed to judge when the force constant refinement has "converged" is to examine the corrections to the force constant parameters,  $|\Delta\phi_i|$ , after each iteration. When all the corrections are less than or equal to an arbitrary constant (0.008 in FADJ), the refinement is terminated and said to have "converged."

The weighted sum of squares of the residuals computed for each iteration is compared with the value computed for the previous iteration. If the weighted sum of squares increases for two consecutive iterations, the refinement is terminated and said to have "diverged."

EVALUATION OF TRANSFERABLE FORCE CONSTANTS

One method of introducing additional constraints is to assume that force constants may be transferred between related molecules. That is, one wishes to refine a set of force constants to give the best fit to a series of molecules. Suppose  $\bar{\Phi}$  is the set of force constants for a series of molecules. One can then partition the perturbation equations and write them in the form

$$\begin{array}{|c} \hline \Delta\bar{\Phi}^{(1)} \\ \hline \Delta\bar{\Phi}^{(2)} \\ \hline \cdot \\ \hline \cdot \\ \hline \cdot \\ \hline \Delta\bar{\Phi}^{(n)} \\ \hline \end{array} = \begin{array}{|c} \hline \tilde{z}_J^{(1)} \tilde{z}_Z^{(1)} \\ \hline \tilde{z}_J^{(2)} \tilde{z}_Z^{(2)} \\ \hline \cdot \\ \hline \cdot \\ \hline \cdot \\ \hline \tilde{z}_J^{(n)} \tilde{z}_Z^{(n)} \\ \hline \end{array} \bar{\Phi} \quad (163)$$

where  $\overline{\Delta\Delta}^{(i)}$  and  $\underset{\sim}{J}^{(i)}\underset{\sim}{Z}^{(i)}$  are the matrices for a single molecule or factored block. The combined equations for a series of large molecules become very large and taxes the memory of even the largest digital computer. However, it follows from Equation (163) that the normal equations for the combined molecules are given by the sum of the normal equations for the individual molecules, thus

$$\sum_{i=1}^n [\underset{\sim}{J}^{(i)}\underset{\sim}{Z}^{(i)}]'\underset{\sim}{P}^{(i)}\overline{\Delta\Delta}^{(i)} = \sum_{i=1}^n [\underset{\sim}{J}^{(i)}\underset{\sim}{Z}^{(i)}]'\underset{\sim}{P}^{(i)}[\underset{\sim}{J}^{(i)}\underset{\sim}{Z}^{(i)}]\overline{\Delta\Delta}^{(i)}. \quad (164)$$

This relation makes it possible to consider one molecule at a time in high-speed storage and to use magnetic tape or disk to collect the normal equations which are then summed as they are read back into the computer. The  $\Phi_i$ 's determined from Equation (164) are by definition transferable among the molecules used in the refinement, and the "goodness of fit" is a measure of the degree of transferability.

#### POTENTIAL ENERGY DISTRIBUTION IN TERMS OF THE FORCE CONSTANTS

The potential energy distribution among the elements of  $\overline{\Phi}$  for each normal mode can be calculated as

$$\text{P.E.} = \underset{\sim}{\Lambda}^{-1}\underset{\sim}{J}\underset{\sim}{Z}\overline{\Phi}. \quad (165)$$

#### ERROR ANALYSIS

The theory of least squares can be applied to estimate the uncertainties in the calculated force constants. The force constant moment matrix is

$$\underset{\sim}{M}(\mathbf{F}) = \sigma^2 (\underset{\sim}{Z}'\underset{\sim}{J}'\underset{\sim}{P}\underset{\sim}{J}\underset{\sim}{Z})^{-1} \quad (166)$$

where  $\sigma^2 = (\overline{\Delta\Delta})'\underset{\sim}{P}(\overline{\Delta\Delta})/\underline{d}$  and  $\underline{d}$  is the number of degrees of freedom. The diagonal elements of  $\underset{\sim}{M}(\mathbf{F})$  give the uncertainties in the calculated force constants, and

the off-diagonal elements give the correlation between the errors in the force constants. One must be cautious about attaching great significance to the uncertainties for several reasons. First, if the number of degrees of freedom is small, the statistical analysis is in doubt. Second, the errors may not be normally distributed due to anharmonicity. Finally, because the force constants and frequency parameters are assumed to be linearly related over the range of errors considered.

However, the analysis does give some indication of the consistency of the data and of the sensitivity of the force constants to the data. For example, if  $(\underline{Z}'\underline{J}'\underline{P}\underline{J}\underline{Z})$  is nearly singular, certain force constants will have a large uncertainty indicating that they are not sensitive to the data.

#### MULTIPLE SOLUTIONS

In many problems, there are a number of distinct solutions to the force field which will fit the data to within acceptable errors. The various solutions represent alternate minima in the hypersurface of the quantity  $(\underline{\Delta}\underline{\lambda}'\underline{P}\underline{\Delta}\underline{\lambda})$  as a function of the force constants,  $\underline{\Phi}$ , and correspond to alternate assignments of the vibrational frequencies. The various minima can be reached by starting the calculation with different initial  $\underline{F}$  matrices. Some of the minima are much higher than others and can be eliminated because of the poorer fit to the data. In other cases, a solution may be unacceptable because the force constants are physically unreasonable. However, in some situations there will be no method of deciding which is the best solution without having some additional data.

MULTIPLE REGRESSION ANALYSIS

Suppose one has a force field defined by a constraint matrix,  $\underline{Z}$ , for which the determinant of  $(\underline{Z}'\underline{J}'\underline{P}\underline{J}\underline{Z})$  is too small to obtain a convergent solution. One then wishes to adjust as many of the force constants in the set  $\underline{\Phi}$  as possible to obtain a least squares fit between the observed and calculated frequencies. One starts with a force field containing the most important force constants. These constants are then refined by the perturbation technique, while holding all other force constants fixed at zero. One then enters a multiple regression analysis in which all the possible interaction constants are added to the normal equations, one at a time, in the order which gives the greatest estimated improvement in the fit between the observed and calculated  $\lambda$ 's, as measured by the variance of  $\lambda$ ,  $V_\lambda$ ,

$$V_\lambda = (\underline{\Delta\lambda})' \underline{P} (\underline{\Delta\lambda}). \tag{167}$$

This procedure is continued until the estimated standard error of the next force constant to be added becomes lower than some preset level. A convenient point to stop the regression is the point at which the standard error in  $\lambda$  begins to increase, that is, the decrease in the variance,  $V_\lambda$ , due to the addition of the next force constant does not compensate for the decrease in  $d$ , the number of degrees of freedom. The standard error in  $\lambda$  is defined by

$$\sigma_\lambda = (V_\lambda/d)^{\frac{1}{2}}. \tag{168}$$

This corresponds to the point at which the next force constant to be added to the force field will have an estimated standard error larger than the value of the constant itself and indicates that the determinant of  $(\underline{Z}'\underline{J}'\underline{P}\underline{J}\underline{Z})$  is becoming small. When the regression is completed, the perturbation cycle is once more entered,

and the force field including those constants selected as significant by the regression is refined. Because the process is iterative,  $\underline{JZ}$  is a function of the force constants, and it may be desirable to again enter the regression after refining the constants to obtain the modified  $\underline{JZ}$  matrix. This process is based on least squares theory and is subject to three criticisms. First, the errors in  $\lambda$  may not be random due to anharmonicity. Second, if the number of degrees of freedom is small, least squares does not apply. Third, if the  $\underline{\Delta\bar{\Phi}}_i$  are large, the linear approximation is poor, and the variance estimates,  $\underline{V}_{-\lambda}$ , will reflect this error.

The method does, however, give one a systematic procedure for selecting a subset of force constants that will give a well-behaved perturbation. In addition, the final estimates of the standard errors in  $\underline{\bar{\Phi}}$  will give some indication of the approximations involved in the regression.

In the stepwise regression, a force constant that may be significant at an early stage may become insignificant after the addition of other force constants. The insignificant force constant is removed from the regression equation before adding additional force constants.

The normal equations are a set of simultaneous linear algebraic equations in  $\underline{\Delta\bar{\Phi}}$  and are solved by the Gaussian elimination method, that is,

$$\underline{Y} = \underline{S}\underline{\Delta\bar{\Phi}} \quad (169)$$

where  $\underline{Y} = (\underline{JZ})' \underline{P} \underline{\Delta\bar{\lambda}}$  and  $\underline{S} = (\underline{JZ})' \underline{P} (\underline{JZ})$ . For convenience, the normal equations are normalized to unity as follows:

$$C_{ij} = S_{ij} / [(S_{ii})^{1/2} (S_{jj})^{1/2}] \quad (170)$$

$$X_i = Y_i / [(S_{ii})^{1/2} \sigma] \quad (171)$$

where  $\sigma = [(\overline{\Delta\lambda})' \underline{P}(\overline{\Delta\lambda})]^{1/2}$ . The matrix  $\underline{C}$  is the correlation matrix and  $\underline{C}^{-1}$  is the variance-covariance matrix. An  $\underline{F}$  level ( $\underline{F}_{in}$ ) for entering a force constant and an  $\underline{F}$  level ( $\underline{F}_{out}$ ) for removing a force constant are entered with the input data. The  $\underline{C}$  matrix at any stage in the regression is partially inverted, that is, the matrix can be partitioned into a matrix for the variables in the regression corresponding to  $\underline{C}^{-1}$  and into a matrix for the variables not in the regression corresponding to  $\underline{C}$ . The variance increase due to the deletion of a variable,  $\underline{j}$ , is estimated by

$$V_j = (X_j^{-1})^2 / (C_{jj}^{-1}) \quad (172)$$

for variables in the regression, and if the minimum  $V_{-j}$ ,  $V_{-min}$ , satisfies

$$V_{min} d/\sigma < F_{out} \quad (173)$$

the variable corresponding to  $V_{-min}$  is removed. If no variable is to be removed, the variance reduction due to the addition of the variables not in the regression is estimated by

$$V_i = X_i^2 / C_{ii} \quad (174)$$

and if the largest  $V_{-i}$ ,  $V_{-max}$ , satisfies the condition

$$V_{max} d/(\sigma - V_{max}) > F_{in} \quad (175)$$

the variable corresponding to  $V_{-max}$  is added to the regression.

It must be emphasized that the regression is a statistical test and is carried out at some intermediate point in the force constant refinement.

NONCONVERGENCE

The refinement procedure is not infallible as may be testified to by several investigators who have reported difficulties, for example, (106-115). There are two conditions which will lead to nonconvergent problems. First, if the initial  $\overline{F}$  matrix is a poor approximation,  $\overline{\Delta\lambda}$  will be large and  $\overline{\Delta F}$  will contain large elements. In this case, the linear approximation given by Equation (101) in the text will be poor. This will be true also if the normal coordinates are very sensitive to certain force constants, causing the elements of  $\overline{J}$  to change drastically on each cycle. This will lead to oscillations because the corrections will tend to overshoot. This can be seen by examining Equation (99) in the main text. This difficulty can sometimes be overcome by finding a better initial  $\overline{F}$  matrix, or by selectively scaling down the large values in  $\overline{\Delta F}$  in the first few cycles of the refinement. In effect, one must guide the calculations into a region where the linear approximation is valid. If the force field is not adequate, that is, if an important interaction constant is missing, it may not be possible to do this and the force field must be modified.

The second cause of nonconvergence is singularity or near-singularity in the normal equations, that is, the determinant of the matrix  $(\overline{Z}'\overline{J}'\overline{P}\overline{J}\overline{Z})$  is very small compared with the product of the diagonal terms,

$$\prod_k (\overline{Z}'\overline{J}'\overline{P}\overline{J}\overline{Z})_{kk}. \quad (176)$$

In this case, the calculations will diverge rapidly or converge very slowly to an ill-defined solution. This problem arises when the frequencies are nearly independent of one or more force constants or if two or more force constants are strongly correlated. In the first situation, one finds that  $[(\underline{L}_{-o})_{ji}(\underline{L}_{-o})_{ki}Z_{jkl}]$



is very small for all values of  $\underline{i}$  and that any reasonable value of  $\Delta F_{-jk}$  will give an acceptable fit to the frequencies. In order to make the calculations converge, this variable must be fixed and eliminated from the normal equations.

$$\underline{\Delta\lambda} = \underline{JZ}\underline{\Delta\Phi} \quad (177)$$

If two or more force constants are strongly correlated, one finds that the corresponding columns of the  $\underline{JZ}$  matrix will be linearly related. In order to cure this cause of singularity, some of the constants of the related set must be fixed or one must use some model to obtain a relation between the two that can be used as a further constraint in the  $\underline{Z}$  matrix.

In some situations, the difficulties caused by oscillation of successive values of  $\underline{\Phi}_i$ , slow convergence, singularity or near-singularity of the normal matrix  $(\underline{Z}'\underline{J}'\underline{P}\underline{J}\underline{Z})$ , and the existence of multiple solutions can be overcome by making the following modification in Equation (111) in the text. This equation may be rewritten as Equation (178) where  $\underline{a}$  and  $\underline{b}$  are constants and  $\underline{E}$  is a unit matrix.

$$\underline{\Delta\Phi} = \underline{a}(\underline{Z}'\underline{J}'\underline{P}\underline{J}\underline{Z} + \underline{b}\underline{E})^{-1}\underline{Z}'\underline{J}'\underline{P}\underline{\Delta\lambda} \quad (178)$$

The first term,  $\underline{a}$ , is a scaling factor by which all of the adjustments are multiplied. This factor was mentioned in the above paragraph, and it ensures that  $\underline{\Delta\Phi}$  does not produce force constants which lie outside the range over which the force constant-frequency relationships are approximately linear. This device is particularly useful in the first few iterations when "overshooting" is most likely to occur. This device has been employed successfully by a number of workers, for instance, Long and Gravenor (116).

The second term,  $\underline{b}$ , represents additions to the diagonal terms of the normal matrix. Inclusion of this factor in the refinement has been labeled "damped least squares" by workers in the field, among them, Schachtschneider (89). The use of this factor in convergence problems was first suggested by Levenberg (117) and later, independently, by Marquardt (118). Marquardt has shown that if a large enough positive value of  $\underline{b}$  is used, convergence must occur. However, in many refinement problems convergence readily occurs without the use of  $\underline{a}$  and/or  $\underline{b}$ , and in these cases, the rate of convergence is inhibited by  $\underline{b}$ , often quite seriously.

Adams and Churchill (119) have offered methods by which the appropriate values for  $\underline{a}$  and  $\underline{b}$  can be determined.

In summary, if the "damped least squares" procedure does not succeed, in order to obtain a stable solution the indeterminant and strongly correlated constants must be eliminated from the normal equations until the determinant assumes an acceptable value. This is equivalent to eliminating rows and columns from the matrix  $(Z'J'PJZ)$ .

The elimination procedure may be carried out by trial and error by repeating the perturbation calculation with various force constants constrained equal to zero or a constant value until one obtains a convergent solution that gives an acceptable fit to the observed data and reasonable uncertainties on all the force constants. This is time consuming, so it is convenient to use the stepwise multiple regression technique previously described to select the most significant subset of force constants out of a set of possible constants.

APPENDIX V

This appendix contains the user instructions, flow diagrams, and listings for the computer programs employed in the normal coordinate analyses of the 1,5-anhydropentitol compounds. These programs form a package of programs which are available on tape from the Computer Center at The Institute of Paper Chemistry, Appleton, Wisconsin 54911 (Code No. IPCTH001).

CART

The computer program CART computes the cartesian coordinates of the atoms in a molecule from the bond distances and bond angles. If desired, the program will also compute the center of mass, moments of inertia, principal moments of inertia, and principal cartesian coordinates. As a check on the computation of the cartesian coordinates, the distances between each atom and every other atom are tabulated. The principal moments of inertia and the coordinate transformation are obtained by diagonalizing the moment of inertia tensor. This is accomplished by the subroutine, HDIAG, which uses the Jacobi method of diagonalization. At the option of the user, the standard cartesian coordinates and/or the principal cartesian coordinates are punched onto cards in the proper format for use in the programs GMAT and EIGV.

The program was written by J. H. Schachtschneider (89) and modified for use in this thesis. CART is coded in FORTRAN IV. The program may be used with the IBM 360/44 RAX operating system.

A flow diagram of CART is given in Fig. 36 and the listing in Table XLVI.

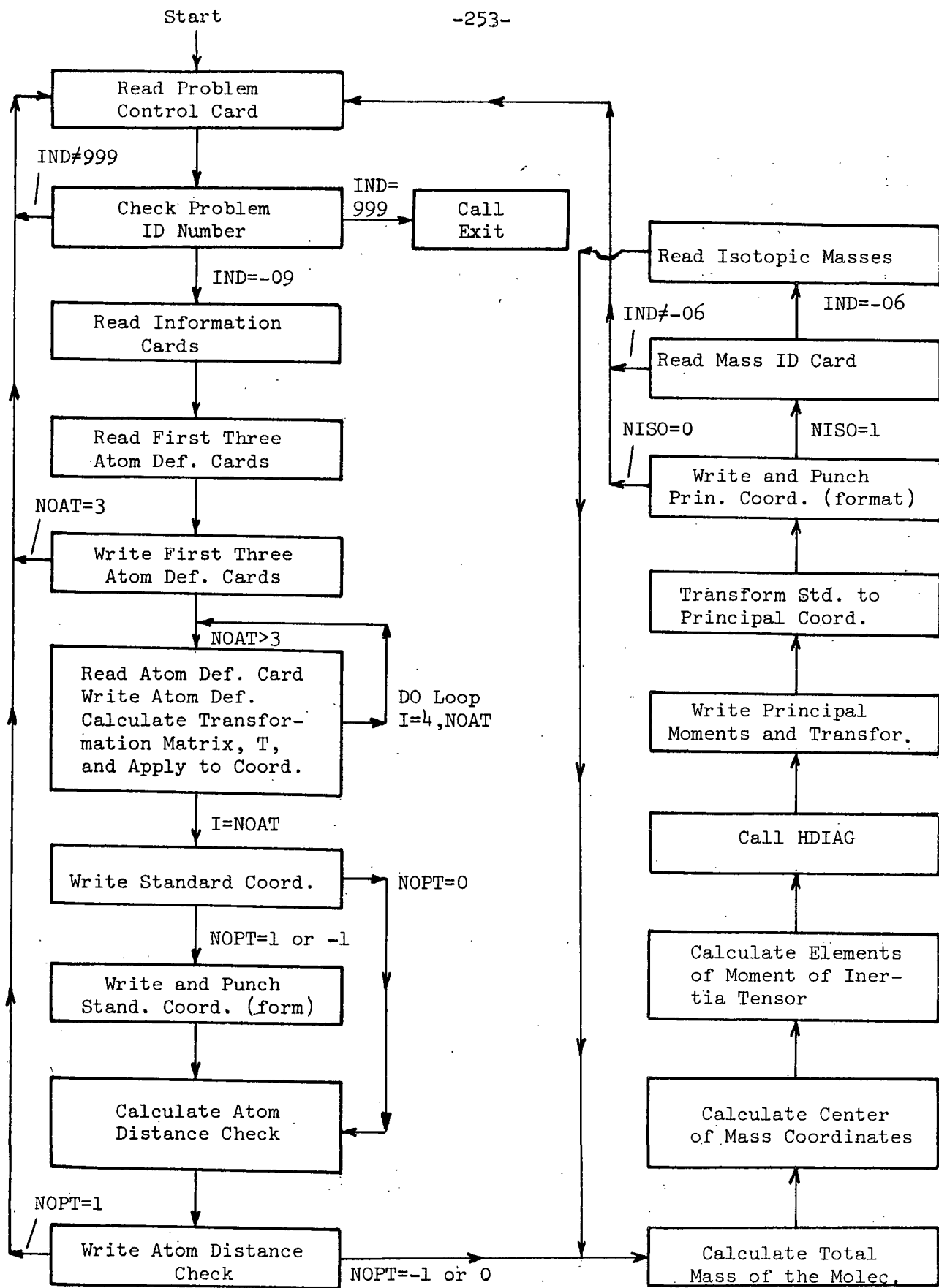


Figure 36. The Flow Diagram of CART

TABLE XLVI  
LISTING OF CART

```

C   CART      SD-4063
C   CARTESIAN COORDINATE PROGRAM
C   SCHACHTSCHNEIDER  9/15/63  REVISED  4/15/64
C   MODIFIED FOR RAX BY L J PITZNER 3/15/71
C   THIS PROGRAM COMPUTES THE CARTESIAN COORDINATES OF THE ATOMS IN
C   A MOLECULE FROM THE BOND DISTANCES AND BOND ANGLES AND IF DESIRED
C   WILL CALCULATE THE PRINCIPAL MOMENTS OF INERTIA AND THE PRINCIPAL
C   CARTESIAN COORDINATES.
C   DIMENSION RECORD(36),COR(50,3),W(50),X(50,3),VBA(3),VCA(3),
1  RJA(3),TRANS(3,3),PRC(3),CAR(50,3),DNER(3,3),CM(3),TR(3,3),
2  RT(50),NR(150),NCO(150),DAT(150),D(50),RR(3),E21(3),E23(3),
3  E13(3)
C   COMMON COR      , X      , CAR      , NR      , NCO      , DAT
C   COMMON D
C   CON=.174532925E-01
C   READ PROBLEM ID CARD
92  READ(5,2)IND
   2  FORMAT(I3)
91  IF(9+IND)900,90,900
900  IF(IND-999) 92,901,92
901  CALL EXIT
C   READ PROBLEM CONTROL CARD
90  READ (5,4) IND,NOAT,NISO,NOPT,IFPUN
   4  FORMAT(I3,3I4,I2)
C   THE PROBLEM CONTROL CARD CONTAINS THE FOLLOWING INFORMATION
C   1.IND=-09 IDENTIFYING THE CONTROL CARD. PUNCHED IN COLUMNS 1-3.
C   2.NOAT, THE NUMBER OF ATOMS IN THE MOLECULE. LESS THAN 51.
C   PUNCHED IN COLUMNS 5-7.
C   3.NISO, THE NUMBER OF ADDITIONAL ISOTOPICALLY SUBSTITUTED
C   MOLECULES . NISO=0 IF NO ISOTOPIC MOLECULES.
C   PUNCHED IN COLUMNS 9-11.
C   4.NOPT, PUNCH AND MOMENT OF INERTIA OPTION CONTROL.
C   IF NOPT=-1 BOTH THE RAW CARTESIANS AND THE PRINCIPAL CARTESIANS
C   ARE PUNCHED ONTO CARDS.
C   IF NOPT=0 ONLY THE PRINCIPAL CARTESIANS ARE PUNCHED ONTO CARDS.
C   IF NOPT=1 THE PRINCIPAL MOMENTS OF INERTIA ARE NOT EVALUATED
C   IF NOPT=1 THE PRINCIPAL MOMENTS OF INERTIA AND PRINCIPAL AXES
C   COORDINATES ARE NOT EVALUATED AND ONLY THE RAW CARTESIANS ARE
C   PUNCHED ONTO CARDS.
C   NOPT IS PUNCHED IN COLUMNS 14 AND 15
C   5.IFPUN, A 1 WILL CAUSE THE PRINCIPAL CARTESIAN COORDINATES TO
C   BE PUNCHED ON CARDS. IFPUN PUNCHED IN COLUMN 17.
C   READ TWO PROBLEM INFORMATION CARDS.
C   READ (5,6)(RECORD(I),I=1,36)
6  FORMAT(18A4)
C   INPUT DATA FOLLOWS, ONE CARD DEFINING EACH ATOM.
C   ATOM DEFINITION CARDS CONTAIN
C   DATA                                COLUMNS
C   NO      NUMBER OF ATOM DEFINED      1-3
C   NA      NUMBERS OF ATOMS DEFINING    4-6
C   NB      ATOM NO                       7-9
C   NC      I.E. ATOMS A,B, AND C        10-12

```

TABLE XLVI (Continued)

```
C          R          DISTANCE NO-NA          13-24 (F12.6)
C          TE          ANGLE NO-NA-NB          25-36 (F12.6)
C          PH          DIHEDRAL ANGLE NO-NA-NB-NC 37-42 (F12.6)
C          WT          MASS OF ATOM NO          49-60 (F12.6)
C  ATOM DEFINITION CARDS MUST BE IN ORDER OF NO=1,2,3, ETC. AND
C  NA,NB, AND NC MUST BE LESS THAN NO.
C  IF TE=0.0 THE ANGLE WILL BE TAKEN TO BE TETRAHEDRAL.
C  NO=1 DEFINES THE ORIGIN
C  THE LINE NO=1 TO NO=2 DFINES THE +X AXIS.
C  ATOMS NO=1,NO=2,NO=3 DEFINE THE XY PLANE
C  FOR A RIGHT HANDED COORDINATE SYSTEM DIHEDRAL ANGLES ARE DEFINED
C  BY VEIING THE CONFIGURATION FROM THE NC DIRECTION ALONG NB-NA
C  AXIS OR THE NA-NB AXIS DEPENDING ON WHETHER ATOM C IS BONDED TO
C  TO ATOM B OR A. THE ANGLE IS DEFINED POSITIVE FOR A CLOCKWISE
C  ROTATION OF ATOM C INTO THE PLANE OF N-A-B.
C  JOKE=0
100 WRITE (6,50)(RECORD(I),I=1,36)
   50 FORMAT(23H1 CARTESIAN COORDINATES /(1X,18A4))
   READ (5,10)NO,NA,NB,NC,R,TE,PH,WT
   10 FORMAT(4I3,4F12.6)
   WRITE (6,19)NO,NA,NB,NC,R,TE,PH,WT
   19 FORMAT(2H 4I4,4F12.6)
      W(NO)=WT
      COR(NO,1)=0.0
      COR(NO,2)=0.0
      COR(NO,3)=0.0
110 READ (5,10)NO,NA,NB,NC,R,TE,PH,WT
   WRITE (6,19)NO,NA,NB,NC,R,TE,PH,WT
      COR(NO,1)=R
      COR(NO,2)=0.0
      COR(NO,3)=0.0
      W(NO)=WT
116 READ (5,10)NO,NA,NB,NC,R,TE,PH,WT
   WRITE (6,19)NO,NA,NB,NC,R,TE,PH,WT
      W(NO)=WT
      IF(TE)120,118,120
118 CS=-0.33333333
   SS= 0.94280907
   GO TO 121
120 CS=COS(CON*TE)
   SS=SIN(CON*TE)
121 IF(NA-1)128,122,128
122 COR(NO,1)=COR(NA,1)+R*CS
   GO TO 129
128 COR(NO,1)=COR(NA,1)-R*CS
129 COR(NO,2)=R*SS
   COR(NO,3)=0.0
   IF (NOAT-3) 92,161,130
130 DO 160 I=4,NOAT
   READ (5,10)NO,NA,NB,NC,R,TE,PH,WT
   WRITE (6,19)NO,NA,NB,NC,R,TE,PH,WT
   W(NO)=WT
```

TABLE XLVI (Continued)

```
IF(TE)133,132,133
132 CS=-0.33333333
SS= 0.94280907
GO TO 135
133 CS=CON(CON*TE)
SS=SIN(CON*TE)
135 DSQ=0
DO 138 M=1,3
VBA(M)=COR(NB,M)-COR(NA,M)
VCA(M)=COR(NC,M)-COR(NA,M)
138 DSQ=DSQ+VBA(M)**2
RAB=SQRT(DSQ)
SCALE=0.0
DO 142 M=1,3
TRANS(M,1)=VBA(M) / RAB
142 SCALE=SCALE+ TRANS(M,1)*VCA(M)
DSQ=0.0
DO 146 M=1,3
RJA(M)=VCA(M)-SCALE*TRANS(M,1)
146 DSQ=DSQ+RJA(M)**2
RAJ=SQRT(DSQ)
DO 148 M=1,3
148 TRANS(M,2)=RJA(M) / RAJ
TRANS(1,3)=TRANS(2,1)*TRANS(3,2)-TRANS(3,1)*TRANS(2,2)
TRANS(2,3)=TRANS(3,1)*TRANS(1,2)-TRANS(1,1)*TRANS(3,2)
TRANS(3,3)=TRANS(1,1)*TRANS(2,2)-TRANS(2,1)*TRANS(1,2)
PRC(1)=R*CS
PRC(2)=R*SS*COS(CON*PH)
PRC(3)=R*SS*SIN(CON*PH)
DO 160 M=1,3
COR(NO,M)=COR(NA,M)
DO 160 K=1,3
160 COR(NO,M)=COR(NO,M)+TRANS(M,K)*PRC(K)
161 WRITE(6,60000)
60000 FORMAT(1H0,' ')
WRITE (6,60)
60 FORMAT(55H0 ATOM NO.          X          Y          Z          MASS)
DO 164 I=1,NOAT
164 WRITE (6,62)I,(COR(I,M),M=1,3),W(I)
62 FORMAT(4X,13,3X,3F12.6,F13.6)
IF(NOPT) 165,1230,165
C PUNCH STANDARD CARTESIANS
165 NX=0
DO 1225 I=1,NOAT
DO 1225 M=1,3
IF(0.000005-ABS(COR(I,M)))1220,1220,1224
1220 NX= NX+1
NR(NX)=M
NCO(NX)=I
DAT(NX)=COR(I,M)
GO TO 1225
1224 COR(I,M)= 0.0
1225 CONTINUE
```

TABLE XLVI (Continued)

```
NX=NX+1
NR(NX)=-1
NCO(NX)=0.0
DAT(NX)=0.0
1228 WRITE (7,70)IND,NOAT,NX,(RECORD(I),I=1,12)
1229 WRITE (7,72)(NR(I),NCO(I),DAT(I),I=1,NX)
1230 WRITE (6,68)(RECORD(I),I=1,36)
68 FORMAT(21H1 ATOM DISTANCE CHECK/(1X,18A4))
DO 1236 I=1,NOAT
DO 1234 J=1,NOAT
DSQ=0.0
DO 1233 M=1,3
RR(M)=COR(J,M)-COR(I,M)
1233 DSQ=DSQ+RR(M)*RR(M)
1234 D(J)=SQRT(DSQ)
1236 WRITE (6,69)I,(D(J),J=1,NOAT)
69 FORMAT(5HOATOMI3/( 7F10.6))
IF(NOPT)168,168,92
C FIND CENTER OF MASS
168 WT=0.0
DO 170 I=1,NOAT
170 WT=WT+W(I)
DO 180 M=1,3
CM(M)=0.0
DO 179 I=1,NOAT
179 CM(M)=CM(M)+W(I)*COR(I,M)
180 CM(M)=CM(M)/ WT
DO 185 I=1,NOAT
RT(I)=0.0
DO 185 M=1,3
X(I,M)=COR(I,M)-CM(M)
185 RT(I)=RT(I)+(X(I,M))**2
DO 190 I=1,3
DO 190 J=1,3
DNER(I,J)=0.0
DO 190 K=1,NOAT
IF(I-J)189,187,189
187 DNER(I,J)=DNER(I,J)+W(K)*(RT(K)-X(K,I)*X(K,I))
GO TO 190
189 DNER(I,J)=DNER(I,J) -W(K)* X(K,I)*X(K,J)
190 CONTINUE
WRITE (6,80)(RECORD(I),I=1,12),WT,(CM(M),M=1,3)
80 FORMAT(27H1 MOMENT OF INERTIA TENSOR.,12A4/13HO TOTAL MASS=F12.6,
116H,CENTER OF MASS=3F12.6)
DO 192 I=1,3
192 WRITE (6,82)(DNER(I,J),J=1,3)
82 FORMAT(1H03F12.6)
N=3
IEGEN=0
C FIND TRANSFORMATION TO PRINCIPAL AXES.
CALL HDIAG(DNER,N,IEGEN,TR,NR)
200 WRITE (6,84)(DNER(I,I),I=1,3)
84 FORMAT(20HO PRINCIPAL MOMENTS 3F12.6,20H AND TRANSFORMATION.)
```



TABLE XLVI (Continued)

```
201 DO 202 I=1,3
202 WRITE (6,82)(TR(I,J),J=1,3)
C   ROTATE TO PRINCIPAL AXES.
    DO 210 I=1,NOAT
    DO 210 J=1,3
    CAR(I,J)=0.0
    DO 210 K=1,3
210 CAR(I,J)=CAR(I,J)+TR(K,J)*X(I,K)
    WRITE (6,86)(RECORD(I),I=1,36)
    86 FORMAT(34H0 PRINCIPAL CARTESIAN COORDINATES/(1X,18A4))
    WRITE (6,60)
    DO 215 I=1,NOAT
215 WRITE (6,62)I,(CAR(I,M),M=1,3),W(I)
    NX=0
C   PUNCH PRINCIPAL CARTESIANS
    IF(IFPUN)240,240,220
220 DO 225 I=1,NOAT
    DO 225 M=1,3
    IF(0.000005-ABS(CAR(I,M)))221,221,224
221 NX=NX+1
    NR(NX)=M
    NCO(NX)=I
    DAT(NX)=CAR(I,M)
    GO TO 225
224 CAR(I,M)=0.0
225 CONTINUE
    NX=NX+1
    NR(NX)=-1
    NCO(NX)=0.0
    DAT(NX)=0.0
236 WRITE (7,70)IND,NOAT,NX,(RECORD(I),I=1,12)
    70 FORMAT(13,6H NOAT=13,4H NX=14,12A4)
238 WRITE (7,72)(NR(I),NCO(I),DAT(I),I=1,NX)
    72 FORMAT(2I3,F12.6,2I3,F12.6,2I3,F12.6,2I3,F12.6)
240 IF(NISO)92,92,242
C   READ MASS ID CARD FOR NISO GREATER THAN ZERO
C   -06 IN COLUMN 1-3 ALPHA-NUMERIC INFORMATION ON REMAINDER
242 READ (5,20)IND,(RECORD(I),I=1,15)
    20 FORMAT(I3,15A4)
    IF(6+IND)92,243,92
C   READ ISOTOPIC MASSES NOAT OF THEM IN ORDER 1-NOAT (6F12.6)
243 READ (5,22)(W(I),I=1,NOAT)
    22 FORMAT(6F12.6)
    GO TO 168
    END
SUBROUTINE HDIAG (H,N,IEGEN,U,NR)
C   MIHDI3,FORTRANIV DIAGONALIZATION OF A REAL SYMMETRIC MATRIX BY
C   THE JACOBI METHOD.
C   PROGRAMMED BY CORBATO AND M. MERWIN OF MIT
C   CALLING SEQUENCE FOR DIAGONALIZATION
C   CALL HDIAG( H, N, IEGEN, U, NR)
C   WHERE H IS THE ARRAY TO BE DIAGONALIZED.
C   N IS THE ORDER OF THE MATRIX, H.
```

TABLE XLVI (Continued)

```
C IEGEN MUST BE SET UNEQUAL TO ZERO IF ONLY EIGENVALUES ARE TO BE
C COMPUTED.
C IEGEN MUST BE SET EQUAL TO ZERO IF EIGENVALUES AND EIGENVECTORS
C ARE TO BE COMPUTED.
C U IS THE UNITARY MATRIX USED FOR FORMATION OF THE EIGENVECTORS.
C NR IS THE NUMBER OF ROTATIONS.
C A DIMENSION STATEMENT MUST BE INSERTED IN THE SUBROUTINE.
C DIMENSION H(N,N), U(N,N), X(N), IQ(N)
C COMPUTER MUST OPERATE IN FLOATING TRAP MODE
C THE SUBROUTINE OPERATES ONLY ON THE ELEMENTS OF H THAT ARE TO THE
C RIGHT OF THE MAIN DIAGONAL. THUS, ONLY A TRIANGULAR
C SECTION NEED BE STORED IN THE ARRAY H.
C DIMENSION H(3,3),U(3,3),X(3),IQ(3)
C EQUIVALENCE (II,IPIV),(JJ,JPIV)
C IF (IEGEN) 15,10,15
10 DO 14 I=1,N
   DO 14 J=1,N
     IF(I-J)12,11,12
11 U(I,J)=1.0
   GO TO 14
12 U(I,J)=0.0
14 CONTINUE
15 NR = 0
   IF (N-1) 1000,1000,17
C SCAN FOR LARGEST OFF DIAGONAL ELEMENT IN EACH ROW
C X(I) CONTAINS LARGEST ELEMENT IN ITH ROW
C IQ(I) HOLDS SECOND SUBSCRIPT DEFINING POSITION OF ELEMENT
17 NM1=N-1
   DO 30 I=1,NM1
     X(I) = 0.0
     IPL1=I+1
     DO 30 J=IPL1,N
       IF(X(I)-ABS( H(I,J))) 20,20,30
20 X(I)=ABS(H(I,J))
     IQ(I)=J
30 CONTINUE
C SET INDICATOR FOR SHUT-OFF.RAP=2**--27,NR=NO.OF ROTATIONS
RAP=.745058059E-08
HDTEST=1.0E38
C FIND MAXIMUM OF X(I) S FOR PIVOT ELEMENT AND
C TEST FOR END OF PROBLEM
40 DO 70 I=1,NM1
   IF (I-1) 60,60,45
45 IF(XMAX-X(I)) 60,70,70
60 XMAX=X(I)
   IPIV=I
   JPIV=IQ(I)
70 CONTINUE
C IS MAX. X(I) EQUAL TO ZERO, IF LESS THAN HDTEST,REVISE HDTEST
IF (XMAX) 1000,1000,80
80 IF( HDTEST) 90,90,85
85 IF (XMAX - HDTEST) 90,90,148
90 HDIMIN = ABS( H (1,1) )
   DO 110 I=2,N
     IF (HDIMIN - ABS( H (I,I))) 110,110,100
```

TABLE XLVI (Continued)

```
100 HDIMIN=ABS(H(I,I))
110 CONTINUE
    HDTEST = HDIMIN*RAP
C   RETURN IF MAX.H(I,J)LESS THAN(2**(-27)ABS(F(H(K,K)-MIN)
    IF (HDTEST-XMAX) 148,1000,1000
148 NR= NR+1
C   COMPUTE TANGENT, SINE AND COSINE,H(I,I),H(J,J)
    XDIF=H(IPIV,IPIV)-H(JPIV,JPIV)
    XO=SIGN(2.0,XDIF)*H(IPIV,JPIV)
    XS=XDIF**2+4.0*H(IPIV,JPIV)**2
150 TANG=XO / (ABS(XDIF) + SQRT(XS))
    COSINE=1.0/SQRT(1.0+TANG**2)
    SINE=TANG*COSINE
    HII=H(IPIV,IPIV)
    H(II,II)=COSINE**2*(HII+TANG*(2.0*H(II,JJ)+TANG*H(JJ,JJ)))
    H(JJ,JJ)=COSINE**2*(H(JJ,JJ)-TANG*(2.0*H(II,JJ)-TANG*HII))
    H(IPIV,JPIV)=0.0
C   PSEUDO RANK THE EIGENVALUES
C   ADJUST SINE AND COS FOR COMPUTATION OF H(IK) AND U(IK)
    IF ( H(IPIV,IPIV) - H(JPIV,JPIV)) 152,153,153
152 HTEMP = H(IPIV,IPIV)
    H(IPIV,IPIV) = H(JPIV,JPIV)
    H(JPIV,JPIV) =HTEMP
C   RECOMPUTE SINE AND COS
    HTEMP = SIGN(1.0, -SINE) * COSINE
    COSINE =ABS(SINE)
    SINE =HTEMP
153 CONTINUE
C   INSPECT THE IQS BETWEEN I+1 AND N-1 TO DETERMINE
C   WHETHER A NEW MAXIMUM VALUE SHOULD BE COMPUTE SINCE
C   THE PRESENT MAXIMUM IS IN THE I OR J ROW.
    DO 350 I=1,NM1
    IF(I-IPIV)210,350,200
200 IF (I-JPIV) 210,350,210
210 IF(IQ(I)-IPIV) 230,240,230
230 IF(IQ(I)-JPIV) 350,240,350
240 K=IQ(I)
250 HTEMP=H(I,K)
    H(I,K)=0.0
    IPL1=I+1
    X(I) =0.0
C   SEARCH IN DEPLETED ROW FOR NEW MAXIMUM
    DO 320 J=IPL1,N
    IF ( X(I) -ABS( H(I,J)) ) 300,300,320
300 X(I) = ABS(H(I,J))
    IQ(I)=J
320 CONTINUE
    H(I,K)=HTEMP
350 CONTINUE
    X(IPIV) =0.0
    X(JPIV) =0.0
C   CHANGE THE ORDER ELEMENTS OF H
```

TABLE XLVI (Continued)

```
DO 530 I=1,N
  IF (I-IPIV) 370,530,420
370 HTEMP = H(I,IPIV)
  H(I,IPIV)= COSINE*HTEMP + SINE*H(I,JPIV)
  IF ( X(I) - ABS( H(I,IPIV)) ) 380,390,390
380 X(I) = ABS(H(I,IPIV))
  IQ(I) = IPIV
390 H(I,JPIV) = - SINE*HTEMP + COSINE*H(I,JPIV)
  IF ( X(I) - ABS( H(I,JPIV)) ) 400,530,530
400 X(I) = ABS(H(I,JPIV))
  IQ(I) = JPIV
  GO TO 530
420 IF(I-JPIV) 430,530,480
430 HTEMP = H(IPIV,I)
  H(IPIV,I) = COSINE*HTEMP + SINE*H(I,JPIV)
  IF ( X(IPIV) - ABS( H(IPIV,I)) ) 440,450,450
440 X(IPIV) = ABS(H(IPIV,I))
  IQ(IPIV) = I
450 H(I,JPIV) = - SINE*HTEMP + COSINE*H(I,JPIV)
  IF (X(I) - ABS( H(I,JPIV)) ) 400,530,530
480 HTEMP = H(IPIV,I)
  H(IPIV,I) = COSINE*HTEMP + SINE*H(JPIV,I)
  IF ( X(IPIV) - ABS( H(IPIV,I)) ) 490,500,500
490 X(IPIV) = ABS(H(IPIV,I))
  IQ(IPIV) = I
500 H(JPIV,I) = - SINE*HTEMP + COSINE*H(JPIV,I)
  IF ( X(JPIV) - ABS( H(JPIV,I)) ) 510,530,530
510 X(JPIV) = ABS(H(JPIV,I))
  IQ(JPIV) = I
530 CONTINUE
C TEST FOR COMPUTATION OF EIGENVECTORS
  IF(IEGEN) 40,540,40
540 DO 550 I=1,N
  HTEMP=U(I,IPIV)
  U(I,IPIV)=COSINE*HTEMP+SINE*U(I,JPIV)
550 U(I,JPIV)= -SINE*HTEMP+COSINE*U(I,JPIV)
  GO TO 40
1000 RETURN
END
```

## INSTRUCTIONS FOR PROGRAM USE

With the RAX operating system, the program deck is preceded by an /ID card and a /JOB GO card. The program deck is followed by the input data deck. The following input data are required for each problem.

1. Problem ID Card. The first card to be read is the problem ID card. This card should contain a -09 in Columns 1-3 (FORMAT I3).
2. Problem Control Card. The next card is the problem control card containing the following information.
  - a. IND, which identifies the problem control card, must be a -09 and punched in Columns 1-3 (FORMAT I3).
  - b. NOAT is the number of atoms in the molecule, currently limited to 50 or less, and punched in Columns 4-7 (FORMAT I4).
  - c. NISO is the number of additional isotopically substituted molecules. In this case, the geometry will be the same for the substituted molecules; however, the masses of the isotopes will be different. NISO is punched in Columns 8-11 (FORMAT I4). If there are to be no isotopically substituted molecules to be included, a zero may be punched in Column 11 or left blank.
  - d. NOPT is the punch and moment of inertia option control. If NOPT = -1, both the standard and principal cartesian coordinates are computed and punched on cards (the principal cartesian coordinates will be punched on cards only for IFPUN = 1). If NOPT = 0, both the standard and the principal cartesian coordinates are punched on cards (i.e., if IFPUN = 1, otherwise neither the principal or standard cartesian coordinates will be punched onto cards). If NOPT = 1, only the standard cartesian coordinates are computed, and they are punched on cards. NOPT is punched in Columns 14-15 (FORMAT I2).
  - e. IFPUN controls the card punching of the principal cartesian coordinates. IFPUN must equal 1 for the cards to be punched. IFPUN is punched in Column 17 (FORMAT I2).
3. Problem Information Cards. The next two cards are the problem information cards. These cards contain any alphanumeric information about the problem that the user may wish to include. The data may fill the first 72 columns of each card with the first three columns left blank (FORMAT 18A4).

Warning: These cards may be left blank, but they must be included with the input.

4. Atom Definition Cards. The next set of cards contains the atom position information. There is one card for each atom in the molecule, i.e., NOAT cards. The following data must appear on each card (this information appeared earlier in the text).
- NO, the number of the atom being defined, punched in Columns 1-3 (FORMAT I3).
  - NA, the number of atom A, punched in Columns 4-6 (FORMAT I3).
  - NB, the number of atom B, punched in Columns 7-9 (FORMAT I3).
  - NC, the number of atom C, punched in Columns 10-12 (FORMAT I3).
  - R, the distance between atom NO and atom NA, i.e., the bond length NO-NA, punched in Columns 13-24 (FORMAT F12.6).
  - TE, the angle between atoms NO, NA, and NB, i.e., the bond angle NO-NA-NB, punched in Columns 25-36 (FORMAT F12.6).  
Note: If TE is left blank or assigned a 0, the angle is assumed to be tetrahedral.
  - PH, the dihedral angle between atoms NO, NA, NB, and NC, punched in Columns 37-48 (FORMAT F12.6).  
Note: The sign convention given in the text must be followed. The convention is reversed for angles less than 90 degrees.
  - WT is the mass of atom NO. This information is only required if the center of mass is to be computed. WT is punched in Columns 49-60 (FORMAT F12.6).

Warning: The atom definition cards must be in the order of NO = 1,2,3,..., etc., and NA, NB, and NC must be less than NO.

5. Mass ID Card. If NISO is greater than zero, the mass ID card for each isotopically substituted molecule must follow the atom definition cards. The mass ID card contains a -06 in Columns 1-3 (FORMAT I3) and may contain descriptive alphanumeric information in Columns 4-63 (FORMAT 15A4).
6. Atom Mass Cards. The masses of the atoms in the isotopically substituted molecule follow the mass ID card in the order 1,2,3,..., NOAT with six masses per card (FORMAT 6F12.6).
7. Data Termination Card. The last card in the input deck designates the end of the input data. This card has a 999 punched in Columns 1-3 (FORMAT I3).

Note: If another problem is to be included, the problem ID card for the next data deck is placed at this point instead of the data termination card. This arrangement permits the stacking of problems.

With the RAX system, the input deck is preceded with a /DATA card and ended with a /END card.

#### OUTPUT INFORMATION

At the option of the user, the following information will be printed out.

