# Vibration Spectra and Rotational Isomerism of Chain Molecules. VII.[1] 1-Chloro-, 1-Bromo-, and 1-Iodopropanes, and 1-Chloro-, 1-Bromo-, and 1-Iodobutanes

Yoshiki OGAWA, Shuji IMAZEKI, Hiroko YAMAGUCHI, Hiroatsu MATSUURA,*
Issei HARADA, and Takehiko SHIMANOUCHI**

*Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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The Raman and infrared spectra of 1-chloro-, 1-bromo-, and 1-iodopropanes, $CH_3CH_2CH_2X$ (X=Cl, Br, and I), and 1-chloro-, 1-bromo-, and 1-iodobutanes, $CH_3CH_2CH_2CH_2X$ (X=Cl, Br, and I), were measured for the gaseous, liquid, glassy, and crystalline states. The normal vibration frequencies were calculated, a consistent set of force constants explaining the frequencies of basic halogenoalkanes being assumed. The rotational isomerism was studied on the basis of the spectral observations and the normal coordinate calculations. The enthalpy differences among the rotational isomers were examined.

The study of the vibration spectra and rotational isomerism of 1-halogenopropanes was started by Mizushima and coworkers[2] and Radinger and Wittek[3] about thirty years ago. Many studies have been made by means of Raman and infrared,[4–17] microwave,[18,19] and electron-diffraction[20] measurements. As a result, it has been established that the *trans* (T) form exists in the crystalline state except 1-fluoropropane for which the *gauche* (G) form exists[7a,b] and both the T and G forms exist in the liquid and gaseous states. The enthalpy difference between the T and G forms has also been determined by many investigators.[4–6,10,11,17–20] However, as has been indicated previously,[17] the reported values of the enthalpy difference are quite different from one another and there are some disagreements in the vibrational assignments among different authors. These problems remain to be settled.

The rotational isomerism of 1-halogenobutanes has been studied also by means of Raman and infrared,[4–9,14,16,21–25] and electron-diffraction[26] measurements. Ukaji and Bonham[26a] concluded that 1-chlorobutane had an isomer distribution of 37% TG, 24% GG', 17% GG, 11% TT, and 11% GT in the gaseous state at room temperature. Snyder and Schachtschneider[14] observed the infrared spectra of $CH_3(CH_2)_n$-Cl ($n$=1—5) in the crystalline (annealed solid) and glassy (unannealed solid) states and obtained the refined valence force field through the normal coordinate analysis. They indicated that the vibrational spectra of 1-chlorobutane in the crystalline state are explained by the existence of the TT form and those in the glassy state by the coexistence of the TT form and the TG form with the *gauche* CC–CCl axis. More recently, Crowder and coworkers[7,8] interpreted the vibrational spectra of 1-fluoro- and 1-iodoalkanes, taking into account only two among various isomers, the all-*trans* form and the form which has a *gauche* conformation about the CC–CX axis and a *trans* conformation about the remaining axes. Thus, the whole aspect of the rotational isomers existing in the various states of 1-halogenobutanes is still unknown and the enthalpy differences among the isomers have not yet been determined.

In the previous papers,[27–31] we compared the Raman and infrared spectra of unbranched ethers, paraffins, and sulfides in the crystalline, glassy, liquid, and gaseous states with the results of normal vibration calculations and determined the rotational isomers existing in each state. As a continuation of such studies, the same method has been applied to 1-halogenopropane and 1-halogenobutane molecules. The results show that the method is useful in the study of rotational isomerism. In the course of the research, several new findings including the identification of less stable rotational isomers and the enthalpy differences among the isomers in the liquid state have been obtained. The present paper describes the rotational isomerism and vibrational assignments of 1-halogenopropanes, $CH_3CH_2CH_2X$, and 1-halogenobutanes, $CH_3CH_2CH_2CH_2X$ (X=Cl, Br, and I).

## Experimental

Samples used in the present study were purchased from Tokyo Kasei Kogyo Co., Ltd. and were distilled prior to the measurements. The Raman and infrared spectra were measured for the gaseous, liquid, glassy, and crystalline states by the method reported previously.[27,28,30]

The glassy state for the Raman measurements was obtained by immersing the sample enclosed in an ampoule in liquid nitrogen for rapid cooling, and that for the infrared measurements by depositing the sample onto a cooled window of KBr or KRS-5.