1. The atom definition cards.
2. The standard cartesian coordinates.
3. The atom distance check.
4. The moment of inertia tensor and center of mass coordinates.
5. The principal moments and the transformation from standard coordinates.
6. The principal cartesian coordinates.

The following information may be punched onto cards at the request of the program user.

1. The standard cartesian coordinates in the sequence NR, NCO, and DAT, four per card [FORMAT 4(I2,F12.6)].
  - a. NR designates the x, y, or z coordinate by a 1, 2, or 3, respectively (FORMAT I2).
  - b. NCO is the atom number (FORMAT I2).
  - c. DAT is the numerical value for the x, y, or z coordinate of atom NCO. The row number following the last element is set equal to -1.
2. The principal cartesian coordinates with the same format as for the standard cartesian coordinates [4(I2,F12.6)].

#### GMAT

This program calculates the Wilson G matrix (i.e., the vibrational inverse kinetic energy matrix) for polyatomic molecules. Input includes the cartesian

coordinates and masses for the atoms in the molecule, the numbers of the atoms defining a complete set of internal valence coordinates, and the symmetry transformation, if desired. The program computes the  $\underline{B}$  matrix (i.e., the transformation from cartesian coordinates to internal coordinates),  $\underline{G}$  matrix, and factored  $\underline{G}$  matrix, if the transformation to symmetry coordinates is included. At the option of the user, the program will punch each of the above matrices on cards in a format suitable for input to FADJ, FLPO, or EIGV. (Only those  $\underline{B}$  and  $\underline{G}$  matrix elements whose absolute value is greater than 0.00005 are considered significant and retained by the program.)

The program was written by J. H. Schachtschneider (89) and modified for use in this thesis. GMAT is coded in FORTRAN IV and may be used with the IBM 360/44 RAX operating system.

A flow diagram of GMAT appears in Fig. 37 and the listing in Table XLVII.

#### INSTRUCTIONS FOR PROGRAM USE

If isotopically substituted molecules are included in the computation, two scratch tapes must be employed. With the RAX system, the program deck is preceded by a /ID and a /JOB GO card followed by two /FILE cards if scratch tapes are required. The program deck is followed by the input data which is comprised of the information below.

1. Problem ID Card. The first card of the input deck is the problem ID card. This card contains a -09 punched in Columns 1-3 (FORMAT I3).
2. Problem Control Card. The problem control card follows the problem ID card with the information given below.
  - a. IND, indicating the start of a problem. IND = -09 which is punched in Columns 1-3 (FORMAT I3).
  - b. NOPROB, the problem number punched in Columns 4-9 (FORMAT I6).



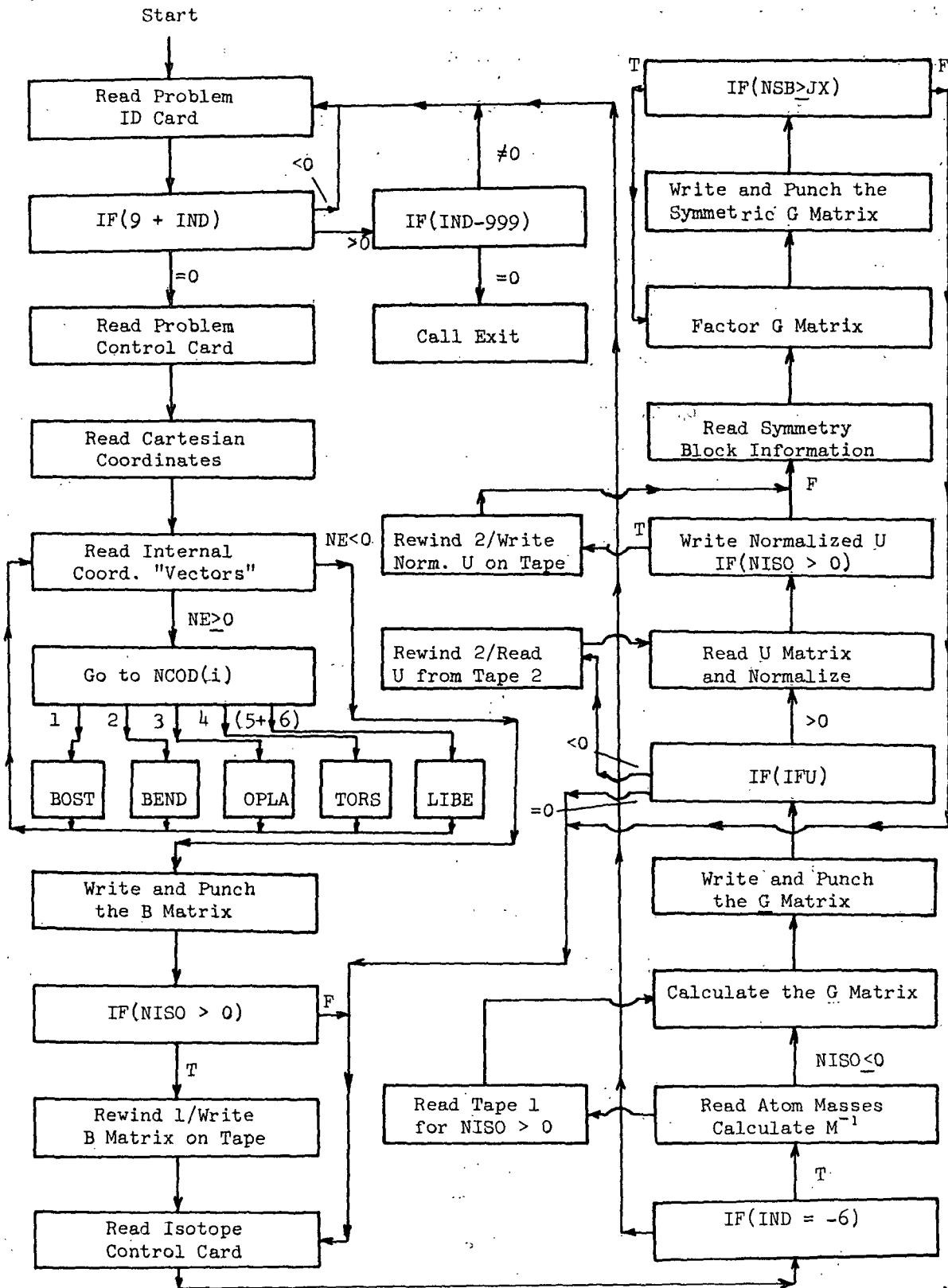


Figure 37. The Flow Diagram for GMAT

TABLE XLVII

LISTING OF GMAT

C GMAT SD-4064 SCHACHTSCHNEIDER  
C CODED IN FORTRAN IV REVISED 4/1/64  
C MODIFIED FOR RAX BY L J PITZNER 3/22/71  
C G MATRIX EVALUATION PROGRAM FOR IBM-360/44  
C PROGRAM USES TAPE 1 AND TAPE 2 FOR SCRATCH TAPES OUTPUT IS DIRECT  
C THIS PROGRAM EVALUATES G AND B MATRIX ELEMENTS FOR UP TO 100  
C INTERNAL COORDINATES FOR MOLECULES CONTAINING UP TO 25 ATOMS.  
C THE G MATRIX MAY BE SYMMETRIZED.  
C G AND B ARE PUNCHED ONTO CARDS IN A FORM SUITABLE FOR INPUT  
C TO THE VIBRATIONAL SECULAR EQUATION PROGRAMS.  
C THE PROGRAM EVALUATES G AND B MATRIX ELEMENTS FOR 5 TYPES OF  
C INTERNAL COORDINATES, (1) BOND STRETCHING, (2) VALENCE ANGLE  
C BENDING, (3) OUT OF PLANE WAGGING, (4) TORSION, (5) LINEAR VALENCE  
C BENDING.  
C INPUT DATA ARE THE MASSES AND CARTESIAN COORDINATES OF THE ATOMS  
C IN AN ARBITRARY REFERENCE FRAME, AND A U MATRIX IF DESIRED.  
C DIMENSION NR( 900), NC( 900), B( 900), NRG(1900), NCG(1900), DG(1900),  
1 NRU(300), NCU(300), DU(300), X(3,25), WT(25), W(100), BB(100),  
2 G(100), GU(100), NRS(101), NCS(101), GS(101), NROW(4), NCOL(4), DAT(4),  
3 NE(4), NCOD(4), NI(4), NJ(4), NK(4), NL(4), NX(4), NY(4), RECORD(36),  
4 REC(18), NB(20), U(100), UG(100), DA(100)  
EQUIVALENCE(NRG(1), X(1,1)), (NCG(1), WT(1)), (NRG(1001), NR(1)),  
1(NCG(1001), NC(1)), (DG(1001), B(1)), (BB(1), GU(1))  
C READ PROBLEM CONTROL CARD  
90 READ(5,11)IND  
11 FORMAT(I3)  
91 IF(9+IND)92,94,92  
92 IF(IND-999)90,93,90  
93 CALL EXIT  
94 READ(5,12) IND,NOPROB,NOAT,NQ,INTC,NISO,IFB,NCON  
12 FORMAT(I3,I6,6I4)  
C RECONVERT PROBLEM CONTROL CARD CONTAINING THE FOLLOWING INFORMATIO  
C 1. IND=-09, INDICATING THE START OF A PROBLEM. IN COLUMNS 1-3.  
C 2. NOPROB, THE PROBLEM NUMBER IN COLUMNS 4-9.  
C 3. NOAT, THE NUMBER OF ATOMS IN THE MOLECULE. COLUMNS 11-13.  
C 4. NQ, THE NUMBER OF INTERNAL COORDINATES. PUNCHED IN COLUMNS 15-1  
C 5. INTC. COLUMNS 18-21. A 1 WILL CAUSE THE UNSYM. G MATRIX TO BE  
C PUNCHED ON CARDS.  
C 6. NISO=0 OR 1 FOR ADDITIONAL ISOTOPIC MOLECULES. COLUMN 25.  
C 7. IFB, B MATRIX OUTPUT OPTIONS. FOR IFB=1 B IS PUNCHED.  
C FOR IFB=0 B IS NOT PUNCHED. IFB IS PUNCHED IN COL. 29.  
C 8. NCON, PRINTOUT SUPPRESSION OPTION. IF NCON = 0, NO SUPPRESSION  
C OCCURS. IF NCON = 1, THE PRINTER OUTPUT OF THE X-MATRIX,  
C B-MATRIX, UNSYMMET. G-MATRIX, U-MATRIX, AND CARD PUNCH OUTPUT  
C OF THE SYMMET. G-MATRIX ARE SUPPRESSED. PUNCHED IN COL. 33.  
C INPUT DATA FOLLOWS PROBLEM CONTROL CARD IN THE ORDER  
C 1. TWO PROBLEM INFORMATION CARDS. COLUMNS 1-3 BLANK  
C 2. THE CARTESIAN COORDINATES  
C 3. INTERNAL COORDINATE DEFINITIONS AND THE CARTESIAN COORDINATES  
C OF THE POINTS GIVING THE ORIENTATIONS OF THE LINEAR BENDING  
C COORDINATES. ONE POINT FOR EACH LINEAR BEND AS DEFINED

TABLE XLVII (Continued)

```
C      5.ISOTOPE CONTROL CARD FOR ISOTOPE 1
C      6.MASSES FOR ISOTOPE 1
C      7.U MATRIX FOR ISOTOPE 1.
C      8.SYMMETRY BLOCK INFORMATION FOR ISOTOPE 1.
C      IF NISO=1 ITEMS 6,7, AND 8 ARE REPEATED FOR EACH ADDITIONAL
C      ISOTOPIC MOLECULE AS DESIRED.
C      READ (5,14)(RECORD(I),I=1,36)
14  FORMAT(18A4)
      NA=3*NOAT
      WRITE (6,50)NOPROB,NOAT,NQ,(RECORD(I),I=1,36)
50  FORMAT(19H1  G MATRIX PROBLEM 7, 7H. NOAT=14,16,22H INTERNAL COORD
      INATES./ (1X,18A4))
      IF(NCON)97576,97576,43125
97576 WRITE(6,1551)
1551 FORMAT(10H0 X-MATRIX)
      JOKER=0
C      READ X MATRIX, THE CARTESIAN COORDINATES OF THE ATOMS.
C      THE X MATRIX IS PUNCHED IN 18 COLUMN FIELDS,4 PER CARD. THE
C      FIRST THREE COLUMNS GIVE THE ROW NUMBER IDENTIFYING THE
C      CARTESIAN AXES, COLUMNS 4-6 GIVE THE COLUMN NUMBER OF THE X
C      MATRIX,THE ATOM NUMBER,AND COLUMNS 7-18 GIVE THE ELEMENT WITH
C      THE DECIMAL POINT BETWEEN COLUMNS 12-13 OR PUNCHED.THE
C      ROW NUMBER FOLLOWING THE LAST ELEMENT IS SET EQUAL TO -1.
43125 DO 102 I=1,3
      DO 102 J=1,NOAT
102  X(I,J)=0.0
104  READ (5,16)(NROW(L),NCOL(L),DAT(L),L=1,4)
16   FORMAT(4(2I3,F12.6))
      IF(NCON)53351,53351,62197
53351 WRITE(6,1221)(NROW(L),NCOL(L),DAT(L),L=1,4)
1221 FORMAT(1H ,4(2I3,F12.6))
62197 DO 110 L=1,4
      IF(NROW(L))112,110,105
105  I=NROW(L)
      J=NCOL(L)
      X(I,J)=DAT(L)
110  CONTINUE
      GO TO 104
112  IF(1+NROW(L))600,115,600
115  NOB=0
      NOINT=0
      IF(NCON)55773,55773,118
55773 WRITE (6,51)
51  FORMAT(34H1  INTERNAL COORDINATE DEFINITIONS/42H0  NO.  CODE  I
1   J   K   L   IX  JX)
C      READ INTERNAL COORDINATE  VECTORS
C      A VECTOR OF 8 NUMBERS NI,NCOD,N1,N2,N3,N4,N5,N6 GIVING THE NO.
C      ASSIGNED TO THE INTERNAL COORDINATE,NI, THE CODE IDENTIFYING
C      THE TYPE OF COORDINATE,NCOD, AND THE NUMBERS OF THE ATOMS
C      DEFINING THE COORDINATE.
C      INTERNAL COORDINATES MUST BE DEFINED IN ORDER 1 TO NQ.
C      IF NI=0 THE DEFINED B. ROW IS ADDED TO THE B ROW FOR THE PREVIOUS
```

TABLE XLVII (Continued)

C	COORDINATE.								
C	TYPE	CODE	N1	N2	N3	N4	N5	N6	
C	STRETCHING	1	I	J					
C	BENDING	2	I	J	K		IX	JX	
C	OUT PLANE WAG	3	I	J	K	L	IX	JX	
C	TORSION	4	I	J	K	L	IX	JX	
C	LINEAR BEND	5	NO2	I	J	K	IX	JX	PAIR
C	LINEAR BEND	6	I	J	K		IX	JX	

IX AND JX GIVE ATOM NUMBERS DEFINING A DISTANCE BY WHICH THE ANGULAR COORDINATES ARE WEIGHTED. IF IX AND JX ARE ZERO THE ANGLES ARE NOT WEIGHTED.

NOTE THAT FOR LINEAR BENDING TYPE 5 A PAIR OF COORDINATES ARE DEFINED AND THAT N1=NO2 THE NUMBER OF THE BENDING COORDINATE PERPENDICULAR TO NI. NO2 MUST BE NI+1.

THE INTERNAL COORDINATE VECTOR IS PUNCHED IN 24 COLUMN FIELDS, 3 COLUMNS FOR EACH OF THE 8 ELEMENTS IN THE ORDER NI,NCOD,N1,N2,N3,N4,N5,N6. THERE ARE 1 TO 3 FIELDS PER CARD

THE CARTESIAN COORDINATES OF POINT GIVING THE DIRECTION OF THE LINEAR BENDING COORDINATE MUST FOLLOW THE CARD ON WHICH THE COORDINATE IS DEFINED. FORMAT(3F12.6) GIVING X,Y, AND Z

COORDINATE DEFINITION CARDS ARE FOLLOWED BY A CARD WITH -02 IN COLUMNS 1-3.

```

118 READ (5,18)(NE(L),NCOD(L),NI(L),NJ(L),NK(L),NL(L),NX(L),NY(L),L=1
1,3)
18 FORMAT(24I3)
120 DO 180 L=1,3
IF(NE(L))182,122,124
122 IF(NCOD(L))180,180,125
124 NOINT=NOINT+1
125 IF(6-NCOD(L))605,126,126
126 MX=NCOD(L)
N1=NI(L)
N2=NJ(L)
N3=NK(L)
N4=NL(L)
N5=NX(L)
N6=NY(L)
IF(NCON)11235,11235,61407
11235 WRITE (6,53)NOINT,MX,N1,N2,N3,N4,N5,N6
53 FORMAT(1H,2I5,I6,5I5)
61407 GO TO(130,140,150,160,170,172),MX
C
STRETCHING SUBROUTINE
130 CALL BOST(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,NQ,
1INTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
GO TO 174
C
BENDING SUBROUTINE
140 CALL BEND(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,NQ,
1INTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
GO TO 174
C
OUT OF PLANE WAGGING SUBROUTINE
150 CALL OPLA(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,NQ,
1INTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
GO TO 174

```

TABLE XLVII (Continued)

```
C   TORSION SUBROUTINE
160 CALL TORS(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,NQ,
    IINTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA,MAP)
    GO TO 174
170 NO2=NOINT+1
C   LINEAR BENDING SUBROUTINE
    CALL LIBE(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,NQ,
    IINTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
    NOINT=NOINT+1
    GO TO 174
172 CALL LIBE(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,NQ,
    IINTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
174 IF(JOKER)180,180,605
180 CONTINUE
    GO TO 118
182 NIB=NOB+1
    NR(NIB)=-5
    NC(NIB)=0
    B(NIB)=0.0
    M=1
    LL=1
    DO 26541 L=1,NOINT
    DO 36751 K=LL,NIB
    IF(NR(K)-L)26119,36751,26119
36751 CONTINUE
26119 JJ=K-2
    LL=K
    NN=K-3
    DO 55000 MM=1,NN
    DO 50000 J=M,JJ
    IF(NC(J+1)-NC(J))60000,50000,50000
60000 D=NC(J)
    C=B(J)
    NC(J)=NC(J+1)
    B(J)=B(J+1)
    NC(J+1)=D
    B(J+1)=C
50000 CONTINUE
55000 CONTINUE
    M=J+2
26541 CONTINUE
    IF(NCON)87653,87653,23123
87653 WRITE(6,2314)
    2314 FORMAT(10H1 B-MATRIX)
23123 IF(IFB)200,19500,19000
C   PUNCH B
19000 IF(NCON)190,190,200
    190 WRITE (7,54)IND,NOB,(RECORD(I),I=1,15)
    54 FORMAT(13,5H NOB=14,15A4)
    192 WRITE (7,56)(NR(K),NC(K),B(K),K=1,NIB)
    56 FORMAT( 2I3,F12.6,2I3,F12.6,2I3,F12.6,2I3,F12.6)
C   WRITE B
19500 IF(NCON)195,195,200
```

TABLE XLVII (Continued)

```
195 WRITE (6,55)NOB,(RECORD(I),I=1,15)
 55 FORMAT(6H0 NOB=I4,15A4)
   WRITE (6,57)(NR(K),NC(K),B(K),K=1,NIB)
 57 FORMAT(1H ,6(2I4,F11.6))
200 IF(NISO)210,210,202
202 REWIND 1
   WRITE(1,111)(NR(K),NC(K),B(K),K=1,NIB)
   END FILE 1
111 FORMAT (2I4,F11.6)
C READ ISOTOPE CONTROL CARD CONTAINING THE FOLLOWING INFORMATION
C 1.IN=-06 IDENTIFYING CARD IN COLUMNS 1-3.
C 2.IFU, U MATRIX READ OPTION CONTROL
C IFU=0 IF U MATRIX IS NOT INCLUDED. G NOT SYMMETRIZED.
C IFU=1 THE U MATRIX IS ENTERED.
C IFU=-1 U IS NOT INCLUDED WITH INPUT AND G IS SYMMETRIZED
C WITH U FROM PREVIOUS ISOTOPIC MOLECULE.
C IFU PUNCHED IN COLUMN 5-6
C 3. NSB, THE NUMBER OF FACTORED BLOCKS + 1. COLUMNS 7-9.
C 4.NS , THE NUMBER OF SYMMETRY COORDINATES. COLUMNS 10-12.
C NAME OF MOLECULE MAY BE PUNCHED ON REST OF CARD.
210 READ (5,20)IND,IFU,NSB,NS,(REC(I),I=1,14)
 20 FORMAT(4I3,14A4)
   IF(IND+6)91,212,91
 212 IF(NCON)57896,57896,66888
57896 WRITE(6,9559) IND,IFU,NSB,NS
 9559 FORMAT(1H0,'IND= ',I3,5X,'IFU= ',I3,5X,'NSB= ',I3,5X,'NS= ',I3)
C READ MASSES . SIX PER CARD IN ORDER 1 THROUGH NOAT.
C FORMAT (6F12.6)
66888 READ (5,22)(WT(L),L=1,NOAT)
 22 FORMAT(6F12.6)
   IF(NCON)33543,33543,31457
33543 WRITE (6,67) (REC(I),I=1,14),(WT(J),J=1,NOAT)
 67 FORMAT(17H1 UNSYMMETRIZED G,14A4/11H FOR MASSES/(9F12.6))
31457 NG=0
   NT=1
   NUB = 1
   DO 216 L=1,NOAT
   DO 216 M=1,3
   K=3*(L-1)+M
   W(K)=1.0 / WT(L)
216 BB(K)=0.0
   DO 218 I=1,NQ
218 G(I)=0.0
   IF(NISO)220,220,219
219 REWIND 1
   READ(1,111) (NR(K),NC(K),B(K),K=1,NIB)
220 DO 250 K=1,NIB
221 IF(NR(K)-NT)382,240,382
382 DO 226 L=NUB,NOB
   I=NR(L)
   J=NC(L)
   G(I)=G(I)+BB(J)*W(J)*B(L)
226 CONTINUE
```

TABLE XLVII (Continued)

```
DO 232 I=NT,NQ
IF(ABS(G(I))-0.00005)232,232,229
229 NG=NG+1
NRG(NG)=NT
NCG(NG)=I
DG(NG)=G(I)
232 CONTINUE
IF(NR(K))252,252,234
234 NT=NT+1
NUB=K
DO 238 I=NT,NQ
238 G(I)=0.0
DO 239 I=1,NA
239 BB(I)=0.0
GO TO 221
240 JX=NC(K)
BB(JX)=BB(JX)+B(K)
250 CONTINUE
252 NOG=NG+1
NRG(NOG)=-1
NCG(NOG)=0
DG(NOG)=0.0
IF(IFU)253,254,253
253 IF(IFB)260,25801,25400
C PUNCH G
25801 IF(INTC)25800,25800,25400
25400 IF(NCON)254,254,260
254 WRITE (7,58)IND,NG,(REC(I),I=1,14)
58 FORMAT(I3,5H NG=I4,14A4)
256 WRITE (7,56)(NRG(L),NCG(L),DG(L),L=1,NOG)
C WRITE G
25800 IF(NCON)258,258,260
258 WRITE (6,59)NG,(REC(I),I=1,14)
59 FORMAT(5H0 NG=I4,14A4)
WRITE(6,57)(NRG(L),NCG(L),DG(L),L=1,NOG)
260 IF(IFU)261,210,263
261 REWIND 2
READ(2,333)(NRU(K),NCU(K),DU(K),K=1,NOU)
333 FORMAT(2I4,F11.6)
GO TO 282
C READ U MATRIX.
C THE U MATRIX IS PUNCHED IN 18 COLUMN FIELDS,1 TO 4 PER CARD
C SIMILAR TO THE X MATRIX, THE ROW NO. FOLLOWING THE LAST ELEMENT
C IS SET EQUAL TO -3. ZERO ELEMENTS NEED NOT BE ENTERED.
C U MUST BE ENTERED IN ROW ORDER. NEED NOT BE NORMALIZED.
263 NOU=0
JX=1
DSQ=0.0
IF(NCON)65653,65653,264
65653 WRITE(6,7557)
7557 FORMAT(10H1 U-MATRIX)
264 READ (5,16)(NRDW(L),NCOL(L),DAT(L),L=1,4)
DO 274 L=1,4
```

TABLE XLVII (Continued)

```
IF(NROW(L))276,274,266
266 IF(NS-NROW(L))615,267,267
267 IF(NROW(L)-JX)615,270,268
268 DA(JX)=1.0 / SQRT(DSQ)
    JX=JX+1
    DSQ=0.0
    GO TO 267
270 DSQ=DSQ +DAT(L)**2
    NOU=NOU+1
    NRU(NOUC)=NROW(L)
    NCU(NOUC)=NCOL(L)
    DU(NOUC)=DAT(L)
274 CONTINUE
    GO TO 264
276 IF(3+NROW(L))615,277,615
277 DA(JX)=1.0 / SQRT(DSQ)
    IF(NS-JX)615,278,615
278 DO 279 I=1,NOU
    J=NRU(I)
279 DU(I)=DA(J)*DU(I)
    NOU=NOU+1
    NRU(NOUC)=-3
    NCU(NOUC)=0
    DU(NOUC)=0.0
    IF(NCON)81985,81985,36631
81985 WRITE(6,4884)(NRU(L),NCU(L),DU(L),L=1,NOU)
4884 FORMAT(1H ,6(2I3,F12.6))
36631 IF(NISO)282,282,280
280 REWIND 2
    WRITE(2,333)(NRU(I),NCU(I),DU(I),I=1,NOU)
    END FILE 2
C READ SYMMETRY BLOCK INFORMATION. NUMBERS OF FIRST ROW OF EACH
C FACTORED BLOCK. LAST NUMBER IS NS+1. PUNCHED IN 24 THREE COLUMN
C FIELDS. I.E. FORMAT(24I3)
282 READ (5,18)(NB(I),I=1,NSB)
    NU=NOU-1
    JL=1
    JX=2
    NUT=1
    NUB=1
    IX=1
290 WRITE (6,60)IND,JL,(REC(I),I=1,14)
    IF(NCON)65987,65987,89981
65987 WRITE (7,71)IND,JL,(REC(I),I=1,14)
C PUNCH SYM. G
60 FORMAT(1H0, I3,12H SYM.G.BLOCKI3,14A4)
71 FORMAT(I3,12H SYM.G.BLOCKI3,14A4)
89981 NT=NB(JX)
    NP=NB(JL)
    NEL=0
300 DO 302 I=1,NQ
    GU(I)=0.0
302 U(I)=0.0
```



TABLE XLVII (Continued)

```
303 DO 320 K=NUB,NOU
    IF(NRU(K)-IX)306,315,306
306 DO 312 L=1,NG
    I=NRG(L)
    J=NCG(L)
309 GU(I)=GU(I)+U(J)*DG(L)
    IF(I-J)310,312,310
310 GU(J)=GU(J)+U(I)*DG(L)
312 CONTINUE
75391 GO TO 322
315 JU=NCU(K)
320 U(JU)=DU(K)
322 NUB=K
    DO 324 I=IX,NS
324 UG(I)=0.0
    JAK=0
    DO 335 L=NUT,NU
    IF(JAK)332,330,332
330 IF(NRU(L)-IX)331,332,331
331 NWY=L
    JAK = 1
332 I=NRU(L)
    J=NCU(L)
335 UG(I)=UG(I)+DU(L)*GU(J)
    NUT=NWY
    DO 350 J=IX,NS
    IF(0.00005-ABS(UG(J)))342,350,350
342 IF(NT-J)343,343,344
343 WRITE (6,72)IX,J
    72 FORMAT(40H ERROR,ERROR,ERROR- G NOT FACTORING.ROWI4,7H COLUMNI4)
344 NEL=NEL+1
    IF(101-NEL)34500,34500,347
34500 IF(NCON)88979,345,68996
    345 WRITE (7,56)(NRS(I),NCS(I),GS(I),I=1,100)
68996 WRITE (6,57)(NRS(I),NCS(I),GS(I),I=1,100)
88979 NEL=1
    347 NRS(NEL)=IX-NP+1
    NCS(NEL)=J-NP+1
    GS(NEL)=UG(J)
350 CONTINUE
    IX=IX+1
    IF(NT-IX)354,354,300
354 NEL=NEL+1
    NRS(NEL)=-1
    NCS(NEL)=0
    GS(NEL)=0.0
    IF(NCON)35427,358,89765
    358 WRITE (7,56)(NRS(I),NCS(I),GS(I),I=1,NEL)
89765 WRITE (6,57)(NRS(I),NCS(I),GS(I),I=1,NEL)
35427 JL=JL+1
    JX=JX+1
360 IF(NSB-JX)210,290,290
600 WRITE (6,80)NOPROB,L,NROW(L),NCOL(L),DAT(L)
```

TABLE XLVII (Continued)

```
80 FORMAT(24H X MATRIX ERROR PROBLEM I7,6H FIELD I3,6H READS 2 I4,F12.6)
GO TO 210
605 WRITE (6,82)L,NE(L),NCOD(L),NI(L),NJ(L),NK(L),NL(L), NX(L),NY(L)
1,JOKER
82 FORMAT(33H INTERNAL COORDINATE ERROR.FIELD I3,6H READS 8 I4, 8H JOKE
IR = I3)
GO TO 210
615 WRITE (6,84)NOPROB,L,NROW(L),NCOL(L),DAT(L)
84 FORMAT(24H U MATRIX ERROR PROBLEM I7,6H FIELD I3,6H READS 2 I4,F12.6)
GO TO 210
END
SUBROUTINE BOST(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,
INQ,INTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
C THIS SUBROUTINE COMPUTES THE B MATRIX ELEMENTS FOR A BOND STRETCH
C AS DEFINED BY WILSON.
DIMENSION NR( 900),NC( 900),B( 900),NRG(1900),NCG(1900),DG(1900),
1 NRU(300),NCU(300),DU(300),X(3,25),
2 RIJ(3)
100 IF(N6)130,101,130
101 IF(N5)130,102,130
102 IF(N4)130,103,130
103 IF(N3)130,104,130
104 IF(NOAT-N2)130,105,105
105 IF(NOAT-N1)130,106,106
106 I=N1
J=N2
DIJSQ=0.0
109 DO 112 M=1,3
RIJ(M)=X(M,J)-X(M,I)
112 DIJSQ=DIJSQ+RIJ(M)*RIJ(M)
114 DO 120 M=1,3
IF(ABS(RIJ(M))-0.00005)120,120,115
115 NOB=NOB+1
NR(NOB)=NOINT
NC(NOB)=3*(I-1)+M
B(NOB)=-RIJ(M) / SQRT(DIJSQ)
NOB=NOB+1
NR(NOB)=NOINT
NC(NOB)=3*(J-1)+M
B(NOB)= RIJ(M) / SQRT(DIJSQ)
120 CONTINUE
GO TO 132
130 JOKER=1
132 RETURN
END
SUBROUTINE BEND(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,
INQ,INTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
C THIS SUBROUTINE COMPUTES THE B MATRIX ELEMENTS OF A VALENCE
C ANGLE BENDING COORDINATE AS DEFINED BY WILSON.
C I AND K ARE THE NUMBERS OF THE END ATOMS.
C J= THE NUMBER OF THE CENTRAL ATOM
DIMENSION NR( 900),NC( 900),B( 900),NRG(1900),NCG(1900),DG(1900),
1 NRU(300),NCU(300),DU(300),X(3,25),
```

TABLE XLVII (Continued)

```
2RJI(3),RJK(3),RIXJX(3),EJI(3),EJK(3)
100 IF(NOAT-N6)150,101,101
101 IF(NOAT-N5)150,102,102
102 IF(N4)150,103,150
103 IF(NOAT-N3)150,104,104
104 IF(NOAT-N2)150,105,105
105 IF(NOAT-N1)150,106,106
106 I=N1
107 J=N2
    K=N3
    IX=N5
    JX=N6
    IF(IX)110,110,112
110 IX=1
    JX=1
112 DJISQ=0.0
    DJKSQ=0.0
    DXSQ=0.0
115 DO 122 M=1,3
    RJI(M)=X(M,I)-X(M,J)
    RJK(M)=X(M,K)-X(M,J)
    RIXJX(M)=X(M,JX)-X(M,IX)
    DJISQ=DJISQ+RJI(M)*RJI(M)
    DJKSQ=DJKSQ+RJK(M)*RJK(M)
122 DXSQ=DXSQ+RIXJX(M)*RIXJX(M)
123 DJI=SQRT(DJISQ)
    DJK=SQRT(DJKSQ)
    DX=SQRT(DXSQ)
    IF(DX)128,127,128
127 DX=1.0
128 DOTJ=0.0
129 DO 132 M=1,3
    EJI(M)=RJI(M)/DJI
    EJK(M)=RJK(M)/DJK
132 DOTJ=DOTJ+EJI(M)*EJK(M)
    IF(1.0-ABS(DOTJ))152,152,134
134 SINJ=SQRT(1.0-DOTJ*DOTJ)
136 DO 144 M=1,3
    SMI=(DX*(DOTJ*EJI(M)-EJK(M)))/(DJI*SINJ)
    IF(ABS(SMI)-0.00005)138,138,137
137 NOB=NOB+1
    NR(NOBI)=NOINT
    NC(NOBI)=3*(I-1)+M
    B(NOBI)=SMI
138 SMK=(DX*(DOTJ*EJK(M)-EJI(M)))/(DJK*SINJ)
    IF(ABS(SMK)-0.00005)140,140,139
139 NOB=NOB+1
    NR(NOBI)=NOINT
    NC(NOBI)=3*(K-1)+M
    B(NOBI)=SMK
140 SUM=SMI+SMK
    IF(ABS(SUM)-0.00005)144,144,142
142 NOB=NOB+1
```

TABLE XLVII (Continued)

```
NR(NO8)=NOINT
NC(NO8)=3*(J-1)+M
B(NO8)=-SUM
144 CONTINUE
GO TO 154
150 JOKER=1
GO TO 154
152 JOKER=2
154 RETURN
END
SUBROUTINE OPLA(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,
INQ,INTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
THIS SUBROUTINE COMPUTES THE B MATRIX ELEMENTS FOR AN OUT OF
PLANE WAGGING COORDINATE AS DEFINED BY WILSON.
I= THE END ATOM
J= THE APEX ATOM
K AND L = THE ANCHOR ATOMS.
DIMENSION NR( 900),NC( 900),B( 900),NRG(1900),NCG(1900),DG(1900),
1 NRU(300),NCU(300),DU(300),X(3,25),
2RJI(3),RJK(3),RJL(3),RIXJX(3),EJI(3),EJK(3),EJL(3),C1(3),C2(3),
3C3(3)
100 IF(NOAT-N6)170,101,101
101 IF(NOAT-N5)170,102,102
102 IF(NOAT-N4)170,103,103
103 IF(NOAT-N3)170,104,104
104 IF(NOAT-N2)170,105,105
105 IF(NOAT-N1)170,106,106
106 I=N1
J=N2
K=N3
L=N4
IX=N5
JX=N6
IF(IX)110,110,112
110 IX=1
JX=1
112 DJISQ=0.0
DJKSQ=0.0
DJLSQ=0.0
115 DXSQ=0.0
116 DO 124 M=1,3
RJI(M)=X(M,I)-X(M,J)
DJISQ=DJISQ+RJI(M)*RJI(M)
RJK(M)=X(M,K)-X(M,J)
DJKSQ=DJKSQ+RJK(M)*RJK(M)
RJL(M)=X(M,L)-X(M,J)
DJLSQ=DJLSQ+RJL(M)*RJL(M)
RIXJX(M)=X(M,JX)-X(M,IX)
124 DXSQ=DXSQ+RIXJX(M)*RIXJX(M)
126 DJI=SQRT(DJISQ)
DJK=SQRT(DJKSQ)
DJL=SQRT(DJLSQ)
DX=SQRT(DXSQ)
```

TABLE XLVII (Continued)

```
130 IF(DX)132,131,132
131 DX=1.0
132 DO 136 M=1,3
    EJI(M)=RJI(M)/DJI
    EJK(M)=RJK(M)/DJK
136 EJI(M)=RJI(M)/DJI
137 C1(1)=EJK(2)*EJL(3)-EJK(3)*EJL(2)
    C1(2)=EJK(3)*EJL(1)-EJK(1)*EJL(3)
    C1(3)=EJK(1)*EJL(2)-EJK(2)*EJL(1)
    C2(1)=EJL(2)*EJI(3)-EJL(3)*EJI(2)
    C2(2)=EJL(3)*EJI(1)-EJL(1)*EJI(3)
    C2(3)=EJL(1)*EJI(2)-EJL(2)*EJI(1)
    C3(1)=EJI(2)*EJK(3)-EJI(3)*EJK(2)
    C3(2)=EJI(3)*EJK(1)-EJI(1)*EJK(3)
139 C3(3)=EJI(1)*EJK(2)-EJI(2)*EJK(1)
140 DET=EJI(1)*C1(1)+EJI(2)*C1(2)+EJI(3)*C1(3)
    DOTI=0.0
142 DO 143 M=1,3
143 DOTI=DOTI+EJK(M)*EJL(M)
144 IF(1.0-ABS(DOTI))172,172,146
146 SINI=SQRT(1.0-DOTI*DOTI)
147 SINT=DET/SINI
148 IF(1.0-ABS(SINT))174,174,149
149 COST=SQRT(1.0-SINT*SINT)
150 TANT=SINT/COST
155 DO 168 M=1,3
157 SMI =((C1(M)/(COST*SINI))-((TANT*EJI(M))))/DJI
    IF(ABS(SMI)-0.00005)160,160,158
158 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(I-1)+M
    B(NOB)=DX*SMI
    COMP1 = SINI*SINI
160 SMK=((C2(M)/(COST*SINI))-((TANT*(EJK(M)-DOTI*EJL(M)))/COMP1))/DJK
    IF(ABS(SMK)-0.00005)163,163,161
161 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(K-1)+M
    B(NOB)=DX*SMK
163 SML=((C3(M)/(COST*SINI))-((TANT*(EJL(M)-DOTI*EJK(M)))/COMP1))/DJL
    IF(ABS(SML)-0.00005)166,166,164
164 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(L-1)+M
    B(NOB)=DX*SML
166 SUM=SMI+SMK+SML
    IF(ABS(SUM)-0.00005)168,168,167
167 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(J-1)+M
    B(NOB)=-DX*SUM
168 CONTINUE
    GO TO 178
```

TABLE XLVII (Continued)

```
170 JOKER=1
    GO TO 178
172 JOKER=2
    GO TO 178
174 JOKER=3
178 RETURN
    END
    SUBROUTINE TORS(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,
    INQ,INTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA,MAP)
C   THIS SUBROUTINE COMPUTES THE B MATRIX ELEMENTS FOR THE TORSION
C   AS DEFINED BY WILSION.
C   I AND L = THE END ATOMS . I NEARER OBSERVER.
C   J AND K = THE CENTRAL ATOMS. J NEARER OBSERVER.
    DIMENSION NR( 900),NC( 900),B( 900),NRG(1900),NCG(1900),DG(1900),
    1 NRU(300),NCU(300),DU(300),X(3,25),
    2 RIJ(3),RJK(3),RKL(3),RIXJX(3),EIJ(3),EJK(3),EKL(3),CR1(3),CR2(3)
100 IF(NOAT-N6)180,101,101
101 IF(NOAT-N6)180,102,102
102 IF(NOAT-N4)180,103,103
103 IF(NOAT-N3)180,104,104
104 IF(NOAT-N2)180,105,105
105 IF(NOAT-N1)180,106,106
106 I=N1
    J=N2
    K=N3
    L=N4
    IX=N5
    JX=N6
    IF(IX)110,110,112
110 IX=1
    JX=1
112 DIJSQ=0.0
    DJKSQ=0.0
    DKLSQ=0.0
115 DXSQ=0.0
116 DO 124 M=1,3
    RIJ(M)=X(M,J)-X(M,I)
    DIJSQ=DIJSQ+RIJ(M)*RIJ(M)
    RJK(M)=X(M,K)-X(M,J)
    DJKSQ=DJKSQ+RJK(M)*RJK(M)
    RKL(M)=X(M,L)-X(M,K)
    DKLSQ=DKLSQ+RKL(M)*RKL(M)
    RIXJX(M)=X(M,JX)-X(M,IX)
124 DXSQ=DXSQ+RIXJX(M)*RIXJX(M)
126 DIJ=SQRT(DIJSQ)
    DJK=SQRT(DJKSQ)
    DKL=SQRT(DKLSQ)
    DX=SQRT(DXSQ)
130 IF(DX)132,131,132
131 DX=1.0
132 DO 136 M=1,3
    EIJ(M)=RIJ(M)/DIJ
```

TABLE XLVII (Continued)

```
EJK(M)=RJK(M)/DJK
136 EKL(M)=RKL(M)/DKL
138 CR1(1)=EIJ(2)*EJK(3)-EIJ(3)*EJK(2)
    CR1(2)=EIJ(3)*EJK(1)-EIJ(1)*EJK(3)
    CR1(3)=EIJ(1)*EJK(2)-EIJ(2)*EJK(1)
    CR2(1)=EJK(2)*EKL(3)-EJK(3)*EKL(2)
    CR2(2)=EJK(3)*EKL(1)-EJK(1)*EKL(3)
142 CR2(3)=EJK(1)*EKL(2)-EJK(2)*EKL(1)
143 DOTPJ=0.0
    DOTPK=0.0
145 DO 147 M=1,3
    DOTPJ=DOTPJ-EIJ(M)*EJK(M)
147 DOTPK=DOTPK-EJK(M)*EKL(M)
148 IF(1.0-ABS(DOTPJ))182,182,149
149 IF(1.0-ABS(DOTPK))182,182,150
150 SINPJ=SQRT(1.0-DOTPJ*DOTPJ)
    SINPK=SQRT(1.0-DOTPK*DOTPK)
152 DO 164 M=1,3
    SMI=-CR1(M)/(DIJ*SINPJ*SINPJ)
    IF(ABS(SMI)-0.00005)156,156,154
154 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(I-1)+M
    B(NOB)=DX*SMI
156 F1=(CR1(M)*(DJK-DIJ*DOTPJ))/(DJK*DIJ*SINPJ*SINPJ)
    F2=(DOTPK*CR2(M))/(DJK*SINPK*SINPK)
    SMJ=F1-F2
    IF(ABS(SMJ)-0.00005)158,158,157
157 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(J-1)+M
    B(NOB)=DX*SMJ
158 SML=CR2(M)/(DKL*SINPK*SINPK)
    IF(ABS(SML)-0.00005)160,160,159
159 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(L-1)+M
    B(NOB)=DX*SML
160 SUM=SMI+SMJ+SML
    IF(ABS(SUM)-0.00005)164,164,162
162 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(K-1)+M
    B(NOB)=-DX*SUM
164 CONTINUE
    GO TO 186
180 JOKER=1
    GO TO 186
182 JOKER=2
186 RETURN
    END
    SUBROUTINE LIBE(NR,NC,B,X,NRG,NRU,NCG,NCU,DG,DU,IND,NOPROB,NOAT,
```

TABLE XLVII (Continued)

```
INQ,INTC,NISO,IFB,NOINT,NO2,N1,N2,N3,N4,N5,N6,MX,JOKER,NOB,NA)
C THIS SUBROUTINE COMPUTES THE B MATRIX ELEMENTS FOR A LINEAR BEND
C OR FOR A PAIR OF PERPENDICULAR LINEAR BENDS.
C NI=NO2 THE NUMBER OF THE SECOND COORDINATE.
C I AND K = THE END ATOMS.
C J= THE CNTRAL ATOM.
C A GIVES THE CARTESIAN COORDINATES OF A POINT IN SPACE, SUCH
C THAT THE VECTOR FROM ATOM J TO POINT A IS PERPENDICULAR TO
C THE LINE I-J-K AND SERVES TO ORIENT THE COORDINATES IN SPACE.
C DIMENSION NR( 900),NC( 900),B( 900),NRG(1900),NCG(1900),DG(1900),
1 NRU(300),NCU(300),DU(300),X(3,25),
2A(3),RJI(3),RJK(3),RIXJX(3),UN(3),UNIT(3),UP(3),EJI(3),EJK(3)
JSTOP=0
100 IF(NOAT-N6)160,101,101
101 IF(NOAT-N5)160,102,102
102 IF(NOAT-N4)160,103,103
103 IF(NOAT-N3)160,104,104
104 IF(NOAT-N2)160,105,105
105 READ (5,24)(A(I),I=1,3)
24 FORMAT(3F12.6)
IF(N4)160,109,108
108 I=N2
J=N3
K=N4
JSTOP=1
GO TO 110
109 I=N1
J=N2
K=N3
110 IX=N5
JX=N6
IF(IX)111,111,112
111 IX=1
JX=1
112 DJISQ=0.0
DJKSQ=0.0
DXSQ=0.0
116 DAJSQ=0.0
117 DO 124 M=1,3
RJI(M)=X(M,I)-X(M,J)
DJISQ=DJISQ+RJI(M)*RJI(M)
RJK(M)=X(M,K)-X(M,J)
DJKSQ=DJKSQ+RJK(M)*RJK(M)
RIXJX(M)=X(M,JX)-X(M,IX)
DXSQ=DXSQ+RIXJX(M)*RIXJX(M)
UN(M)=A(M)-X(M,J)
124 DAJSQ=DAJSQ+UN(M)*UN(M)
126 DJI=SQRT(DJISQ)
DJK=SQRT(DJKSQ)
DX=SQRT(DXSQ)
DAJ=SQRT(DAJSQ)
130 IF(DX)132,131,132
131 DX=1.0
```



TABLE XLVII (Continued)

```
132 DOTJ=0.0
    DOTP=0.0
134 DO 140 M=1,3
    EJI(M)=RJI(M)/DJI
    EJK(M)=RJK(M)/DJK
    UNIT(M)=UN(M)/DAJ
    DOTJ=DOTJ+EJI(M)*EJK(M)
140 DOTP=DOTP+EJI(M)*UNIT(M)
    TEST=(ABS(DOTJ)-1.0)
    IF(0.0001-ABS(TEST))162,142,142
142 IF(0.00005-ABS(DOTP))162,143,143
143 UP(1)=EJK(2)*UNIT(3)-EJK(3)*UNIT(2)
    UP(2)=EJK(3)*UNIT(1)-EJK(1)*UNIT(3)
    UP(3)=EJK(1)*UNIT(2)-EJK(2)*UNIT(1)
146 DO 149 M=1,3
    IF(ABS(UNIT(M))-0.00005)149,149,147
147 NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(I-1)+M
    B(NOB)=-DX*UNIT(M)/ DJI
    NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(K-1)+M
    B(NOB)=-DX*UNIT(M)/ DJK
    NOB=NOB+1
    NR(NOB)=NOINT
    NC(NOB)=3*(J-1)+M
    B(NOB)=DX*(1.0/ DJI +1.0/DJK)*UNIT(M)
149 CONTINUE
    IF(IJSTOP)164,164,150
150 DO 158 M=1,3
    IF(ABS(UP(M))-0.00005)158,158,151
151 NOB=NOB+1
    NR(NOB)=NO2
    NC(NOB)=3*(I-1)+M
    B(NOB)=-DX*UP(M)/ DJI
    NOB=NOB+1
    NR(NOB)=NO2
    NC(NOB)=3*(K-1)+M
    B(NOB)=-DX*UP(M) / DJK
    NOB=NOB+1
    NR(NOB)=NO2
    NC(NOB)=3*(J-1)+M
    B(NOB)=DX*(1.0/DJI + 1.0/DJK)*UP(M)
158 CONTINUE
    GO TO 164
160 JOKER=1
    GO TO 164
162 JOKER=2
164 RETURN
    END
```

- c. NOAT, the number of atoms in the molecule. NOAT punched in Columns 11-13 (FORMAT I4).  
Note: The maximum number of atoms permitted is 25.
- d. NQ, the number of internal coordinates, punched in Columns 14-17 (FORMAT I4).
- e. INTC, must be a 1 for the unsymmetric G matrix to be punched on cards. INTC is punched in Column 21 (FORMAT I4).
- f. NISO, the number of isotopically substituted molecules punched in Columns 22-25 (FORMAT I4).
- g. IFB, may be 1, 0, or -1. IFB is the B matrix suppression option. For IFB = -1, the B and G matrices are not printed or punched onto cards. For IFB = 0, the B matrix is printed, but not punched onto cards if NCON = 0, and the printing and punching of the G matrix depends on the values of INTC and NCON. For IFB = 1, the B matrix and G matrix are printed and punched onto cards for NCON = 0. IFB is punched in Columns 26-29 (FORMAT I4).
- h. NCON is the output suppression option. If NCON = 1, all output, both printer and card punch, is suppressed, except the printout of the symmetric G matrix. There is no suppression for NCON = 0. NCON is punched in Column 33 (FORMAT I4).

- 3. Problem Information Cards. The problem control card is followed by two problem information cards. These cards may contain any desired alphanumeric information about the problem. The data can be punched in any column of the card except 1-3, which should be left blank, through Column 72 (FORMAT 18A4).

Warning: These two cards must be included with the input data even if they are left blank.

- 4. Cartesian Coordinates. The next set of cards contain the cartesian coordinates, standard or principal, obtained as output data from CART [FORMAT 4(2I3,F12.6)]. The row number following the last element should be -1. This should have been accomplished by CART already.
- 5. Internal Coordinate Definition Cards. The next set of cards defines the internal coordinates. There are three internal coordinate "vectors" describing the internal coordinates per card. Each internal coordinate "vector" is denoted by eight numbers: NI, NCOD, N1, N2, N3, N4, N5, and N6. NI gives the number assigned to the internal coordinate, NCOD is the code number identifying the type of internal coordinate, and N1, N2, N3, N4, N5, and N6 are the numbers of the atoms defining the coordinate. A description of the internal coordinate coding system was presented earlier in this text which may also be found in Schachtschneider's manual (89) (FORMAT 24I3). The internal coordinate definition cards are followed by a card with -02 in Columns 1-3 which designates the end of the internal coordinate information.

Warning: The internal coordinates must be defined in the order 1 through NQ.

Note: If  $NI = 0$ , the defined B matrix row is added to the B matrix row for the previous coordinate, i.e., the internal coordinate becomes a linear sum of the two defined coordinates.

6. Isotope Control Card. There must be one of these cards for each molecule in the problem. The following information is contained on this card.
  - a. IN, identifies the isotope control card.  $IN = -06$  which is punched in Columns 1-3 (FORMAT I3).
  - b. IFU, the U matrix read option control. (The U matrix is the transformation from internal coordinates to symmetry coordinates.) IFU may be a 1, 0, or -1.  $IFU = 0$ , the U matrix is not included with the input and the G matrix is not symmetrized.  $IFU = 1$ , the U matrix is entered and the G matrix is symmetrized.  $IFU = -1$ , the U matrix is not entered with the input, but the G matrix is symmetrized with the U matrix from the previous isotopically substituted molecule. IFU is punched in Columns 4-6 (FORMAT I3).
  - c. NSB is the number of factored blocks or symmetry species plus 1 which is punched in Columns 7-9 (FORMAT I3).
  - d. NS is the number of symmetry coordinates which is punched in Columns 10-12 (FORMAT I3).

Note: The rest of the isotope control card through Column 68 may be used for descriptive alphanumeric information (FORMAT 14A4).

Warning: The isotope control card must be included with the input data even though there may not be any isotopically substituted molecules included in the problem.

7. Atomic Masses. The atomic masses, six per card, follow the isotope control card. The masses must follow in the order 1 through NOAT. (FORMAT 6F12.6).
8. U Matrix. If  $IFU = 1$ , the U matrix must be included next. The U matrix is punched in 18 column fields, 1 to 4 per card, in a manner similar to the cartesian coordinates. The row number following the last element is set equal to -3. [See Schachtschneider (89) for a description of the U matrix.] The zero elements of the U matrix need not be included and the matrix does not have to be normalized. The row elements must be entered in order [FORMAT 4(2I3,F12.6)].
9. Symmetry Block Information. If  $IFU = 1$ , the U matrix is followed by a symmetry block information card giving the numbers of the first row of each factored block with the last number being  $NS + 1$ . These numbers are punched in 24 three column fields (FORMAT 24I3).
10. Data Termination Card. The data are followed by a card denoting the end of the problem. This card consists of 999 punched in Columns 1-3.

Note: If another problem is to be included with the input data, the problem ID card of the next set of data is placed at this point instead of the data termination card.

Warning: The B matrix is limited to 900 elements and the G matrix to 1900 elements.

Warning: If the G matrix does not factor, a user error is signified.

With the RAX system the input deck is preceded by a /DATA card and ended with a /END card.

#### OUTPUT INFORMATION

At the option of the program user, the following data will be printed out.

1. The cartesian coordinates (X matrix).
2. The internal coordinate definition "vectors."
3. The B matrix.
4. The atomic masses.
5. The unsymmetrized G matrix.
6. The normalized U matrix.
7. The symmetrized G matrix.

The data below will be punched on cards if desired by the user.

1. The B matrix in the format row, column, and numerical value [FORMAT 4(2I3,F12.6)]. The row number following the last element is set equal to -5.
2. The G matrix in the format row, column, and numerical value [FORMAT 4(2I3,F12.6)]. The row following the last element is set equal to -1.
3. The symmetrized or factored G matrix [FORMAT 4(2I3,F12.6)]. The row number following the last element is set equal to -1.

UBZM

This program is designed to evaluate the transformation,  $\underline{Z}$ , from force constant space to internal coordinate space. The program is specifically designed to calculate the SVQFF or UBFF which were described earlier in this text. The use of the program to compute the  $\underline{Z}$  matrix for a Urey-Bradley force field will not be discussed here, but the reader will find a detailed description in Schachtschneider's manual (89). The employment of UBZM shall instead be oriented toward the computation of a simplified valence quadratic force field. The input data to UBZM consists of a specification of the  $\underline{Z}$  matrix in terms of the position of the  $\underline{F}$  matrix elements by row and column number and the number of the corresponding force constant parameters. The program then punches the  $\underline{Z}$  matrix on cards in a form suitable for use as input to ZSYM, FADJ, FLPO, and EIGV.

The program was written by J. H. Schachtschneider (89) and modified for use in this thesis. The program may be run with the IBM 360/44 RAX operating system.

A flow diagram of UBZM is presented in Fig. 38 and a listing in Table XLVIII [the UBFF subroutines are not included; see (89)].

INSTRUCTIONS FOR PROGRAM USE

The program deck must be preceded by a /ID and a /JOB GO card when the program is run with the RAX operating system.

Warning: If this program is to be required to compute the  $\underline{F}$  matrix, the array  $F(I,J)$  in the dimension statement must be changed to  $F(50,50)$  which will permit the evaluation of  $\underline{F}$  up to 50 force constants.

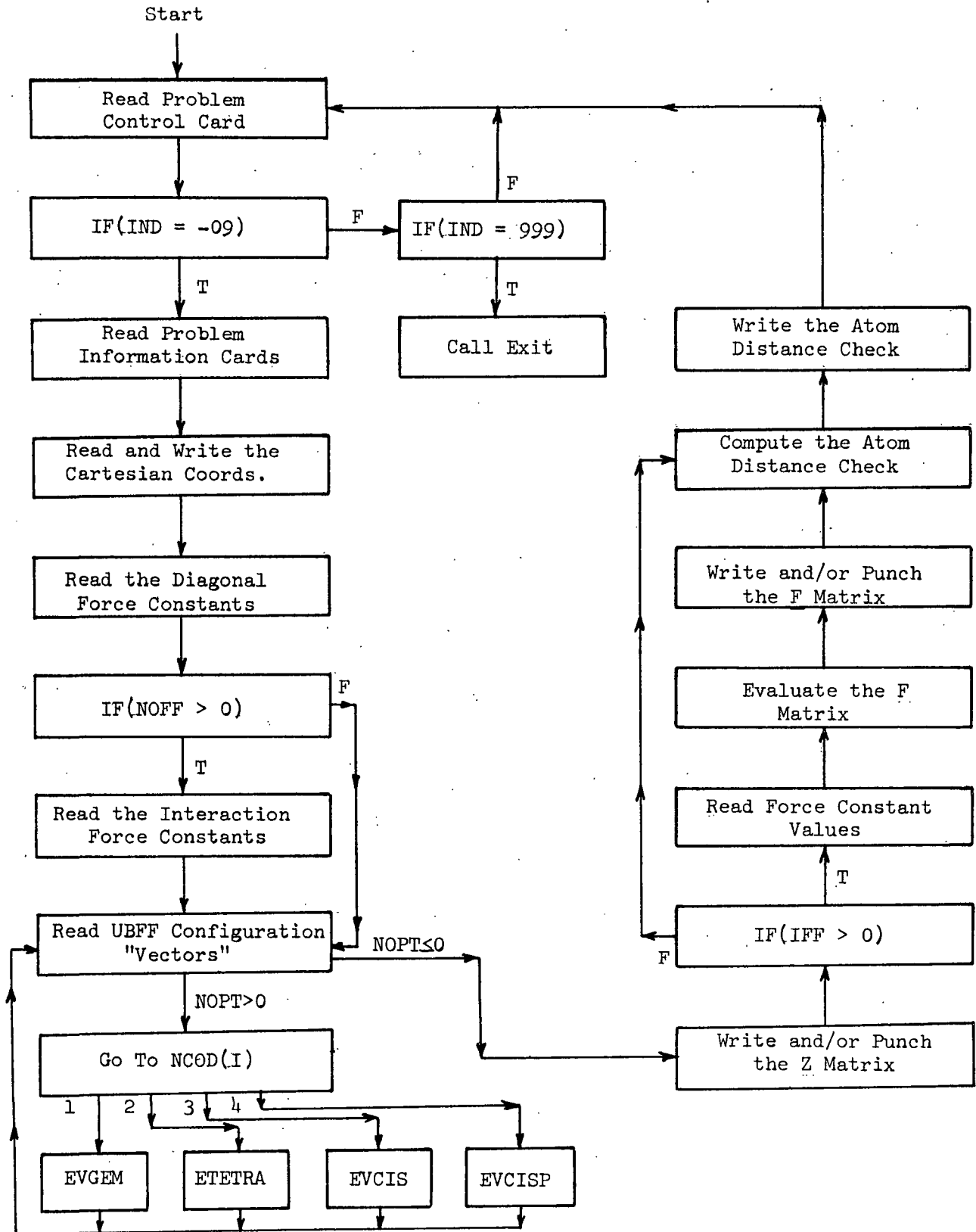


Figure 38. The Flow Diagram of UBZM

TABLE XLVIII

LISTING OF UBZM

```
C UBZM SD-4080 CODED IN FORTRAN IV FOR THE IBM-360/44 RAX
C SCHACHTSCHNEIDER 9/1/60 REVISED 10/1/63
C MODIFIED FOR RAX BY L J PITZNER 4/1/71
C THIS PROGRAM EVALUATES THE TRANSFORMATION FROM UREY-BRADLEY
C SPACE TO INTERNAL COORDINATE SPACE FOR THREE TYPES OF
C CONFIGURATIONS GIVEN THE CARTESIAN COORDINATES OF THE ATOMS.
C THE CONFIGURATIONS ARE 1.GEM,2.TETRA,AND 3. CIS.
C DIMENSION D( 57,57 ),NC1( 800),NC2( 800),NFO( 800),DATINZ( 800),
C 1X(3, 25),NA(5),KOOOFX(10),NFOR(700),NINT(700),N1(700),N2(700),
C 2NROWX(4),NCOLX(4),DATINX(4),RECORD(36),UBF(100),R(3),F( 1, 1)
C INTEGER PUNCH
C EQUIVALENCE (D( 1),NC1(1)),(D( 810),NC2(1)),(D(1620),NFO(1)),
C 1(D(2430),DATINZ(1))
C READ CONTROL CARD
C CONTROL CARD CONTAINS THE FOLLOWING INFORMATION
C 1.IND=-09,INDICATING THE START OF A PROBLEM. IN COLUMNS 1-3.
C 2.NOPROB, THE PROBLEM NUMBER, COLUMNS 4-9.
C 3.NOAT, THE NUMBER OF ATOMS. IN COLUMNS 10-12. LESS THAN 25.
C 4.NCOR, THE NUMBER OF INTERNAL COORDINATES. IN COLUMNS 13-15.
C 5.NF, THE NUMBER OF FORCE CONSTANTS. IF COLUMNS 16-18.
C 6.IFF=1,IF THE VALUES OF THE FORCE CONSTANTS ARE INCLUDED WITH
C THE INPUT.
C IFF=0,IF NOT. PUNCHED IN COLUMN 20.
C 7.NOFF, THE NUMBER OF NON UREY-BRADLEY CONSTANTS TO BE FILLED
C IN. IN COLUMNS 21-23
C 8.INFRA=1, IF THE INTERMEDIATE GEM,TETRA,AND CIS MATRICES ARE
C TO BE WRITTEN.
C INFR=0 IF NOT.
C PUNCHED IN COLUMN 25.
C 9.PUNCH =1, IF THE PUNCHING OF THE Z-MATRIX IS TO BE SUPRESSED.
C OTHERWISE PUNCH =0. IN COL. 27.
C 10.NOX, IF NOX=1, THE X-MATRIX IS NOT READ IN AND THE ATOM
C DISTANCE CHECK IS NOT COMPUTED. THIS OPTION APPLYS TO THE VFF
C ONLY. NOX IS PUNCHED IN COLUMN 29.
C 90 READ(5,4) IND,NOPROB,NOAT,NCOR,NF,IFF,NOFF,INFRA,PUNCH,NOX
C 4 FORMAT(I3,I6,3I3,I2,I3,I2,I2,I2)
C 91 IF(IND+9)94,92,94
C 94 IF(IND-999)90,95,90
C 95 CALL EXIT
C 92 CONTINUE
C INPUT DATA FOLLOWS CONTROL CARD IN THE ORDER
C 1.PROBLEM INFORMATION CARDS. 2 CARDS
C 2.THE X MATRIX, IF NOX =0.
C 3.THE NUMBERS OF THE DIAGONAL FORCE CONSTANTS.
C 4.NUMBERS FOR THE NON UB OFF DIAGONAL ELEMENTS.
C 5.CONFIGURATION VECTORS
C 6.THE VALUES OF THE FORCE CONSTANTS.
C 7.FOLLOW DATA WITH TWO BLANK CARDS.
C READ PROBLEM INFORMATION CARDS
C 100 READ (5,6)(RECORD(I),I=1,36)
C 6 FORMAT(18A4)
```

TABLE XLVIII (Continued)

```
102 WRITE (6,50)NOPROB,(RECORD(I),I=1,36)
 50 FORMAT(22H1 Z MATRIX PROBLEM NO.18/(12X,18A4))
C   READ X MATRIX
   IF(NOX)8175,8175,130
8175 WRITE(6,3773)
3773 FORMAT(10H0 X-MATRIX)
 105 DO 107 I=1,3
     DO 107 J=1,NOAT
 107 X(I,J)=0.0
 110 READ (5,8)(NROWX(L),NCOLX(L),DATINX(L),L=1,4)
     WRITE(6,2772)(NROWX(L),NCOLX(L),DATINX(L),L=1,4)
2772 FORMAT(1H ,4(2I3,F12.6))
   8 FORMAT(4(2I3,F12.6))
 112 DO 118 L=1,4
     IF(NROWX(L))120,605,114
 114 IF(3-NROWX(L))605,115,115
 115 IF(NOAT-NCOLX(L))605,116,116
 116 I=NROWX(L)
     J=NCOLX(L)
 118 X(I,J)=DATINX(L)
     GO TO 110
 120 IF(1+NROWX(L))605,130,605
 130 READ (5,10)(NINT(J),NFOR(J),J=1,NCOR)
  10 FORMAT(24I3)
     WRITE(6,1771)
1771 FORMAT(34H0 DIAGONAL VALENCE FORCE CONSTANTS)
     WRITE(6,7557)(NINT(J),NFOR(J),J=1,NCOR)
7557 FORMAT(1H ,24I3)
 132 NZ=0
 140 DO 145 K=1,NCOR
     IF(NCOR-NINT(K))610,142,142
 142 IF(NF-NFOR(K))610,143,143
 143 NZ=NZ+1
     NC1(NZ)=NINT(K)
     NC2(NZ)=NINT(K)
     NFO(NZ)=NFOR(K)
 145 DATINZ(NZ)=1.0
 150 IF(NOFF)170,170,152
 152 READ (5,10)(N1(I),N2(I),NFOR(I),I=1,NOFF)
     WRITE(6,9339)
9339 FORMAT(37H0 VALENCE FORCE INTERACTION CONSTANTS)
     WRITE(6,7557)(N1(I),N2(I),NFOR(I),I=1,NOFF)
 160 DO 168 K=1,NOFF
     IF(NCOR-N2(K))610,162,162
 162 IF(N2(K)-N1(K))610,163,163
 163 IF(NF-NFOR(K))610,164,164
 164 NZ=NZ+1
     NC1(NZ)=N1(K)
     NC2(NZ)=N2(K)
     NFO(NZ)=NFOR(K)
 168 DATINZ(NZ)=1.0
 170 JOKE=0
```



TABLE XLVIII (Continued)

```
172 READ (5,10)NOPT,NCOD,(NA(I),I=1,5),(K00FX(J),J=1,10),      (NFOR(
    1K),K=1,13)
    WRITE (6,80)NCOD,NOPT,(NA(I),I=1,5)
80 FORMAT(24H0 SUBCONFIGURATION CODEI4,8H, OPTIONI3/14H ATOM NUMBER
    1S/1H 5I4)
    WRITE (6,81)(K00FX(J),J=1,10)
81 FORMAT(29H INTERNAL COORDINATE NUMBERS/1H 10I4)
    WRITE (6,82)(NFOR(K),K=1,13)
82 FORMAT(25H FORCE CONSTANT NUMBERS /1H 13I4)
174 IF(NOPT)400,400,180
180 IF(NCOD)615,615,181
181 IF(4-NCOD)615,182,182
182 DO 184 I=1,5
    IF(NA(I))615,183,183
183 IF(NOAT-NA(I))615,184,184
184 CONTINUE
186 DO 189 I=1,10
    IF(K00FX(I))615,188,188
188 IF(NCOR-K00FX(I))615,189,189
189 CONTINUE
190 DO 193 I=1,13
    IF(NFOR(I))615,192,192
192 IF(NF-NFOR(I))615,193,193
193 CONTINUE
200 MX=NCOD
    GO TO (210,220,230,240),MX
210 CALL EVGEM (D,NC1,NC2,NFO,DATINZ,X,NA,K00FX,NFOR,NOPT,INFRA,
    INOPROB,JOKE,NOAT,NF,NZ)
    IF(JOKE)172,172,620
220 CALL ETETRA(D,NC1,NC2,NFO,DATINZ,X,NA,K00FX,NFOR,NOPT,INFRA,
    INOPROB,JOKE,NOAT,NF,NZ)
    IF(JOKE)172,172,620
230 CALL EVCIS (D,NC1,NC2,NFO,DATINZ,X,NA,K00FX,NFOR,NOPT,INFRA,
    INOPROB,JOKE,NOAT,NF,NZ)
    IF (JOKE)172,172,620
240 CALL EVCISP(D,NC1,NC2,NFO,DATINZ,X,NA,K00FX,NFOR,NOPT,INFRA,
    INOPROB,JOKE,NOAT,NF,NZ)
    IF(JOKE)172,172,620
400 WRITE (6,53)IND,NOPROB,NZ
53 FORMAT(1H1I3,17H Z MATRIX PROBLEM I8,5H NZ=I6)
    IF(NOPT)63631,63631,11443
63631 NUM=1
    KK=1
11554 DO 96315 J=1,NZ
    ITEM=NC1(J)
    IF(ITEM-NUM)96315,88887,96315
88887 NFOR(KK)=ITEM
    NINT(KK)=NC2(J)
    N1(KK)=NFO(J)
    KK=KK+1
96315 CONTINUE
    NUM=NUM+1
    IF(NUM-NCOR)11554,11554,12021
```

TABLE XLVIII (Continued)

```
12021 DO 87635 I=1,NZ
      NC1(I)=NFOR(I)
      NC2(I)=NINT(I)
      NFO(I)=N1(I)
87635 CONTINUE
11443 IF(PUNCH)89735,89735,402
89735 WRITE(7,5335)IND,NOPROB,NZ
      5335 FORMAT(13,17H Z MATRIX PROBLEM18,5H NZ=16)
      402 WRITE (6,54)(NC1(I),NC2(I),NFO(I),DATINZ(I),I=1,NZ)
      54 FORMAT(1H 3I3,F9.6,3I3,F9.6,3I3,F9.6,3I3,F9.6,3I3,F9.6,3I3,F9.6)
      IF(PUNCH)63571,63571,420
63571 WRITE(7,2992) (NC1(I),NC2(I),NFO(I),DATINZ(I),I=1,NZ)
2992 FORMAT(3I3,F9.6,3I3,F9.6,3I3,F9.6,3I3,F9.6)
420 IF(IFF)462,462,421
421 IF(50-NCOR)462,422,422
422 READ (5,14)(UBF(I),I=1,NF)
      14 FORMAT(6F12.6)
424 DO 426 I=1,NCOR
      DO 426 J=I,NCOR
426 F(I,J)=0.0
428 DO 434 K=1,NZ
      I=NC1(K)
      J=NC2(K)
      M=NFO(K)
434 F(I,J)=F(I,J)+DATINZ(K)*UBF(M)
      NX=0
436 DO 444 I=1,NCOR
      DO 444 J=I,NCOR
438 IF(0.0001-ABS(F(I,J)))439,439,444
439 NX=NX+1
      NC2(NX)=I
      NFO(NX)=J
      DATINZ(NX)=F(I,J)
444 CONTINUE
      NX=NX+1
      NC2(NX)=-2
      NFO(NX)=0
      DATINZ(NX)=0.0
448 WRITE (6,57)IND,NOPROB,NX
      57 FORMAT(2H1 I3,17H F MATRIX PROBLEM18,5H NO=16)
450 WRITE (6,58)(NC2(I),NFO(I),DATINZ(I),I=1,NX)
      58 FORMAT(2H 2I3,F12.6,2I3,F12.6,2I3,F12.6,2I3,F12.6)
462 IF(NOX)88462,88462,90
88462 DO 470 I=1,NOAT
      DO 470 J=1,NOAT
      DSQ=0.0
466 DO 468 M=1,3
      R(M) =X(M,J)-X(M,I)
468 DSQ=DSQ+R(M)*R(M)
470 D(I,J)=SQRT(DSQ)
471 WRITE (6,60)NOPROB
      60 FORMAT(28H1ATOM DISTANCE CHECK PROBLEM18)
472 DO 474 I=1,NOAT
```

TABLE XLVIII (Continued)

```
474 WRITE (6,62)I,(D(I,J),J=1,NOAT)
   62 FORMAT(5HOATOMI3/(10F12.6))
   GO TO 90
605 WRITE (6,70)NOPROB
   70 FORMAT(24HO X MATRIX ERROR PROBLEM18)
   GO TO 90
610 WRITE (6,72)NOPROB
   72 FORMAT(38HODIAGONAL FORCE CONSTANT ERROR PROBLEM18)
   GO TO 90
615 WRITE (6,74)NOPROB,NOPT,NCOD,I
   74 FORMAT(14HOERROR PROBLEM18,5H NOPTI3,5H CODEI3,3H I=I3)
   GO TO 90
620 WRITE (6,76)NOPROB,NOPT,NCOD,JOKE,(NA(I),I=1,5),(K000FX(J),J=1,10)
   1,(NFOR(K),K=1,13)
   76 FORMAT(28HOERROR IN SUBROUTINE PROBLEM18,5H NOPTI3,5H CODEI3,5H JO
   1KEI3/28I3)
   GO TO 90
   END
```

The data deck follows the program deck with the following information.

1. Problem Control Card. The problem control card is the first card in the data deck. This card contains the information given below.

a. IND, indicates the start of a problem. A -09 must be punched in Columns 1-3 (FORMAT I3).

b. NOPROB is the problem number punched in Columns 4-9 (FORMAT I6).

c. NOAT, the number of atoms, punched in Columns 10-12 (FORMAT I3).

Note: The number of atoms must be less than or equal to 25.

d. NCOR, the number of internal coordinates. NCOR is punched in Columns 13-15 (FORMAT I3).

e. NF, the number of force constants, punched in Columns 16-18 (FORMAT I3).

Note: The number of force constants must be 100 or less, except in those cases where F is to be evaluated, then the number of force constants must be 50 or less. (Force constant is used here to mean, more specifically, force constant parameter.)

f. IFF, a 1 signifies that the force constants are included with the input and that the F matrix is to be evaluated. IFF is punched in Column 20 or is left blank (FORMAT I2).

g. NOFF is the number of non-Urey-Bradley constants to be specified or the number of SVQFF interaction constants. NOFF is punched in Columns 21-23 (FORMAT I3).

h. INFRA, a 1 will cause the intermediate GEM, TETRA, and CIS matrices (UBFF) to be written out. INFRA is punched in Column 25 or left blank (FORMAT I2).

i. PUNCH, a 1 will suppress the card punching of the  $\tilde{Z}$  matrix. PUNCH is placed in Column 27 (FORMAT I2).

j. NOX, if NOX = 1, the cartesian coordinates are not read in, and the atom distance check is not computed. NOX is punched in Column 29 (FORMAT I2).

Warning: This option is available for the SVQFF only; the cartesian coordinates must be included for the UBFF.

2. Problem Information Cards. Two problem information cards follow the problem control card. These cards contain any desired alphanumeric information about the problem or may be left blank. The data may be punched in any column through 72, but Columns 1-3 should be left blank (FORMAT 18A4).

Warning: The problem information cards must be included with the input data, even if they are left blank.

3. The Cartesian Coordinates. If  $NOX = 0$ , the cartesian coordinates must be included at this point in the data deck. The cards should have been punched in proper format by CART, and the last row number should be a -1 [FORMAT 4(2I3,F12.6)].
4. Diagonal Force Constants. The position of the element (row or column number) and force constant parameter number of the diagonal elements of the UBFF or SVQFF are punched on cards in 24 fields of three columns each (FORMAT 24I3).
5. Interaction Force Constants. The row, column, and force constant parameter number for each of the off-diagonal elements of the SVQFF or for each non-Urey-Bradley interaction constant (FORMAT 24I3).
6. Two Blank Cards. For the computation of a UBFF, the configuration "vectors" are placed at this point [see Schachtschneider (89) for details] (FORMAT 24I3) followed by two blank cards. For a SVQFF one only needs the two blank cards at this point in the data deck.
7. Force Constant Parameters. If  $IFF = 1$ , i.e., the  $F$  matrix is to be evaluated, the force constant parameters are included in the data deck, six constants per card (FORMAT 6F12.6).  
Warning: In this case, the number of force constants must not exceed 50. Also, the dimension statement must be modified so that one has  $F(50,50)$ .
8. Data Termination Card. The data are followed by a card denoting the end of the problem. This card must have a 999 punched in Columns 1-3 (FORMAT I3).

Note: If another problem is to be included in the data deck, it may be placed at this point with the problem control card replacing the data termination card which then goes to the end of the second problem.

In the RAX operating system, the data deck is preceded by a /DATA card and the deck ended with a /END card.

#### OUTPUT INFORMATION

The following data are printed out at the option of the user.

1. The cartesian coordinates, if included with the input.
2. The diagonal elements of the  $\underline{Z}$  matrix.
3. The non-Urey-Bradley interaction elements or the SVQFF off-diagonal elements.

4. The Urey-Bradley configuration "vectors."
5. The intermediate GEM, TETRA, and CIS matrices.
6. The  $\underline{Z}$  matrix.
7. The  $\underline{F}$  matrix.
8. The atom distance check, if the cartesian coordinates are included with the input data.

The  $\underline{Z}$  matrix is punched on cards, if requested, in a form suitable for use in ZSYM, FADJ, FLPO, and EIGV. The data are arranged in the order of row, column, force constant number, and numerical value of  $\underline{Z}$  matrix element [FORMAT (6(3I3,F9.6))].

#### ZSYM

This program symmetrizes the  $\underline{Z}$  matrix by transforming the internal coordinates to symmetry coordinates. Input to ZSYM includes the  $\underline{Z}$  matrix elements and the  $\underline{U}$  matrix (the transformation matrix from internal coordinates to symmetry coordinates). ZSYM can be used to factor the  $\underline{Z}$  matrix for the UBFF, SVQFF, VFF, and other constrained force fields. The resulting factored  $\underline{Z}$  matrix is punched onto cards in the proper format for input to FADJ, FLPO, and EIGV.

The program was written by J. H. Schachtschneider (89) and modified for use in this investigation. The program may be used with the IBM 360/44 RAX operating system.

A flow diagram for ZSYM is presented in Fig. 39 and the program listing in Table XLIX.

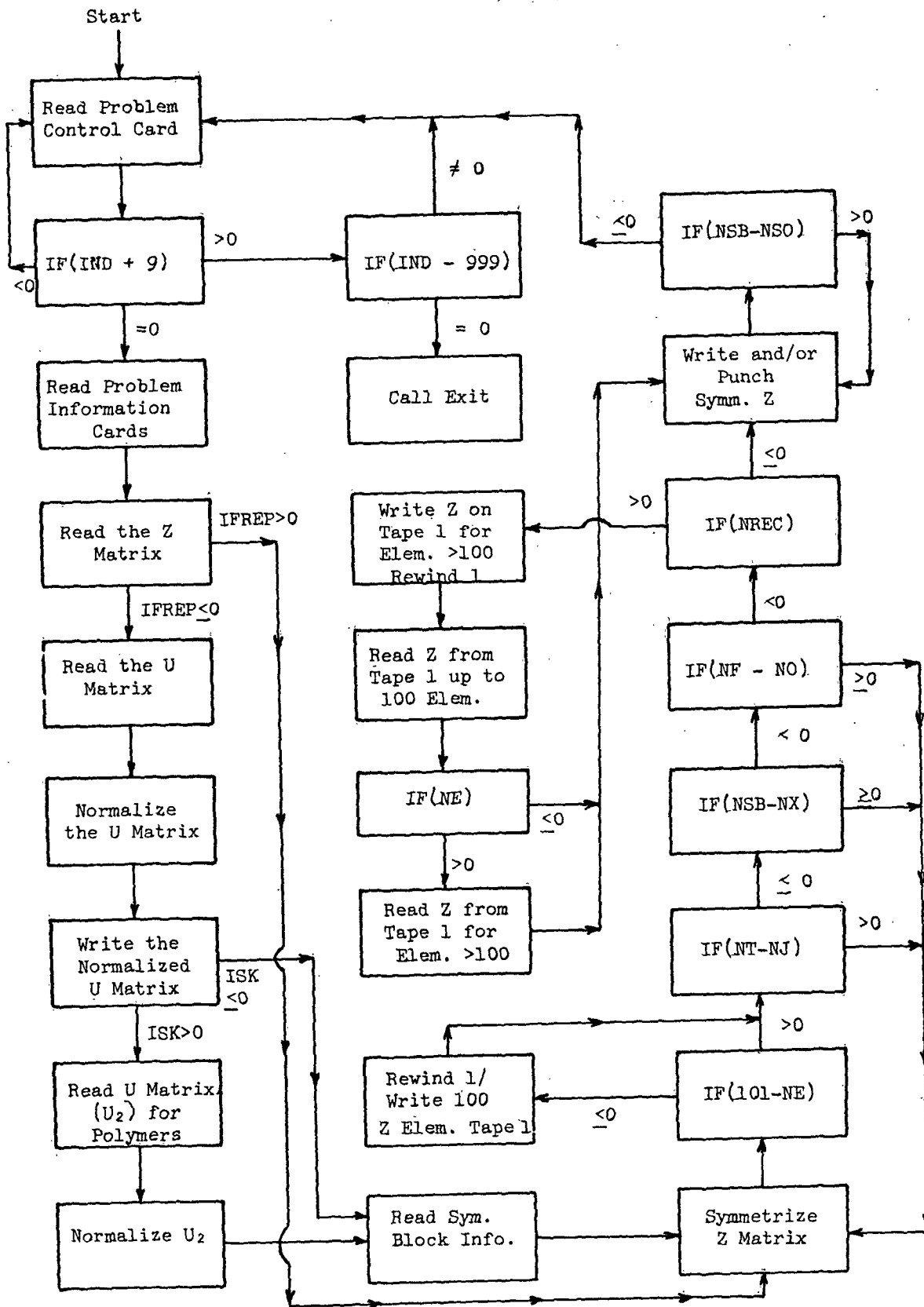


Figure 39. The Flow Diagram of ZSYM

TABLE XLIX

LISTING OF ZSYM

```
C ZSYM SD-4082 Z SYMMETRIZE POLYMER OPTION
C CODED IN FORTRAN IV FOR THE IBM-360/44 SCHACHTSCHNEIDER
C MODIFIED FOR RAX BY L J PITZNER 4/2/71
C THIS PROGRAM SYMMETRIZES A Z MATRIX. F MATRIX ELEMENTS IN
C VALENCE FORCE SPACE ARE SPECIFIED BY AN ARRAY Z(I,J,K) WHERE
C I IS ROW NUMBER OF F MATRIX ELEMENT
C J IS COLUMN NUMBER OF F MATRIX ELEMENT
C K IS THE NUMBER OF AN INDEPENDENT FORCE CONSTANT
C THE ELEMENT F(I,J) IS DEFINED AS Z(I,J,K)*VALUE OF FORCE CONSTANT
C DIMENSION NR(1500),NC(1500),NFO(1500),DZ(1500),NRU( 150),
1 NCU( 150),DU( 150),NRI( 150),NCI( 150),DU1( 150),NRZ(250),
2 NCZ(250),Z(250),NBL(101),NRS(101),NCS(101),NFC(101),FS(101),
3 NB1(1500),DA(250),U(250),FU(250),UF(250),RECORD(36),NB(20),NRO(4),
4 NCO(4),NPI(4),DAT(4)
C EQUIVALENCE(DA(1),U(1),UF(1)),(NB1(1),NRZ(1)),(NB1(251),NCZ(1)),
1(NB1(502),Z(1))
C RECONVERT PROBLEM CONTROL CARD CONTAINING FOLLOWING INFORMATION
C 1.IND=-09 INDICATING THE START OF A PROBLEM IN COLUMNS 1-3.
C 2.NQ, THE NUMBER OF INTERNAL COORDINATES. LESS THAN 601. PUNCHED
C IN COLUMNS 4-7.
C 3.NF, THE NUMBER OF FORCE CONSTANTS IN COLUMNS 8-11.
C 4.NS, THE NUMBER OF SYMMETRY COORDINATES IN COLUMNS 12-15.
C 5.NSB, THE NUMBER OF FACTORED BLOCKS+1 IN COLUMNS 16-19.
C 6.IFSK, POLYMER CONTROL OPTION
C IFSK=0, NORMAL MOLECULE READ ONE U MATRIX.
C IFSK=1, POLYMER READ U1 AND U2.
C IFSK PUNCHED IN COLUMN 23.
C 7.IFREP, REPEAT OPTION CONTROL
C FOR IFREP=1 ONLY NEW Z MATRIX IS READ AND U FROM PREVIOUS
C PROBLEM IS USED TO SYMMETRIZE.
C IF IFREP=0 NEW PROBLEM
C PUNCHED IN COLUMN 27.
C 8.NST, STARTING INDEX FOR DO LOOP ON FORCE CONSTANTS FOR
C IFREP=1. NST IS PUNCHED IN COLUMNS 28-31.
C 9.FPUN, CARD-PUNCH SUPPRESSION OPTION FOR THE SYMMET.Z-MATRIX.
C IF FPUN =1 CARD-PUNCHING OF THE Z-MATRIX IS SUPPRESSED. IF FPUN
C =0 THERE IS NO SUPPRESSION. PUNCHED IN COL. 35.
C READ PROBLEM CONTROL CARD
90 READ ( 5,12)IND,NQ,NF,NS,NSB,IFSK,IFREP,NST,FPUN
12 FORMAT(I3,8I4)
IF(IND+9)90,92,94
C INPUT DATA FOLLOWS IN ORDER
C 1.TWO PROBLEM INFORMATION CARDS.
C 2.Z MATRIX ELEMENTS
C 3.U MATRIX(U1 FOLLOWED BY U2 FOR IFSK=1)
C 4.SYMMETRY BLOCK INFORMATION
94 IF(IND-999)90,96,90
96 CALL EXIT
92 CONTINUE
READ (5,14)(RECORD(I),I=1,36)
```



TABLE XLIX (Continued)

```
GO TO 141
145 DSQ=DSQ+DAT(L)**2
    NOU=NOU+1
    NRU(NO)=NRD(L)
    NCU(NO)=NCO(L)
    DU(NO)=DAT(L)
150 CONTINUE
    GO TO 130
152 IF(3+NRD(L))605,154,605
154 DA(NX)= 1.0 / SQRT(DSQ)
    IF(NS-NX)605,156,605
156 WRITE(6,13352)NOU
13352 FORMAT(1H , 'NOU= ',I4)
    DO 158 I=1,NOU
    J=NRU(I)
158 DU(I)=DA(J)*DU(I)
    NOU=NOU+1
    NRU(NO)=-3
    NCU(NO)=0
    DU(NO)=0.0
    WRITE(6,75875)
75875 FORMAT(1H0, 'NORMALIZED U-MATRIX')
    WRITE(6,18)(NRU(I),NCU(I),DU(I),I=1,NOU)
    IF(IFSK)180,180,160
160 NU=0
    NX=1
C   READ U2 (SAME FORMAT AS U1)
162 READ (5,18)(NRD(L),NCO(L),DAT(L),L=1,4)
    DO 174 L=1,4
    IF(NRD(L))176,174,164
164 IF(NS-NRD(L))605,165,165
165 IF(NRD(L)-NX)605,168,166
166 NX=NX+1
    GO TO 165
168 NU=NU+1
    NR1(NU)=NX
    NC1(NU)=NCO(L)
    DU1(NU)=DAT(L)*DA(NX)
174 CONTINUE
    GO TO 162
176 IF(3+NRD(L))605,75812,605
75812 WRITE(6,37812)NU
37812 FORMAT(1H , 'NU = ',I4)
    GO TO 185
180 NU=NOU-1
    DO 184 K=1,NU
    NR1(K)=NRU(K)
    NC1(K)=NCU(K)
184 DU1(K)=DU(K)
C   READ SYMMETRY BLOCK INFORMATION. ROW NUMBERS OF THE BEGINNING OF
C   EACH FACTORED BLOCK. LAST ELEMENT IS NS+1. PUNCHED IN 3 COLUMN
C   FIELDS 24 PER CARD.
```

TABLE XLIX (Continued)

```
185 READ (5,20){NB(I),I=1,NSB)
20 FORMAT(24I3)
NO=1
186 NZ=0
DO 190 K=1,NOZ
IF(NO-NFD(K))190,188,190
188 NZ=NZ+1
NRZ(NZ)=NR(K)
NCZ(NZ)=NC(K)
Z(NZ)=DZ(K)
190 CONTINUE
WRITE(6,99853)NO,NZ
99853 FORMAT(1H,'NO = ',I4,4X,'NZ = ',I4)
63521 IF(NZ)600,192,220
192 NO=NO+1
IF(NO-NF)186,186,295
220 NL=1
NX=2
NUT=1
NUB=1
NJ=1
230 NP=NB(NL)
NT=NB(NX)
236 DO 238 I=1,NQ
FU(I)=0.0
238 U(I)=0.0
DO 250 K=NUB,NOU
IF(NRU(K)-NJ)240,248,240
240 DO 246 L=1,NZ
I=NRZ(L)
J=NCZ(L)
FU(I)=FU(I)+Z(L)*U(J)
IF(I-J)244,246,244
244 FU(J)=FU(J)+Z(L)*U(I)
246 CONTINUE
GO TO 252
248 JU=NCU(K)
250 U(JU)=DU(K)
252 NUB=K
88971 DO 254 I=NJ,NS
254 UF(I)=0.0
LL = 0
41411 DO 265 L=NUT,NU
IF(LL)262,262,264
262 IF(NR1(L)-NJ)605,264,263
263 LL = 1
NWY=L
264 I=NR1(L)
J=NC1(L)
265 UF(I)=UF(I)+DU1(L)*FU(J)
NUT=NWY
DO 280 J=NJ,NS
IF(0.00005-ABS(UF(J)))270,280,280
```

TABLE XLIX (Continued)

```
270 IF(NT-J)271,271,272
271 WRITE (6,72)NJ,J
72 FORMAT(40H0 ERROR,ERROR,ERROR- Z NOT FACTORING.ROWI4,7H COLUMNI4)
272 NE=NE+1
IF(101-NE)273,273,274
273 WRITE(1)(NBL(I),NRS(I),NCS(I),NFC(I),FS(I),I=1,100)
NREC=NREC+1
NE=1
274 NRS(NE)=NJ-NP+1
NCS(NE)=J-NP+1
NBL(NE)=NL
NFC(NE)=NO
FS(NE)=UF(J)
280 CONTINUE
NJ=NJ+1
IF(NT-NJ)284,284,236
284 NL=NL+1
NX=NX+1
IF(NSB-NX)290,230,230
290 NO=NO+1
IF(NF-NO)295,186,186
295 IF(NREC)296,296,298
296 NOZ=0
GO TO 321
298 WRITE(1)(NBL(I),NRS(I),NCS(I),NFC(I),FS(I),I=1,NE)
300 END FILE 1
REWIND 1
302 DO 312 L=1,NREC
READ (1)(NBL(I),NRS(I),NCS(I),NFC(I),FS(I),I=1,100)
DO 312 K=1,100
NZ=100*(L-1)+K
NBL(NZ)=NBL(K)
NR(NZ)=NRS(K)
NC(NZ)=NCS(K)
NFO(NZ)=NFC(K)
312 DZ(NZ)=FS(K)
NOZ=NZ
315 IF(NE)330,330,320
320 READ (1)(NBL(I),NRS(I),NCS(I),NFC(I),FS(I),I=1,NE)
321 DO 324 K=1,NE
NZ=NOZ+K
NBL(NZ)=NBL(K)
NR(NZ)=NRS(K)
NC(NZ)=NCS(K)
NFO(NZ)=NFC(K)
324 DZ(NZ)=FS(K)
330 NSO=1
331 NT=0
NX=0
332 WRITE (6,64)IND,NSO,(RECORD(I),I=1,12)
IF(FPUN)87551,87551,75571
87551 WRITE (7,9119)IND,NSO,(RECORD(I),I=1,12)
```

TABLE XLIX (Continued)

```
64 FORMAT(1H0I3,15H Z MATRIX BLOCKI3,12A4)
9119 FORMAT(I3,15H Z MATRIX BLOCKI3,12A4)
75571 DO 340 I=1,NZ
      IF(NSO-NB1(I))340,336,340
336 NX=NX+1
      IF(101-NX)337,337,338
337 WRITE (6,66)(NRS(L),NCS(L),NFC(L),FS(L),L=1,100)
      IF(FPUN)52151,52151,37751
52151 WRITE (7,7131)(NRS(L),NCS(L),NFC(L),FS(L),L=1,100)
66 FORMAT(1H 3I3,F9.6,3I3,F9.6,3I3,F9.6,3I3,F9.6,3I3,F9.6,3I3,F9.6)
7131 FORMAT(3I3,F9.6,3I3,F9.6,3I3,F9.6,3I3,F9.6)
37751 NT=NT+100
      NX=1
338 NRS(NX)=NR(I)
      NCS(NX)=NC(I)
      NFC(NX)=NFO(I)
      FS(NX)=DZ(I)
340 CONTINUE
      IF(NX)344,344,342
342 WRITE (6,66)(NRS(L),NCS(L),NFC(L),FS(L),L=1,NX)
      IF(FPUN)58888,58888,63333
58888 WRITE (7,7131)(NRS(L),NCS(L),NFC(L),FS(L),L=1,NX)
63333 NT=NT+NX
344 WRITE (6,76)NT
      IF(FPUN)85851,85851,99887
85851 WRITE (7,1211)NT
76 FORMAT(1H0,5H NOZ=I4)
1211 FORMAT(5H NOZ=I4)
99887 NSO=NSO+1
      IF(NSB-NSO)90,90,331
600 WRITE (6,56)L,NRO(L),NCO(L),NPI(L),DAT(L)
56 FORMAT(23H0 Z MATRIX ERROR FIELDI3,6H READS3I4,F12.6)
GO TO 90
605 WRITE (6,58)L,NRO(L),NCO(L),DAT(L)
58 FORMAT(23H0 U MATRIX ERROR FIELDI3,6H READS2I4,F12.6)
GO TO 90
END
```

INSTRUCTIONS FOR PROGRAM USE

ZSYM requires the use of a scratch tape. If the program is being used with the RAX system, the program deck is preceded by /ID, /JOB GO, and /FILE cards.

The program deck is followed by the input data which consist of the following information.

1. Problem Control Card. This is the first card of the data deck. The following data are punched on each problem control card.
  - a. IND, indicates the start of a problem. IND must be set equal to -09 and is punched in Columns 1-3 (FORMAT I3).
  - b. NQ is the number of internal coordinates, punched in Columns 4-7 (FORMAT I4).
  - c. NF is the number of force constant parameters, punched in Columns 8-11 (FORMAT I4).
  - d. NSB, denotes the number of factored blocks plus 1 and is punched in Columns 16-19 (FORMAT I4).
  - e. IFSK is the polymer control option. For a normal molecule, IFSK = 0 and only one U matrix is read in. For a polymer, IFSK = 1 and two U matrices,  $U_1$  and  $U_2$ , are read in. IFSK is punched in Column 23 (FORMAT I4).
  - f. IFREP is the repeat option control. If a new problem is to be started, IFREP = 0, and new Z and U matrices are read in. If IFREP = 1, a new Z matrix is read in, but the U matrix from the previous problem is used for symmetrization. IFREP is punched in Column 27 (FORMAT I4).
  - g. NST is the starting index for the DO loop on force constants. This constant must be entered when IFREP = 1, otherwise, NST = 0 or is left blank. NST is punched in Columns 28-31 (FORMAT I4).
  - h. FPUN is the card punch suppression option. If FPUN = 1, the factored Z matrix is not punched on cards. FPUN is positioned in Column 35 (FORMAT I4).

2. Problem Information Cards. Two problem information cards follow the control card. These cards contain whatever alphanumeric information about the problem may be desired by the user. The information may be punched in any of the columns through Column 72 except that Columns 1-3 should be left blank (FORMAT 18A4).

Warning: These cards must be included in the data deck even if they are left blank.

3. Z Matrix. The Z matrix, punched in the proper format by UBZM, follows the problem information cards in the data deck. There are four Z matrix elements per card; each element consists of row number, column number, force constant parameter number, and numerical Z matrix element [FORMAT 4(3I3,F9.6)]. The row number after the last element must be -2.

4. U Matrix. The U matrix follows with the form: row, column, and U matrix element [FORMAT 4(2I3,F12.6)]. The row number after the last element must be -3.

Note: The zero elements need not be included or the matrix normalized.

5. U<sub>2</sub> Matrix. If IFSK = 1, the second U matrix, U<sub>2</sub>, must follow the first U matrix. The format is the same for the first matrix.

6. Symmetry Block Information Card. This card contains the row numbers of the beginning of each factored block. The last element is NS + 1. These data are punched in 3 column fields of which there are 24 per card (FORMAT 24I3).

7. Data Termination Card. This card is placed at the end of the data deck and is used to denote the end of the input data for the problem(s) to be worked. The data termination card is marked by a 999 punched in Columns 1-3 (FORMAT I3).

Note: If another problem is to be included with the input data, the problem control card for the next problem is placed at this point in the deck, and the data termination card is placed at the end of the second problem.

Warning: Failure of the Z matrix to factor most often indicates a user error.

With the RAX system, the data deck is preceded by a /DATA card and terminated by a /END card.

#### OUTPUT INFORMATION

The factored Z matrix is printed out and at the user's option, punched on cards in the proper format.

FADJ

This program solves the vibrational secular equation by the method of successive orthogonalization followed by diagonalization. The diagonalization is performed by the subroutine HDIAG which employs the Jacobi method. This program will also refine an initial set of force constants to give a linear weighted least squares "fit" between the calculated and observed frequencies. (This program is based on the Gauss-Newton-Raphson method.) At the user's option, a regression analysis is performed by the subroutine, REGRS, which may aid in the selection of the proper force field.

This program was written by J. H. Schachtschneider (89) and modified for this investigation. The program may be used with the IBM 360/44 OS operating system. FADJ employs a phase overlay procedure for the subroutines and is permanently stored on disk at the Institute.

A flow diagram of FADJ is given in Fig. 40 and 41. A listing of the JCL cards for the stored version of FADJ are listed in Table L. These cards are to be placed in front of the data deck and replace the program deck which is stored on disk in compiled form. A listing of FADJ appears in Table LI.

INSTRUCTIONS FOR PROGRAM USE

FADJ requires two scratch tapes or disks. (Two scratch disks have been allotted for the stored version of FADJ.) The following data comprise the input information.

1. Problem ID Card. This card designates the start of a new problem. This card must have a -09 punched in Columns 1-3 (FORMAT I3).
2. Problem Control Card.

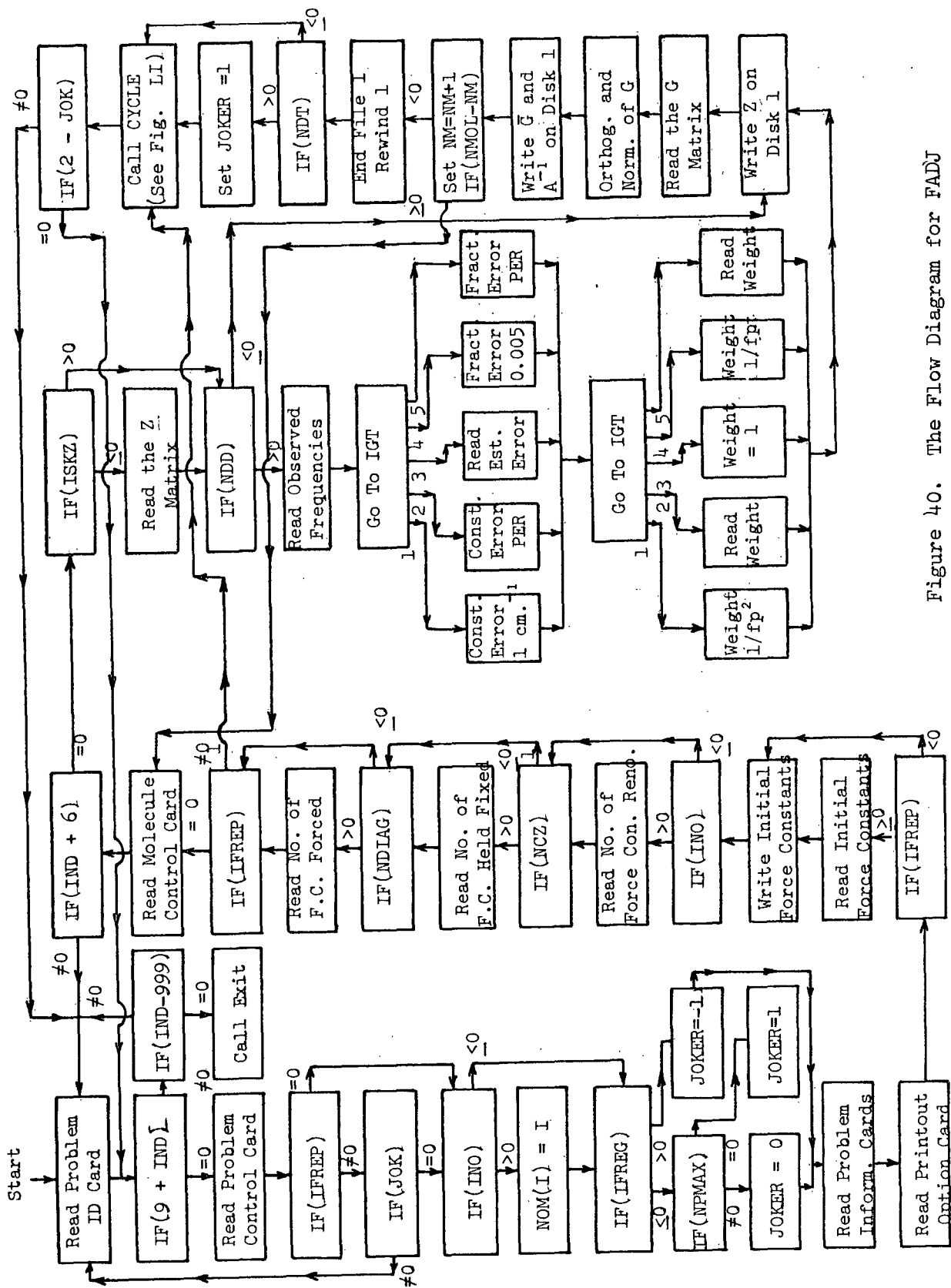


Figure 40. The Flow Diagram for FADJ



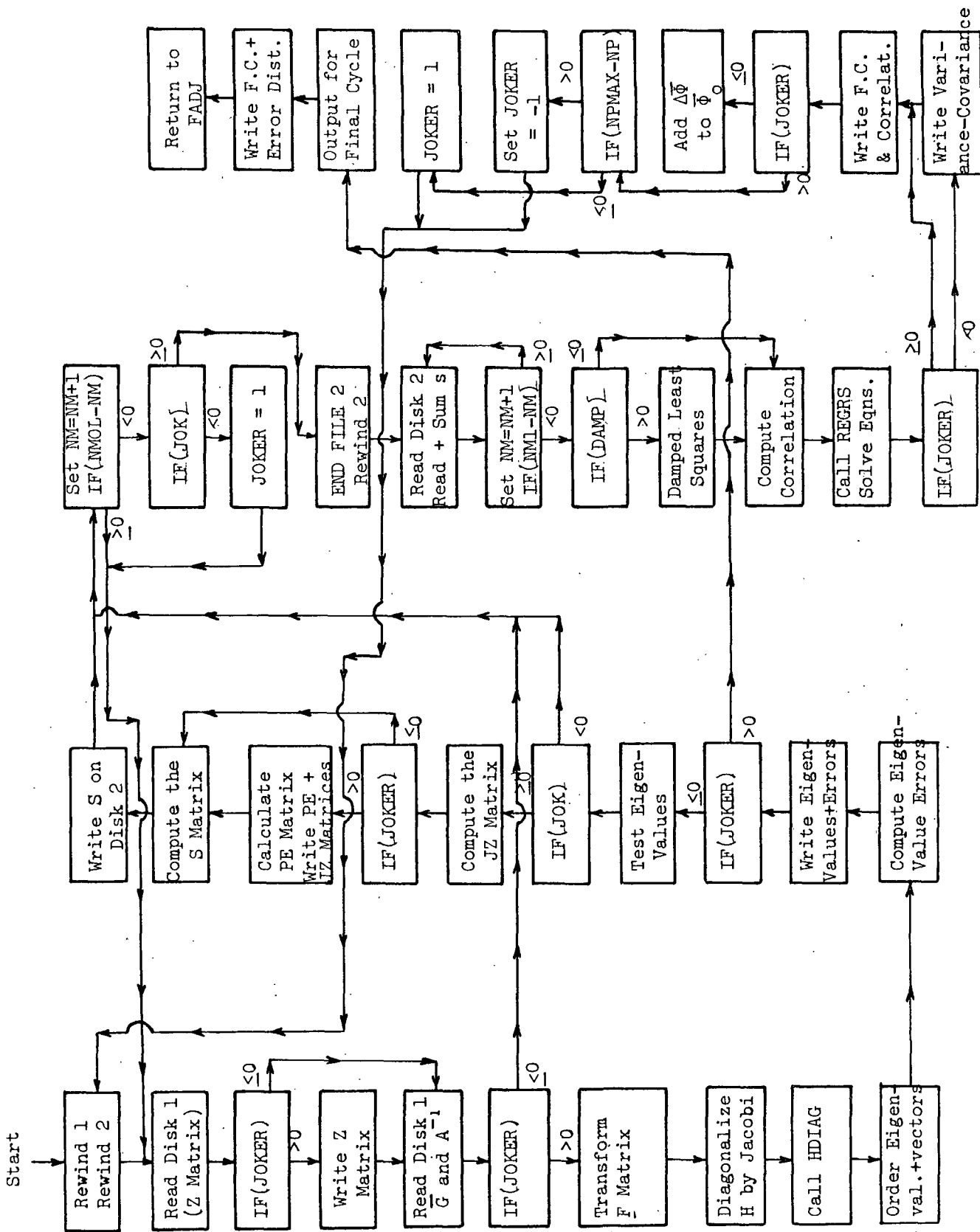


Figure 41. The Flow Diagram for Subroutine CYCLE

TABLE LI (Continued)

- 1. IND=-09, INDICATING THE START OF A PROBLEM IN COLUMNS 1-3.
- 2. NOPROB, THE PROBLEM NUMBER. IN COLUMNS 4-9.
- 3. NMOL, THE NUMBER OF MOLECULES, IN COLUMNS 10-12.
- 4. NF, THE NUMBER OF FORCE CONSTANTS IN COLUMNS 13-15.  
LESS THAN 71
- 5. NPMAX, THE MAXIMUM NUMBER OF PERTURBATIONS DESIRED, COLUMNS  
16-18. (LESS THAN 20)
- 6. NCZ, THE NUMBER OF FORCE CONSTANTS TO BE HELD FIXED, IN COLUMNS  
19-21. (LESS THAN 71)
- 7. IFREP=1, IF ONLY A NEW SET OF FI(I), AND NCF(I) ARE TO BE  
READ IN. DE, P, W, U, Z, AND G FROM PREVIOUS PROBLEM ARE USED.  
IFREP=0, IF A NEW PROBLEM IS TO BE STARTED.  
IFREP=-1, FINAL FI(I) FROM PREVIOUS PROBLEM ARE USED AS INITIAL  
FI(I). NEW NCF(I) ARE READ. ZS FROM PREVIOUS PROBLEM MAY BE  
RENUMBERED. PUNCHED IN COLUMNS 22-23.
- 8. IFER=-3, -2, -1, 0, 1 PUNCHED IN COLUMNS 24-25  
FOR IFER=1 PER IS READ IN AND USED AS A FRACTIONAL ERROR  
FOR IFER=0 PER= 0.005 USED AS A FRACTION  
FOR IFER=-1 ESTIMATED ERRORS ARE READ IN FOR EACH OBS.FREQ.  
INPUT FOLLOWS OBS.FREQ.  
FOR IFER=-2 ERROR IN ALL FREQ. ASSUMED TO BE PER CM-1  
FOR IFER=-3 PER=1.0 CM-1 FOR ALL OBS. FREQ.
- 9. PER AN ERROR TO BE ASSUMED FOR ALL OBS.FREQ.  
A FRACTION IF IFER=1 IN CM-1 IF IFER=-2  
PUNCHED IN COLUMNS 26 TO 33 WITH DECIMAL BETWEEN COL.  
27 AND 28 OR PUNCHED

CONTINUE

- 10. DMX, A FRACTIONAL FACTOR TO BE APPLIED TO THE FORCE  
CONSTANT PERTURBATION ON EACH CYCLE ( FOR DAMPING OSCILATION)  
PUNCHED IN COLUMNS 34 TO 41 WITH THE DECIMAL BETWEEN COLUMNS  
37 AND 38 OR PUNCHED.
- 11. IFREG PUNCHED IN COLUMNS 42 AND 43  
IFREG=0 FOR NO REGRESSION  
IFREG=-1 FOR REGRESSION ON CYCLE 4.  
IFREG=1 FOR REGRESSION ON CYCLE 1
- 12. NDIAG, THE NUMBER OF FORCE CONSTANTS TO BE INCLUDED IN  
ALL REGRESSIONS. PUNCHED IN COLUMNS 44 THROUGH 46.
- 13. INO, THE NUMBER OF FORCE CONSTANTS TO BE RENUMBERED.  
PUNCHED IN COLUMNS 47-49.
- 14. NIP PUNCHED IN COLUMNS 50 THROUGH 52.  
SPACING BETWEEN REGRESSIONS EQUALS 3-NIP. NIP MAY BE NEGATIVE.
- 15. DAMP, DAMPING FACTOR FOR DAMPED LEAST SQUARES. FOR DAMP GREATER  
THAN ZERO DAMP\*MAX(S(I,I)) IS ADDED TO THE DIAGONAL TERMS OF  
THE NORMAL EQUATIONS ON EACH PERTURBATION CYCLE. A VALUE OF  
DAMP=0.001 WILL USUALLY CAUSE VERY ILL-CONDITIONED PROBLEMS TO  
CONVERGE. DAMP IS PUNCHED IN COLUMNS 53-58 WITH THE DECIMAL  
BETWEEN COLUMNS 53 AND 54 OR PUNCHED.
- 16. RAP, THE CUT-OFF FACTOR FOR THE JACOBI DIAGONALIZATION.  
THE JACOBI ROTATIONS ARE STOPPED WHEN MAX(H(I,J)) IS LESS  
THAN RAP\*MIN(H(I,I)). IF RAP IS NOT ENTERED IT IS TAKEN EQUAL  
TO 0.5E-2. ON THE THE FINAL CYCLE RAP IS SET EQUAL TO  
0.5E-3 GIVING EIGENVALUES TO 6 SIGNIFICANT FIGURES AND EIGEN-

TABLE LI (Continued)

```
C      VECTORS TO 3 OR 4 FIGURES.
C      RAP IS PUNCHED IN COLUMNS 59-63 WITH THE DECIMAL BETWEEN
C      COLUMNS 59 AND 60 OR PUNCHED.
      CONTINUE
C      17.FRAC, A FRACTIONAL FACTOR FOR DECREASING RAP ON EACH CYCLE.
C      AFTER EACH PERTURBATION RAP IS SET EQUAL TO FRAC*RAP.
C      IF FRAC IS NOT ENTERED IT IS TAKEN EQUAL TO 0.9.
C      FRAC IS PUNCHED IN COLUMNS 64-67 WITH THE DECIMAL BETWEEN
C      COLUMNS 64 AND 65 OR PUNCHED.
C      18.CUTOF, THE NUMBER OF PERTURBATIONS AFTER WHICH DMX SET = 0.0
C      PUNCHED IN COLUMNS 68-72.
      90 READ(5,96001)IND
96001  FORMAT(I3)
      IF(9+IND)901,91,901
      901 IF(IND-999)90,9020,90
      9020 CALL EXIT
      91 READ ( 5,4)IND,NOPROB,NMOL,NF,NPMAX,NCZ,IFREP,IFER,PERC, DMX,IFREG
      1,NDIAG,INO,NIP,DAMP,RAP,FRAC,CUTOF
      4  FORMAT(I3,I6,4I3,2I2,F8.6,F8.4,I2,I3,I3,I3,F6.5,F5.4,F4.3,I5)
      REWIND 1
      REWIND 2
      93 IF(IFREP)800,802,800
      800 IF(JOK)90,801,90
      801 IF(INO)805,805,803
      802 PER=PERC
      803 DO 804 I=1,70
      804 NOM(I)=I
      805 NP=0
      NX=1
      ER=0.0
      ERP=0.0
      DO 806 I=1,50
      NPN(I)=0
      806 NPL(I)=0
      NCZS=NCZ
      NCYC=1
      LIMIT=2*(NF-NCZ)
      NOVAR=NF+1
      NOVMI=NF
      IF(RAP)807,807,808
      807 RAP=0.5E-2
      808 DO 810 I=1,NF
      810 NFX(I)=0
      IF(FRAC)811,811,812
      811 FRAC=0.9
      812 JOK=0
      JET=0
      IF(IFREG)94,94,95
      94 IF(NPMAX)940,942,940
      940 JOKER=0
      GO TO 96
      942 JOKER=1
```

TABLE LI (Continued)

```
GO TO 96
95 JOKER=-1
C READ PROBLEM INFORMATION CARDS. 3 CARDS CONTAINING INFORMATION
C ABOUT THE PROBLEM. CARDS MUST BE INCLUDED EVEN IF BLANK.
96 READ (5,6)(RECORD(I),I=1,54)
6 FORMAT(18A4)
WRITE (6,8)NOPROB,NMOL,NF,NPMAX,NCZ,(RECORD(I),I=1,54)
8 FORMAT(13H1 PROBLEM NO.18,6H NMOL=14,4H NF=14,7H NPMAX=14,5H NCZ=I
14/(12X,18A4))
C READ PRINT-OUT OPTION CARD
C A VALUE OF 0 FOR IXX CAUSES PRINT-OUT OF THE INFORMATION IXX
C CONTROLS.
C A VALUE OF 1 FOR IXX WILL SUPPRESS THE PRINT-OUT OF THE INFORMATION
C CONTROLLED BY IXX.
C IXX IS OF FORMAT 11.
C THE PRINTED INFORMATION CONTROLLED BY THE VARIOUS IXX ARE DEFINED
C BELOW
C IXX CONTROLS THE PRINT-OUT OF
C 1). 101 THE Z MATRIX.
C 2). 102 THE EIGEN VALUES AND EIGENVECTORS.
C 3). 103 THE JX MATRIX.
C 4). 104 THE POTENTIAL ENERGY MATRIX.
C 5). 105 THE CORRELATION MATRIX.
C 6). 106 THE VARIANCE-COVARIANCE MATRIX.
C 7). 107 THE ERROR DISTRIBUTION
C 8). 108 A 1 CAUSES PRINT-OUT OF FINAL SET OF FORCE CONSTANTS.
C 9). 109 A 1 CAUSES BYPASS OF TEST FOR UNREASONABLE EIGENVALUES.
READ(5,90041)I01,I02,I03,I04,I05,I06,I07,I08,I09
90041 FORMAT( 9I1)
IF(IFREP)9602,9601,9601
C READ INTIAL FORCE CONSTANTS
C THE FORCE CONSTANTS ARE PUNCHED IN 12 COLUMN FIELDS 6 PER CARD
C WITH THE DECIMAL BETWEEN COLUMNS 6 AND 7 OR PUNCHED. IN ORDER
C 1 THROUGH NF.
9601 READ (5,20)(FI(I),I=1,NF)
20 FORMAT(6F12.6)
9602 WRITE (6,61)NP,(I,FI(I),I=1,NF)
61 FORMAT(23H0 FORCE CONSTANTS AFTER14,15H PERTURBATIONS./(16,F12.6))
90042 IF(INO)9610,9610,9603
C READ FORCE CONSTANT RENUMBERING
C NF1(I)=OLD NUMBER NF2(I)= NEW NUMBER
9603 READ (5,7) (NF1(I),NF2(I),I=1,INO)
7 FORMAT(24I3)
DO 9605 I=1,INO
JX=NF1(I)
9605 NOM(JX)=NF2(I)
90002 WRITE (6,9) (NF1(I),NF2(I),I=1,INO)
9 FORMAT(14H0 Z RENUMBERED / (16,4H TO I3))
9610 IF(NCZ)9614,9614,9612
C READ NUMBERS OF FORCE CONSTANTS TO BE HELD FIXED
C THESE NUMBERS ARE USED TO ELIMINATE ROWS AND COLUMNS FROM
C THE PERTURBATION MATRIX S.
C PUNCHED IN 3 COLUMN FIELDS 24 PER CARD. IF NCZ=0 ALL FORCE
C CONSTANTS ARE ADJUSTED.
```

TABLE LI (Continued)

```
9612 READ (5,7) (NCF(L),L=1,NCZ)
      DO 9613 I=1,NCZ
        JX=NCF(I)
9613 NFX(JX)=-1
9614 IF(NDIAG)9615,9615,9620
9615 NDIAG=NF-NCZ
      NIO=0
      DO 9617 I=1,NF
        IF(NFX(I))9617,9616,9617
9616 NIO=NIO+1
      NCON(NIO)=I
9617 CONTINUE
      GO TO 9624
C     READ NUMBERS OF FORCE CONSTANTS TO BE FORCED INTO REGRESSION.
C     FORCE CONSTANTS IN THIS LIST ARE ENTERED INTO THE REGRESSION
C     EQUATION WITHOUT REGARD TO TESTS FOR SIGNIFICANCE
C     ON THE REGRESSION OPTION FORCE CONSTANTS IN THIS LIST
C     ARE ADJUSTED ON EACH CYCLE.
9620 READ (5,7) (NCON(I),I=1,NDIAG)
90003 WRITE (6,13) (NCON(I),I=1,NDIAG)
      13 FORMAT(47H0 FORCE CONSTANTS ALWAYS INCLUDED IN REGRESSION/(15I4))
9624 IF(NCZ)9630,9630,9625
9625 WRITE (6,25) (NCF(L),L=1,NCZ)
      25 FORMAT(39H0 NUMBERS OF FORCE CONSTANTS HELD FIXED/(15I4))
9630 NM=1
      IF(IFREP)470,99,470
      99 SUM=0.0
      NDT=0
      PTOT=0.
      SCALE=1.0
C     READ MOLECULE CONTROL CARD.CONTAINING THE FOLLOWING INFORMATION
C     1.IND=-06, IDENTIFYING CONTROL CARD. IN COLUMNS 1-3
C     2.NQ, THE DIMENSION OF THE SECULAR EQUATION. COLUMNS 4-6.
C     3.NDD,THE NUMBER OF NON-ZERO EXPERIMENTAL FREQUENCIES. IN
C     COLUMNS 7-9.
C     4.NZZ, THE NUMBER OF Z MATRIX ELEMENTS. IN COLUMNS 10-13.
C     5. IFU IN COLUMNS 14-15 IGNORED BY PROGRAM.
C     6. IFW=1 OR -2, IF WEIGHTING ELEMENTS ARE INCLUDED WITH THE INPUT
C     IFW=0,-1,OR-3, IFWEIGHTING ELEMENTS ARE NOT INCLUDED.COLS.16-17
C     7. ISKZ=0, IF A NEW Z MATRIX IS TO BE READ IN FOR THE MOLECULE.
C     ISKZ=1, IF THE Z MATRIX FROM THE PREVIOUS MOLECULE IS TO BE
C     USED. E.G. ISOTOPIC MOLECULES . PUNCHED IN COLUMN 19.
100 READ (5,14)IND,NQ,NDD,NZZ,IFU,IFW,ISKZ
      14 FORMAT(3I3,14,3I2)
      IF(IND+6)900,101,900
C     INPUT DATA FOR EACH MOLECULE FOLLOW THE MOLECULE CONTROL
C     CARD IN THE ORDER
C     1.MOLECULE INFORMATION CARD, 1 CARD CONTAINING THE NAME OF THE
C     MOLECULE OR BLANK. (COLUMNS 1-3 MUST BE LEFT BLANK)
C     2.THE Z MATRIX
C     3.EXPERIMENTAL FREQUENCIES, NQ OF THEM FOR NDD GREATER THAN ZERO
C     IF NDD=0 NO FREQ. ARE ENTERED.
C     4.ESTIMATED ERRORS IN OBS.FREQ. FOR IFER=-1.
C     5.WEIGHTING ELEMENTS, IF IFW=1 OR -2
```

TABLE LI (Continued)

```

C      6. THE G MATRIX.
C      READ MOLECULE INFORMATION CARD
101 READ (5,6) (REC(I),I=1,18)
      ND=0
      IF(ISKZ)190,190,203
C      READ Z MATRIX
C      Z IS NOT STORED AS A MATRIX, BUT RATHER AS 4 ONE DIMENSIONAL
C      ARRAYS NR GIVING THE ROW NUMBER OF THE F MATRIX ELEMENT, NC
C      GIVING THE COLUMN NUMBER OF THE F MATRIX ELEMENT, NFO GIVING
C      THE NUMBER OF THE DISTINCT FORCE CONSTANT AND Z GIVING THE Z
C      MATRIX ELEMENT. NC MUST BE GREATER THAN OR EQUAL TO NR
C      ONLY NON-ZERO ELEMENTS ARE ENTERED.
C      THE Z ELEMENTS ARE PUNCHED IN 18 COLUMN FIELDS, 1 TO 4 PER CARD
C      COLUMNS 1-3 GIVE NR , COLUMNS 4-6 GIVE NC , COLUMNS 7-9 GIVE NFO,
C      AND Z IS PUNCHED IN COLUMNS 10-18 WITH THE DECIMAL BETWEEN
C      COLUMNS 12 AND 13 OR PUNCHED. NROW=-2 AFTER LAST ELEMENT.
C      TOTAL NUMBER OF Z MATRIX ELEMENTS MUST BE LESS THAN 651.
190 NOZ=0
191 READ (5,18) (NROW(L),NCOL(L),NPO(L),DATIN(L),L=1,4)
      18 FORMAT(4(3I3,F9.6))
      DO 196 L=1,4
      IF(NROW(L))198,196,192
192 IF(NQ-NCOL(L))1920,193,193
193 NOZ=NOZ+1
      NR(NOZ)=NROW(L)
      NC(NOZ)=NCOL(L)
      IXX=NPO(L)
      NFO(NOZ)=NOM(IXX)
      Z(NOZ)=DATIN(L)
196 CONTINUE
      GO TO 191
198 IF(NROW(L)+2)1920,203,920
203 IF( 650-NOZ)1920,204,204
204 IF(NDD)205,205,207
205 DO 206 I=1,NQ
      DX(I)=0.0
206 P(I)=0.0
      GO TO 270
C      READ OBSERVED FREQUENCIES. IF NDD IS GREATER THAN ZERO.
C      PUNCHED IN 12 COLUMN FIELDS 6 PER CARD, DECIMAL BETWEEN COLUMNS
C      6 AND 7 OR PUNCHED. ENTERED IN DECREASING ORDER IN EACH FACTORED
C      BLOCK. IF THE FREQUENCIES ARE UNKNOWN OR UNCERTIAN, OR ZERO
C      (REDUNDANCIES) ENTER A ZERO, FOR DEGENERATE ROOTS ENTER ONE
C      FREQUENCY AND THE REST ZERO. ANY FREQUENCY MAY BE GIVEN ZERO
C      WEIGHT IN THE PERTURBATION BY ENTERING A ZERO INSTEAD OF THE
C      ACTUAL FREQUENCY. FREQUENCIES ARE ENTERED IN WAVENUMBERS.
C      A TOTAL OF NQ ENTRIES, ND OF THEM MUST BE NON-ZERO.
207 READ (5,20) (DE(I),I=1,NQ)
C      COMPUTE THE FREQUENCY PARAMETERS FROM THE FREQUENCIES
      DO 209 I=1,NQ
      IF(DE(I))209,209,208
208 ND=ND+1
209 DX(I)=5.88852E-7*DE(I)*DE(I)
      N1=0

```

TABLE LI (Continued)

```
C      WEIGHT =E(I) / FREQ.PAR.      FOR IFW=1
241 DO 248 I=1,NQ
      IF(DX(I))247,247,242
242 N1=N1+1
      P(I)=E(N1) / (DX(I))
      PTOT=PTOT+P(I)
      IF(P(I))248,248,246
246 N2=N2+1
      GO TO 248
247 P(I)=0.0
248 CONTINUE
      NDT=NDT+N2
      GO TO 260

C      WEIGHT =1.0      FOR IFW=-1
250 DO 254 I=1,NQ
      IF(DX(I))253,253,251
251 P(I)=1.0
      PTOT=PTOT+1.0
      GO TO 254
253 P(I)=0.0
254 CONTINUE
      NDT=NDT+ND
      GO TO 260

C      WEIGHT= 1/ FREQ. PAR.      FOR IFW=0
255 DO 259 I=1,NQ
      IF(DX(I))258,258,256
256 P(I)=1.0 / DX(I)
      PTOT=PTOT+P(I)
      GO TO 259
258 P(I)=0.0
259 CONTINUE
      NDT=NDT+ND
260 N1=0
      DO 266 I=1,NQ
      IF(DX(I))266,266,262
262 N1=N1+1
      DCS=DC(N1)*DC(N1)
      SUM=SUM+DX(I)*DX(I)*P(I)*DCS*(DCS+4.0*DC(N1)+4.0)
266 CONTINUE
      IF(ND-N1)925,270,925
270 WRITE (1)NQ,ND,NOZ
      WRITE (1) (REC(I),I=1,18)
      WRITE (1) (NR(K),NC(K),NFO(K),Z(K),K=1,NOZ)

C      READ G MATRIX
C      READ NON-ZERO G MATRIX ELEMENTS ,G(I,J).
C      G ELEMENTS ENTERED IN 18 COLUMN FIELD 1 TO 4 PER CARD GIVING
C      COLUMNS      ITEM
C      1-3          NROW=I      (ROW NO.)
C      4-6          NCOL=J      (COLUMN NO.) (I LESS THAN OR=J)
C      7-18         DATIN=G(I,J) (DECIMAL BETWEEN 12-13 OR PUNCHED)
C      NROW IS SET =-1 AFTER LAST G ELEMENT.
C      SINCE THE G MATRIX IS SYMMETRIC ONLY DIAGONAL ELEMENTS AND THE
C      ELEMENTS ABOVE THE DIAGONAL ARE ENTERED. THAT IS, COLUMN NO.
C      GREATER THAN OR EQUAL TO THE ROW NO.
```

TABLE LI (Continued)

```
140 DO 142 I=1,NQ
    DO 142 J=I,NQ
142 G(I,J)=0.0
144 READ (5,16)(NROW(L),NCOL(L),DATIN(L),L=1,4)
    16 FORMAT(4(2I3,F12.6))
    DO 150 L=1,4
        IF(NROW(L))152,150,146
146 IF(NCOL(L)-NROW(L))910,147,147
147 IF(NQ-NCOL(L))910,148,148
148 I=NROW(L)
    J=NCOL(L)
    G(I,J)=DATIN(L)
150 CONTINUE
    GO TO 144
152 IF(1+NROW(L))910,154,910
C     SCHMIDT ORTHOGONALIZATION OF G
C     STORE INVERSE TRANSFORMATION IN LOWER TRIANGLE OF G
154 NO=1
    NL=2
155 GD=1.0 /G(NO,NO)
    DO 156 J=NL,NQ
156 G(J,NO)=G(NO,J)*GD
    IF(NL-NQ)158,158,170
158 DO 160 I=NL,NQ
    DO 160 J=I,NQ
160 G(I,J)=G(I,J)-(G(NO,I)*G(NO,J)*GD)
161 NO=NO+1
    NL=NO+1
163 IF(G(NO,NO)-0.000001)164,164,155
164 IF(NL-NQ)165,165,170
165 DO 166 J=NL,NQ
166 G(J,NO)=G(NO,J)
    GO TO 161
170 DO 175 I=1,NQ
    IF(G(I,I)-0.00005)173,173,172
172 DG(I)=SQRT(G(I,I))
    GO TO 174
173 DG(I)=0.0
174 G(I,I)=1.0
    DO 175 J=I,NQ
175 G(J,I)=G(J,I)*DG(I)
    DO 178 J=1,NQ
178 WRITE (1) (G(I,J),I=J,NQ)
    WRITE (1) (DG(I),I=1,NQ)
    WRITE (1) (DX(I),I=1,NQ)
    WRITE (1) (P(I),I=1,NQ)
    NM=NM+1
    IF(NMOL-NM)286,100,100
286 END FILE 1
    REWIND 1
    IF(NDT)287,287,288
287 JOKER=1
    FREQ=NF
    SCALE=1.0
```



TABLE LI (Continued)

```
GO TO 470
288  FREQ=NDT
      SCALE=FREQ/ PTOT
      SUM=SCALE*SUM
470  CALL CYCLE
      IF(2-JOK)90,901,90
900  WRITE (6,81)NOPROB,NM
      81  FORMAT(40H0 ERROR IN MOLECULE CONTROL CARD.PROBLEM18,4H.NM=13)
      IF(NM-1)902,902,903
902  JOK=1
      GO TO 90
903  NMOL=NM-1
      JOK=2
      GO TO 286
910  WRITE (6,85)NM,NOPROB,L,NROW(L),NCOL(L),DATIN(L)
      85  FORMAT(25H0 G MATRIX ERROR MOLECULE13,8H PROBLEM18,6H FIELD13,6H R
1EADSI4,I4,F12.6)
      JOK=1
      GO TO 90
920  WRITE (6,87)NM,NOPROB,NOZ,NROW(L),NCOL(L),NPO(L),DATIN(L)
      87  FORMAT(25H0 Z MATRIX ERROR MOLECULE13,8H PROBLEM18,8H ELEMENT14,6H
1 READSI4,I4,I4,F9.6)
      JOK=1
      GO TO 90
925  WRITE (6,88)NM,NOPROB,N1
      88  FORMAT(27H0 EIGENVALUE ERROR MOLECULE13,8H PROBLEM18,4H ND=13)
      JOK=1
      GO TO 90
      END
      SUBROUTINE CYCLE
      DIMENSION S( 84,84 ),EIG(66,66),NR( 650),NC( 650),NFO( 650),
1 Z( 650),BZ(66,71) ,G(66,66),INDEX( 71),DX(71),DE(71),DG(71),
2 NFX( 71),FF( 71),SI( 71),EC(71),Y( 71),NF1( 71),NF2( 71),DD( 71),
3 COEN( 71),SIGMCO( 71),NOM( 71),EX( 71),PE( 71),E( 71),DV(71),
4 DC( 71),FI( 71),NCON( 71),NCF( 71),NPL(50),NPN(50),RECORD(54),
5 REC(18),P(71),NROW(4),NCOL(4),NPO(4),DATIN(4),SUMDD(20)
      EQUIVALENCE (S,EIG),(S(4365),NR),(S(5020),NC),(S(5675),NFO),
1 (S(6330),Z),(BZ,G),(BZ(4360),INDEX,DX),(BZ(4440),DE,DG),
2 (BZ(4520),NFX,FF, EC),(BZ(4600),Y,NF1),(SIGMCO,NOM),
3 (COEN,NF2,DD),(EX,PE),(E,DV)
      COMMON S,BZ,SIGMCO,COEN,EX,E,DC,FI,NCON,NCF,NPL,NPN,RECORD,REC,
1P,SUMDD,NROW,NCOL,NPO,DATIN,NF,NCZ,NCZS,NDT,DET,JOKER,JOK,DMX,
2 DEFR,FR,JET,NX,NP,NOIN,NOSTEP,NOVAR,NOVMI,EFOUT,EFIN,NCYC,
3NOPROB,NOZ,NQ,LIMIT,TOL,NDIAG,NPMAX,IFREG,PROD,FREQ,ERPO,ERO,DAMP,
4RAP,FRAC,TIME,PER,INO,IFREP,IFER,NIP,NMOL,IND,SCALE,ER,ERP,PTOT,
5 NM,NM1,ND,NDD,SUM,I01,I02,I03,I04,I05,I06,I07,I08,I09,CUTOF
      INTEGER CUTOF
470  REWIND 1
      REWIND 2
      NM=1
      NM1=0
480  READ (1) NQ,ND,NOZ
      READ (1) (REC(I),I=1,18)
      READ (1) (NR(K),NC(K),NFO(K),Z(K),K=1,NOZ)
```

TABLE LI (Continued)

```
      IF(IFREP)484,490,484
484 IF(INO)490,490,485
485 DO 488 K=1,NOZ
      I=NFO(K)
488 NFO(K)=NOM(I)
490 IF(JOKER)300,300,492
492 RAP=0.5E-3
      IF(I01)300,90005,300
90005 WRITE (6,80)NM,(REC(K),K=1,18),NQ,NO,NOZ
      80 FORMAT(23H1 Z MATRIX FOR MOLECULEI4,3X,18A4/I6,12H COORDINATESI3,
      125H EXPERIMENTAL FREQUENCIESI8,19H Z MATRIX ELEMENTS.)
      WRITE (6,81) (NR(I),NC(I),NFO(I),Z(I),I=1,NOZ)
      81 FORMAT(4(I4,2(I3,F9.6))
300 DO 301 J=1,NQ
301 READ (1) (G(I,J),I=J,NQ)
      READ (1) (DG(I),I=1,NQ)
      READ (1) (DX(I),I=1,NQ)
      READ (1) (P(I),I=1,NQ)
      IF(ND)304,304,306
304 IF(JOKER)468,468,306
C COMPUTE TRANSFORMED F MATRIX AND STORE IN UPPER TRIANGLE OF G.
306 DO 328 J=1,NQ
      P(J)=SCALE*P(J)
      DO 308 I=1,NQ
308 DD(I)=0.0
      DO 320 K=1,NOZ
      IX=NR(K)
      IF(IX-J)320,312,312
312 JX=NC(K)
      LX=NFO(K)
      DD(IX)=DD(IX)+FI(LX)*Z(K)*G(JX,J)
      IF(IX-JX)318,320,318
318 DD(JX)=DD(JX)+FI(LX)*Z(K)*G(IX,J)
320 CONTINUE
      DO 324 K=J,NQ
      DC(K)=0.0
      DO 324 L=K,NQ
324 DC(K)=DC(K)+G(L,K)*DD(L)
      DO 328 K=J,NQ
328 G(J,K)=DC(K)
      NR2=0
      IEGEN=0
C DIAGONALIZE TRANSFORMED F MATRIX BY JACOBI METHOD
      CALL HDIAG(G,NQ,IEGEN,EIG,NR2,RAP)
C COMPUTE EIGEN VECTORS
      DO 330 I=1,NQ
      DC(I)=G(I,I)
330 G(I,I)=DG(I)
      DO 335 I=1,NQ
      DO 333 J=1,NQ
      DD(J)=0.0
      DO 333 K=1,J
333 DD(J)=DD(J)+G(J,K)*EIG(K,I)
      DO 335 J=1,NQ
```

TABLE LI (Continued)

```
335 EIG(J,I)=DD(J)
C   ORDER EIGENVALUES AND EIGENVECTORS
    II=NQ-1
    DO 340 J=1,II
    LOW=J+1
    DO 340 K=LOW,NQ
    IF(DC(J)-DC(K))337,340,340
337 TEM=DC(J)
    DC(J)=DC(K)
    DC(K)=TEM
    DO 338 I=1,NQ
338 DD(I)=EIG(I,J)
    DO 339 I=1,NQ
    EIG(I,J)=EIG(I,K)
339 EIG(I,K)=DD(I)
340 CONTINUE
C   COMPUTE EIGENVALUE ERRORS
341 DO 350 I=1,NQ
    IF(DX(I))348,348,344
344 DD(I)=DX(I)-DC(I)
    SUMDD(NX)=SUMDD(NX)+DD(I)*DD(I)*P(I)
    GO TO 350
348 DD(I)=0.0
350 CONTINUE
352 WRITE (6,24)NM,NP,NR2,RAP,(DC(I),I=1,NQ)
    24 FORMAT(37H0 EIGENVALUES AND ERRORS FOR MOLECULEI4,6H AFTERI3,15H P
    1ERTURBATIONS.15,11H ROTATIONS./6H RAP=E12.4/(1H ,9F8.5))
    WRITE (6,26)(DD(J),J=1,NQ)
    26 FORMAT(8H0 ERRORS/(1H ,9F8.5))
90007 IF(JOKER)354,354,364
C   TEST FOR UNREASONABLE EIGENVALUES
354 IF(109)61712,61712,91919
61712 DO 359 J=1,NQ
    IF(DC(J)+0.001)360,3550,3550
3550 IF(DC(J))3552,3552,355
3552 IF(P(J))355,355,360
355 IF(9.0-DC(J))360,360,356
356 IF(2.5-DC(J))357,357,358
357 IF(0.8-ABS(DD(J)))360,360,359
358 IF(0.4-ABS(DD(J)))360,360,359
359 CONTINUE
91919 CONTINUE
    IF(JOK)468,400,400
360 JOK=-1
    WRITE (6,74)NM,NP
    74 FORMAT(26H0 EIGENVALUES FOR MOLECULEI4,31H NOT REASONABLE ON PERTU
    1RBATIONI4)
    GO TO 468
C   OUTPUT FOR FINAL CYCLE
364 ERO=0.0
    ERPO=0.0
    DO 368 I=1,NQ
    DE(I)=SQRT(DX(I)/5.88852E-7)
    DV(I)=SQRT(DC(I)/5.88852E-7)
```

TABLE LI (Continued)

```

      IF(DE(I))365,365,366
365  EC(I)=0.0
      EX(I)=0.0
      GO TO 368
366  EX(I)=DE(I)-DV(I)
      EC(I)=100.0*EX(I)/DE(I)
      IF(P(I))368,368,367
367  ERO=ERO+ABS(EX(I))
      ERPO=ERPO+ABS(EC(I))
368  CONTINUE
      ER=ER+ERO
      ERP=ERP+ERPO
      ERO=ERO / FLOAT(ND)
      ERPO=ERPO / FLOAT(ND)
90008 WRITE (6,28)NM,SCALE,(REC(I),I=1,18)
      28 FORMAT(75H1 OBSERVED AND CALCULATED FREQUENCIES AND FREQUENCY PARA
      1METERS FOR MOLECULEI3/26H SCALE FACTOR FOR WEIGHTS=F10.6/12X,18A4)
369  WRITE (6,29)(I,DE(I),DV(I),EX(I),EC(I), P(I),DX(I),DC(I),I=1,NQ)
      29 FORMAT(95H0   OBS.FREQ.   CALC.FREQ.   DIFFERENCE   PERCENT ERROR
      1 WEIGHT   OBS.FREQ.PAR.   CALC.FREQ.PAR.   /6X,6H(CM-1),6X,6H(CM-1
      2),7X,6H(CM-1)/(14,F9.1,4X,F8.1,4X,F6.1,7X,F7.3,6X,F9.4,F10.5,F14.5
      3))
      WRITE (6,31) ERO,ERPO
      31 FORMAT(17H0 AVERAGE ERROR=F6.2,10H CM-1 ,OR F6.3,8H PERCENT)
90009 DO 3680 I=1,50
      K=51-I
      TES=FLOAT(K)-0.5
      DO 3680 J=1,NQ
      IF(DX(J))3680,3680,3670
3670 IF(TES-ABS(EX(J)))3672,3680,3680
3672 IF(EX(J))3673,3680,3674
3673 NPN(K)=NPN(K)+1
      GO TO 3675
3674 NPL(K)=NPL(K)+1
3675 EX(J)=0.0
3680 CONTINUE
      370 IF(I02)400,90010,400
90010 WRITE (6,30)NOPROB,NM,NP,(REC(I),I=1,18)
      30 FORMAT(37H1EIGENVALUES AND EIGENVECTORS PROBLEM18,9H MOLECULEI3,13
      1H PERTURBATIONI4/12X,18A4)
      DO 372 J=1,NQ
372  WRITE (6,32)J,DV(J),(EIG(I,J),I=1,NQ)
      32 FORMAT(10H0FREQUENCYI3,2H =F8.1,5H CM-1,20H EIGENVECTOR FOLLOWS/
      1(1H ,9F8.4))
C      COMPUTE THE JZ MATRIX ( CALLED BZ)
400  DO 421 K=1,NQ
      DO 410 N=1,NF
410  BZ(K,N)=0.0
      DO 420 L=1,NOZ
      I=NR(L)
      J=NC(L)
      M=NFO(L)
      IF(I-J)418,416,418

```

TABLE LI (Continued)

```
416 BZ(K,M)=BZ(K,M)+EIG(I,K )*EIG(J,K )*Z(L)
GO TO 420
418 BZ(K,M)=BZ(K,M)+2.0*EIG(I,K )*EIG(J,K )*Z(L)
420 CONTINUE
421 CONTINUE
422 IF(JOKER)438,438,424
424 IF(I03)90012,90011,90012
90011 WRITE (6,38)NP,NM,(REC(I),I=1,18)
38 FORMAT(28H1 THE JZ MATRIX PERTURBATIONI4,9H MOLECULEI4/12X,18A4)
DO 426 I=1,NQ
426 WRITE (6,41)I,DC(I),DD(I),P(I),(BZ(I,J),J=1,NF)
41 FORMAT(11H0 FREQ.PAR.I3,2H =F12.6,7H ERROR=F12.6,8H WEIGHT=F12.6/(
1 9F8.4))
90012 IF(I04)90014,90013,90014
90013 WRITE (6,42)(REC(I),I=1,18)
42 FORMAT(31H1 POTENTIAL ENERGY DISTRIBUTION/3X,18A4)
90014 DO 435 I=1,NQ
IF(DC(I)-0.0001)435,435,430
430 DO 432 J=1,NF
432 PE(J)=(BZ(I,J)*FI(J))/ DC(I)
IF(I04)435,90015,435
90015 WRITE (6,45)I,DV(I),(PE(J),J=1,NF)
45 FORMAT(11H0 FREQUENCYI3,2H =F6.1,5H CM-1/(1H ,9F8.4))
435 CONTINUE
C COMPUTE S
438 DO 442 I=1,NQ
P(I)=SQRT(P(I))
BZ(I,NOVAR)=DD(I)
DO 442 J=1,NOVAR
442 BZ(I,J)=P(I)*BZ(I,J)
DO 458 I=1,NOVAR
DO 456 J=I,NOVAR
SI(J)=0.0
DO 456 K=1,NQ
456 SI(J)=SI(J)+BZ(K,I)*BZ(K,J)
458 WRITE (2) (SI(J),J=I,NOVAR)
463 NM1=NM1+1
468 NM=NM+1
IF(NMOL-NM)600,480,480
600 IF(JOK)601,602,602
601 JOK=1
JOKER=1
GO TO 470
602 CONTINUE
END FILE 2
REWIND 2
FR=NDT-NF+NCZ
DO 604 I=1,NOVAR
DO 604 J=I,NOVAR
604 S(I,J)=0.0
NM=1
C READ AND SUM S MATRICES
608 DO 610 I=1,NOVAR
READ (2) (SI(J),J=I,NOVAR)
```

TABLE LI (Continued)

```
DO 610 J=1,NOVAR
610 S(I,J)=S(I,J)+SI(J)
    NM=NM+1
    IF(NM1-NM)612,608,608
612 IF(NP)613,613,620
613 DO 618 I=1,NF
    IF(S(I,I))614,614,618
614 IF(NCZ)617,617,615
615 DO 616 J=1,NCZ
    IF(I-NCF(J))616,618,616
616 CONTINUE
617 NCZ=NCZ+1
    NCZS=NCZ
    NCF(NCZ)=I
    WRITE (6,1)I
    1 FORMAT(16H0 FORCE CONSTANTI3,42H NOT A FUNCTION OF FREQ.,FIXED ON
1CYCLE 1.)
618 CONTINUE
    DO 6185 I=1,NDIAG
    KX=NCON(I)
6185 NFX(KX)=1
    IF(NCZ)6189,6189,6186
6186 DO 6187 I=1,NCZ
    KX=NCF(I)
6187 NFX(KX)=-1
6189 DO 6192 I=1,NF
    IF(NFX(I))6192,6190,6192
6190 NCZS=NCZS+1
    NCF(NCZS)=I
6192 CONTINUE
620 PROD=1.0
    IF(DAMP)6207,6207,6201
6201 IF(JOKER)6207,6202,6207
6202 SMAX=S(I,I)
    DO 6205 I=2,NF
    IF(S(I,I)-SMAX)6205,6205,6203
6203 SMAX=S(I,I)
6205 CONTINUE
    DB=DAMP*SMAX
    WRITE (6,43) DAMP,DB
    43 FORMAT(37H0 DAMPED LEAST SQUARES.DAMPING FACTORF8.4,11H*S(I,I)MAX=
1F8.4)
    GO TO 621
6207 DB=0.0
621 CONTINUE
    DO 628 I=1,NOVAR
    IF(S(I,I))622,622,623
622 EX(I)=1.0
    GO TO 628
623 S(I,I)=S(I,I)+DB
    EX(I)=SQRT(S(I,I))
628 CONTINUE
C COMPUTE CORRELATION MATRIX
DO 630 I=1,NOVAR
```

TABLE LI (Continued)

```
DO 630 J=1,NOVAR
S(I,J)=S(I,J)/(EX(I)*EX(J))
630 S(J,I)=S(I,J)
IF(JOKER)631,634,631
631 IF(105)634,90016,634
90016 WRITE (6,53)NP,(RECORD(I),I=1,54)
53 FORMAT(29H1 CORRELATION MATRIX ON CYCLEI3/(3X,18A4))
DO 632 I=1,NOVAR
632 WRITE (6,40) I,(S(I,J),J=1,NOVAR)
40 FORMAT(4HOROWI3/(1H ,9F8.4))
WRITE (6,63) (EX(I),I=1,NF)
63 FORMAT(61H0 SQUARE ROOTS OF THE DIAGONAL TERMS OF THE NORMAL EQUAT
IONS./(1H ,9F8.4))
C ELIMINATE ROWS AND COLUMNS FROM CORRELATION MATRIX
634 IF(JOKER)635,636,636
635 NVO=NCZ
GO TO 637
636 NVO=NCZS
637 IF(NVO)642,642,638
638 DO 640 I=1,NVO
K=NCF(I)
DO 639 J=1,NOVAR
S(K,J)=0.0
639 S(J,K)=0.0
640 S(K,K)=1.0
642 DEFR=FREQ
C CALL REGRES TO SOLVE PERTUBATION EQUATIONS OR REGRESSION
CALL REGRES
NFA=NF-NCZS
DO 700 I=1,NDIAG
KX=INDEX(I)
PROD=PROD*EX(KX)*EX(KX)
700 FF(I)=FI(KX)
IF(JOKER)702,710,702
702 IF(106)710,90017,710
90017 WRITE (6,52)DET,NFA,NDT,(RECORD(I),I=1,54)
52 FORMAT(43H1 VARIANCE-COVARIANCE MATRIX. DETERMINANT= E12.4/18,32H
1FORCE CONSTANTS ADJUSTED TO FITI5,13H FREQUENCIES./(3X,18A4))
DO 704 I=1,NOVAR
704 WRITE (6,40) I,(S(I,J),J=1,NOVAR)
710 CONTINUE
90018 WRITE (6,61)NP, DET,PROD,RAP,(INDEX(I),FF(I),COEN(I),
ISIGMCO(I),I=1,NDIAG)
61 FORMAT(23H1 FORCE CONSTANTS AFTERI3,14H PERTURBATIONS /15H
1.DETERMINANT =E12.4,19H PRODUCT OF S(I,I)=E12.4/5H RAP=E14.4/
252H I FORCE CONSTANT(I) DELTA(I) EST.DISPERSION/
3(I4,4X,F12.6,F14.6,F16.6))
90019 IF(NCZS)715,715,712
712 WRITE (6,66) (NCF(I),I=1,NCZS)
66 FORMAT(28H0 FORCE CONSTANTS HELD FIXED/(24I3))
715 IF(JOKER)718,718,780
718 DO 720 I=1,NDIAG
IF(2.0-ABS(COEN(I)))722,722,720
720 CONTINUE
```

TABLE LI (Continued)

```
GO TO 735
722 CMAX=ABS(COEN(I))
    MAX=I+1
    LX=I
    DO 724 I=MAX,NDIAG
    IF(CMAX-ABS(COEN(I)))723,724,724
723 CMAX=ABS(COEN(I))
    LX=I
724 CONTINUE
    NFIX=INDEX(LX)
90021 WRITE (6,17)NFIX,COEN(LX),SIGMCO(LX)
    17 FORMAT(16H0 FORCE CONSTANTI3,13H FIXED.DELTA= F10.6,8H SIGMCO=F10.
16)
90022 DO 726 I=1,NCZS
    JX=NCZS-I+1
    LX=JX+1
726 NCF(LX)=NCF(JX)
    NCF(1)=NFIX
    NCZ=NCZ+1
    NCZS=NCZS+1
    NLC=0
    DO 728 I=1,NDIAG
    IF(INDEX(I)-NFIX)727,728,727
727 NLC=NLC+1
    NCON(NLC)=INDEX(I)
728 CONTINUE
    NDIAG=NLC
    SUMDD(NX)=0.0
    IF(NDIAG)729,729,470
729 JOKER=1
    NPMAX=1
    GO TO 470
735 DO 736 I=1,NDIAG
    IF(0.008-ABS(COEN(I)))738,738,736
736 CONTINUE
    NPMAX=0
    GO TO 751
738 IF(DMX)750,742,739
739 DO 740 I=1,NDIAG
740 COEN(I)=DMX*COEN(I)
    IF(CUTOF-NP)63152,63152,91516
63152 DMX=0.0
91516 GO TO 750
742 DO 746 I=1,NDIAG
    IF(1.0-ABS(COEN(I)))743,744,744
743 COEN(I)=0.7*COEN(I)
744 IF(0.5-ABS(COEN(I)))745,746,746
745 COEN(I)=0.8*COEN(I)
746 CONTINUE
750 IF(NPMAX)758,751,751
751 DO 753 I=1,NDIAG
    JX=INDEX(I)
753 FI(JX)=FI(JX)+COEN(I)
    IF(NP)758,758,754
```



TABLE LI (Continued)

```

754 IF(SUMDD(NP)-SUMDD(NX))756,756,758
756 JET=JET+1
      IF(2-JET)757,757,758
757 WRITE (6,51)NOPROB,NP
      51 FORMAT(9H0 PROBLEMI7,14H DIVERGING NP=I3)
      NPMAX=0
758 NP=NP+1
      NX=NP+1
      NCYC=NCYC+1
      SUMDD(NX)=0.0
      RAP=FRAC*RAP
      IF(NPMAX-NP)762,762,765
762 JOKER=1
      GO TO 470
765 IF(IFREG)770,470,770
770 IF(NIP+3-NCYC)771,470,470
771 JOKER=-1
      GO TO 470
780 IF(NCZS)802,802,800
800 DO 801 I=1,NCZS
      K=NCF(I)
801 S(K,K)=0.0
802 E3=SQRT(SUMDD(NX)/DEFR)
      E4=SQRT(SUM / DEFR)
      DO 810 I=1,NF
      TEM=ABS(S(I,I))
      E(I)=E4*SQRT(TEM)/ EX(I)
810 Y(I)=E3*SQRT(TEM)/ EX(I)
815 WRITE (6,55)NOPROB,(RECORD(I),I=1,54)
      55 FORMAT(1H1,5X,8H PROBLEMI8/(12X,18A4))
816 WRITE (6,60)NP,(I,FI(I),Y(I),E(I),I=1,NF)
      60 FORMAT(44H0 FORCE CONSTANTS AND ESTIMATED ERRORS AFTERI4,15H PERTU
      IRBATIONS.//47H I FORCE CONSTANT(I) ERROR * ERROR **/(14,
      23X,F12.6,5X,F9.6,5X,F8.6))
90024 FR=DEFR
      NAD=NF-NCZS
      IF(108)817,817,99887
99887 WRITE(7,21121)(FI(I),I=1,NF)
21121 FORMAT(6F12.6)
817 WRITE (6,62)SUMDD(NX),E3,SUM,E4
      62 FORMAT(33H0 * STANDARD ERROR ESTIMATED FROM/54H SUMDD=SUM((LAMB
      1DA(I)OBS.-LAMBDA(I)CALC.)**2)*P(I)=E13.6/47H STANDARD ERROR IN
      2LAMBDA = SQRT(SUMDD/ FR)=E13.6 //33H ** STANDARD ERROR ESTIMATED F
      3ROM/39H SUMD=SUM(DELTA LAMBDA(I)**2)*P(I)=E13.6/19H SQRT(SU
      4MD/ FR)=E13.6/37H WHERE DELTA LAMBDA ESTIMATED FROM/
      549H 1.IFER=-3,DELTA FREQ(I)=1.0 CM-1 FOR ALL I/
      649H 2.IFER=-2,DELTA FREQ(I)=PER CM-1 FOR ALL I/
      745H 3.IFER=-1,DELTA FREQ(I) READ IN (CM-1)/
      848H 4.IFER= 0,DELTA FREQ(I)=0.005*OBS.FREQ(I)/
      946H OR 5.IFER= 1,DELTA FREQ(I)=PER*OBS.FREQ(I))
90026 IF(NDT)825,825,820
820 WRITE (6,64)IFER,PER,NF,NAD,NDT,FR,(SUMDD(I),I=1,NX)
      64 FORMAT(10H IFER=I3, 9H AND PER=F8.4/ 16,17H FORCE CONSTANTS.16
      1,16H ADJUSTED TO FITI6,13H FREQUENCIES./ 2X,F5.1,41H DEGREES OF FR

```

TABLE LI (Continued)

```

2EEDOM. SUMDD FOR EACH CYCLE /(5E13.6))
90028 CON=FREQ
      E5=ER/CON
      E6=ERP/CON
90029 WRITE (6,65)E5,E6
      65 FORMAT(30HO AVERAGE ERROR IN FREQUENCIES=F7.1,9H CM-1 OR F8.4,9H PE
1RCENT.)
90030 NZER=NDT
      DO 824 I=1,50
      824 NZER=NZER-NPN(I)-NPL(I)
90031 IF(I07)26261,26261,825
26261 WRITE (6,55)NOPROB,(RECORD(I),I=1,54)
      WRITE (6,82)NDT,NMOL,NZER,(I,NPL(I),NPN(I),I=1,50)
      82 FORMAT(24HO ERROR DISTRIBUTION FOR I5,13H FREQUENCIES.I4,11H MOLECU
1LES./20H 0.5 TO-0.5 CM-1 =I8/26H CM-1 PLUS MINUS/
2(I6,2I10))
825 RETURN
      END

```

/\*

SUBROUTINE REGRES

C           MODIFICATION OF A PROGRAM FOR STEPWISE MULTIPLE  
C           REGRESSION PROGRAMED BY M.A. EFROYMSON OF ESSO RESEARCH  
C           THE SUBROUTINE IS ALSO USED FOR MATRIX INVERSION AND FOR  
C           SOLVING THE LINEAR EQUATION ON CYCLES NOT USING THE REGRESSION  
C           TECHNIQUE

```

DIMENSION S( 84,84 ),EIG(66,66),NR( 650),NC( 650),NFO( 650),
1 Z( 650),BZ(66,71) ,G(66,66),INDEX( 71),DX(71),DE(71),DG(71),
2 NFX( 71),FF( 71),SI( 71),EC(71),Y( 71),NF1( 71),NF2( 71),DD( 71),
3 COEN( 71),SIGMCO( 71),NOM( 71),EX( 71),PE( 71),E( 71),DV(71),
4 DC( 71),FI( 71),NCON( 71),NCF( 71),NPL(50),NPN(50),RECORD(54),
5 REC(18),P(71),NROW(4),NCOL(4),NPO(4),DATIN(4),SUMDD(20)
EQUIVALENCE (S,EIG),(S(4365),NR),(S(5020),NC),(S(5675),NFO),
1 (S(6330),Z),(BZ,G),(BZ(4360),INDEX,DX),(BZ(4440),DE,DG),
2 (BZ(4520),NFX,FF, EC),(BZ(4600),Y,NF1),(SIGMCO,NOM),
3 (COEN,NF2,DD),(EX,PE),(E,DV)
COMMON S,BZ,SIGMCO,COEN,EX,E,DC,FI,NCON,NCF,NPL,NPN,RECORD,REC,
1P,SUMDD,NROW,NCOL,NPO,DATIN,NF,NCZ,NCZS,NDT,DET,JOKER,JOK,DMX,
2 DEFR,FR,JET,NX,NP,NOIN,NOSTEP,NOVAR,NOVMI,EFOUT,EFIN,NCYC,
3NOPROB,NOZ,NQ,LIMIT,TOL,NDIAG,NPMAX,IFREG,PROD,FREQ,ERPO,ERO,DAMP,
4RAP,FRAC,TIME,PER,INO,IFREP,IFER,NIP,NMOL,IND,SCALE,ER,ERP,PTOT,
5 NM,NM1,ND,NDD,SUM,I01,I02,I03,I04,I05,I06

```

DET=1.0

NOIN=0

DO 650 I=1,NF

650 NFX(I)=0

IF(JOKER)656,699,699

656 WRITE (6,22)

22 FORMAT(35H1 CONSTANTS FORCED INTO REGRESSION.)

VAR=0.0

NOSTEP=-1

IFSTEP=0

TOL=0.001

NIN=0

ASSIGN 1320 TO NUMBER

TABLE LI (Continued)

```
C      ENTER FORCE CONSTANTS IN THE LIST NCON(I), I=1, NDIAG INTO
C      THE REGRESSION EQUATIONS WITHOUT REGARD TO THE STATISTICAL
C      TESTS. THIS LIST SHOULD INCLUDE ALL DIAGONAL FORCE CONSTANTS
C      PLUS ANY KNOWN LARGE INTERACTION CONSTANTS.
699 IX=1
      ASSIGN 710 TO NO1
700 DEFR=DEFR-1.0
      JX=NCON(IX)
      NFX(JX)=1
      K=JX
      GO TO 1400
710 NOIN=NOIN+1
      INDEX(NOIN)=JX
      IX=IX+1
      IF(NDIAG-IX)711,700,700
711 FLEVEL=0.0
      SIGY=EX(NOVAR)*SQRT(S(NOVAR,NOVAR)/DEFR)
      DO 720 I=1,NOIN
      KX=INDEX(I)
      COEN(I)=S(KX,NOVAR)*EX(NOVAR)/EX(KX)
720 SIGMCO(I)=(SIGY/EX(KX))*SQRT(S(KX,KX))
      IF(JOKER)721,200,200
721 WRITE (6,70)FLEVEL,SIGY,(INDEX(J),COEN(J),SIGMCO(J),J=1,NOIN)
722 IF(IFREG)730,723,730
723 EFIN=2.0
      EFOUT=1.0
      GO TO 731
730 READ (5,20) EFIN,EFOUT
      20 FORMAT(2F12.6)
731 WRITE (6,26) EFIN,EFOUT
      26 FORMAT(36H0 REGRESSION, F LEVEL FOR ENTERING =F10.6,23H F LEVEL FO
IR REMOVING =F10.6)
790 DEFR=DEFR+1.0
799 ASSIGN 1000 TO NO1
      AO=1
      NOMIN=0
      NOMAX=0
      NOENT=0
      K=0
1000 NOSTEP=NOSTEP+1
      IF(NOSTEP-LIMIT)1001,3001,3001
3001 WRITE (6,3005)
3005 FORMAT(36H000 MANY STEPS, PROBLEM TERMINATED )
      JOKER=1
      GO TO 1381
1001 IF(S(NOVAR,NOVAR))1002,1002,1010
1002 NSTPM1=NOSTEP-1
      WRITE (6,1004)NSTPM1
1004 FORMAT(1H037HY SQUARE NON-POSITIVE,TERMINATE STEP 15)
      GO TO 1381
1010 SIGY=EX(NOVAR)*SQRT(S(NOVAR,NOVAR)/DEFR)
1015 DEFR=DEFR-AO
1016 IF(DEFR) 1017,1017,1020
1017 WRITE (6,1019)NOSTEP
```

TABLE LI (Continued)

```
1019 FORMAT(1H029H NO MORE DEGREES FREEDOM STEP 15)
GO TO 1381
1020 VMIN=0.0
1030 VMAX=0.0
1035 NOIN=0
1040 DO 1050 I=1,NOVMI
IF(NFX(I))1041,1041,1080
1041 IF(S(I,I))1046,1050,1060
1043 WRITE (6,1044)I,NOSTEP
1044 FORMAT(1H010H SQUARE S-15,17H NEGATIVE. SOLONG 15,6H STEPS)
GO TO 1381
1046 IF(S(I,I)+TOL)1043,1050,1050
1060 IF(S(I,I)-TOL) 1050,1080,1080
1080 VAR=S(I,NOVAR)*S(NOVAR,I)/ S(I,I)
1090 IF(VAR)1100,1050,1110
1100 NOIN=NOIN+1
1120 INDEX(NOIN)=I
1130 COEN(NOIN)=S(I,NOVAR)*EX(NOVAR)/EX(I)
1140 SIGMCO(NOIN)=(SIGY/ EX(I))* SQRT(S(I,I))
IF(NFX(I))1150,1150,1050
1150 IF(VMIN)1160,1170,904
904 WRITE (6,906)
906 FORMAT(24H ERROR,VMIN PLUS,SOLONG )
GO TO 900
1170 VMIN=VAR
1180 NOMIN=I
1190 GO TO 1050
1160 IF(VAR-VMIN)1050,1050,1170
1110 IF(VAR-VMAX)1050,1050,1210
1210 VMAX=VAR
1220 NOMAX=I
1050 CONTINUE
1230 IF(NIN)903,1240,1300
903 WRITE (6,907)
907 FORMAT(26H ERROR,NOIN MINUS, SOLONG )
GO TO 900
1240 WRITE (6,65)SIGY
65 FORMAT(39H0 START REGRESSION.STANDARD ERROR OF Y=F12.6)
NIN=1
GO TO 1350
1300 IF(IFSTEP)900,1310,1320
1310 IF(INDENT) 1311,1311,1313
1311 WRITE (6,91)NOSTEP,K
91 FORMAT(9H0STEP NO.15/19H VARIABLE REMOVED 18)
1312 GO TO 1314
1313 WRITE (6,92)NOSTEP,K
92 FORMAT(9H0STEP NO.15/20H VARIABLE ENTERING 18)
1314 WRITE (6,70)FLEVEL,SIGY,(INDEX(J),COEN(J),SIGMCO(J),J=1,NOIN)
70 FORMAT(12H F LEVEL =F12.6/24H STANDARD ERROR OF Y =F12.6/47H
1 CONSTANT PERTURBATION STANDARD ERROR/(17,8X,F10.6,8X,F10
2.6))
1315 GO TO NUMBER,(1320,1580)
1320 FLEVEL=VMIN*DEFR/ S(NOVAR,NOVAR)
1330 IF(EFOUT+FLEVEL)1350,1350,1340
```

TABLE LI (Continued)

```
1340 K=NOMIN
1345 NOENT=0
      AO=-1.0
      GO TO 1391
1350 FLEVEL=VMAX*DEFR/ (S(NOVAR,NOVAR)-VMAX)
      AO=1.0
1360 IF(EFIN-FLEVEL)1370,1361,1380
1361 IF(EFIN)1380,1380,1370
1370 K=NOMAX
1390 NOENT=K
1391 IF(K) 1392,1392,1400
1392 WRITE (6,1395)
1395 FORMAT(12H K=0. STEP 16,7H SOLONG)
      GO TO 900
1400 DO 1410 I=1,NOVAR
1420 IF(I-K) 1430,1410,1430
1430 DO 1440 J=1,NOVAR
1450 IF(J-K) 1460,1440,1460
1460 S(I,J)=S(I,J)-(S(I,K)*S(K,J)/S(K,K))
1440 CONTINUE
1410 CONTINUE
      DET=S(K,K)*DET
1470 DO 1480 I=1,NOVAR
1490 IF(I-K) 1500,1480,1500
1500 S(I,K)= -S(I,K)/S(K,K)
1480 CONTINUE
1510 DO 1520 J=1,NOVAR
1530 IF(J-K)1540,1520,1540
1540 S(K,J)= S(K,J)/S(K,K)
1520 CONTINUE
1550 S(K,K)= 1.0 / S(K,K)
1560 GO TO N01,(710,1000)
1380 WRITE (6,75)NOSTEP
      75 FORMAT(10HOCOMPLETED 15,20H STEPS OF REGRESSION)
1381 IF(IFSTEP)900,1580,1570
1570 ASSIGN 1580 TO NUMBER
1571 GO TO 1310
1580 WRITE (6,1586)(L,S(L,L),L=1,NOVAR)
1586 FORMAT(22H      DIAGONAL ELEMENTS//20H      VAR.NO.      VALUE //(1H 17,
1F16.6))
910 NCZS=NCZ
      IF(NCZ)913,913,911
911 DO 912 I=1,NCZ
      K=NCF(I)
912 NFX(K)=-1
913 DO 914 I=1,NOIN
      K=INDEX(I)
      NCON(I)=K
914 NFX(K)=1
      DO 916 I=1,NF
      IF(NFX(I))916,915,916
915 NCZS=NCZS+1
      NCF(NCZS)=I
      IF(0.01-ABS(FI(I)))916,916,917
```

TABLE LI (Continued)

```
917 FI(1)=0.0
916 CONTINUE
    NCYC=0
    JOKER=0
200 NDIAG=NOIN
201 RETURN
900 JOKER=1
    GO TO 201
    END
```

```
/*
    SUBROUTINE HDIAG(H,N,IEGEN,U,NR,RAP)
```

Subroutine HDIAG has been presented earlier in Table XXXIV and will not be repeated here because of space limitations.

- a. IND = -09 and indicates the start of a new problem. IND is punched in Columns 1-3 (FORMAT I3).
- b. NOPROB is the problem number, punched in Columns 4-9 (FORMAT I6).
- c. NMOL, denotes the number of molecules included in the problem. NMOL is punched in Columns 10-12 (FORMAT I3).
- d. NF is the number of force constants, punched in Columns 13-15 (FORMAT I3).

Warning: NF must not exceed 71.

- e. NPMAX, represents the maximum number of perturbations desired in the refinement. The refinement will terminate when the number of iterations exceeds NPMAX, even though the refinement may not have converged. NPMAX is punched in Columns 16-18 (FORMAT I3).

Note: If NPMAX is set equal to zero or left blank, the force constants will not be refined, and the frequencies will be calculated for the initial set of force constants.

- f. NCZ, refers to the number of force constants to be held fixed. These force constants are not perturbed by the refinement. NCZ is punched in Columns 19-21 (FORMAT I3).
- g. IFREP is the problem repeat option. If IFREP = 0, a new problem is to be started. For IFREP = 1, only a new set of force constants and identification of those constants to be held fixed need be entered; the remaining data are taken from the previous problem. If IFREP = -1, the final set of force constants from the previous problem are used as the initial set in the new problem. IFREP is punched in Columns 22-23 (FORMAT I2).
- h. IFER is the error control. For IFER = 1, the fractional error, PER, is read in. For IFER = 0, the fractional error, PER, is set equal to 0.005. If IFER = -1, the estimated errors for each of the observed frequencies are read in.

Note: These errors must follow the observed frequencies. For IFER = -2, the error in the observed frequencies in  $\text{cm.}^{-1}$ , PER, is read in. If IFER = -3, the error in the frequencies, PER, is set equal to 1  $\text{cm.}^{-1}$  IFER is punched in Columns 24-25 (FORMAT I2).

- i. PER is the error referred to in above paragraph. If IFER = 1, PER is a fraction. If IFER = -2, PER is in  $\text{cm.}^{-1}$  PER is punched in Columns 26-33 (FORMAT F8.6).
- j. DMX, a fractional factor which is multiplied by the force constant perturbations to result in the "damped" perturbation. This factor is used in those situations where the initial force constant corrections are very large. DMX is punched in Columns 34-41 (FORMAT F8.4).

- k. IFREG is the regression option control. If IFREG = 0, there is no regression analysis. For IFREG = 1, the regression is performed on the first iteration. If IFREG = -1, the regression is initiated on the fourth iteration. IFREG is punched in Columns 42-43 (FORMAT I2).
  - l. NDIAG, represents the number of force constants to be included in all the regressions, punched in Columns 44-46 (FORMAT I3).
  - m. INQ is the number of force constants to be renumbered, punched in Columns 47-49 (FORMAT I3).
  - n. NIP, represents the spacing between the regressions. The spacing is 3 - NIP where NIP may be negative. NIP is positioned in Columns 50-52 (FORMAT I3).
  - o. DAMP is the damping factor for "damped least squares." For DAMP greater than zero,  $DAMP \cdot \text{MAX}[S(I,I)]$  is added to the diagonal terms of the normal equations on each perturbation cycle. Schachtschneider (89) suggests using DAMP = 0.001. DAMP is punched in Columns 53-58 (FORMAT F6.5).
  - p. RAP is the cut-off factor for the Jacobi diagonalization. The rotations are terminated when  $\text{MAX}[H(I,J)]$  is less than  $RAP \cdot \text{MIN}[H(I,I)]$ . If RAP is not entered or left blank, it is assigned a value of 0.5E-2 in the program. On the final iteration, RAP is automatically set equal to 0.5E-3 which gives eigenvalues to six significant figures and eigenvectors to three or four significant figures. RAP is punched in Columns 59-63 (FORMAT F5.4).
  - q. FRAC is a fractional factor for decreasing RAP after each iteration. After each iteration, RAP is set equal to  $\text{FRAC} \cdot \text{RAP}$ . If FRAC is not entered, it is assigned a value of 0.9 by the program. FRAC is punched in Columns 64-67 (FORMAT F4.3).
  - r. CUTOF is the number of iterations after which DMX is set equal to zero, punched in Columns 68-72 (FORMAT I5).
3. Problem Information Cards. Three cards containing any alphanumeric information about the problem the user may wish to enter. The first three columns, i.e., Columns 1-3, should be left blank. Therefore, the alphanumeric information may be punched in Columns 4-72 on each of the cards.
- Warning: These three cards must always be included with the input data even if left blank.
4. Printout Option Cards. A 1 in the appropriate column will suppress the printout of the following information.
- a. I01, the Z matrix suppression option, punched in Column 1.
  - b. I02, the eigenvalues and eigenvectors suppression option, punched in Column 2.



- c. I03, the JZ matrix suppression option, punched in Column 3.
  - d. I04, the potential energy matrix suppression option, punched in Column 4.
  - e. I05, the correlation matrix suppression option, punched in Column 5.
  - f. I06, the variance-covariance matrix suppression option, punched in Column 6.
  - g. I07, the error distribution suppression option, punched in Column 7.
  - h. I08, a 1 will result in the final set of force constants being punched onto cards in a format suitable for input to FADJ, FLPO, and EIGV. I08 is punched in Column 8.
  - i. I09, a 1 will result in the test for unreasonable eigenvalues being bypassed. This option is useful if the initial set of force constants is not a good approximation. In this case, the refinement would terminate on the first iteration if the eigenvalues are not considered reasonable by the test built into the program. I09 is punched in Column 9.
5. Initial Set of Force Constants. The initial set of force constant parameters are punched on cards in 12 column fields, six per card, in the order 1 through NF (FORMAT 6F12.6).
  6. Force Constants to be Renumbered. If INO is greater than zero, the force constants to be renumbered along with their new numbers must be included in the data deck. The format is: NF1(I) = the old force constant number and NF2(I) = the new force constant number, where I = 1 through INO. NF1(I) and NF2(I) each occupy three columns and they are punched in pairs. There are 24 fields of 3 columns each per card (FORMAT 24I3).
  7. Force Constants Held Fixed. If NCZ is greater than zero, the numbers of the force constants to be held fixed, NCF(L), are punched on cards in 3 column fields, 24 per card, for L = 1 through NCZ (FORMAT 24I3).  
Note: These force constants do not enter the refinement, and their final value is the same as their initial value.
  8. Force Constants Forced Into the Regression. If NDIAG is greater than zero, the numbers of the force constants forced into the regression, NCON(I), must be included with the data. These numbers are punched in 3 column fields, 24 per card, for I = 1 through NDIAG (FORMAT 24I3).  
Note: The force constants identified here are entered into the regression equation without regard to the tests for significance.
  9. Molecule Control Card.
    - a. IND = -06, identifies the molecule control card and is punched in Columns 1-3 (FORMAT I3).

- b. NQ is the number of internal coordinates, punched in Columns 4-6 (FORMAT I3).

Warning: NQ cannot exceed 66.

- c. NDD is the number of nonzero experimental frequencies to be included with the input data. NDD is punched in Columns 7-9 (FORMAT I3).

Note: If no experimental frequencies are entered with the data, NDD is set = 0 or left blank. This option may be used if one only wishes to solve the secular equation to obtain the calculated frequencies.

Warning: If NPMAX is greater than zero, so must be NDD.

- d. NZZ, signifies the number of Z matrix elements, punched in Columns 10-13 (FORMAT I4).

Warning: NZZ cannot exceed 650.

- e. IFU is ignored by the program. The Columns 14-15 may be left blank.

- f. IFW, represents the weighting element option for the weighted least squares refinement. If IFW = 1 or -2, the weighting elements, E(I), are read in and must be included with the input data, one for each nonzero experimental frequency. For IFW = -2, the weight(I) then becomes = E(I). For IFW = 1, the weight(I) = E(I)/frequency parameter(I). If IFW = 0, the weight(I) = 1/frequency parameter(I). For IFW = -1, the weight(I) = 1.0 and all frequencies are weighted equally. Finally, if IFW = -3, the weight(I) = 1/[frequency parameter(I)]<sup>2</sup>. IFW is punched in Columns 16-17 (FORMAT I2).

- g. ISKZ is the Z matrix repeat option. If ISKZ = 0, the Z matrix is included in the input data. For ISKZ = 1, the Z matrix from the previous problem is used and a new Z matrix is not included with the data deck. ISKZ is punched in Columns 18-19 (FORMAT I2).

Note: This option is specifically suitable for isotopically substituted molecules.

10. Molecule Information Card. One card containing the name of the molecule or other pertinent alphanumeric information. The first three columns should be left blank with the Columns 4-72 open for the alphanumeric data (FORMAT 18A4).

11. The Z Matrix. The constraint matrix from UBZM or ZSYM is placed at this point in the data deck. The Z matrix elements are punched in 18 column fields, 1 to 4 per card [FORMAT 4(3I3,F9.6)].

Warning: The row number following the last element must be -2.

12. Experimental Frequencies. If NDD is greater than zero, the experimental frequencies, in wave numbers, must be included with the input data. The frequencies are entered in decreasing order and are punched in 12 column fields, 6 per card (FORMAT 6F12.6).

Note: If the frequencies are unknown or uncertain, enter a zero. For degenerate roots, enter one frequency and zeros for the rest. Any frequency may be given a zero weight in the refinement by entering a zero instead of the actual value.

Warning: For NDD greater than zero, one must make NQ entries of which NDD must be nonzero. A zero should be entered for each of the redundancies. Blanks are read as zeros.

13. Estimated Errors in the Observed Frequencies. If IFER = -1, the estimated errors in the observed frequencies, in  $\text{cm.}^{-1}$ , must be included with the input data, one for each nonzero frequency. The estimated frequency errors must be entered in the same order as the experimental frequencies, with zeros being entered corresponding to zeros in the frequency list. The estimated errors are entered in 12 column fields, six per card (FORMAT 6F12.6).

Warning: There must be NQ error entries for IFER = -1, NDD of them nonzero.

14. The Weighting Elements. If IFW = 1 or -2, the weighting elements are read in, one element for each nonzero frequency. The weighting elements are punched in 12 column fields, six per card (FORMAT 6F12.6).

Note: There are a total of NDD weighting elements arranged in the same order as the nonzero experimental frequencies.

15. The G Matrix. The G matrix from GMAT is inserted in the data deck at this point. The data are punched in 18 column fields, four per card [FORMAT 4(2I3,F12.6)].

Warning: The row number after the last element must be -1.

16. Data Termination Card. This card designates the end of the data deck by a 999 punched in Columns 1-3 (FORMAT I3).

Note: If another problem is to be included, the problem ID card is placed at this position and the data termination is moved to the end of the second problem data.

If the same set of force constants is to be used in the refinement for more than one molecule, the data cards starting with the molecule control card through the  $\overline{G}$  matrix cards must be included, one set after another, for each molecule in the refinement, i.e., NMOL sets of data. For symmetry factored blocks, NMOL must be set equal to the number of factored blocks. The blocks are then treated as separate molecules with the data handled in the manner just described for several molecules.

The data deck is terminated with a card having /\* punched in Columns 1-2 with the OS system.

#### OUTPUT INFORMATION

The following information is printed out at the option of the user.

1. The initial set of force constants.
2. The renumbered force constants, old and new numbers.
3. The force constants to be held fixed.
4. The force constants to be forced into the regression.
5. The  $\underline{Z}$  matrix.
6. The eigenvalues and errors for each cycle.
7. The force constant perturbations after each iteration.
8. The regression data.
9. The final set of calculated frequencies, frequency parameters, observed frequencies, errors, and weighting information.
10. The eigenvalues and eigenvectors for the final set of force constants.
11. The final  $\underline{JZ}$  matrix.
12. The potential energy distribution.
13. The correlation matrix.
14. The variance-covariance matrix.
15. The final set of force constants.
16. The estimated error in the final force constants.
17. The error distribution for the frequencies.

The final set of force constants is punched on cards, if desired.

FLPO

This program solves the vibrational secular equation by the method of successive orthogonalization followed by diagonalization. The diagonalization is accomplished by the subroutine HDIAG which employs the Jacobi method. The program will also refine an initial set of force constant parameters to provide a linear or nonlinear (depending on the problem) weighted least squares "fit" of the calculated frequencies to the experimental frequencies by the Fletcher-Powell method (121).

This program was constructed by the author of this text during the investigation of the 1,5-anhydropentitol spectra. FLPO was developed from sections of FADJ (the section involving the solution of the secular equation) and from an IBM subroutine, FMFP, (which is the basis of the Fletcher-Powell method) obtained from their scientific subroutine package (122). The adaptation of the Fletcher-Powell method is based on the paper by Gans (120). FLPO may be used with the IBM 360/44 OS operating system. The program requires a phase overlay procedure available with OS. The current version of FLPO is stored on disk at the Institute's computer center.

A flow diagram for FLPO appears in Fig. 42, 43, and 44. The JCL cards required to run the stored version of FLPO at the Institute are listed in Table LII. These cards must precede the data deck. A listing of FLPO follows the JCL cards in Table LIII.

INSTRUCTIONS FOR PROGRAM USE

The program, FLPO, requires a scratch tape or disk. This has already been accounted for with the stored version of FLPO. The following information comprises the input data deck.



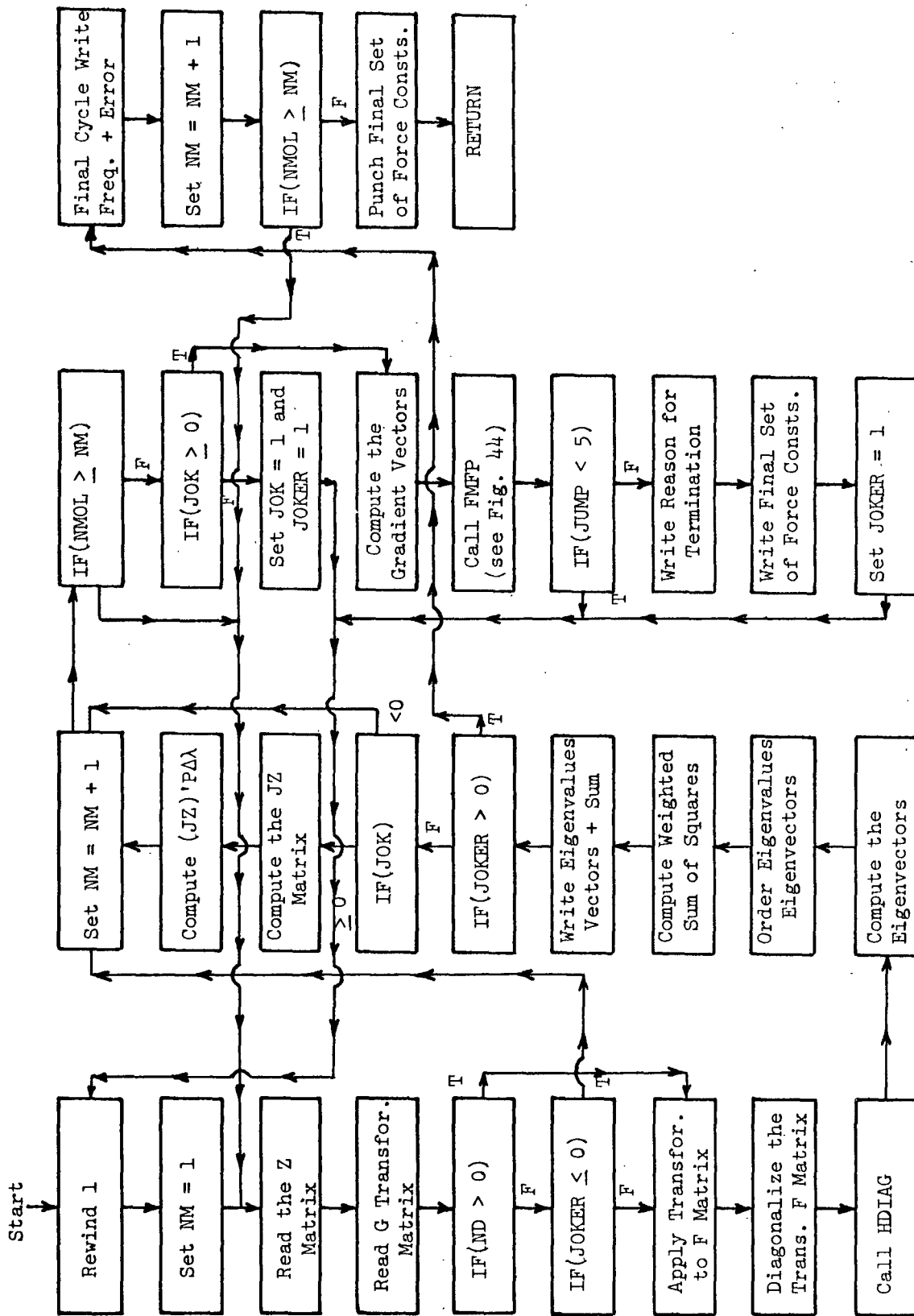


Figure 43. The Flow Diagram of Subroutine CYCLE

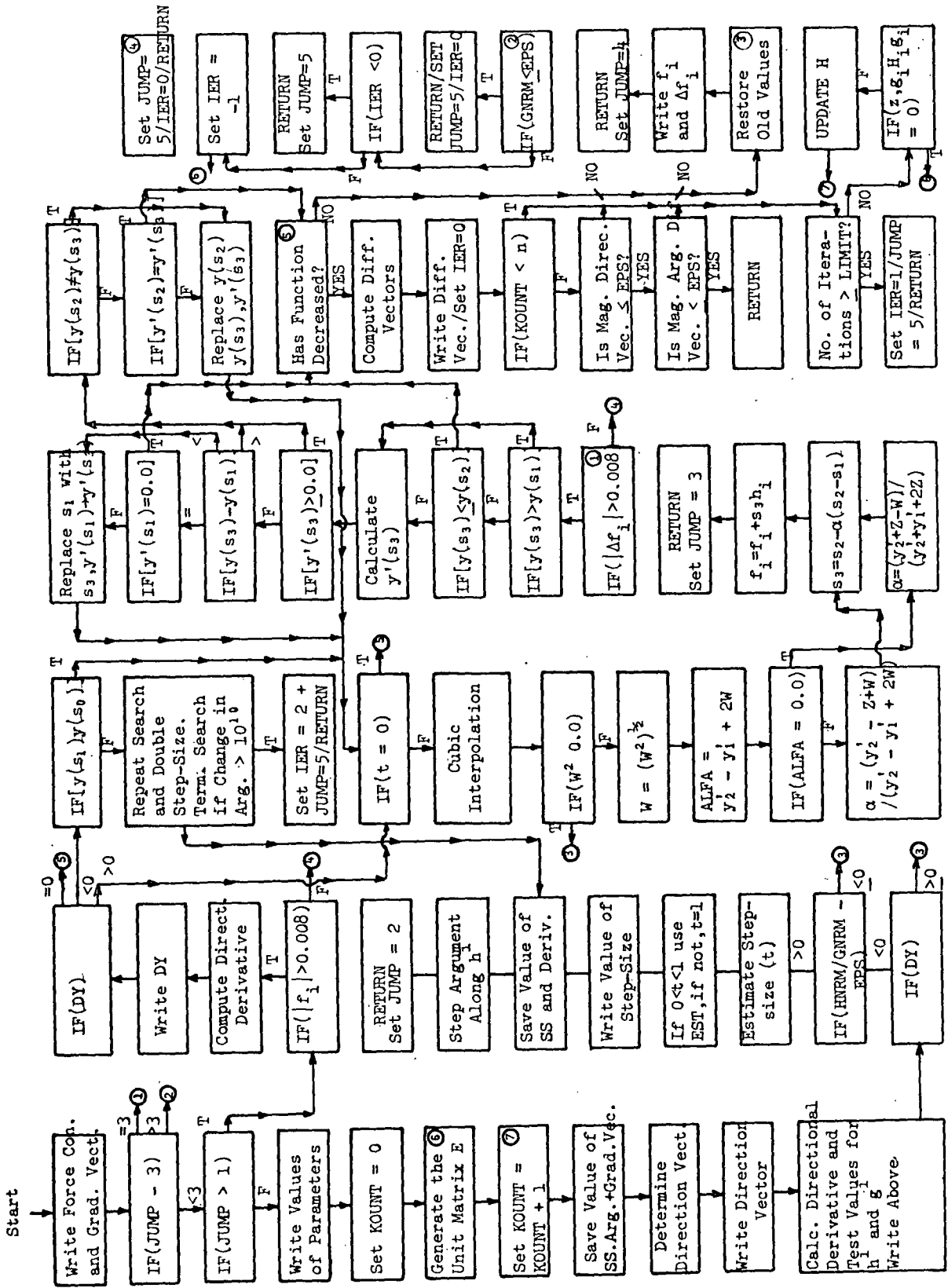


Figure 44. The Flow Diagram of Subroutine FMFP



TABLE LII

LISTING OF THE JCL CARDS NEEDED TO RUN THE  
STORED VERSION OF FLPO

```
//FLPO JOB 94000110,LAR,MSGLEVEL=1
//JOB LIB DD DSN=LAR,VOL=SER=DLIB03,DISP=OLD,UNIT=SYSDA
// EXEC PGM=FLPO
//FT05F001 DD DDNAME=SYSIN
//FT06F001 DD SYSOUT=A
//FT07F001 DD SYSOUT=B
//FT01F001 DD UNIT=SYSDA,DSN=TAPE01,DISP=(NEW,DELETE),
// VOL=SER=DLIB01,
// SPACE=(CYL,(20,1)),DCB=(RECFM=VS,BLKSIZE=120)
//SYSIN DD *
```

TABLE LIII

LISTING OF FLPO

```
C PROGRAM FLPO. SOLUTION OF THE SECULAR EQUATION AND REFINEMENT
C OF A SET OF FORCE CONSTANTS BY THE METHOD OF LEAST SQUARES.
C SCHACHTSCHNEIDER 9/1/65
C MODIFIED FOR OS BY L J PITZNER 10/1/71
C MANY MOLECULE PERTURBATION USING FLETCHER-POWELL MINIMIZATION.
C THIS PROGRAM USES SUBROUTINE FMFP FROM IBM'S SCIENTIFIC SUB. PACK.
C THIS PROGRAM ADJUSTS UP TO 70 FORCE CONSTANTS FOR A
C LARGE NUMBER OF MOLECULES OR BLOCKS OF ORDER 70 OR LESS.
C CODED IN FORTRAN IV FOR USE WITH THE IBSYS SYSTEM.
C THE SECULAR EQUATIONS OF THE SYMMETRIC PROBLEMS ARE SOLVED BY
C A SHARE SUBROUTINE MIHDI3 PROGRAMED BY F.J.CORBATO AND M.MERWIN
C OF M.I.T.
C DISCS ARE USED INSTEAD OF SCRATCH TAPES
C DIMENSION EIG(66,66),NR(650),NC(650),NFO(650),Z(650),NCF(71),
C 1SI(71),SIS(71),FF(71),EX(71),BZ(66,71),G(66,66),DX(71),DE(71),
C 2DG(71),EC(71),E(71),DV(71),DD(71),DC(71),FI(71),RECORD(54),
C 3REC(18),P(71),NFX(71),H(2734),NROW(4),NCOL(4),NPO(4),DATIN(4)
C EQUIVALENCE(EIG(2640),NCF),(EIG(2720),SI),(EIG(2880),FF),
C 2(EIG(2960),EX),(BZ,G),(BZ(4360),DX),(BZ(4440),DE,DG),
C 3(BZ(4520),EC),(E,DV,SIS)
C COMMON BZ,EIG,DD,E,DC,FI,RECORD,REC,P,NFX,NROW,NCOL,NPO,DATIN,
C INCZ,NCZS,NDT,JOKER,JOK,EST,EPS,SUMDD,DEFR,FR,NP,NOIN,NOPROB,NOZ,
C 2NF,NQ,TOL,NPMAX,FREQ,ERPO,ERO,RAP,FRAC,PER,IFREP,IFER,NMOL,IND,
C 3SCALE,ER,ERP,PTOT,NM,NM1,ND,NDD,SUM,NVAR,JUMP,NOVAR,NR,NC,NFO,Z,H,
C 4LEAP,CONV,STUT,IFU,IFDEL,RATIO,WSRO,ITERM,NCOND
C HN(A)=5.88852E-7*A*A
C FNC(B)=SQRT(B)
C READ PROBLEM CONTROL CARD
C PROBLEM CONTROL CARD CONTAINS THE FOLLOWING INFORMATION
C 1.IND=-09, INDICATING THE START OF A PROBLEM IN COLUMNS 1-3.
C 2.NOPROB, THE PROBLEM NUMBER. IN COLUMNS 4-9.
C 3.NMOL, THE NUMBER OF MOLECULES, IN COLUMNS 10-12.
```

TABLE LIII (Continued)

- C 4.NF, THE NUMBER OF FORCE CONSTANTS IN COLUMNS 13-15.  
C LESS THAN 71
- C 5.NPMAX, THE MAXIMUM NUMBER OF PERTURBATIONS DESIRED, COLUMNS  
C 16-18.
- C 6.NCZ, THE NUMBER OF FORCE CONSTANTS TO BE HELD FIXED, IN COLUMNS  
C 19-21. (LESS THAN 71)
- C 7.IFREP=1, IF ONLY A NEW SET OF  $F_i(i)$ , AND  $NCF(i)$  ARE TO BE  
C READ IN. DE, P, W, U, Z, AND G FROM PREVIOUS PROBLEM ARE USED.  
C IFREP=0, IF A NEW PROBLEM IS TO BE STARTED.  
C IFREP=-1, FINAL  $F_i(i)$  FROM PREVIOUS PROBLEM ARE USED AS INITIAL  
C  $F_i(i)$ . NEW  $NCF(i)$  ARE READ. ZS FROM PREVIOUS PROBLEM MAY BE  
C RENUMBERED. PUNCHED IN COLUMNS 22-23.
- C 8.IFER=-3,-2,-1,0,1 PUNCHED IN COLUMNS 24-25  
C FOR IFER=1 PER IS READ IN AND USED AS A FRACTIONAL ERROR  
C FOR IFER=0 PER=0.005 USED AS A FRACTION  
C FOR IFER=-1 ESTIMATED ERRORS ARE READ IN FOR EACH OBS.FREQ.  
C INPUT FOLLOWS OBS.FREQ.  
C FOR IFER=-2 ERROR IN ALL FREQ. ASSUMED TO BE PER CM-1  
C FOR IFER=-3 PER=1.0 CM-1 FOR ALL OBS. FREQ.
- C 9.PER AN ERROR TO BE ASSUMED FOR ALL OBS.FREQ.  
C A FRACTION IF IFER=1 IN CM-1 IF IFER=-2  
C PUNCHED IN COLUMNS 26 TO 33 WITH DECIMAL BETWEEN COL.  
C 27 AND 28 OR PUNCHED  
C CONTINUE
- C 10. EST, AN ESTIMATE OF THE MINIMUM FUNCTION VALUE.  
C PUNCHED IN COLUMNS 34 TO 41 WITH THE DECIMAL BETWEEN COLUMNS  
C 37 AND 38 OR PUNCHED.
- C 11. EPS, A TEST VALUE REPRESENTING THE EXPECTED ABSOLUTE ERROR.  
C A REASONABLE CHOICE IS  $0.1E-05$ . PUNCHED IN COLUMNS 42-51. (RIGHT  
C JUSTIFIED)
- C 12.RAP, THE CUT-OFF FACTOR FOR THE JACOBI DIAGONALIZATION.  
C THE JACOBI ROTATIONS ARE STOPPED WHEN  $MAX(H(i,j))$  IS LESS  
C THAN  $RAP * MIN(H(i,i))$ . IF RAP IS NOT ENTERED IT IS TAKEN EQUAL  
C TO  $0.5E-2$ . ON THE THE FINAL CYCLE RAP IS SET EQUAL TO  
C  $0.5E-3$  GIVING EIGENVALUES TO 6 SIGNIFICANT FIGURES AND EIGEN-  
C VECTORS TO 3 OR 4 FIGURES.  
C RAP IS PUNCHED IN COLUMNS 52-56 WITH THE DECIMAL BETWEEN  
C COLUMNS 52 AND 53 OR PUNCHED.  
C CONTINUE
- C 13.FRAC, A FRACTIONAL FACTOR FOR DECREASING RAP ON EACH CYCLE.  
C AFTER EACH PERTURBATION RAP IS SET EQUAL TO  $FRAC * RAP$ .  
C IF FRAC IS NOT ENTERED IT IS TAKEN EQUAL TO 0.9.  
C FRAC IS PUNCHED IN COLUMNS 57-60 WITH THE DECIMAL BETWEEN  
C COLUMNS 57 AND 58 OR PUNCHED.
- C 14.LEAP, EITHER 1 OR 0. A 1 CAUSES THE PRINT OUT OF THE EIGEN-  
C VALUES AND ERRORS, GRAD. VEC., ARG. VEC., DIR. VEC., ARG. DIFF.  
C VEC., AND GRAD. DIFF. VEC. TO BE SUPRESSED. A ZERO WILL PERMIT  
C THEIR PRINT OUT. LEAP IS PUNCHED IN COLUMNS 61 AND 62.
- C 15.CONV, AN ARBITRARY CONSTANT USED TO JUDGE THE FORCE CONSTANT  
C CORRECTIONS FOR SATISFACTORY CONVERGENCE. IF CONV. IS NOT  
C ENTERED IT IS TAKEN TO BE 0.008 WHICH IS SCHACHTSCHNEIDER'S  
C CHOICE FOR THIS CONSTANT. CONV IS PUNCHED IN COLUMNS 63-70.
- C 16.IFDEL, A 1 WILL CAUSE THE PRINTOUT OF THE DIFFERENCE BETWEEN  
C OBSERVED AND CALCULATED FREQUENCIES FOR EACH ITERATION.

TABLE LIII (Continued)

```
C      IFDEL PUNCHED IN COLUMNS 71-72.MAY BE USED ONLY WHEN NMOL=1.
 90 READ(5,96001)IND
96001 FORMAT(I3)
      IF(IND.EQ.-9)GO TO 91
 901 IF(IND.NE.999)GO TO 90
 902 CALL EXIT
 91 READ ( 5,4)IND,NOPROB,NMOL,NF,NPMAX,NCZ,IFREP,IFER,PERC,EST,EPS,
  IRAP,FRAC,LEAP,CONV,IFDEL
  4 FORMAT(I3,I6,4I3,2I2,F8.6,F8.4,E10.2,F5.4,F4.3,I2,F8.6,I2)
      WSRO=1000.0
      REWIND 1
 93 IF(IFREP.EQ.0)GO TO 802
 800 IF(JOK)90,805,90
 802 PER=PERC
 805 NP=0
      NCOND=0
      JUMP=1
      NVAR = NF - NCZ
      NX=1
      ER=0.0
      ERP=0.0
      NCZS=NCZ
      IF(CONV.GT.0.0)GO TO 51311
      CONV=0.008
51311 NCYC=1
      NOVAR=NF+1
      IF(RAP.GT.0.0)GO TO 808
 807 RAP=0.5E-2
 808 DD 810 I=1,NF
 810 NFX(I)=1
      IF(FRAC.GT.0.0)GO TO 812
 811 FRAC=0.9
 812 JOK=0
  94 IF(NPMAX.EQ.0)GO TO 942
 940 JOKER=0
      GO TO 96
 942 JOKER=1
C      READ PROBLEM INFORMATION CARDS. 3 CARDS CONTAINING INFORMATION
C      ABOUT THE PROBLEM. CARDS MUST BE INCLUDED EVEN IF BLANK.
 96 READ (5,6)RECORD
  6 FORMAT(18A4)
      WRITE (6,8)NOPROB,NMOL,NF,NPMAX,NCZ,EST,EPS
  8 FORMAT(13H1 PROBLEM NO.18,6H NMOL=14,4H NF=14,7H NPMAX=14,5H NCZ=1
 14,5H EST=F6.4,5H EPS=E10.2)
      WRITE(6,8080)RECORD
 8080 FORMAT(1H ,12X,18A4)
      IF(IFREP.LT.0)GO TO 9602
C      READ INTIAL FORCE CONSTANTS
C      THE FORCE CONSTANTS ARE PUNCHED IN 12 COLUMN FIELDS 6 PER CARD
C      WITH THE DECIMAL BETWEEN COLUMNS 6 AND 7 OR PUNCHED. IN ORDER
C      1 THROUGH NF.
 9601 READ (5,20)(FI(I),I=1,NF)
  20 FORMAT(6F12.6)
 9602 WRITE (6,61)NP,(I,FI(I),I=1,NF)
```

TABLE LIII (Continued)

```
61 FORMAT(23H0 FORCE CONSTANTS AFTER 14,15H PERTURBATIONS./(16,F12.6))
9610 IF(NCZ.LE.0)GO TO 9614
C   READ NUMBERS OF FORCE CONSTANTS TO BE HELD FIXED
C   PUNCHED IN 3 COLUMN FIELDS 24 PER CARD. IF NCZ=0 ALL FORCE
C   CONSTANTS ARE ADJUSTED.
9612 READ (5,7) (NCF(L),L=1,NCZ)
7   FORMAT(24I3)
DO 9613 I=1,NCZ
   JX=NCF(I)
9613 NFX(JX)=-1
9614 CONTINUE
9624 IF(NCZ.LE.0)GO TO 9630
9625 WRITE (6,25) (NCF(L),L=1,NCZ)
25  FORMAT(39H0 NUMBERS OF FORCE CONSTANTS HELD FIXED/(15I4))
9630 NM=1
   IF(IFREP.NE.0)GO TO 470
99  SUM=0.0
   NDT=0
   PTOT=0.0
   SCALE=1.0
C   READ MOLECULE CONTROL CARD.CONTAINING THE FOLLOWING INFORMATION
C   1.IND=-06, IDENTIFYING CONTROL CARD. IN COLUMNS 1-3
C   2.NQ, THE DIMENSION OF THE SECULAR EQUATION. COLUMNS 4-6.
C   3.NDD,THE NUMBER OF NON-ZERO EXPERIMENTAL FREQUENCIES. IN
C   COLUMNS 7-9.
C   4.NZZ, THE NUMBER OF Z MATRIX ELEMENTS. IN COLUMNS 10-13.
C   5.IFU, A 1 WILL CAUSE PRINTOUT OF THE FINAL H MATRIX. PUNCHED
C   IN COLUMNS 14-15.
C   6.IFW=1 OR -2, IF WEIGHTING ELEMENTS ARE INCLUDED WITH THE INPUT
C   IFW=0,-1,OR-3, IFWEIGHTING ELEMENTS ARE NOT INCLUDED.COLS.16-17
C   7.ISKZ=0, IF A NEW Z MATRIX IS TO BE READ IN FOR THE MOLECULE.
C   ISKZ=1, IF THE Z MATRIX FROM THE PREVIOUS MOLECULE IS TO BE
C   USED. E.G. ISOTOPIC MOLECULES . PUNCHED IN COLUMN 19.
C   8.STUT, THE VALUE FROM STUDENT'S T DISTRIBUTION NEEDED TO CALC-
C   ULATE THE 95 PERCENT CONFIDENCE INTERVALS. STUT=T(N-P,.975)
C   WHERE N=NO. OF NONZERO FREQ. AND P=NO. OF FORCE CONSTANTS
C   BEING REFINED. PUNCHED IN COLUMNS 20-27.
C   9.RATIO, IF THE RATIO OF SUCCESSIVE WEIGHTED SUM OF SQUARES
C   OF RESIDUALS IS = OR GT THIS VALUE, THE REFINEMENT WILL BE
C   TERMINATED AND SAID TO HAVE CONVERGED. RATIO IS PUNCHED IN
C   COLUMNS 28-35.
C   10.ITEM, NO. OF TIMES THE RATIO CONDITION FOR TERMINATION MUST BE
C   MET BEFORE ACTUAL TERMINATION OF THE REFINEMENT. COLS.36-39.
100 READ (5,14)IND,NQ,NDD,NZZ,IFU,IFW,ISKZ,STUT,RATIO,ITEM
14  FORMAT(3I3,I4,3I2,F8.4,F8.6,I4)
   IF(IND.NE.-6)GO TO 900
C   INPUT DATA FOR EACH MOLECULE FOLLOW THE MOLECULE CONTROL
C   CARD IN THE ORDER
C   1.MOLECULE INFORMATION CARD, 1 CARD CONTAINING THE NAME OF THE
C   MOLECULE OR BLANK. (COLUMNS 1-3 MUST BE LEFT BLANK)
C   2.THE Z MATRIX
C   3.EXPERIMENTAL FREQUENCIES, NQ OF THEM FOR NDD GREATER THAN ZERO
C   IF NDD=0 NO FREQ. ARE ENTERED.
C   4.ESTIMATED ERRORS IN OBS.FREQ. FOR IFER=-1.
```

TABLE LIII (Continued)

```
C      5.WEIGHTING ELEMENTS, IF IFW=1 OR -2
C      6. THE G MATRIX.
C      READ MOLECULE INFORMATION CARD
101 READ (5,6)REC
      ND=0
      IF(ISKZ.GT.0)GO TO 203
C      READ Z MATRIX
C      Z IS NOT STORED AS A MATRIX, BUT RATHER AS 4 ONE DIMENSIONAL
C      ARRAYS NR GIVING THE ROW NUMBER OF THE F MATRIX ELEMENT, NC
C      GIVING THE COLUMN NUMBER OF THE F MATRIX ELEMENT, NFO GIVING
C      THE NUMBER OF THE DISTINCT FORCE CONSTANT AND Z GIVING THE Z
C      MATRIX ELEMENT. NC MUST BE GREATER THAN OR EQUAL TO NR
C      ONLY NON-ZERO ELEMENTS ARE ENTERED.
C      THE Z ELEMENTS ARE PUNCHED IN 18 COLUMN FIELDS, 1 TO 4 PER CARD.
C      COLUMNS 1-3 GIVE NR , COLUMNS 4-6 GIVE NC , COLUMNS 7-9 GIVE NFO,
C      AND Z IS PUNCHED IN COLUMNS 10-18 WITH THE DECIMAL BETWEEN
C      COLUMNS 12 AND 13 OR PUNCHED.NROW=-2 AFTER LAST ELEMENT.
C      TOTAL NUMBER OF Z MATRIX ELEMENTS MUST BE LESS THAN 651.
190 NOZ=0
191 READ (5,18) (NROW(L),NCOL(L),NPO(L),DATIN(L),L=1,4)
      18 FORMAT(4(3I3,F9.6))
      DO 196 L=1,4
      IF(NROW(L))198,196,192
192 IF(NQ.LT.NCOL(L))GO TO 920
193 NOZ=NOZ+1
      NR(NOZ)=NROW(L)
      NC(NOZ)=NCOL(L)
      NFO(NOZ)=NPO(L)
      Z(NOZ)=DATIN(L)
196 CONTINUE
      GO TO 191
198 IF(NROW(L).NE.-2)GO TO 920
203 IF(NOZ.GT.650)GO TO 920
204 IF(NDD.GT.0)GO TO 207
205 DO 206 I=1,NQ
      DX(I)=0.0
206 P(I)=0.0
      GO TO 270
C      READ OBSERVED FREQUENCIES. IF NDD IS GREATER THAN ZERO.
C      PUNCHED IN 12 COLUMN FIELDS 6 PER CARD, DECIMAL BETWEEN COLUMNS
C      6 AND 7 OR PUNCHED. ENTERED IN DECREASING ORDER IN EACH FACTORED
C      BLOCK. IF THE FREQUENCIES ARE UNKNOWN OR UNCERTIAN, OR ZERO
C      (REDUNDANCIES) ENTER A ZERO, FOR DEGENERATE ROOTS ENTER ONE
C      FREQUENCY AND THE REST ZERO. ANY FREQUENCY MAY BE GIVEN ZERO
C      WEIGHT IN THE PERTURBATION BY ENTERING A ZERO INSTEAD OF THE
C      ACTUAL FREQUENCY. FREQUENCIES ARE ENTERED IN WAVENUMBERS.
C      A TOTAL OF NQ ENTRIES, ND OF THEM MUST BE NON-ZERO.
207 READ (5,20) (DE(I),I=1,NQ)
C      COMPUTE THE FREQUENCY PARAMETERS FROM THE FREQUENCIES
      DO 209 I=1,NQ
      TEM=DE(I)
      IF(TEM.LE.0.0)GO TO 209
208 ND=ND+1
209 DX(I)=HN(TEM)
```

TABLE LIII (Continued)

```

N1=0
IF(IFER+2)210,211,1122
1122 IF(IFER)215,220,221
C   CONSTANT ERROR OF 1 CM-1 IN EACH OBS.FREQ. FOR IFER=-3
210 PER=1.0
C   CONSTANT ERROR OF PER CM-1 IN EACH OBS. FREQ. FOR IFER=-2
211 DO 212 I=1,NQ
212 E(I)=PER
    GO TO 217
C   READ ESTIMATED ERRORS IN OBS.FREQ.IN CM-1. ONE FOR EACH
C   NON-ZERO DE(I), I.E. NQ ENTRIES, ND OF THEM NON-ZERO FOR IFER=-1.
215 READ (5,20)(E(I),I=1,NQ)
217 DO 219 I=1,NQ
    TEMP=DE(I)
    IF(TEMP)925,219,218
218 N1=N1+1
    DC(N1)=E(I)/TEMP
219 CONTINUE
    GO TO 225
C   CONSTANT FRACTIONAL ERROR OF 0.005 IN EACH OBS. FREQ. FOR
C   IFER=0
220 PER=0.005
C   CONSTANT FRACTIONAL ERROR =PER IN EACH OBS. FREQ. FOR IFER=1.
221 DO 222 I=1,ND
222 DC(I)=PER
225 IF(IFW+2)230,235,1311
1311 IF(IFW)250,255,235
C   WEIGHT= 1.0/ (FREQ.PAR.)*2           FOR IFW=-3
230 DO 234 I=1,NQ
    TEM=DX(I)
    IF(TEM.LE.0.0)GO TO 232
231 P(I)=1.0/(TEM*TEM)
    PTOT=PTOT+P(I)
    GO TO 234
232 P(I)=0.0
234 CONTINUE
    NDT=NDT+ND
    GO TO 260
C   READ WEIGHTING ELEMENTS ONE FOR EACH NON-ZERO OBS. FREQ. FOR
C   IFW=1 OR IFW=-2
235 READ (5,20)(E(I),I=1,ND)
    N1=0
    N2=0
    IF(IFW.GT.0)GO TO 241
C   WEIGHT =E(I)   FOR IFW=-2
236 DO 240 I=1,NQ
    IF(DX(I).LE.0.0)GO TO 239
237 N1=N1+1
    P(I)=E(N1)
    TEM = P(I)
    PTOT=PTOT+TEM
    IF(TEM.LE.0.0)GO TO 240
238 N2=N2+1
    GO TO 240
```

TABLE LIII (Continued)

```
239 P(I)=0.0
240 CONTINUE
    NDT=NDT+N2
    GO TO 260
C   WEIGHT =E(I) / FREQ.PAR.      FOR IFW=1
241 DO 248 I=1,NQ
    TEM=DX(I)
    IF(TEM.LE.0.0)GO TO 247
242 N1=N1+1
    P(I)=E(N1)/TEM
    TEMP=P(I)
    PTOT=PTOT+TEMP
    IF(TEMP.LE.0.0)GO TO 248
246 N2=N2+1
    GO TO 248
247 P(I)=0.0
248 CONTINUE
    NDT=NDT+N2
    GO TO 260
C   WEIGHT =1.0      FOR IFW=-1
250 DO 254 I=1,NQ
    IF(DX(I).LE.0.0)GO TO 253
251 P(I)=1.0
    PTOT=PTOT+1.0
    GO TO 254
253 P(I)=0.0
254 CONTINUE
    NDT=NDT+ND
    GO TO 260
C   WEIGHT= 1/ FREQ. PAR.      FOR IFW=0
255 DO 259 I=1,NQ
    TEM=DX(I)
    IF(TEM.LE.0.0)GO TO 258
256 P(I)=1.0/TEM
    PTOT=PTOT+P(I)
    GO TO 259
258 P(I)=0.0
259 CONTINUE
    NDT=NDT+ND
260 N1=0
    DO 266 I=1,NQ
    TEMP=DX(I)
    IF(TEMP.LE.0.0)GO TO 266
262 N1=N1+1
    TEM=DC(N1)
    DCS=TEM*TEM
    SUM=SUM+TEMP*TEMP*P(I)*DCS*(DCS+4.0*TEM+4.0)
266 CONTINUE
    IF(ND-N1)925,270,925
270 WRITE (1)NQ,ND,NOZ
    WRITE (1)(REC(I),I=1,18)
    WRITE (1) (NR(K),NC(K),NFO(K),Z(K),K=1,NOZ)
C   READ G MATRIX
C   READ NON-ZERO G MATRIX ELEMENTS ,G(I,J).
```

TABLE LIII (Continued)

```
C      G ELEMENTS ENTERED IN 18 COLUMN FIELD 1 TO 4 PER CARD GIVING
C      COLUMNS          ITEM
C      1-3              NROW=I      (ROW NO.)
C      4-6              NCOL=J      (COLUMN NO.) (I LESS THAN OR=J)
C      7-18            DATIN=G(I,J) (DECIMAL BETWEEN 12-13 OR PUNCHED)
C      NROW IS SET =-1 AFTER LAST G ELEMENT.
C      SINCE THE G MATRIX IS SYMMETRIC ONLY DIAGONAL ELEMENTS AND THE
C      ELEMENTS ABOVE THE DIAGONAL ARE ENTERED. THAT IS, COLUMN NO.
C      GREATER THAN OR EQUAL TO THE ROW NO.
140 DO 142 I=1,NQ
      DO 142 J=I,NQ
142 G(I,J)=0.0
144 READ (5,16)(NROW(L),NCOL(L),DATIN(L),L=1,4)
      16 FORMAT(4(2I3,F12.6))
      DO 150 L=1,4
      ITEM=NROW(L)
      ITEMP=NCOL(L)
      IF(ITEM)152,150,146
146 IF(ITEMP.LT.ITEM)GO TO 910
147 IF(NQ.LT.ITEMP)GO TO 910
148 I=ITEM
      J=ITEMP
      G(I,J)=DATIN(L)
150 CONTINUE
      GO TO 144
152 IF(ITEM.NE.-1)GO TO 910
C      SCHMIDT ORTHOGONALIZATION OF G
C      STORE INVERSE TRANSFORMATION IN LOWER TRIANGLE OF G
154 NQ=1
      NL=2
155 GD=1.0 /G(NQ,NQ)
      DO 156 J=NL,NQ
156 G(J,NQ)=G(NQ,J)*GD
      IF(NL.GT.NQ)GO TO 170
158 DO 160 I=NL,NQ
      DO 160 J=I,NQ
160 G(I,J)=G(I,J)-(G(NQ,I)*G(NQ,J)*GD)
161 NQ=NQ+1
      NL=NQ+1
163 IF(G(NQ,NQ)-0.000001)164,164,155
164 IF(NL.GT.NQ)GO TO 170
165 DO 166 J=NL,NQ
166 G(J,NQ)=G(NQ,J)
      GO TO 161
170 DO 175 I=1,NQ
      TEM=G(I,I)
      IF(TEM.LE.0.00005)GO TO 173
172 DG(I)=FNC(TEM)
      GO TO 174
173 DG(I)=0.0
174 G(I,I)=1.0
      DO 175 J=I,NQ
175 G(J,I)=G(J,I)+DG(I)
      DO 178 J=1,NQ
```



TABLE LIII (Continued)

```
178 WRITE (1) (G(I,J),I=J,NQ)
    WRITE (1) (DG(I),I=1,NQ)
    WRITE (1) (DX(I),I=1,NQ)
    WRITE (1) (P(I),I=1,NQ)
    NM=NM+1
    IF(NMOL.GE.NM)GO TO 100
286 END FILE 1
    REWIND 1
    IF(NDT.GT.0)GO TO 288
287 JOKER=1
    FREQ=NF
    SCALE=1.0
    GO TO 470
288 FREQ=NDT
    SCALE=FREQ/ PTOT
    SUM=SCALE*SUM
    DEFR = FREQ
470 CALL CYCLE
    IF(2-JOK)90,901,90
900 WRITE (6,81)NOPROB,NM
    81 FORMAT(40H0 ERROR IN MOLECULE CONTROL CARD.PROBLEM18,4H.NM=13)
    IF(NM.GT.1)GO TO 903
902 JOK=1
    GO TO 90
903 NMOL=NM-1
    JOK=2
    GO TO 286
910 WRITE (6,85)NM,NOPROB,L,NROW(L),NCOL(L),DATIN(L)
    85 FORMAT(25H0 G MATRIX ERROR MOLECULE13,8H PROBLEM18,6H FIELD13,6H R
1 LEADSI4,I4,F12.6)
    JOK=1
    GO TO 90
920 WRITE (6,87)NM,NOPROB,NOZ,NROW(L),NCOL(L),NPO(L),DATIN(L)
    87 FORMAT(25H0 Z MATRIX ERROR MOLECULE13,8H PROBLEM18,8H ELEMENT14,6H
1 READSI4,I4,I4,F9.6)
    JOK=1
    GO TO 90
925 WRITE (6,88)NM,NOPROB,N1
    88 FORMAT(27H0 EIGENVALUE ERROR MOLECULE13,8H PROBLEM18,4H ND=13)
    JOK=1
    GO TO 90
    END
    SUBROUTINE CYCLE
    DIMENSION EIG(66,66),NR(650),NC(650),NFO(650),Z(650),NCF(71),
1 SI(71),SIS(71),FF(71),EX(71),BZ(66,71),G(66,66),DX(71),DE(71),
2 DG(71),EC(71),E(71),DV(71),DD(71),DC(71),FI(71),RECORD(54),
3 REC(18),P(71),NFX(71),H(2734),NROW(4),NCOL(4),NPO(4),DATIN(4)
    EQUIVALENCE(EIG(2640),NCF),(EIG(2720),SI),(EIG(2880),FF),
2 (EIG(2960),EX),(BZ,G),(BZ(4360),DX),(BZ(4440),DE,DG),
3 (BZ(4520),EC),(E,DV,SIS)
    COMMON BZ,EIG,DD,E,DC,FI,RECORD,REC,P,NFX,NROW,NCOL,NPO,DATIN,
1 INCZ,NCZS,NDT,JOKER,JOK,EST,EPS,SUMDD,DEFR,FR,NP,NOIN,NOPROB,NOZ,
2 NF,NQ,TOL,NPMAX,FREQ,ERPO,ERO,RAP,FRAC,PER,IFREP,IFER,NMOL,IND,
3 SCALE,ER,ERP,PTOT,NM,NM1,ND,NDD,SUM,NVAR,JUMP,NOVAR,NR,NC,NFO,Z,H,
```

TABLE LIII (Continued)

```
4LEAP, CONV , STUT, IFU, IFDEL, RATIO, WSRU, ITERM, NCOND
  FN(A)=SQRT(A/5.88852E-7)
  GN(A)=A/ND
470 REWIND 1
  NM=1
  SUMDD=0.0
480 READ (1) NQ, ND, NOZ
  READ (1) (REC(I), I=1, 18)
  READ (1) (NR(K), NC(K), NFO(K), Z(K), K=1, NOZ)
490 IF(JOKER.LE.0)GO TO 300
492 RAP=0.5E-3
300 DO 301 J=1, NQ
301 READ (1) (G(I, J), I=J, NQ)
  READ (1) (DG(I), I=1, NQ)
  READ (1) (DX(I), I=1, NQ)
  READ (1) (P(I), I=1, NQ)
  IF(ND.GT.0)GO TO 306
304 IF(JOKER.LE.0)GO TO 468
C COMPUTE TRANSFORMED F MATRIX AND STORE IN UPPER TRIANGLE OF G.
306 DO 328 J=1, NQ
  P(J)=SCALE*P(J)
  DO 308 I=1, NQ
308 DD(I)=0.0
  DO 320 K=1, NOZ
  IX=NR(K)
  IF(IX.LT.J)GO TO 320
312 JX=NC(K)
  LX=NFO(K)
  TEM = F((LX)*Z(K)
  DD(IX)=DD(IX)+TEM*G(JX, J)
  IF(IX-JX)318, 320, 318
318 DD(JX)=DD(JX)+TEM*G(IX, J)
320 CONTINUE
  DO 324 K=J, NQ
  DC(K)=0.0
  DO 324 L=K, NQ
324 DC(K)=DC(K)+G(L, K)*DD(L)
  DO 328 K=J, NQ
328 G(J, K)=DC(K)
  NR2=0
  IEGEN=0
C DIAGONALIZE TRANSFORMED F MATRIX BY JACOBI METHOD
CALL HDIAG(G, NQ, IEGEN, EIG, NR2, RAP)
C COMPUTE EIGEN VECTORS
DO 330 I=1, NQ
DC(I)=G(I, I)
330 G(I, I)=DG(I)
DO 335 I=1, NQ
DO 333 J=1, NQ
DD(J)=0.0
DO 333 K=1, J
333 DD(J)=DD(J)+G(J, K)*EIG(K, I)
DO 335 J=1, NQ
335 EIG(J, I)=DD(J)
```

TABLE LIII (Continued)

```
C      ORDER EIGENVALUES AND EIGENVECTORS
      II=NQ-1
      DO 340 J=1,II
      LOW=J+1
      DO 340 K=LOW,NQ
      IF(DC(J)-DC(K))337,340,340
337  TEM=DC(J)
      DC(J)=DC(K)
      DC(K)=TEM
      DO 338 I=1,NQ
338  DD(I)=EIG(I,J)
      DO 339 I=1,NQ
      EIG(I,J)=EIG(I,K)
339  EIG(I,K)=DD(I)
340  CONTINUE
C      COMPUTE EIGENVALUE ERRORS
341  DO 350 I=1,NQ
      IF(DX(I))348,348,344
344  DD(I)=DX(I)-DC(I)
      SUMDD=SUMDD+DD(I)*DD(I)*P(I)
      GO TO 350
348  DD(I)=0.0
350  CONTINUE
352  IF(LEAP.NE.0)GO TO 63999
      WRITE (6,24)NM,NP,NR2,RAP,(DC(I),I=1,NQ)
24  FORMAT(37H0 EIGENVALUES AND ERRORS FOR MOLECULEI4,6H AFTERI3,15H P
      1ERTURBATIONS.I5,11H ROTATIONS./6H  RAP=E12.4/(1H ,9F8.5))
      WRITE (6,26)(DD(J),J=1,NQ)
26  FORMAT(8H0 ERRORS/(1H ,9F8.5))
63999 WRITE(6,87787)SUMDD,NP
87787 FORMAT(26H0 WEIGHTED SUM OF SQUARES=E14.6,6H AFTERI3,15H PERTURBAT
      IONS.)
      IF(IFDEL.LE.0)GO TO 90007
      WRITE(6,10113)NP
10113 FORMAT(1H0,'THE DIFFERENCE BETWEEN OBS. AND CALC. FREQUENCIES AFTE
      IR',I4,2X,'PERTURBATIONS')
      WRITE(6,21012)
21012 FORMAT(1H0,3X,'I',5X,'DELTA FREQ.')
```

```
      DO 61531 J=1,NQ
61531 SIS(J)=0.0
      DO 61532 J=1,NQ
      IF(DX(J).LE.0.)GO TO 10011
      TEMP1=FN(DX(J))
      TEMP2=FN(DC(J))
      SIS(J)=TEMP1-TEMP2
10011 WRITE(6,20022)J,SIS(J)
20022 FORMAT(1H ,I4,5X,F12.6)
61532 CONTINUE
90007 IF(JOKER.GT.0)GO TO 364
354  CONTINUE
      IF(JOK)468,400,400
C      OUTPUT FOR FINAL CYCLE
364  ERO=0.0
      ERPO=0.0
```

TABLE LIII (Continued)

```
DO 368 I=1,NQ
DE(I)=FN(DX(I))
DV(I)=FN(DC(I))
TEM=DE(I)
IF(TEM.LE.0.)GO TO 365
GO TO 366
365 EC(I)=0.0
EX(I)=0.0
DE(I)=0.0
GO TO 368
366 EX(I)=TEM-DV(I)
EC(I)=100.0*EX(I)/TEM
IF(P(I).LE.0.0)GO TO 368
367 ERO=ERO+ABS(EX(I))
ERPO=ERPO+ABS(EC(I))
368 CONTINUE
81180 ER=ER+ERO
ERP=ERP+ERPO
ERO=GN(ERO)
ERPO=GN(ERPO)
90008 WRITE (6,28)NM,SCALE,REC
28 FORMAT(75H1 OBSERVED AND CALCULATED FREQUENCIES AND FREQUENCY PARA
METERS FOR MOLECULEI3/26H SCALE FACTOR FOR WEIGHTS=F10.6/12X,18A4)
369 WRITE (6,29)(I,DE(I),DV(I),EX(I),EC(I), P(I),DX(I),DC(I),I=1,NQ)
29 FORMAT(95H0 OBS.FREQ. CALC.FREQ. DIFFERENCE PERCENT ERROR
1 WEIGHT OBS.FREQ.PAR. CALC.FREQ.PAR. /6X,6H(CM-1),6X,6H(CM-1
2),7X,6H(CM-1)/(14,F9.1,4X,F8.1,4X,F6.1,7X,F7.3,6X,F9.4,F10.5,F14.5
3))
WRITE (6,31) ERO,ERPO
31 FORMAT(17H0 AVERAGE ERROR=F6.2,10H CM-1 ,OR F6.3,8H PERCENT)
SIGMA = SQRT(SUMDD/DEFR)
NM=NM+1
IF(NMOL-NM)825,480,480
C COMPUTE THE JZ MATRIX ( CALLED BZ)
400 IF(NM.NE.1)GO TO 401
DO 19156 I=1,NQ
19156 SIS(I)=0.0
401 DO 421 K=1,NQ
DO 410 N=1,NF
410 BZ(K,N)=0.0
DO 420 L=1,NOZ
I=NR(L)
J=NC(L)
M=NFO(L)
TEM=EIG(I,K)*EIG(J,K)*Z(L)
IF(I.NE.J)GO TO 418
416 BZ(K,M)=BZ(K,M)+TEM
GO TO 420
418 BZ(K,M)=BZ(K,M)+TEM+TEM
420 CONTINUE
421 CONTINUE
C COMPUTE S
438 DO 442 I=1,NQ
P(I)=SQRT(P(I))
```

TABLE LIII (Continued)

```
BZ(I,NOVAR)=DD(I)
DO 442 J=1,NOVAR
442 BZ(I,J)=P(I)*BZ(I,J)
DO 458 I=1,NOVAR
DO 456 J=I,NOVAR
SI(J)=0.0
DO 456 K=1,NQ
456 SI(J)=SI(J)+BZ(K,I)*BZ(K,J)
458 SIS(I)=SI(NOVAR) + SIS(I)
463 CONTINUE
468 NM=NM+1
IF(NMOL.GE.NM)GO TO 480
RAP=FRAC*RAP
600 IF(JOK.GE.0)GO TO 602
601 JOK=1
JOKER=1
GO TO 470
602 FR=NDT-NF+NCZ
608 DO 610 I=1,NF
SI(I)=-2.*SIS(I)
610 CONTINUE
642 DEFR=FREQ
IF(NCZ.GT.0)GO TO 3286
9119 DO 47813 I=1,NF
SIS(I)=SI(I)
47813 FF(I)=FI(I)
GO TO 31311
3286 NCN=1
DO 31444 I=1,NF
IF(NFX(I).LT.0)GO TO 31444
66222 FF(NCN)=FI(I)
SIS(NCN)=SI(I)
NCN=NCN+1
31444 CONTINUE
C CALL FMFP TO MINIMIZE WEIGHTED SUM OF SQUARES OF RESIDUALS.
31311 CALL FMFP(H,NVAR,FF,SUMDD,SIS,EST,EPS,NPMAX,IER,JUMP,NP,NN2,NN3,
IN31,OLDF,TT,HNRM,GNRM,DDX,FFY,ALFA,AMBDA,FFX,DDY,ZZ,DALFA,WW,LEAP,
ICONV,RATIO,WSRO,ITERM,NGOND)
IF(NCZ.GT.0)GO TO 32121
11211 DO 26162 I=1,NF
26162 FI(I)=FF(I)
GO TO 66871
32121 NCN=1
DO 81181 I=1,NF
IF(NFX(I).LT.0)GO TO 81181
21381 FI(I)=FF(NCN)
NCN=NCN+1
81181 CONTINUE
66871 IF(JUMP.LT.5)GO TO 470
8887 IF(IER)10101,20202,66666
10101 WRITE(6,81918)
81918 FORMAT(1H0,5X,'ERRORS IN GRADIENT CALCULATION')
GO TO 90018
20202 WRITE(6,72135)NP
```

TABLE LIII (Continued)

```
72135 FORMAT(1H0,'ONE OF THE CONDITIONS FOR TERMINATION WAS MET AFTER',
1I3,' PERTURBATIONS.')
GO TO 90018
66666 IF(IER.GT.1)GO TO 40404
30303 WRITE(6,83562)
83562 FORMAT(1H0,5X,'NONE OF THE CONDITIONS FOR TERMINATION WERE MET IN
INPMAX ITERATIONS')
GO TO 90018
40404 WRITE(6,75321)
75321 FORMAT(1H0,5X,'LINEAR SEARCH TECHNIQUE INDICATES IT IS LIKELY NO
1MINIMUM EXITS')
90018 JOKER =1
GO TO 470
825 IF(NPMAX.EQ.0)GO TO 100
WRITE(7,55445)(FI(I),I=1,NF)
55445 FORMAT(6F12.6)
N =NVAR
N2=N+N
N3=N2+N
N31=N3+1
K=N31
IF(IFU.LE.0)GO TO 10201
WRITE(6,20302)
20302 FORMAT(1H1,5X,'THE FINAL H MATRIX')
KK=N31
KM=N3+N
DO 30403 L=1,N
WRITE(6,50404)(H(KJ),KJ=KK,KM)
50404 FORMAT(1H ,10F12.6)
KK=KM+1
KM=KM+N-L
30403 CONTINUE
10201 DO 4000 J=1,NVAR
TEM=ABS(H(K))
E(J)=SQRT(2.*TEM)*SIGMA
NJ=N-J
IF(NJ)5000,5000,2000
2000 DO 3000 L=1,NJ
KL=K+L
3000 CONTINUE
4000 K=KL+1
5000 IF(NCZ.LE.0)GO TO 85361
NCN=1
DO 95959 J=1,NF
IF(NFX(J).LT.0)GO TO 95958
EC(J)=E(NCN)
NCN = NCN + 1
GO TO 95959
95958 EC(J)=0.
95959 CONTINUE
DO 85364 I=1,NF
85364 E(I)=EC(I)*STUT
GO TO 95119
85361 DO 88771 M=1,NF
```



TABLE LIII (Continued)

C IER - ERROR PARAMETER  
 C IER = 0 MEANS CONVERGENCE WAS OBTAINED  
 C IER = 1 MEANS NO CONVERGENCE IN LIMIT ITERATIONS  
 C IER = -1 MEANS ERRORS IN GRADIENT CALCULATION  
 C IER = 2 MEANS LINEAR SEARCH TECHNIQUE INDICATES  
 C IT IS LIKELY THAT THERE EXISTS NO MINIMUM.  
 C H - WORKING STORAGE OF DIMENSION N\*(N+7)/2.  
 C CONTINUE  
 C CONV -ARBITRARY CONSTANT TO WHICH DELTA VALUES IN FORCE  
 C CONSTANTS ARE COMPARED TO CHECK FOR SATISFACTORY  
 C CONVERGENCE.

REMARKS

- C I) THE SUBROUTINE NAME REPLACING THE DUMMY ARGUMENT FUNCT  
 C MUST BE DECLARED AS EXTERNAL IN THE CALLING PROGRAM.  
 C II) IER IS SET TO 2 IF , STEPPING IN ONE OF THE COMPUTED  
 C DIRECTIONS, THE FUNCTION WILL NEVER INCREASE WITHIN  
 C A TOLERABLE RANGE OF ARGUMENT.  
 C IER = 2 MAY OCCUR ALSO IF THE INTERVAL WHERE F  
 C INCREASES IS SMALL AND THE INITIAL ARGUMENT WAS  
 C RELATIVELY FAR AWAY FROM THE MINIMUM SUCH THAT THE  
 C MINIMUM WAS OVERLEAPED. THIS IS DUE TO THE SEARCH  
 C TECHNIQUE WHICH DOUBLES THE STEPSIZE UNTIL A POINT  
 C IS FOUND WHERE THE FUNCTION INCREASES.

SUBROUTINES AND FUNCTION SUBPROGRAMS REQUIRED  
FUNCT

METHOD

C THE METHOD IS DESCRIBED IN THE FOLLOWING ARTICLE  
 C R. FLETCHER AND M.J.D. POWELL, A RAPID DESCENT METHOD FOR  
 C MINIMIZATION,  
 C COMPUTER JOURNAL VOL.6, ISS. 2, 1963, PP.163-168.

CONTINUE

C PROGRAM TAKEN FROM IBM'S SCIENTIFIC SUBROUTINE PACKAGE.  
 C MODIFIED FOR USE WITH FLPO BY L.J.PITZNER 10/5/71

.....

DIMENSIONED DUMMY VARIABLES

```

WSRN=F
IF(WSRN.GT.WSRO)GO TO 61179
TEMP=WSRN/WSRO
WRITE(6,80934)TEMP
80934 FORMAT(1H0,'RATIO OF SUCCESSIVE WEIGHTED SUM OF SQUARES = ',F8.6)
IF(TEMP.LT.RATIO)GO TO 61179
NCOND=NCOND+1
WRITE(6,12345)NCOND
12345 FORMAT(1H0,'NCOND=',I4)
IF(NCOND.GT.ITERM)GO TO 55
61179 IF(LEAP.NE.0)GO TO 67761
WRITE(6,1010)

```



TABLE LIII (Continued)

```
1010 FORMAT(1H0,5X,'N',6X,'FORCE CONSTANTS',4X,'GRADIENT VECTOR')
111 WRITE(6,5213)(I,X(I),G(I),I=1,N)
5213 FORMAT(1H ,4X,I2,7X,F10.6,8X,E14.6)
67761 IF(JUMP-3)3333,1002,1003
3333 IF(JUMP.GT.1)GO TO 1001
C   FUNCTION VALUE AND GRADIENT VECTOR FOR INITIAL ARGUMENT
C
C   RESET ITERATION COUNTER AND GENERATE IDENTITY MATRIX
1000 WRITE(6,999)N,F,EST,EPS,LIMIT,KOUNT,CONV,RATIO,ITERM
999  FORMAT(3HON=I2,3H F=E14.6,5H EST=F10.6,5H EPS=E10.2,7H LIMIT=I4,7H
1  KOUNT=I2,6H CONV=F8.6,7H RATIO=F8.6,7H ITERM=I4)
IER=0
KOUNT=0
N2=N+N
N3=N2+N
N31=N3+1
1  K=N31
DO 4 J=1,N
H(K)=1.
NJ=N-J
IF(NJ)5,5,2
2 DO 3 L=1,NJ
KL=K+L
3 H(KL)=0.
4 K=KL+1
C
C   START ITERATION LOOP
5 KOUNT=KOUNT +1
C
C   SAVE FUNCTION VALUE, ARGUMENT VECTOR AND GRADIENT-VECTOR
IF(LEAP.NE.0)GO TO 63331
WRITE(6,121)
121  FORMAT(1H0,5X,'N',5X,'DIRECTION VECTOR')
63331 OLDF=F
DO 9 J=1,N
K=N+J
H(K)=G(J)
K=K+N
H(K)=X(J)
C
C   DETERMINE DIRECTION VECTOR H
K=J+N3
T=0.
DO 8 L=1,N
T=T-G(L)*H(K)
IF(L.GE.J)GO TO 7
6 K=K+N-L
GO TO 8
7 K=K+1
8 CONTINUE
H(J)=T
IF(LEAP.NE.0)GO TO 9
WRITE(6,965)J,H(J)
965  FORMAT(1H ,4X,I2,6X,E14.6)
```

TABLE LIII (Continued)

9 CONTINUE

```
C
C      CHECK WHETHER FUNCTION WILL DECREASE STEPPING ALONG H.
C      DY=0.
C      HNRM=0.
C      GNRM=0.
C
C      CALCULATE DIRECTIONAL DERIVATIVE AND TESTVALUES FOR DIRECTION
C      VECTOR H AND GRADIENT VECTOR G.
C      DO 10 J=1,N
C      TEM=H(J)
C      TEMP=G(J)
C      HNRM=HNRM+R(TEM)
C      GNRM=GNRM+R(TEMP)
C      10 DY=DY+TEM*TEMP
C      WRITE(6,353)HNRM,GNRM,DY
C      353 FORMAT(1H0,'MAG. OF DIR. VEC. = ',E14.6,4X,'MAG. OF GRAD. VEC.= ',
C      1E14.6,4X,'DIRECTIONAL DERIVATIVE= ',E14.6)
C
C      REPEAT SEARCH IN DIRECTION OF STEEPEST DESCENT IF DIRECTIONAL
C      DERIVATIVE APPEARS TO BE POSITIVE OR ZERO.
C      IF(DY)11,51,51
C
C      REPEAT SEARCH IN DIRECTION OF STEEPEST DESCENT IF DIRECTION
C      VECTOR H IS SMALL COMPARED TO GRADIENT VECTOR G.
C      11 IF(HNRM/GNRM-EPS)51,51,12
C
C      SEARCH MINIMUM ALONG DIRECTION H
C
C      SEARCH ALONG H FOR POSITIVE DIRECTIONAL DERIVATIVE
C      12 FY=F
C      ALFA=2.*(EST-F)/DY
C      AMBDA=1.
C
C      USE ESTIMATE FOR STEPSIZE ONLY IF IT IS POSITIVE AND LESS THAN
C      1. OTHERWISE TAKE 1. AS STEPSIZE
C      IF(ALFA.LE.0.0)GO TO 15
C      13 IF(ALFA.GE.AMBDA)GO TO 15
C      14 AMBDA=ALFA
C      15 ALFA=0.
C
C      SAVE FUNCTION AND DERIVATIVE VALUES FOR OLD ARGUMENT
C      16 FX=FY
C      DX=DY
C      WRITE(6,91326)AMBDA
C      91326 FORMAT(1H0,'STEPSIZE = ',E14.6)
C
C      STEP ARGUMENT ALONG H
C      WRITE(6,201)
C      201 FORMAT(1H0,5X,'N',5X,'FORCE CONSTANTS',9X,'DELTA')
C      DO 17 I=1,N
C      DELTA = AMBDA*H(I)
C      WRITE(6,951)I,X(I),DELTA
C      951 FORMAT(1H ,4X,12,4X,F12.6,8X,F12.6)
C      17 X(I)=X(I)+DELTA
C
```

TABLE LIII (Continued)

```
C      COMPUTE FUNCTION VALUE AND GRADIENT FOR NEW ARGUMENT
      JUMP = 2
      GO TO 56
1001  FY=F
C
C      CHECK FOR SATISFACTORY CONVERGENCE
      DO 96581 I=1,N
      DELTA = AMBDA*H(I)
      IF(R(DELTA).GT.CONV)GO TO 75381
96581  CONTINUE
      GO TO 55
C      COMPUTE DIRECTIONAL DERIVATIVE DY FOR NEW ARGUMENT.  TERMINATE
C      SEARCH, IF DY IS POSITIVE.  IF DY IS ZERO THE MINIMUM IS FOUND.
75381  DY=0.
      DO 18 I=1,N
      18  DY=DY+G(I)*H(I)
      WRITE(6,752)DY
752   FORMAT(1H0,'THE DIRECTIONAL DERIVATIVE = ',E14.6)
      IF(DY)19,36,22
C
C      TERMINATE SEARCH ALSO IF THE FUNCTION VALUE INDICATES THAT
C      A MINIMUM HAS BEEN PASSED.
19   IF(FY.GE.FX)GO TO 22
C
C      REPEAT SEARCH AND DOUBLE STEPSIZE FOR FURTHER SEARCHES
20   AMBDA=AMBDA+ALFA
      ALFA=AMBDA
C      END OF SEARCH LOOP
C
C      TERMINATE IF THE CHANGE IN ARGUMENT GETS VERY LARGE
      CHARG = HNRM*AMBDA
      WRITE(6,954)CHARG
954   FORMAT(1H0,'CHANGE IN ARGUMENT VECTOR = ',E14.6)
      IF(CHARG-1.E10)16,16,21
C
C      LINEAR SEARCH TECHNIQUE INDICATES THAT NO MINIMUM EXISTS
21   IER=2
      JUMP = 5
      RETURN
C
C      INTERPOLATE CUBICALLY IN THE INTERVAL DEFINED BY THE SEARCH
C      ABOVE AND COMPUTE THE ARGUMENT X FOR WHICH THE INTERPOLATION
C      POLYNOMIAL IS MINIMIZED
22   T=0.
23   IF(AMBDA.EQ.0.0)GO TO 36
24   Z=3.*(FX-FY)/AMBDA+DX+DY
      ALFA=AMAX1(R(Z),R(DX),R(DY))
      DALFA=Z/ALFA
      DALFA=DALFA*DALFA-DX/ALFA*DY/ALFA
      WRITE(6,81351)DALFA
81351  FORMAT(1H0,'DALFA = ',E14.6)
      IF(DALFA.LT.0.0)GO TO 51
25   W=ALFA*SQRT(DALFA)
      ALFA = DY-DX+W+W
      IF(ALFA.EQ.0.0)GO TO 251
```

TABLE LIII (Continued)

```
250 ALFA =(DY-Z+W)/ALFA
    GO TO 252
251 ALFA =(Z+DY-W)/(Z+DX+Z+DY)
252 ALFA = ALFA*AMBDA
    WRITE(6,201)
    DO 26 I=1,N
    DELTA =(T-ALFA)*H(I)
    WRITE(6,951)I,X(I),DELTA
26 X(I)=X(I)+DELTA
C
C     TERMINATE, IF THE VALUE OF THE ACTUAL FUNCTION AT X IS LESS
C     THAN THE FUNCTION VALUES AT THE INTERVAL ENDS. OTHERWISE REDUCE
C     THE INTERVAL BY CHOOSING ONE END-POINT EQUAL TO X AND REPEAT
C     THE INTERPOLATION. WHICH END-POINT IS CHOSEN DEPENDS ON THE
C     VALUE OF THE FUNCTION AND ITS GRADIENT AT X
C
    JUMP = 3
    GO TO 56
C     CHECK FOR SATISFACTORY CONVERGENCE.
1002 DO 51131 I=1,N
    DELTA=(T-ALFA)*H(I)
    IF(R(DELTA).GT.CONV)GO TO 61318
51131 CONTINUE
    GO TO 55
61318 IF(F.GT.FX)GO TO 28
    27 IF(F.LE.FY)GO TO 36
    28 DALFA=0.
    DO 29 I=1,N
    29 DALFA=DALFA+G(I)*H(I)
    IF(DALFA.GE.0.0)GO TO 33
    30 IF(F-FX)32,31,33
    31 IF(DX.EQ.0.0)GO TO 36
    32 FX=F
    DX=DALFA
    T=ALFA
    AMBDA=ALFA
    GO TO 23
    33 IF(FY.NE.F)GO TO 35
    34 IF(DY.EQ.DALFA)GO TO 36
    35 FY=F
    DY=DALFA
    AMBDA=AMBDA-ALFA
    GO TO 22
C     TERMINATE, IF FUNCTION HAS NOT DECREASED DURING LAST ITERATION
36 IF(OLDF-F+EPS)51,38,38
C
C     COMPUTE DIFFERENCE VECTORS OF ARGUMENT AND GRADIENT FROM
C     TWO CONSECUTIVE ITERATIONS
38 IF(LEAP.NE.0)GO TO 31113
    WRITE(6,10011)
10011 FORMAT(1H0,5X,'N',5X,'ARG. DIFF. VEC.',3X,'GRAD. DIFF. VEC.')
31113 DO 37 J=1,N
    K=N+J
    H(K)=G(J)-H(K)
```

TABLE LIII (Continued)

```
K=N+K
H(K)=X(J)-H(K)
IF(LEAP.NE.0)GO TO 37
WRITE(6,97533)J,H(N+J),H(N+N+J)
97533 FORMAT(1H ,4X,I2,5X,E14.6,5X,E14.6)
37 CONTINUE

C
C
C      TEST LENGTH OF ARGUMENT DIFFERENCE VECTOR AND DIRECTION VECTOR
C      IF AT LEAST N ITERATIONS HAVE BEEN EXECUTED. TERMINATE, IF
C      BOTH ARE LESS THAN EPS
IER=0
IF(KOUNT.LT.N)GO TO 42
39 T=0.
Z=0.
DO 40 J=1,N
K=N+J
W=H(K)
K=K+N
TEM=H(K)
T=T+R(TEM)
40 Z=Z+W*TEM
WRITE(6,893)T,Z
893 FORMAT(1H0,'LENGTH OF ARG. DIFF. VECTOR = ',E14.6,10X,'LENGTH OF D
IIRECTION VECTOR = ',E14.6)
IF(HNRM.GT.EPS)GO TO 42
41 IF(T.LE.EPS)GO TO 56

C
C      TERMINATE, IF NUMBER OF ITERATIONS.WOULD EXCEED LIMIT
42 IF(KOUNT.GE.LIMIT)GO TO 50

C
C      PREPARE UPDATING OF MATRIX H
43 ALFA=0.
DO 47 J=1,N
K=J+N3
W=0.
DO 46 L=1,N
KL=N+L
W=W+H(KL)*H(K)
IF(L.GE.J)GO TO 45
44 K=K+N-L
GO TO 46
45 K=K+1
46 CONTINUE
K=N+J
ALFA=ALFA+W*H(K)
47 H(J)=W

C
C      REPEAT SEARCH IN DIRECTION OF STEEPEST DESCENT IF RESULTS
C      ARE NOT SATISFACTORY
TEM =Z*ALFA
WRITE(6,96512)TEM
96512 FORMAT(1H0,'Z*ALFA= ',E14.6)
IF(TEM.EQ.0.0)GO TO 1
```

TABLE LIII (Continued)

```
C
C      UPDATE MATRIX H
48 K=N31
   DO 49 L=1,N
   KL=N2+L
   DO 49 J=L,N
   NJ=N2+J
   H(K)=H(K)+H(KL)*H(NJ)/Z-H(L)*H(J)/ALFA
49 K=K+1
   GO TO 5
C      END OF ITERATION LOOP
C
C      NO CONVERGENCE AFTER LIMIT ITERATIONS
50 IER=1
   JUMP = 5
   RETURN
C
C      RESTORE OLD VALUES OF FUNCTION AND ARGUMENTS
51 WRITE(6,201)
   DO 52 J=1,N
   DELTA = 0.0
   K=N2+J
   X(J)=H(K)
52 WRITE(6,951)J,X(J),DELTA
   JUMP = 4
   GO TO 56
C
C      REPEAT SEARCH IN DIRECTION OF STEEPEST DESCENT IF DERIVATIVE
C      FAILS TO BE SUFFICIENTLY SMALL
1003 IF(GNRM.LE.EPS)GO TO 55
C
C      TEST FOR REPEATED FAILURE OF ITERATION
53 IF(IER.LT.0)GO TO 59
54 IER=-1
   GOTO 1
55 IER=0
59 JUMP = 5
56 WSRO=WSRN
   RETURN
   END
SUBROUTINE HDIAG(H,N,IEGEN,U,NR,RAP)
A listing of the subroutine HDIAG was presented in Table
XXXIV and will not be repeated here because of space limita-
tions.
```

1. Problem ID Card. This card identifies the beginning of a problem. This card must have a -09 punched in Columns 1-3 (FORMAT I3).
2. Problem Control Card.
  - a. IND = -09, identifies the problem control card. IND is punched in Columns 1-3 (FORMAT I3).
  - b. NOPROB is the problem number, punched in Columns 4-9 (FORMAT I6).
  - c. NMOL, designates the number of molecules, punched in Columns 10-12 (FORMAT I3).
  - d. NF, signifies the number of force constant parameters. NF is punched in Columns 13-15 (FORMAT I3).

Warning: NF must not exceed 71.
  - e. NPMAX is the maximum number of desired iterations. The refinement will terminate when NPMAX is exceeded, even if convergence has not been reached. NPMAX is positioned in Columns 16-18 (FORMAT I3).

Note: If NPMAX is set equal to zero or left blank, there will be no refinement of the force constant parameters, and the frequencies will be calculated for the problem based on the initial set of parameters.
  - f. NCZ, represents the number of force constants to be held fixed. These force constants do not enter the refinement, and their final value is identical to their initial value. NCZ is punched in Columns 19-21 (FORMAT I3).
  - g. IFREP is the problem repeat option. For IFREP = 0, a new problem is started. If IFREP = 1, only a new set of force constants and list of those force constants to be held fixed are read in; the rest of the problem information is taken from the previous problem. For IFREP = -1, the final set of force constants from the previous problem are used as the initial set in the new problem; the rest of the problem data must be included with the input data. IFREP is punched in Columns 22-23 (FORMAT I2).
  - h. IFER is the error option control. For IFER = 1, the fractional error in the experimental frequencies, PER, is read in. If IFER = 0, the fractional error, PER, is assumed to be 0.005. For IFER = -1, the estimated errors in the frequencies, in  $\text{cm}^{-1}$ , are read in. For IFER = -3, the error is assumed to be  $\text{PER} = 1.0 \text{ cm}^{-1}$ . IFER is punched in Columns 24-25 (FORMAT I2).
  - i. PER is the error in the frequencies described in the above paragraph. If PER is not needed, it may be left blank. PER is punched in Columns 26-33 (FORMAT F8.6).
  - j. EST is the estimate of the value of the weighted sum of squares of the residuals at the minimum. If a value cannot be estimated for EST, one may set it equal to 0.0. EST is punched in Columns 34-41 (FORMAT 8.4).

- k. EPS is a test value representing the expected absolute error. A reasonable choice for EPS is 0.1E-05. EPS is punched in Columns 42-51 (FORMAT E10.2).

Warning: EPS must be right justified.

- l. RAP, the cutoff factor for the Jacobi diagonalization. The plane rotations are terminated when  $\text{MAX}[H(I,J)]$  is less than  $\text{RAP} \cdot \text{MIN}[H(I,I)]$ . If RAP is not entered, the program assigns a value of 0.5E-2. On the final cycle, RAP is set equal to 0.5E-3 which results in eigenvalues significant to 6 figures and eigenvectors significant to 3 or 4 figures. RAP is punched in Columns 52-56 (FORMAT F5.4).
- m. FRAC is a fractional factor for decreasing RAP on each cycle. After each perturbation, RAP is set equal to  $\text{FRAC} \cdot \text{RAP}$ . If FRAC is not entered, it is assigned a value of 0.9 by the program. FRAC is punched in Columns 57-60 (FORMAT F4.3).
- n. LEAP is a printer output suppression option. A 1 will result in the printer suppression of the eigenvalues and errors, gradient vector, argument vector, direction vector, argument difference vector, and gradient difference vector for each perturbation. LEAP is punched in Columns 61-62 (FORMAT I2).
- o. CONV is the convergence criterion. The refinement will terminate when the corrections to the force constant parameters are all less than or equal to CONV (i.e., the absolute value). CONV is punched in Columns 63-70 (FORMAT F8.6).

Note: Schachtschneider (89) suggests a value of 0.008 for CONV; however, the author suggests a value of 0.0001 for a more rigorous criterion.

- p. IFDEL, a 1 will cause the printout of the difference between the calculated and observed frequencies for each perturbation. If IFDEL is left blank the difference will not be printed. IFDEL is punched in Columns 71-72 (FORMAT I2).

Warning: IFDEL can be set equal to 1 only when  $\text{NMOL} = 1$ .

3. Problem Information Cards. Three cards containing alphanumeric information about the problem. The first three columns of each card should be left blank, so that the alphanumeric information may be punched in any column, 4-72 (FORMAT 18A4).

Warning: These cards must be included in the data deck even if they are left blank.

4. Initial Set of Force Constant Parameters. The force constants are punched in 12 column fields, six per card, in the order 1 through NF (FORMAT 6F12.6).
5. Force Constants to be Held Fixed. If NCZ is greater than zero, the numbers of the force constants to be held fixed are punched on cards in 3 column fields, 24 per card, up to NCZ entries (FORMAT 24I3).



Note: The force constants designated on these cards are not entered into the refinement and their final values are identical to their initial values.

6. Molecule Control Card.

a. IND = -06, identifies the molecule control card. IND is punched in Columns 1-3 (FORMAT I3).

b. NQ is the number of internal coordinates, punched in Columns 4-6 (FORMAT I3).

Warning: NQ cannot exceed 66.

c. NDD is the number of nonzero experimental frequencies included with the input data. NDD is punched in Columns 7-9 (FORMAT I3).

Note: If one wishes to solve the secular equation to obtain the calculated frequencies, but no refinement, the experimental frequencies need not be included so that NDD = 0 or left blank.

d. NZZ, the number of  $\underline{Z}$  matrix elements, punched in Columns 10-13 (FORMAT I4).

Warning: NZZ cannot exceed 650.

e. IFU, a 1 will result in the final  $\overline{H}$  matrix being printed out, punched in Columns 14-15 (FORMAT I2).

f. IFW is the weighting element option for the weighted least squares refinement. If IFW = 1 or -2, the weighting elements, E(I), are read in, one for each nonzero experimental frequency. For IFW = -2, the weight(I) = E(I), and for IFW = 1, the weight(I) = E(I)/frequency parameter(I). If IFW = 0, the weight(I) = 1/frequency parameter(I). For IFW = -1, the weight = 1.0 for all the frequencies. Finally, if IFW = -3, the weight(I) = 1/[frequency parameter(I)]<sup>2</sup>. IFW is punched in Columns 16-17 (FORMAT I2).

g. ISKZ is the  $\underline{Z}$  matrix repeat option. If ISKZ = 0, the  $\underline{Z}$  matrix is included with the input data. For ISKZ = 1, the  $\underline{Z}$  matrix from the previous problem is used so that a new  $\underline{Z}$  matrix does not need to be included with the input data. ISKZ is punched in Columns 18-19 (FORMAT I2).

Note: This option is useful for isotopically substituted molecules.

h. STUT is the value from Student's  $t$  distribution needed to compute the 95% confidence intervals for the final set of force constants. STUT =  $t(\underline{n-p}, 0.975)$  where  $\underline{n}$  = NDD, the number of nonzero experimental frequencies, and  $\underline{p}$  = NF - NCZ, the number of force constant parameters being refined. STUT is punched in Columns 20-27 (FORMAT F8.4).

Note: If STUT is set equal to 1.0, the standard errors in the force constants are printed instead of the 95% confidence intervals.

- i. **RATIO**, establishes another criterion to judge the convergence of the refinement and upon which to base termination of the refinement. When the ratio of successive weighted sum of squares is equal to or greater than **RATIO**, the force constant refinement will be terminated and said to have converged if the condition has been met previously **ITERM** times. **RATIO** is punched in Columns 28-35 (FORMAT F8.6).

Note: A reasonable choice for **RATIO** is 0.995.

- j. **ITERM** is the number of times that **RATIO** must be equaled or exceeded before the refinement is actually terminated. **ITERM** is punched in Columns 36-39 (FORMAT I4).

Note: The refinement is terminated when **RATIO** has been equaled or exceeded **ITERM** + 1 times. This device is a check against premature termination.

7. **Molecule Information Card**. One card containing the name of the molecule or other alphanumeric information. The first three columns should be left blank with the alphanumeric data following in any of the columns through 72 (FORMAT 18A4).

Warning: This card must be included with the input data even if left blank.

8. **The Z Matrix**. The programs **UBZM** and **ZSYM** punch the **Z** matrix in the proper format for use in this program. The **Z** elements are punched in 18 column fields, 1 to 4 per card [FORMAT 4(3I3,F9.6)].

Warning: The row following the last **Z** matrix element must be set equal to -2.

9. **The Experimental Frequencies**. If **NDD** is greater than zero, the experimental frequencies, in  $\text{cm}^{-1}$ , are included with the input data. The frequencies are entered in decreasing order being punched in 12 column fields, 6 per card (FORMAT 6F12.6).

Note: If the frequencies are unknown, uncertain, or zero (redundancies), one should enter a zero. For degenerate roots, one should enter one frequency and set the rest equal to zero. Any frequency may be given zero weight in the refinement by entering a zero instead of the actual frequency.

Warning: For **NDD** greater than zero, one must make **NQ** frequency entries, **NDD** of which must be nonzero. Blanks are read as zeros.

10. **The Estimated Errors in the Experimental Frequencies**. If **IFER** = -1, the estimated errors in the observed frequencies, in  $\text{cm}^{-1}$ , must be included with the input data, one for each nonzero frequency. The estimated errors are entered in the same order as the experimental frequencies, with zeros or blanks positioned properly corresponding to zeros in the list of experimental frequencies. The estimated errors are entered in 12 column fields, six per card (FORMAT 6F12.6).

Warning: There must be **NQ** error entries, **NDD** of the nonzero for **IFER** = -1.

11. The Weighting Elements. If IFW = -2 or 1, the weighting elements must be included with the data deck, one element for each nonzero frequency. The weighting elements are punched in 12 column fields, six per card (FORMAT 6F12.6).

Note: There are NDD weighting elements which must be arranged in the same order as the nonzero experimental frequencies.

12. The G Matrix. The G matrix from GMAT is included at this point in the data deck. The information is punched in 18 column fields, four per card [FORMAT 4(2I3,F12.6)].

Warning: The row number following the last G matrix element must be set equal to -1.

13. Data Termination Card. This card must have a 999 punched in Columns 1-3 (FORMAT I3) and designates the end of the data.

Note: If another problem is to be included in the data deck, the problem ID card for the next problem should be placed at this point and the data termination card moved to the end of the second problem.

If the same set of force constants is to be refined for more than one molecule, the data cards starting with the molecule control card and going through the G matrix cards must be included, one set after another, for each molecule in the refinement, i.e., NMOL sets of data. For symmetry factored blocks, NMOL must be set equal to the number of factored blocks. Each of the factored blocks may be treated as separate molecules and the data cards from the molecule control card through the G matrix cards included, one set after another, for all the factored blocks in a manner similar to the refinement for several molecules simultaneously.

With the OS operating system, a /\* must be punched in Columns 1-2 on a card which is placed at the end of the data deck and follows the data termination card.

#### OUTPUT INFORMATION

The following information is printed out at the option of the user.

1. The initial set of force constants.
2. The force constants being held fixed.
3. The eigenvalues and errors for each perturbation.

4. The gradient vector for each perturbation.
5. The direction vector for each perturbation.
6. The force constant corrections for each perturbation.
7. The calculated and experimental frequencies and frequency parameters along with the differences, weights, and percent error.
8. The final  $\underline{\underline{H}}$  matrix.
9. The final set of force constants along with the 95% confidence intervals.

At the user's option, the final set of force constants are punched on cards with the proper format for use in FADJ, FLPO, and EIGV.

Warning: If the data output is terminated before completion because of an error, namely, the attempt to take the square root of a negative number, an error or errors in the refinement, usually user induced, are indicated. Such an error may be generated when the refinement has caused one of the diagonal  $\underline{\underline{F}}$  matrix elements to become negative (usually elements of normally small magnitude, such as the torsional elements). This error may also be generated if a calculated frequency parameter becomes small compared to the accuracy of the computation. If such an error message should occur after the interrupted printout of data, the user should examine the set of refined force constants and set of calculated frequencies and frequency parameters for unusual values. Extraordinary values for these items may signal errors in the  $\underline{\underline{F}}$  and  $\underline{\underline{G}}$  matrix.

#### EIGV

This program solves the vibrational secular equation by the method of successive orthogonalization followed by Jacobi diagonalization. The eigenvalues and eigenvectors are computed, the latter computation at the request of the user. The  $\underline{\underline{L}}$  matrix and potential energy distribution among the diagonal elements of  $\underline{\underline{F}}$  may be computed by EIGV if the user so specifies. If the  $\underline{\underline{B}}$  matrix is included

with the input data, the cartesian displacement coordinates and mean square amplitudes for each normal mode may also be computed. In addition, EIGV has been modified to permit the computation of the "squared amplitudes" of vibration for each of the internal coordinates for each normal mode. The discussion of the "squared amplitudes" appeared earlier in this text. The cartesian coriolis coupling coefficients may also be calculated with EIGV.

This program was written by J. H. Schachtschneider (89) and modified for use in the investigation of the 1,5-anhydropentitol vibrational spectra. EIGV may be used with the IBM 360/44 OS operating system. A flow diagram of EIGV appears in Fig. 45 and a listing in Table LIV.

#### INSTRUCTIONS FOR PROGRAM USE

EIGV requires three scratch tapes or disks for normal operation. The disks are favored over tapes because of the faster operation of the disks during data input/output. If the user wishes to exercise the option to write the potential energy distribution and "squared amplitudes" on tape, an additional scratch tape must be provided. This option results in the potential energy distribution and "squared amplitudes" being written on tape with the proper format to be used as input data to SASORT.

The following information embodies the data deck which is included after the program deck.

1. Problem ID Card. This card indicates the start of a new problem. The problem ID card must have a -09 punched in Columns 1-3 (FORMAT I3).
2. Problem Control Card.
  - a. IND = -09, identifies the problem control card. IND is punched in Columns 1-3 (FORMAT I3).
  - b. NOPROB is the problem number, punched in Columns 4-9 (FORMAT I6).



TABLE LIV

LISTING OF EIGV

```
C      EIGV      SCHACHTSCHNEIDER      7/19/65
C      MODIFIED FOR OS BY L.J.PITZNER  1/5/72
C      THIS PROGRAM SOLVES THE WILSON GF VIBRATIONAL SECULAR EQUATION
C      BY AN ORTHOGONALIZATION OF THE BASIS OF G FOLLOWED BY A JACOBI
C      DIAGONALIZATION OF THE TRANSFORMED F MATRIX. INPUT INCLUDES THE G
C      MATRIX AND THE POTENTIAL ENERGY IN THE FORM OF THE Z MATRIX.
C      F MATRIX ELEMENTS F(I,J) ARE DEFINED AS THE SUM OVER K OF
C      (Z(I,J,K)*FI(K)) WHERE FI(K) GIVES THE VALUE OF FORCE CONSTANT
C      NUMBER K. THE SYMMETRIC MATRICES ARE DIAGONALIZED BY SUBROUTINE
C      HDIAG (MIHDI3) PROGRAMED BY F.J. CORBATO AND M. MERWIN OF MIT.
C      RAP=0.5E-3 UNLESS SPECIFIED.
C      UNDER NORMAL OPERATION THIS PROGRAM COMPUTES EIGENVALUES AND
C      EIGENVECTORS.      AT THE OPTION OF THE USER ONLY THE EIGENVALUES
C      ARE COMPUTED.
C      AT THE OPTION OF THE USER THE CARTESIAN COORDINATES OF THE ATOMS
C      THE MASSES AND THE B MATRIX ARE READ IN AND THE CARTESIAN
C      DISPLACEMENT COORDINATES AND MEAN SQUARE AMPLITUDES FOR EACH
C      NORMAL MODE ARE CALCULATED
C      DIMENSION G( 66, 66),D( 66, 66),NR( 650),NC( 650),NFO( 650),
C      IZ( 650),FI( 71),NOL(71),NEW(71),DG( 71),FF( 71),DE( 71),
C      2DC( 71),DV( 71),DD( 71),HJ( 71),DJ( 71),XO(22,3),X(22,3),WT(22),
C      3W(71),NRD(4),NCD(4),NPO(4),DAT(4),REC(18),PE( 71),T(3),TT(22),
C      4TSUM(22),NIP( 71),TEMP(5),DEL( 71),RECORD(54),ASQ(71),DES(72),
C      1XDIFF(22,3)
C      EQUIVALENCE (D,NR),(D( 661),NC),(D(1321),NFO),(D(1971),Z),
C      1 (DD,XO),(DE,X),(DC,NOL),(DV,NEW),(DG,DEL),(FF,W)
C      COMMON G,D
C      RECONVERT PROBLEM CONTROL CARD CONTAINING THE FOLLOWING DATA
C      1.IND=-09 INDICATING THE START OF A PROBLEM AND IDENTIFYING
C      CONTROL CARD. PUNCHED IN COLUMNS 1-3.
C      2.NOPROB, THE PROBLEM NUMBER IN COLUMNS 4-9.
C      3.NMOL, THE NUMBER OF MOLECULES IN COLUMNS 10-12.
C      4.NF, THE NUMBER OF FORCE CONSTANTS IN COLUMNS 13-15. (71 MAX).
C      5.INO, THE NUMBER OF FORCE CONSTANTS TO BE RENUMBERED IN THE
C      Z MATRIX. PUNCHED IN COLUMNS 16-18. (INO LESS THAN 100)
C      6.IEG, FOR EIGENVALUES ONLY SET IEG=1. PUNCH IN COLUMNS 19-21.
C      7.IFF , FOR F MATRIX OUTPUT SET EQUAL TO 1      COL. 22-24.
C      8.RAP, INDICATOR FOR SHUT-OFF IN HDIAG. PUNCHED IN COLUMNS 25-34.
C      WITH THE DECIMAL BETWEEN COL.25 AND 26 OR PUNCHED.
C      JACOBI DIAGONALIZATION STOPS WHEN MAX(H(I,J)) LESS THAN
C      RAP*MIN(H(I,I)). IF COL.25-34 ARE BLANK RAP IS SET EQUAL .0005
C      READ PROBLEM CONTROL CARD
C      REWIND 4
C      90 READ (5,2)IND
C      2 FORMAT(I3)
C      91 IF(9+IND)900,92,900
C      900 IF(IND-999)90,901,90
C      901 END FILE 4
C      REWIND 4
C      CALL EXIT
C      92 READ ( 5,4)IND,NOPROB,NMOL,NF,INO,IEG,IFF,RAP
C      4 FORMAT(I3,I6,5I3,F10.9)
```

TABLE LIV (Continued)

```

IF(RAP)93,93,94
93 RAP=0.5E-3
94 IF(IEG)96,96,95
95 IEGEN=1
RAP=0.5E-2
GO TO 97
96 IEGEN=0
C READ 3 PROBLEM INFORMATION CARDS. (COLUMNS 1-3 MUST BE BLANK)
97 READ (5,6)RECORD
6 FORMAT(18A4)
C READ FORCE CONSTANTS IN ORDER 1 TO NF PUNCHED IN 12 COLUMN FIELDS
C 6 PER CARD WITH DECIMAL BETWEEN COL.6 AND 7 OR PUNCHED.
READ (5,8) (FI(I),I=1,NF)
8 FORMAT(6F12.6)
NM=0
WRITE (6,50)NOPROB,NMOL,RAP,RECORD
50 FORMAT(39H1 VIBRATIONAL SECULAR EQUATION. PROBLEM I6,10H,NO.MOL. =I
13,5H RAP=E14.6/(18A4))
WRITE (6,52)NF,(I,FI(I),I=1,NF)
52 FORMAT(4HO 13,16H FORCE CONSTANTS/17H I FI(I)/(16,F12.6
1))
DO 98 I=1,71
98 NIP(I)=I
IF(INO)110,110,99
C READ NUMBERS FOR RENUMBERING FORCE CONSTANTS IN Z MATRIX.
C NOL(I),NEW(I),I=1,IND NOL GIVES OLD FORCE CONSTANT NO. AND
C NEW GIVES NEW FORCE CONSTANT NUMBER. PUNCHED IN 6 COLUMN FIELDS
C 12 PER CARD . COL. 1-3 GIVE NOL AND COL.4-6 GIVE NEW.
99 READ (5,10) (NOL(I),NEW(I),I=1,IND)
10 FORMAT(24I3)
WRITE (6,53)(NOL(I),NEW(I),I=1,IND)
53 FORMAT(40HO FORCE CONSTANTS RENUMBERED IN Z MATRIX/(16,4H TO 13))
DO 100 I=1,IND
IX=NOL(I)
100 NIP(IX)=NEW(I)
C READ MOLECULE CONTROL CARD GIVING THE FOLLOWING DATA
C 1.IND=-06 IDENTIFYING CARD IN COLUMNS 1-3.
C 2.NQ, THE DIMENSION OF THE SECULAR EQUATION. LESS THAN 101.
C PUNCHED IN COLUMNS 4-6.
C 3.ND, OBS.FREQ.READ CONTROL. FOR ND=0 NO FREQ. ARE READ.
C FOR ND GREATER THAN ZERO FREQ. ARE ENTERED. COLUMNS 7-9.
C 4.NZ, THE NUMBER OF Z MATRIX ELEMENTS(LESS THAN 650) PUNCHED IN
C COLUMNS 10-13. NZ IS NOT USED BY THE PROGRAM AND COL. 10-13
C MAY BE LEFT BLANK.
C 5.IFU,A 1 WILL SUPPRESS PRINTOUT OF THE Z MATRIX. COLUMNS 14-15.
C 6.IFW, A 1 WILL SUPPRESS PRINT OUT OF THE L MATRIX AND P.E. DIST.
C PUNCHED IN COLUMNS 16-17. A -1 WILL RESULT IN L MATRIX ONLY.
C 7.ISKZ, Z MATRIX READ OPTION. PUNCHED IN COLUMN 19.
C FOR ISKZ=0 A Z MATRIX IS ENTERED.
C FOR ISKZ=1 THE Z MATRIX FROM THE PREVIOUS MOLECULE IS USED.
C 8.IFINV, INVERSE COMPUTATION CONTROL. PUNCHED IN COLUMN 21.
C FOR IFINV=1 THE INVERSE EIGEN VECTORS ARE CALCULATED.
C FOR IFINV=0 INVERSE NOT EVALUATED.
C 9.IFMA, A 1 WILL SUPPRESS PRINT OUT OF L INVERSE MATRIX.

```



TABLE LIV (Continued)

C PUNCHED IN COLUMNS 22-23.  
C 10. IFB, CARTESIAN NORMAL COORDINATE CONTROL. PUNCHED IN COL. 25.  
C FOR IFB=1 THE B MATRIX AND MASSES ARE ENTERED AND CARTESIAN  
C NORMAL COORDINATES ARE CALCULATED. IFINV MUST=1 FOR IFB=1  
C FOR IFB=0 CARTESIAN NORMAL COORDINATES ARE NOT CALCULATED.  
C 11. NOAT, THE NUMBER OF ATOMS. MUST BE ENTERED FOR IFB=1  
C PUNCHED IN COLUMNS 27-28. (22 MAX).  
C 12. IFCOR, A 1 WILL CAUSE CALCULATION OF THE INTERNAL MEAN SQUARE  
C AMPLITUDE MATRIX. PUNCHED IN COLUMNS 29-30.  
C CONTINUE  
C 13. NOTEP, NO. OF TEMPERATURES FOR WHICH MEAN SQ. AMP. CALC. IS  
C TO BE CALCULATED FOR. IF NOTEMP = 0 CALC. FOR ROOM TEMP.  
C PUNCHED IN COLUMNS 31-32.  
C 14. SCALE, SCALE FACTOR FOR CARTESIAN DISPLACEMENTS. PUNCHED IN COL  
C 33-38 WITH DECIMAL BETWEEN 37-38 OR PUNCHED.  
C IF COLUMNS 33-38 ARE LEFT BLANK SCALE IS SET EQUAL TO 2.0.  
C 15. ICAR, A 1 WILL SUPPRESS PRINT OUT OF CARTESIAN DISPLACEMENT  
C COORDINATES. PUNCHED IN COLUMNS 39-40.  
C 16. IMSC, A1 WILL SUPPRESS PRINTOUT OF THE CARTESIAN MEAN SQUARE  
C AMPLITUDES. PUNCHED IN COLUMNS 41-42.  
C 17. ICOR, A 1 WILL CAUSE CALCULATION OF THE CARTESIAN CORIOLIS  
C COEFFICIENTS. PUNCHED IN COLUMN 44.  
C CONTINUE  
C 18. ITEMP, INTERNAL MEAN SQUARE AMP. CALCULATED FOR 0 DEG K IF  
C ITEMP=0. IF ITEMP=1, THE INTERNAL MEAN SQ. AMP. IS CALC. FOR  
C ABST DEG K. ITEMP PUNCHED IN COLUMN 46.  
C 19. ABST, IF ITEMP =1, ABST IS THE TEMP IN DEG K FOR WHICH THE  
C INTERNAL MEAN SQUARE AMP. IS TO BE CALC. PUNCHED IN COLUMNS  
C 47-56.  
C 20. ICD, IF ICD=1, ONE MAY ENTER THE DESCRIPTION OF THE INTERNAL  
C COORDINATES (4 CHAR.) TO BE PRINTED WITH THE INTERNAL MEAN  
C SQ. AMP. (A\*\*2). ICD PUNCHED IN COL. 58.  
C 21. IPUN, IF IPUN=1 THE MEAN SQ. AMP. AND PE DISTR. FOR INTERNAL  
C COORDINATES WILL BE WRITTEN ON TAPE. IPUN PUNCHED IN COL. 60.  
C 22. IFL, A 1 WILL CAUSE THE L MATRIX TO BE WRITTEN ON TAPE BY  
C COLUMNS. PUNCHED IN COLUMN 62.  
C  
C 110 READ (5,12)IND,NQ,NDD,NZZ,IFU,IFW,ISKZ,IFINV,IFMA,IFB,NOAT,IFCOR,  
C INOTEP,SCALE,ICAR,IMSC,ICOR,ITEMP,ABST,ICD,IPUN,IFL  
C 12 FORMAT(3I3,14,6I2,13,2I2,F6.1,4I2,F10.2,3I2)  
C IF(IND+6)91,112,91  
C INPUT DATA FOR EACH MOLECULE FOLLOWS IN THE ORDER  
C 1. MOLECULE INFORMATION CARD (COL. 1-3 BLANK)  
C 1'. INTERNAL COORDINATE DESCRIPTION IF ICD=1.  
C 2. Z MATRIX (FOR ISKZ=0)  
C 3. OBSERVED FREQ. (FOR ND GREATER THAN ZERO)  
C 4. G MATRIX  
C 5. X MATRIX (I.E. CARTESIAN COORD. OF ATOMS IN EQUILIBRIUM CONFIG)  
C 6. MASSES  
C 7. B MATRIX  
C ITEMS 5-7 ENTERED ONLY FOR IFB=1  
C READ MOLECULE INFORMATION CARD  
C 112 READ (5,6)REC  
C IF(ICD)39539,39539,66661

## TABLE LIV (Continued)

```

66661 READ(5,7771)(DES(J),J=1,NQ)
 7771 FORMAT(18A4)
    WRITE(6,8881)
 8881 FORMAT(1H1,'INTERNAL COORDINATE DESCRIPTION')
    WRITE(6,9991)(I,DES(I),I=1,NQ)
 9991 FORMAT(1H ,16,4X,A4)
39539 REWIND 1
    REWIND 2
    REWIND 3
    NM=NM+1
    IF(SCALE)113,113,114
 113 SCALE=2.0
 114 IF(ISKZ)115,115,134
C   READ NON-ZERO Z MATRIX ELEMENTS Z(I,J,K) ENTERED AS FOUR ONE
C   DIMENSIONAL ARRAYS ,(NR(L),NC(L),NFO(L),Z(L),L=1,NZ WHERE NR(L)=I,
C   NC(L)=J,NFO(L)=K, AND Z(L)=Z(I,J,K)) NZ=NO. OF NON-ZERO Z ELEMENTS
C   ENTERED IN 18 COLUMN FIELDS 1 TO 4 PER CARD GIVING
C   COLUMNS          ITEM
C   1-3              NR(L)=I
C   4-6              NC(L)=J      (I LESS THAN OR EQUAL TO J)
C   7-9              NFO(L)=K    (NO. OF FORCE CONSTANT)
C   10-18            Z(L)=Z(I,J,K) (DECIMAL BETWEEN COL.12 AND 13 OR
C                                   PUNCHED)
C   NR IS SET = -2 AFTER LAST ELEMENT.
 115 NOZ=0
 116 READ (5,16) (NRO(L),NCO(L),NPO(L),DAT(L),L=1,4)
 16  FORMAT(4(3I3,F9.6))
    DO 120 L=1,4
    IF(NRO(L))122,120,117
 117 NOZ=NOZ+1
    NR(NOZ)=NRO(L)
    NC(NOZ)=NCO(L)
    I=NPO(L)
    NFO(NOZ)=NIP(I)
    IF(DAT(L))118,119,118
 118 Z(NOZ)=DAT(L)
    GO TO 120
 119 Z(NOZ)=1.0
 120 CONTINUE
    GO TO 116
 122 IF(NRO(L)+2)605,127,605
 127 REWIND 2
    WRITE (2)(NR(I),NC(I),NFO(I),Z(I),I=1,NOZ)
    END FILE 2
    IF(IFU)128,3511,128
3511 WRITE (6,68)NM,NOZ,REC
 68  FORMAT(19H1 Z MATRIX MOLECULEI3,6H NOZ=I4/(18A4))
    WRITE (6,69)(NR(I),NC(I),NFO(I),Z(I),I=1,NOZ)
 69  FORMAT(4(I4,2I3,F9.6))
 128 DO 130 I=1,NQ
    DO 130 J=1,NQ
 130 G(I,J)=0.0
    DO 132 K=1,NOZ
    I=NR(K)

```

TABLE LIV (Continued)

```
J=NC(K)
LX=NFO(K)
132 G(I,J)=G(I,J)+FI(LX)*Z(K)
    IF(IFF) 1136,1136,1128
1128 WRITE (6,70)NM,RECORD
    70 FORMAT(19H1 F MATRIX MOLECULEI3/(18A4))
1136 DO 133 I=1,NQ
    FF(I)=G(I,I)
    IF(IFF)133,133,1133
1133 WRITE (6,56)I,(G(I,J),J=1,NQ)
    56 FORMAT(5H0 ROWI3/(9F8.4))
133 CONTINUE
    GO TO 136
134 REWIND 2
    READ (2) (NR(I),NC(I),NFO(I),Z(I),I=1,NOZ)
136 IF(NDD)137,137,139
137 DO 138 I=1,NQ
138 DE(I)=0.0
    GO TO 140
C    READ OBSERVED FREQ. IN ORDER 1 TO NQ PUNCHED IN 12 COLUMN FIELDS
C    6 PER CARD WITH DECIMAL BETWEEN COL.6 AND 7 OR PUNCHED.
C    CALC. FREQ. ARE IN DECREASING ORDER WITHIN EACH FACTORED
C    (ENTER ZEROS FOR UNKNOWN FREQ. AND REDUNDANCIES)IN CM-1
139 READ (5,8) (DE(I),I=1,NQ)
140 DO 141 I=1,NQ
    DO 141 J=I,NQ
141 G(I,J)=0.0
C    READ NON-ZERO G MATRIX ELEMENTS ,G(I,J).
C    G ELEMENTS ENTERED IN 18 COLUMN FIELD 1 TO 4 PER CARD GIVING
C    COLUMNS      ITEM
C    1-3          NRO =I      (ROW NO.)
C    4-6          NCO =J      (COLUMN NO.) (I LESS THAN OR=J)
C    7-18         DAT=G(I,J) (DECIMAL BETWEEN 12-13 OR PUNCHED)
C    NRO IS SET =-1 AFTER LAST G ELEMENT.
142 READ (5,14) (NRO(L),NCO(L),DAT(L),L=1,4)
    14 FORMAT(4(2I3,F12.6))
    DO 146 L=1,4
    IF(NRO(L))148,146,144
144 I=NRO(L)
    J=NCO(L)
    G(I,J)=DAT(L)
146 CONTINUE
    GO TO 142
148 IF(NRO(L)+1)600,150,600
C    SCHMIDT ORTHOGONALIZATION OF G
C    STORE INVERSE TRANSFORMATION IN LOWER TRIANGLE OF G.
150 NRED=0
    NO=1
    NL=2
154 GD=1.0/ G(NO,NO)
    DO 156 J=NL,NQ
156 G(J,NO)=G(NO,J)*GD
    IF(NL-NQ)158,158,170
158 DO 160 I=NL,NQ
```

TABLE LIV (Continued)

```
      DO 160 J=1,NQ
160 G(I,J)=G(I,J)-(G(NO,I)*G(NO,J)*GD)
161 NO=NO+1
      NL=NO+1
163 IF(G(NO,NO)-0.000001)164,164,154
164 NRED=NRED+1
      IF(NL-NQ)165,165,170
165 DO 166 J=NL,NQ
166 G(J,NO)=G(NO,J)
      GO TO 161
170 DO 175 I=1,NQ
      IF(G(I,I)-0.00005)173,173,172
172 DG(I)=SQRT(G(I,I))
      GO TO 174
173 DG(I)=0.0
174 G(I,I)=1.0
      DO 175 J=1,NQ
175 G(J,I)=G(J,I)*DG(I)
C   COMPUTE TRANSFORMED F MATRIX AND STORE IN UPPER TRIANGLE OF G
      DO 200 J=1,NQ
      DO 178 I=1,NQ
178 DJ(I)=0.0
      DO 190 K=1,NOZ
      IX=NR(K)
      IF(IX-J)190,182,182
182 JX=NC(K)
      LX=NFO(K)
      DJ(IX)=DJ(IX)+FI(LX)*Z(K)*G(JX,J)
      IF(IX-JX)186,190,186
186 DJ(JX)=DJ(JX)+FI(LX)*Z(K)*G(IX,J)
190 CONTINUE
      DO 196 K=J,NQ
      HJ(K)=0.0
      DO 196 L=K,NQ
196 HJ(K)=HJ(K)+G(L,K)*DJ(L)
      DO 200 K=J,NQ
200 G(J,K)=HJ(K)
      IF(IFF)203,203,201
201 WRITE (6,61) RECORD
61 FORMAT(22H1 TRANSFORMED F MATRIX/(18A4))
      DO 202 I=1,NQ
202 WRITE (6,56)I,(G(I,J),J=1,NQ)
203 CONTINUE
C   DIAGONALIZE TRANSFORMED F MATRIX BY JACOBI METHOD
      NR2=0
      CALL HDIAG(G,NQ,IEGEN,D,NR2,RAP)
      WRITE (6,62) NM,NR2,RECORD
62 FORMAT(9H1MOLECULEI3,21H NUMBER OF ROTATIONS=I6/(1H ,18A4))
      N1=0
      PT=0.0
      SUM=0.0
      DO 204 I=1,NQ
      DC(I)=G(I,I)
      G(I,I)=DG(I)
```

TABLE LIV (Continued)

```
204 HJ(I)=DC(I)
C   FOR COMPARISON WITH OBS. FREQ. THE CALC. FREQ. ARE ORDERED HIGH
C   TO LOW.
    II=NQ-1
    DO 206 I=1,II
    LOW=I+1
    DO 206 J=LOW,NQ
    IF(HJ(I)-HJ(J))205,206,206
205 TEM=HJ(I)
    HJ(I)=HJ(J)
    HJ(J)=TEM
206 CONTINUE
    DO 209 I=1,NQ
    DV(I)=SQRT(HJ(I)/5.88852E-7)
    IF(DE(I))207,207,208
207 DD(I)=0.0
    DJ(I)=0.0
    GO TO 209
208 DD(I)=DE(I)-DV(I)
    DJ(I)=100.0*DD(I)/DE(I)
    N1=N1+1
    PT=PT+ABS(DJ(I))
    SUM=SUM+ABS(DD(I))
209 CONTINUE
    IF(N1)211,211,210
210 SUM=SUM/ FLOAT(N1)
    PT=PT/ FLOAT(N1)
211 WRITE (6,76)REC,(J,DE(J),DV(J),DD(J),DJ(J),HJ(J),J=1,NQ)
    76 FORMAT(37H0 OBSERVED AND CALCULATED FREQUENCIES/ 18A4 /71H0   OBS
    1.FREQ.   CALC.FREQ. DIFFERENCE PERCENT ERROR   CALC.FREQ.PAR./6X
    26H(CM-1),7X,6H(CM-1),5X,6H(CM-1)/ (I4,F9.1,4X,F8.1,4X,F6.1,7X,F7.3
    3,9X,F9.5))
    WRITE (6,77)SUM,PT
    77 FORMAT(17H0 AVERAGE ERROR=F5.1,9H CM-1 OR ,F5.2,9H PERCENT.)
    IF(IEGEN)500,212,500
212 DO 2121 I=1,NQ
2121 DV(I)=SQRT(DC(I)/5.88852E-7)
    IF(IFW)63154,12111,63154
12111 WRITE (6,63)NM,NR2,RECORD
    63 FORMAT(56H1 L MATRIX BY COLUMNS AND POTENTIAL ENERGY DISTRIBUTION
    1/41H AMONG DIAGONAL ELEMENTS OF F. MOLECULEI3,14H NO.ROTATIONS=I
    26/(18A4))
63154 DO 220 I=1,NQ
    IF(DC(I)-0.000050)220,220,213
    213 IF(ITEMP)2631,2631,4444
4444 C2=(0.7193392/ABST)*DV(I)
    ET=(16.8612/DV(I))/TANH(C2)
    GO TO 65316
    2631 ET=16.8612/DV(I)
65316 DO 215 J=1,NQ
    HJ(J)=0.0
    DO 214 K=1,J
214 HJ(J)=HJ(J)+G(J,K)*D(K,I)
    ASQ(J)=ET*HJ(J)*HJ(J)
```

TABLE LIV (Continued)

```
215 PE(J)=FF(J)*HJ(J)*HJ(J) / DC(I)
    IF(IFL)216,216,23475
23475 WRITE(4,86378)(HJ(J),J=1,NQ)
86378 FORMAT(6F12.6)
    216 WRITE (1) (HJ(J),J=1,NQ)
    IF(IFW)217,217,22002
    217 WRITE (6,64)DV(I),(HJ(J),DES(J),J=1,NQ)
    64 FORMAT(13HO FREQUENCY =F8.2,6H(CM-1),10H L COLUMN/(8(F8.4,1X,A4))
    1)
22002 IF(IPUN)21888,21888,66543
66543 WRITE(4,23151)I,DV(I)
23151 FORMAT(13,F8.2)
    WRITE(4,11114)(PE(J),J=1,NQ)
11114 FORMAT(9F8.4)
    WRITE(4,22224)(ASQ(J),J=1,NQ)
22224 FORMAT(6E12.4)
21888 IF(IFW)220,218,220
    218 WRITE (6,66) (PE(J),J=1,NQ)
    66 FORMAT(18H POTENTIAL ENERGY/(9F8.4))
    IF(ICD)75357,75357,86586
86586 WRITE(6,93999)ABST,(ASQ(J),DES(J),J=1,NQ)
93999 FORMAT(26H MEAN SQUARE AMP. (A**2) F8.2,7H DEG. K/(6(E12.4,2X,A4)
    1))
    GO TO 220
75357 WRITE(6,75321)ABST,(ASQ(J),J=1,NQ)
75321 FORMAT(26H MEAN SQUARE AMP. (A**2) F8.2,7H DEG. K/(9E12.4))
    220 CONTINUE
    END FILE 1
    IF(IFINV)400,400,230
C    INVERT ORTHOGONALIZATION MATRIX AND STORE ITS TRANSPOSE IN
C    UPPER TRIANGLE OF G
    230 DO 234 I=1,NQ
        IF(DG(I))234,234,232
    232 DG(I)= 1.0/ DG(I)
        DO 233 J=I,NQ
    233 G(J,I)=G(J,I)*DG(I)
    234 CONTINUE
        DO 240 K=1,NQ
            NX=K+1
            DO 240 I=NX,NQ
                LIM=I-1
                DO 240 J=K,LIM
    240 G(K,I)=G(K,I)-G(I,J)*G(K,J)
                DO 244 I=1,NQ
                DO 244 J=I,NQ
    244 G(I,J)=G(I,J)*DG(J)
C    COMPUTE L INVERSE
        DO 250 I=1,NQ
        DO 248 J=1,NQ
            HJ(J)=0.0
            DO 248 K=J,NQ
    248 HJ(J)=HJ(J)+G(J,K)*D(K,I)
            DO 250 J=1,NQ
    250 D(J,I)=HJ(J)
```

TABLE LIV (Continued)

```
IF(IFMA)21315,61611,21315
61611 WRITE (6,67)RECORD
  67 FORMAT(26H1 INVERSE L MATRIX BY ROWS/(18A4))
  DO 260 J=1,NQ
  260 WRITE (6,65)J,DV(J),(D(I,J),I=1,NQ)
  65 FORMAT(11H0 FREQUENCY13,2H =F8.1,6H(CM-1)/(1H ,9F8.4))
21315 IF(IFB)400,400,300
  300 DO 320 I=1,NOAT
  DO 320 J=1,3
  320 XO(I,J)=0.0
C READ NON-ZERO X MATRIX ELEMENTS PUNCHED IN 18 COLUMN FIELDS 1 TO 4
C PER CARD GIVING
C COLUMNS ITEM
C 1-3 NRO =I (I=1,2,OR 3 FOR X,Y,OR Z RESPT.)
C 4-6 NCO =J (ATOM NUMBER)
C 7-18 DAT=X(I,J) (DECIMAL BETWEEN 12-13 OR PUNCHED)
C NRO SET =-1 AFTER LAST X ELEMENT.
  322 READ (5,14) (NRO(L),NCO(L),DAT(L),L=1,4)
  DO 330 L=1,4
  IF(NRO(L))332,330,324
  324 I=NCO(L)
  J=NRO(L)
  XO(I,J)=DAT(L)
  330 CONTINUE
  GO TO 322
  332 IF(NRO(L)+1)615,314,615
  314 NA=3*NOAT
C READ MASSES IN ORDER 1 TO NOAT PUNCHED IN 12 COLUMN FIELDS 6 PER
C CARD WITH DECIMAL BETWEEN COL.6-7 OR PUNCHED.
  READ (5,8) (WT(I),I=1,NOAT)
  DO 316 I=1,NOAT
  DO 316 M=1,3
  L=3*(I-1)+M
  316 W(L)=1.0 / WT(I)
C READ B MATRIX
  DO 302 I=1,NQ
  DO 302 J=1,NA
  302 G(I,J)=0.0
C READ NON-ZERO B MATRIX ELEMENTS ,B(I,J).
C B ELEMENTS ENTERED IN 18 COLUMN FIELD 1 TO 4 PER CARD GIVING
C COLUMNS ITEM
C 1-3 NRO =I (ROW NO.)
C 4-6 NCO =J (COLUMN NO.)
C 7-18 DAT=B(I,J) (DECIMAL BETWEEN 12-13 OR PUNCHED)
C NRO IS SET =-5 AFTER LAST B ELEMENT.
  304 READ (5,14) (NRO(L),NCO(L),DAT(L),L=1,4)
  DO 310 L=1,4
  IF(NRO(L))312,310,306
  306 I=NRO(L)
  J=NCO(L)
  G(I,J)=DAT(L)
  310 CONTINUE
  GO TO 304
  312 IF(NRO(L)+5)610,334,610
```

## TABLE LIV (Continued)

```

334 IF(ICAR)61836,20102,61836
20102 WRITE (6,72) NM,RECORD
      72 FORMAT(43H1EQUILIBRIUM CARTESIAN COORDINATES.MOLECULEI3/(18A4))
      WRITE (6,73)
      73 FORMAT(5X,39H ATOM      MASS      X      Y      Z)
61836 DO 336 L=1,NOAT
      TSUM(L)=0.0
      IF(ICAR)336,5155,336
5155 WRITE (6,74)L,WT(L),XD(L,1),XD(L,2),XD(L,3)
      336 CONTINUE
      REWIND 3
      74 FORMAT(1H ,5X,I4,F9.4,F9.4,F10.4,F10.4)
C      COMPUTE CARTESIAN DISPLACEMENT COORDINATES AND THE MEAN SQUARE
C      AMPLITUDE FOR EACH ATOM IN EACH NORMAL MODE      0 DEG. K
      DO 360 I=1,NQ
      IF(DC(I)-0.000050)360,360,350
350 ET=16.8612/DV(I)
      DO 353 J=1,NOAT
      TT(J)=0.0
      DO 352 M=1,3
      L=3*(J-1)+M
      T(M)=0.0
      DO 351 K=1,NQ
351 T(M)=T(M)+G(K,L)*D(K,I)*W(L)
      HJ(L)=T(M)
      TT(J)=TT(J)+ET*T(M)*T(M)
      X(J,M)=XD(J,M)+SCALE*T(M)
352 XDIFF(J,M)=SCALE*T(M)
353 TSUM(J)=TSUM(J)+TT(J)
      IF(ICAR)6352,8888,6352
8888 WRITE (6,75)SCALE,I,DV(I),ET,REC
      75 FORMAT(46H0 CARTESIAN COORDINATES FOR ATOMS DISPLACED BYF6.1,21H U
      INITS OF NORMAL MODEI3/13H FREQUENCY=F10.2,7H DELTA=E12.4/18A4)
      WRITE (6,78)
      78 FORMAT(1H ,4X,' ATOM      MASS      X      Y      Z      MEAN
      1 SQUARE AMP.(A**2) 0 K      DELTA X      DELTA Y      DELTA Z')
359 WRITE (6,79) (J,WT(J),X(J,1),X(J,2),X(J,3),TT(J),XDIFF(J,1),
      1XDIFF(J,2),XDIFF(J,3),J=1,NOAT)
      79 FORMAT(1H ,5X,I4,F9.4,F9.4,F10.4,F10.4,7X,E12.4,12X,3F10.4)
6352 WRITE (3) (HJ(J),J=1,NA)
360 CONTINUE
      END FILE 3
      DO 362 J=1,NOAT
362 TT(J)=SQRT(TSUM(J))
      IF(IMSC)400,6355,400
6355 WRITE (6,84) (J,TSUM(J),TT(J),J=1,NOAT)
      84 FORMAT(49H0MEAN AMP. FOR ATOMS SUMMED OVER ALL NORMAL MODES/5X,44H
      1 ATOM      MEAN SQUARE      ROOT MEAN SQUARE/(1H ,5X,I4,6X,E12.4,
      26X,E12.4))
400 IF(NOTEP)401,401,403
401 NOTEP=1
      TEMP(1)=298.16
      GO TO 405
403 READ (5,8) (TEMP(I),I=1,NOTEP)
405 IF(IFCOR)500,500,406

```



TABLE LIV (Continued)

```
406 REWIND 1
    REWIND 3
    NUM = 1
    NII=NQ
    WRITE (6,54)REC
54 FORMAT(56H1INTERNAL COORDINATE MEAN SQUARE AMPLITUDE MATRIX(X 100)
1/3X,18A4)
407 DO 412 I=1,NQ
    IF(DC(I)-0.000050)410,410,408
408 READ (NUM) (HJ(L),L=1,NII)
    DO 409 L=1,NII
409 G(L,I)=HJ(L)
    GO TO 412
410 DO 411 L=1,NII
411 G(L,I)=0.0
412 CONTINUE
    C1=16.8612*100.0
    DO 429 L=1,NOTEP
    C2=0.7193392 / TEMP(L)
    WRITE (6,55) TEMP(L)
55 FORMAT(15H0 TEMPERATURE=F10.2,6H DEG.K)
    DO 418 I=1,NQ
    IF(0.01-ABS(DV(I)))415,416,416
415 DEL(I)=C1 / (TANH(C2*DV(I))*DV(I))
    GO TO 418
416 DEL(I)=0.0
418 CONTINUE
    DO 420 I=1,NII
    DO 420 J=1,NII
    D(I,J)=0.0
    DO 420 K=1,NQ
420 D(I,J)=D(I,J)+G(I,K)*DEL(K)*G(J,K)
    DO 426 I=1,NII
    DD(I)=SQRT(D(I,I))/10.0
    DO 426 J=1,NII
426 D(J,I)=D(I,J)
    DO 427 I=1,NII
427 WRITE (6,56)I,(D(I,J),J=1,NII)
    WRITE (6,57) TEMP(L),REC,(J,DD(J),J=1,NII)
57 FORMAT(1H0,22H ROOT MEAN AMPLITUDES.,F10.2,6H DEG,K/3X,18A4/5X,33H
1COORDINATE ROOT MEAN AMPLITUDE/(9X,I3,9X,F9.7))
429 CONTINUE
430 IF(IFB)450,500,431
431 IFB=-1
    NII=NA
    NUM = 3
    WRITE (6,85)REC
85 FORMAT(47H1 CARTESIAN MEAN SQUARE AMPLITUDE MATRIX(X 100)/3X,18A4)
    GO TO 407
450 IF(ICOR)500,500,452
452 IF(IFB)453,500,500
453 DO 455 I=1,NA
    W(I)=SQRT(1.0 / W(I))
    DO 455 J=1,NQ
```

c. NMOL, the number of molecules in the problem, punched in Columns 10-12 (FORMAT I3).

d. NF is the number of force constants, punched in Columns 13-15 (FORMAT I3).

Warning: NF may not exceed 71.

e. INO, designates the number of force constants to be renumbered. INO is punched in Columns 16-18 (FORMAT I3).

f. IEG, a 1 will result in the termination of the problem after the secular equation has been solved and the eigenvalues determined. IEG is punched in Columns 19-21 (FORMAT I3).

g. IFF, a 1 will result in the printout of the  $\underline{F}$  matrix.

h. RAP is the cutoff factor for the Jacobi diagonalization. The plane rotations are terminated when  $\text{MAX}[H(I,J)]$  is less than  $\text{RAP} * \text{MIN}[H(I,I)]$ . If RAP is left blank, a value of  $0.5E-3$  is assumed. RAP is punched in Columns 25-34 (FORMAT F10.9).

3. Problem Information Cards. Three cards containing alphanumeric information about the problem. The first three columns of each card should be left blank with the alphanumeric information following in any of the Columns 4-72 (FORMAT 18A4).

Warning: These three cards must be included with the input data, even if they are left blank.

4. The Force Constants. The force constants are read in order 1 through NF and are punched in 12 column fields, six per card (FORMAT 6F12.6).

5. The Force Constants to be Renumbered. If INO is greater than zero, the force constants to be renumbered are entered with the old force constant number listed first followed by the new number. There are INO sets of numbers, each number punched in a 3 column field of which there are 24 per card (FORMAT 24I3).

6. Molecule Control Card.

a. IND = -06, identifies the molecule control card, punched in Columns 1-3 (FORMAT I3).

b. NQ is the number of internal coordinates, punched in Columns 4-6 (FORMAT I3).

Warning: NQ must not exceed 66.

c. NDD is the number of nonzero experimental frequencies entered with the data. For NDD = 0 or blank, no frequencies are entered. NDD is punched in Columns 7-9 (FORMAT I3).

- p. IMSC, a 1 will result in the suppression of the printout of the cartesian "squared amplitudes" of vibration, punched in Columns 41-42 (FORMAT I2).
- q. ICOR, a 1 will result in the calculation of the cartesian coriolis coefficients being bypassed, punched in Columns 43-44 (FORMAT I2).
- r. ITEMP is the temperature option control for the internal "squared amplitudes" of vibration. If ITEMP = 0, the computations are completed for a temperature of 0°K. If ITEMP = 1, the internal "squared amplitudes" are calculated for a temperature of ABST °K. ITEMP is punched in Columns 45-46 (FORMAT I2).
- s. ABST is the temperature in °K for which the internal "squared amplitudes" are to be computed. ABST is punched in Columns 47-56 (FORMAT F10.2).

Note: ABST need only be entered in those instances when ITEMP = 1.

- t. ICD is the internal coordinate description code control. If ICD = 1, a description code identifying the internal coordinates must be entered with the data. These four character codes are printed next to the corresponding "squared amplitudes," potential energy component, or L matrix element to simplify their identification. ICD is punched in Columns 57-58 (FORMAT I2).
- u. IPUN, for IPUN = 1, the "squared amplitudes" and potential energy distribution are written on tape in the proper format for use as input to SASORT. IPUN is punched in Columns 59-60 (FORMAT I2).

Warning: If IPUN = 1, an additional tape (Number 4) must be provided.

- v. IFL, if IFL = 1, the L matrix will be written on tape by columns. IFL is punched in Columns 61-62 (FORMAT I2).

Warning: If IFL = 1, an additional tape (Number 4) must be provided.

Warning: Both IFL and IPUN should not be set = 1 in the same problem because the data format will not be correct for use with SASORT.

- 7. Molecule Information Card. This card contains the name of the molecule or any other alphanumeric data pertinent to the problem. The first three columns of the card should be left blank with the alphanumeric information following in any of the Columns 4-72 (FORMAT 18A4).

Warning: This card must be included with the input data even if it is left blank.

- 8. Internal Coordinate Identification Cards. If ICD = 1, four character alphanumeric codes must be entered which identify the internal coordinates. The codes must appear in the same order as the internal coordinates which they are representing. The codes are punched in four column fields, 18 per card (FORMAT 18A4).

9. The Z Matrix. The Z matrix elements are read in as four one-dimensional arrays and are punched in 18 column fields, 1-4 per card [FORMAT 4(3I3,F9.6)]. The Z matrix is punched in the proper format by UBZM or ZSYM.

Warning: The row after the last element must be set equal to -2.

10. The Experimental Frequencies. If NDD is greater than zero, the experimental frequencies must be entered with the input data. The frequencies are entered in decreasing order 1 through NQ, of which NDD are nonzero. For frequencies which are uncertain, unknown, or redundant a zero is entered. The frequencies are punched in 12 column fields, 6 per card (FORMAT 6F12.6).

Warning: There must be NQ frequency entries, NDD of these entries must be nonzero.

11. The G Matrix. The nonzero G matrix elements are entered as three arrays and are punched in 18 column fields, four per card [FORMAT 4(2I3,F12.6)]. The G matrix is punched in proper format by GMAT.

Warning: The row number after the last element must be set equal to -1.

12. The Cartesian Coordinates. If IFB = 1, the cartesian coordinates must be entered with the input data. The nonzero cartesian coordinates are described by three arrays. The elements are punched in 18 column fields, four per card [FORMAT 4(2I3,F12.6)]. The cartesian coordinates are punched in the proper format by CART.

Warning: The row number after the last element must be = -1.

13. The Masses. If IFB = 1, the atomic masses must be entered with the input data in the order 1 through NOAT. The masses are punched in 12 column fields, six per card (FORMAT 6F12.6).

14. B Matrix. If IFB = 1, the B matrix must be entered with the input data. The B matrix elements are entered as three arrays, punched in 18 column fields, four per card [FORMAT 4(2I3,F12.6)]. The B matrix is punched in the proper format by GMAT.

Warning: The row number following the last element must be set equal to -5.

15. Data Termination Card. The data termination card designates the end of the input data. This card must have a 999 punched in Columns 1-3 (FORMAT I3).

Note: If another problem is to be included in the data deck, the problem ID card of the next problem should be placed at this point and the data termination card moved to the end of the second problem.

With the OS operating system, a card with a /\* punched in Columns 1-2 must be placed at the very end of the data deck, after the data termination card.

OUTPUT INFORMATION

At the option of the user, the following information is printed out.

1. The set of force constants.
2. The force constants to be renumbered.
3. The  $\underline{Z}$  matrix.
4. The  $\underline{F}$  matrix.
5. The calculated and observed frequencies and their difference.
6. The  $\underline{L}$  matrix.
7. The potential energy distribution among the diagonal  $\underline{F}$  elements.
8. The internal "squared amplitudes" of vibration.

Note: These elements are improperly labeled mean square amplitudes in the printout; however, this title is immediately followed by (A\*\*2) which should lessen the confusion.

9. The  $\underline{L}^{-1}$  matrix.
10. The equilibrium cartesian coordinates.
11. The cartesian displacement coordinates and the cartesian "squared amplitudes" of vibration.

Note: These latter elements are also improperly labeled mean square amplitudes, but are followed by the designation (A\*\*2) which should reduce the confusion.

12. The cartesian mean amplitudes for the atoms summed over all the normal modes and the root mean squares.
13. The internal coordinate root mean square amplitudes.
14. The internal coordinate mean square amplitude matrix.
15. The cartesian mean square amplitude matrix.
16. The cartesian coriolis coupling coefficients.

At the option of the user, the internal coordinate "squared amplitudes" of vibration and the potential energy distribution for the normal modes are written on tape in a format suitable for input to SASORT. The  $\underline{L}$  matrix may also be written on tape by columns.

PAMOLE

This program employs the Calcomp 110 digital plotter to draw three dimensional "ball and stick" representations of molecules from any viewpoint at any reasonable distance away and is based on the cartesian coordinates of the atoms.

This program was written by P. G. Adamson (90) and modified at the Institute for use on our IBM 360/44 computer. The program may be used with the IBM 360/44 OS operating system. A version of PAMOLE is stored on disk at the Institute. A listing of the JCL cards required to run the stored version of PAMOLE appears in Table LV. These cards are placed in front of the data deck. A listing of PAMOLE cannot be included in this text because of space considerations. However, a sample data input to PAMOLE is presented in Table LVI.

INSTRUCTIONS FOR PROGRAM USE

The following information is required to complete the data deck for PAMOLE.

1. Problem Definition Card.

- a. IND = -09, identifies the problem definition card, punched in Columns 1-3 (FORMAT I3).
- b. NOAT is the number of atoms in the molecule. NOAT is punched in Columns 4-7 (FORMAT I4).
- c. NVW, designates the number of views to be drawn for this molecule, punched in Columns 8-11 (FORMAT I4).
- d. ITITLE, a 1 will permit alphanumeric information describing the drawing to be written on plotter output, punched in Columns 12-15 (FORMAT I4).

Warning: For more than one view of a molecule with or without a label, the plotter should be manually zeroed to the right after each drawing.

- e. XSTAR is the desired starting position along the x-axis, in inches from the origin, for the alphanumeric lettering. XSTAR is punched in Columns 16-21 (FORMAT F6.2).

Note: If ITITLE = 0, XSTAR may be left blank.

TABLE LV

JCL CARDS REQUIRED TO RUN THE STORED  
VERSION OF PAMOLE

```
//PAMOLE JOB 94000110,LJP,MSGLEVEL=1
//JOB LIB DD DSN=PAM,VOL=SER=DLIB03,DISP=OLD,UNIT=SYSDA
// EXEC PGM=PAMOLE
//FT05F001 DD DDNAME=SYSIN
//FJ06F001 DD SYSOUT=A
//FT07F001 DD SYSOUT=B
//PLOT PLOT DD UNIT=PLOTTER
//SENSE DD UNIT=AFF=PLOT PLOT
//SYSIN DD *
```

TABLE LVI

SAMPLE INPUT DATA TO PAMOLE

```
-9 19 1
SCALE 1.2
SIZES C .290 .27H .12
O1 0.000 0.000 0.000 C2 C3
C2 1.423 0.000 0.00001 H7 H8 C4
C3 -0.543 1.315 0.000 O1 H9 H10 C5
C4 1.931 0.718 1.244C2 C6 O18 H17
C5 -0.074 2.059 1.244 C3 C6 H11 O12
C6 1.446 2.162 1.230 C4 C5 H14 O15
H7 1.788 -1.033 0.000C2
H8 1.788 0.517 -0.895 C2
H9 -1.638 1.258 0.000 C3
H10 -0.205 1.850 -0.895 C3
H11 -0.394 1.515 2.136 C5
O12 -0.635 3.358 1.256 C5 H13
H13 -0.350 3.840 0.465 O12
H14 1.770 2.646 0.305 C6
O15 1.885 2.818 2.404 C6 H16
H16 1.563 2.337 3.183 O15
H17 1.550 0.214 2.136 C4
O18 3.345 0.696 1.256 C4 H19
H19 3.683 1.143 0.465 O18
VIEW 5. 5. -5.
999
/*
```

- f. YSTAR is the desired starting position along the y-axis, in inches from the origin, for the alphanumeric lettering. YSTAR is punched in Columns 22-27 (FORMAT F6.2). YSTAR is left blank if there is to be no labeling of the drawing.
- g. LHGT is the desired lettering height in inches, which must be an integer multiple of 0.07. LHGT is punched in Columns 28-33 (FORMAT F6.2).

Note: LHGT is left blank if there is to be no label on the drawing.

- 2. Alphanumeric Information. If ITITLE = 1, the alphanumeric labeling to appear on the drawing must be punched on a card in any of the Columns 1-80 and must be included with the input data (FORMAT 20A4).

Note: This card must be included with the input data even if blank and ITITLE = 0. In this case the alphanumeric information will appear only with the printer output.

- 3. BIG. This card requests that the wide paper (29½") be used. If this card is omitted, the more commonly used narrow paper (10½") is required. The characters BIG are punched in Columns 1-3 (FORMAT A4,A2,3F4.0).
- 4. SCALE XXXX. This card indicates the scale factor to be used in the drawing. If this card is omitted, a scale factor of 1 is assumed. SCALE is punched in Columns 1-6 and the numerical scale factor in Columns 7-10 (FORMAT A4,2,3F4.0).

Note: The scale factor punched in Columns 7-10 may be decimal and the Format F4.0 will be overruled, e.g., SCALE 1.2.

- 5. ANGLES  $\alpha, \beta, \gamma$ . This card supplies the angles between the coordinates (if not rectangular) where  $\alpha$  is the angle between the y- and z-axes,  $\beta$  is the angle between the x- and z-axes, and  $\gamma$  is the angle between the x- and y-axes. If this card is omitted, rectangular axes are assumed. ANGLES is punched in Columns 1-6,  $\alpha$  in Columns 7-10,  $\beta$  in Columns 11-14, and  $\gamma$  in Columns 15-18 (FORMAT A4,A2,3F4.0).

Note: If decimal angles are entered, the Format F4.0 is overruled.

- 6. SIZES name r name r ..... . This card indicates the general atom names (name), e.g., C, H, O, Cl, Br, etc., and the corresponding radius of the "ball" representation (r) in atomic units. There can be up to 10 atom names. SIZES is punched in Columns 1-6, the atom name in Columns 7-10, and the atom radius in Columns 11-13 with the next atom names and radii following in groups of 4 columns and 3 columns through 10 atom names [FORMAT 6X,10(4A1,F3.2)].

Warning: The atom names must be left justified.

- 7. CELL x,y,z. This card indicates the fractional coordinates for the atom positions, and is optional. This option is used when the coordinates are x-ray crystallographic fractional coordinates. The unit cell dimensions are specified in atomic units. If this card is included with the input data, all subsequent atom coordinates will be assumed fractional. CELL is punched in Columns 1-4, x in Columns 5-11, y in Columns 12-18, and z in Columns 19-25 (FORMAT 4A1,3F7.3).



8. Name x y z name1 name2 ..... . The next set of cards specify individual atoms, up to 100. Each card refers to one atom giving its name with up to four characters in Columns 1-4; its position in space by the cartesian or fractional coordinates (x is punched in Columns 5-11, y in Columns 12-18, and z in Columns 19-25); and the names of the atoms connected to it, up to 8 atoms, punched in four column fields with a blank separating each entry [FORMAT 4A1,3F7.3,8(4A1,1X)].

Note: There should be NOAT cards in this group. The program checks for duplicate names. The order of the drawing of atoms is the same as the order of their specification on the data cards.

Note: The first one or two columns of the atom names should contain the general atom name as it appears on the SIZES card. The remaining two or three columns should contain an atom numbering code or some other identification code to distinguish the individual atoms in the molecule. (For an example, see Table LVI.)

Warning: The atom names should be left justified.

9. VIEW x,y,z. This card(s) specifies the coordinates of the viewpoint(s) desired. The view is drawn from a point looking down the line joining the viewpoint to the center (i.e., the average of the extremities) of the molecule. VIEW is punched in Columns 1-4 with Columns 5-6 left blank. Then x is punched in Columns 7-10, y in Columns 11-14, and z in Columns 15-18 (FORMAT 6X,3F4.0). There should be NVW viewpoint cards in this section.
10. Data Termination Card. This card indicates the end of the data deck and has a 999 punched in Columns 1-3 (FORMAT I3). If another problem is to be included in the data deck, the problem definition card for the next problem should be placed at this point in the deck and the data termination card moved to the end of the second problem.

The data termination card is followed by a card with a /\* punched in Columns 1-2 if the OS operating system is being used.

Warning: For best results, the plotter should be manually zeroed, i.e., the pen moved to the extreme right, after each drawing is completed.

#### OUTPUT INFORMATION

Besides the plotter drawing, the following information is written out by the printer.

1. Alphanumeric information about the drawing (if this card is not blank).
2. Scale factor.

3. Sizes of atoms.
4. Cartesian coordinates (fractional coordinates if specified) and bond information.
5. Viewpoint coordinates.
6. Listing of those atoms hidden from view in the drawing.

#### PESORT AND SASORT

These programs read the potential energy and "squared amplitude" data from tape, arrange the information in decreasing order, and label the numerical data with an identifying code.

These programs were written by the author during the investigation of the 1,5-anhydropentitol spectra to arrange the potential energy and "squared amplitude" data in a more convenient way. PESORT sorts the potential energy data in terms of the force constants in decreasing order. The data is read from the output tape from NFAD which is a simplified version of FADJ. PESORT reads four character codes, one for each force constant, which identify the force constants. These force constant codes are then printed beside the corresponding potential energy element when the ordered distributions are printed out by PESORT. PESORT also converts the fractional elements to percent. SASORT reads the potential energy data in terms of the internal coordinates (diagonal  $\underline{F}$  matrix elements) and "squared amplitude" data for internal coordinates from the output tape from EIGV. These data are then arranged in decreasing order and labeled with a four character code that identifies the internal coordinates.

Both PESORT and SASORT may be used with the IBM 360/44 RAX operating system. A listing of PESORT is presented in Table LVII and a listing of SASORT in Table LVIII.

TABLE LVII

LISTING OF PESORT

DIMENSION DES(100),PE(100),DUM(100),INDEX(100),REC(18)

PROGRAM PESORT

DESIGNED TO RUN ON RAX AND READ PE DISTRIBUTION OFF TAPE FROM PROGRAM NFAD.

PESORT SORTS THE PE DISTRIBUTION DATA FOR EACH CALCULATED FREQ. AND ARRANGES THE DATA IN DESCENDING ORDER.

A DESCRIPTION OF THE FORCE CONSTANTS IS READ IN FROM CARDS AND IS REPRODUCED ALONG WITH THE OUTPUT. (FORMAT A4).

PESORT WAS WRITTEN BY L.J.PITZNER 1/13/72

READ PROBLEM CONTROL CARD

NOTE EACH PROBLEM CONTROL CARD IS PRECEDED BY A CARD WITH -09 IN COLUMNS 1-3.

- 1). IND=-09 PUNCHED IN COLUMNS 1-3.
- 2). NOPROB= PROBLEM NUMBER PUNCHED IN COLUMNS 4-9.
- 3). NF= THE NUMBER OF FORCE CONSTANTS PUNCHED IN COLUMNS 10-12.
- 4). NFR= THE NUMBER OF FREQUENCIES PUNCHED IN COLUMNS 13-15.

REWIND 1

4 READ(5,1)IND

1 FORMAT(I3)

IF(IND+9)2,3,2

2 IF(IND-999)4,5,4

5 REWIND 1

CALL EXIT

3 READ(5,6)IND,NOPROB,NF,NFR

6 FORMAT(I3,I6,2I3)

READ PROBLEM INFORMATION CARD.

READ(5,18)REC

18 FORMAT(18A4)

WRITE(6,19)NOPROB,REC

19 FORMAT(1H1,'APPROXIMATE POTENTIAL ENERGY DISTRIBUTION FOR PROBLEM',

1I6/(1H ,12X,18A4))

READ FORCE CONSTANT DESCRIPTION CARDS

READ(5,7)(DES(J),J=1,NF)

7 FORMAT(18A4)

DO 15 J=1,NFR

READ(1,70)NUM,FREQ

70 FORMAT(I3,F8.2)

READ(1,80)(PE(L),L=1,NF)

80 FORMAT(9F8.4)

DO 66 I=1,NF

66 INDEX(I)=I

MU=1

NU=2

9 DO 11 K=NU,NF

IF(PE(K)-PE(MU))11,11,10

10 TEM=PE(K)

PE(K)=PE(MU)

PE(MU)=TEM

ITEM=INDEX(K)

TABLE LVII (Continued)

```
INDEX(K)=INDEX(MU)
INDEX(MU)=ITEM
11 CONTINUE
  MU=MU+1
  NU=MU+1
  IF(MU-NF)9,200,200
200 DO 13 JJ=1,NF
  KK=INDEX(JJ)
13 DUM(JJ)=DES(KK)
  DO 14 I=1,NF
14 PE(I)=100.*PE(I)
  WRITE(6,21)NUM,FREQ
  WRITE(6,22)(PE(L),DUM(L),L=1,NF)
21 FORMAT(1H0,'FREQUENCY',I3,' =',F6.1,' CM-1')
22 FORMAT(1H ,8(F8.2,2X,A4))
15 CONTINUE
  GO TO 4
  END

/ DATA
-09
-09 5009 56 51
  1,5-ANHYDROXYLITOL CORRECTED TETRAHEDRAL STRUCTURE.
COR CO ACH CH CC OHCCCCOCOCOCOCHCCCHCHCHCOOHHCORCCORAHGCHCH° HCC CCO
COH CCC HCOCORC SB1 SB2 SB3 SB4 SB5 SB6 SB7 SB8 SB9SB10 BB1 BB2 BB3 BB4
BB5 BB6 BB7 BB8 BB9BB10BB11BB12BB13BB14BB15BB16BB17BB18BB19 TCC TCOTCOR
BB0BB20
-09
-09 5009 56 51
  1,5-ANHYDRORIBITOL CORRECTED TETRAHEDRAL STRUCTURE.
COR CO ACH CH CC OHCCCCOCOCOCOCHCCCHCHCHCHCOOHHCORCCORAHGCHCH° HCC CCO
COH CCC HCOCORC SB1 SB2 SB3 SB4 SB5 SB6 SB7 SB8 SB9SB10 BB1 BB2 BB3 BB4
BB5 BB6 BB7 BB8 BB9BB10BB11BB12BB13BB14BB15BB16BB17BB18BB19 TCC TCOTCOR
BB0BB20
-09
-09 5009 56 51
  1,5-ANHYDRO-L-ARABINITOL CORRECTED TETRAHEDRAL STRUCTURE.
COR CO ACH CH CC OHCCCCOCOCOCOCHCCCHCHCHCHCOOHHCORCCORAHGCHCH° HCC CCO
COH CCC HCOCORC SB1 SB2 SB3 SB4 SB5 SB6 SB7 SB8 SB9SB10 BB1 BB2 BB3 BB4
BB5 BB6 BB7 BB8 BB9BB10BB11BB12BB13BB14BB15BB16BB17BB18BB19 TCC TCOTCOR
BB0BB20
999
```

TABLE LVIII

LISTING OF SASORT

DIMENSION DES(100),PE(100),ASQ(100),DUM(100),INDEX(100),REC(18)  
PROGRAM SASORT  
DESIGNED TO RUN ON RAX AND READ PE DISTRIBUTION OFF TAPE FROM  
PROGRAM EIGV. THE MEAN SQ. AMP. (A\*\*2) IS ALSO READ FROM TAPE.  
SASORT SORTS THE PE AND MEAN SQ. AMP. DATA FOR EACH CALC. FREQ.  
AND ARRANGES THE DATA IN DESCENDING ORDER.  
A DESCRIPTION OF THE INTERNAL COORDINATES IS READ IN FROM CARDS  
AND IS REPRODUCED ALONG WITH THE OUTPUT. (FORMAT A4).  
SASORT WAS WRITTEN BY L.J.PITZNER 1/13/72

NOTE EACH PROBLEM CONTROL CARD IS PRECEDED BY A CARD WITH -09 IN  
COLUMNS 1-3.

- 1). IND=-09 PUNCHED IN COLUMNS 1-3.
  - 2). NOPROB= PROBLEM NUMBER PUNCHED IN COLUMNS 4-9.
  - 3). NQ= THE NUMBER OF INTERNAL COORDINATES PUNCHED IN COLUMNS 10-12.
  - 4). NFR= THE NUMBER OF FREQUENCIES PUNCHED IN COLUMNS 13-15.
- READ PROBLEM CONTROL CARD

```
REWIND 1
4 READ(5,1)IND
1 FORMAT(I3)
  IF(IND+9)2,3,2
2 IF(IND-999)4,5,4
5 REWIND 1
  CALL EXIT
3 READ(5,6)IND,NOPROB,NQ,NFR
6 FORMAT(I3,I6,2I3)
  READ PROBLEM INFORMATION CARD.
  READ(5,18)REC
18 FORMAT(18A4)
  WRITE(6,19)NOPROB,REC
19 FORMAT(1H1,'APPROXIMATE PE AND MEAN SQ. AMP. DISTRIBUTION FOR PROBLEM'
1',I6/(1H ,12X,18A4))
  READ INTERNAL COORDINATE DESCRIPTION
  READ(5,7)(DES(J),J=1,NQ)
7 FORMAT(18A4)
  DO 15 J=1,NFR
  READ(1,70)NUM,FREQ
70 FORMAT(I3,F8.2)
  READ(1,80)(PE(L),L=1,NQ)
80 FORMAT(9F8.4)
  READ(1,90)(ASQ(K),K=1,NQ)
90 FORMAT(6E12.4)
400 NUM = J
  DO 66 I=1,NQ
66 INDEX(I)=I
  MU=1
  NU=2
  DO 11 K=NU,NQ
  IF(PE(K)-PE(MU))11,11,10
10 TEM=PE(K)
```

TABLE LVIII(Continued)

```
PE(K)=PE(MU)
PE(MU)=TEM
ITEM=INDEX(K)
INDEX(K)=INDEX(MU)
INDEX(MU)=ITEM
11 CONTINUE
MU=MU+1
NU=MU+1
IF(MU-NQ)9,200,200
200 DO 13 JJ=1,NQ
KK=INDEX(JJ)
13 DUM(JJ)=DES(KK)
DO 14 I=1,NQ
14 PE(I)=100.*PE(I)
WRITE(6,21)NUM,FREQ
21 FORMAT(1H0,'FREQUENCY',I3,' =',F6.1,' CM-1')
WRITE(6,30)
WRITE(6,31)(PE(L),DUM(L),L=1,NQ)
30 FORMAT(1H,'POTENTIAL ENERGY DISTRIBUTION')
31 FORMAT(1H,8(F8.2,2X,A4))
DO 50 I=1,NQ
50 INDEX(I)=I
MU=1
NU=2
39 DO 41 K=NU,NQ
IF(ASQ(K)-ASQ(MU))41,41,40
40 TEM=ASQ(K)
ASQ(K)=ASQ(MU)
ASQ(MU)=TEM
ITEM=INDEX(K)
INDEX(K)=INDEX(MU)
INDEX(MU)=ITEM
41 CONTINUE
MU=MU+1
NU=MU+1
IF(MU-NQ)39,300,300
300 DO 43 JJ=1,NQ
KK=INDEX(JJ)
43 DUM(JJ)=DES(KK)
WRITE(6,51)
WRITE(6,52)(ASQ(L),DUM(L),L=1,NQ)
51 FORMAT(1H,'MEAN SQ. AMP. (A**2)')
52 FORMAT(1H,6(E12.4,2X,A4))
15 CONTINUE
GO TO 4
END
```

## INSTRUCTIONS FOR PROGRAM USE

The input data appear on tape which is the output from EIGV or NFAD. The following information embodies the data deck. The program deck, which precedes the data deck, must be started with a /ID card, a /JOB GO card, and a /FILE card with the RAX system. The data deck is preceded by a /DATA card.

1. Problem ID Card. This card indicates the start of a problem. A -09 is punched in Columns 1-3 (FORMAT I3).
2. Problem Control Card.
  - a. IND = -09, identifies the problem control card, punched in Columns 1-3 (FORMAT I3).
  - b. NOPROB is the problem number, punched in Columns 4-9 (FORMAT I6).
  - c. NF (in PESORT) or NQ (in SASORT), NF is the number of force constants and NQ the number of internal coordinates, punched in Columns 10-12 (FORMAT I3).
  - d. NFR is the number of nonzero calculated frequencies, punched in Columns 13-15 (FORMAT I3).
3. The Force Constant Identification Codes (PESORT) or The Internal Coordinate Identification Codes (SASORT). These four character alphanumeric codes should provide easy identification of the force constants or internal coordinates. They are punched in four column fields, 18 per card, in order 1 through NF (PESORT) or 1 through NQ (SASORT) (FORMAT 18A4).
4. Data Termination Card. This card indicates the end of the problem and is characterized by a 999 in Columns 1-3 (FORMAT I3). If another problem is to be included, the problem ID card for the next problem is placed at this point. The data termination card is then moved to the end of the second problem.

With the RAX operating system, the data deck is terminated by a /END card. Printer output for PESORT includes the sorted potential energy distribution (in decreasing order) in terms of the force constants. Printer output for SASORT includes the sorted (in decreasing order) potential energy distribution in terms of the diagonal  $\underline{F}$  matrix elements and the internal coordinate "squared amplitudes." In both cases, the data are labeled with the identifying code characters.

NFAD

This program is a condensed version of FADJ. NFAD solves the secular determinant and computes the potential energy distribution in terms of the force constants; however, the force constants are not refined. NFAD will write the potential energy distribution on tape in the proper format for input to PESORT. NFAD may be used with the IBM 360/44 OS operating system. NFAD will not be listed in this text because of the similarity to FADJ which has been discussed earlier in this appendix.



APPENDIX VI

CALCULATED FREQUENCIES FOR BOTH CONFORMERS OF THE  
1,5-ANHYDRO-PENTITOL MODELS

This appendix contains the listings of the calculated frequencies for the 1,5-AP models for both conformers and is based on the set of force constant parameters listed in Table XX in the main text. The calculated frequencies for 1,5-AX, 1,5-AR, and 1,5-ALA follow in Tables LIX, LX, and LXI, respectively.

TABLE LIX

CALCULATED FREQUENCIES FOR BOTH CONFORMERS OF THE  
1,5-ANHYDROXYLITOL MODEL, BASED ON THE FORCE  
CONSTANTS IN TABLE XX

Stable Conf., $\nu$ , cm. <sup>-1</sup>	Alternate Conf. $\nu$ , cm. <sup>-1</sup>	Stable Conf., $\nu$ , cm. <sup>-1</sup>	Alternate Conf., $\nu$ , cm. <sup>-1</sup>
3356	3356	1131	1133
3356	3356	1110	1108
3356	3356	1096	1076
2982	2980	1095	1028
2979	2976	1049	971
2946	2930	1014	956
2926	2924	950	948
2911	2923	927	903
2882	2881	901	854
2880	2880	882	815
1468	1469	655	795
1460	1463	563	596
1437	1389	533	572
1410	1382	467	539
1388	1382	429	458
1363	1350	420	434
1347	1328	368	365
1345	1328	318	310
1329	1319	297	286
1298	1303	278	241
1292	1289	241	238
1272	1253	230	230
1257	1239	228	199
1207	1224	200	170
1201	1213	131	131
1141	1162		

TABLE LX

CALCULATED FREQUENCIES FOR BOTH CONFORMERS OF THE  
1,5-ANHYDRORIBITOL MODEL BASED ON THE FORCE  
CONSTANTS IN TABLE XX

Stable Conf., $\nu$ , cm. <sup>-1</sup>	Alternate Conf., $\nu$ , cm. <sup>-1</sup>	Stable Conf., $\nu$ , cm. <sup>-1</sup>	Alternate Conf., $\nu$ , cm. <sup>-1</sup>
3356	3356	1131	1136
3356	3356	1106	1089
3356	3356	1096	1059
2982	2980	1042	1037
2979	2976	1024	994
2931	2930	1010	963
2925	2924	981	946
2921	2922	926	889
2882	2881	876	865
2880	2880	850	809
1468	1469	676	786
1460	1461	641	666
1418	1373	599	601
1412	1371	463	470
1393	1365	446	451
1367	1353	413	433
1344	1329	342	354
1320	1324	308	301
1317	1302	283	297
1295	1284	255	258
1289	1283	240	239
1265	1272	227	230
1255	1240	220	226
1233	1222	202	170
1220	1214	137	132
1155	1139		

TABLE LXI

CALCULATED FREQUENCIES FOR BOTH CONFORMERS OF THE  
1,5-ANHYDRO-L-ARABINITOL MODEL BASED ON THE FORCE  
CONSTANTS IN TABLE XX

Stable Conf., $\nu$ , cm. <sup>-1</sup>	Alternate Conf., $\nu$ , cm. <sup>-1</sup>	Stable Conf., $\nu$ , cm. <sup>-1</sup>	Alternate Conf., $\nu$ , cm. <sup>-1</sup>
3356	3356	1130	1122
3356	3356	1108	1093
3356	3356	1097	1086
2981	2981	1074	1045
2978	2977	1061	1018
2940	2929	988	978
2926	2925	941	947
2915	2921	931	929
2882	2881	873	874
2880	2880	851	831
1469	1469	743	720
1461	1460	637	640
1419	1391	540	548
1395	1383	487	518
1378	1377	441	451
1372	1348	403	419
1341	1333	380	387
1326	1320	302	313
1313	1303	285	288
1304	1295	260	243
1284	1278	237	238
1263	1255	236	238
1251	1232	236	228
1234	1230	222	214
1199	1220	185	190
1163	1149	132	135