For the determination of the enthalpy difference, the Raman spectra in the liquid state were recorded twice at each of nine different temperatures between −105 and 15 °C for 1-chloropropane, nine different temperatures between −100 and 15 °C for 1-bromopropane, eight different temperatures between −85 and 15 °C for 1-iodopropane, and eight different temperatures between −90 and 15 °C for 1-chloro-, 1-bromo-, and 1-iodobutanes. The Raman spectra in the gaseous state were also measured three times at each of four different temperatures between 23 and 80 °C for 1-chloropropane.

## Normal Coordinate Treatment

The normal coordinate treatment of the unbranched halogenoalkanes (see Table 1) was carried out with a computer program NCTB2[32] and a HITAC 8700/8800

* Present address: Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730.

** Present address: College of Information Sciences, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 300-31.

Table 1. Procedure of the least-squares calculation

(i) Chloroalkanes

| Step | $C_3H_7Cl$[a] | $C_4H_9Cl$[b] | $C_5H_{11}Cl$[c] | $ClC_3H_6Cl$[d] | $ClC_4H_8Cl$[c] |
|---|---|---|---|---|---|
| 1 | T (19) | TT (26) | | | |
| 2 | G (17) | TG (13) | | | |
| 3 | | | TTT (29) | | |
| 4 | | | TTG (18) | GG (19) | GTG′ (24) |
| | | | | TG (12) | |
| | | | | TT (13) | |
| 5 | | GT (5) | TGT (14) | | TTT (17) |
| | | GG (11) | TGG (11) | | TTG (20) |
| | | | GTG (9) | | TGG (18) |
| | | | GTG′ (8) | | GTG (16) |
| | | | | | GGG (17) |

(ii) Bromoalkanes

| Step | $C_3H_7Br$[a] | $C_4H_9Br$[b] | $C_5H_{11}Br$[c] | $BrC_3H_6Br$[d] | $BrC_4H_8Br$[c] |
|---|---|---|---|---|---|
| 1 | T (19) | TT (24) | | | |
| 2 | G (16) | TG (14) | | | |
| 3 | | | TTT (31) | | |
| 4 | | | TTG (29) | GG (19) | GTG′ (24) |
| | | | | TG (10) | |
| | | | | TT (7) | |
| 5 | | GT (4) | TGT (10) | | TTT (19) |
| | | GG (8) | GTT (7) | | TTG (20) |
| | | | TGG (10) | | TGT (17) |
| | | | GTG (10) | | TGG (20) |
| | | | GTG′ (7) | | GTG (16) |
| | | | | | GGG (19) |
| 6 | $CH_3CHDCH_2Br$[e] | T (17) G (6) | G′ (6) | | |
| | $CH_3CH_2CHDBr$[e] | T (16) G (5) | G′ (9) | | |

(iii) Iodoalkanes

| Step | $C_3H_7I$[a] | $C_4H_9I$[b] | $C_5H_{11}I$[c] | $IC_3H_6I$[d] |
|---|---|---|---|---|
| 1 | T (19) | TT (24) | | |
| 2 | G (13) | TG (15) | | |
| 3 | | | TTT (28) | |
| 4 | | | TTG (16) | GG (19) |
| | | | | TG (13) |
| | | | | TT (19) |
| 5 | | GT (7) | TGT (12) | |
| | | GG (13) | GTT (9) | |
| | | | TGG (14) | |
| | | | GTG (10) | |
| | | | GTG′ (11) | |

(iv) Fluoroalkanes

| Step | $C_3H_7F$[f] | $C_4H_9F$[f] | $C_5H_{11}F$[f] |
|---|---|---|---|
| 1 | G (17) | TG (24) | |
| 2 | | | TTG (27) |
| 3 | T (9) | TT (7) | |
| 4 | | | TTT (6) |
| 5 | | GT (3) | TGT (3) |
| | | GG (1) | GTT (3) |

Table 1. Continued

The least-squares calculation begins with the simplest halogenoalkanes given in the first step and the first set of force constants is determined so as to give the best fit between the observed and calculated frequencies. This set of force constants gives the definite vibrational assignments of the halogenoalkanes given in the second step and the second set of force constants is subsequently determined from the observed frequencies in this step in addition to those in the first step. By repeating this procedure, the final set of force constants is obtained. The figures in parentheses give the numbers of observed frequencies used for the least-squares calculation. The observed frequencies of the CH and CD stretching vibrations are not included in the calculation and accordingly the force constants associated with these vibrations are not refined. The results of the following references are utilized in the least-squares calculation. a) This study and Ref. 13. b) This study. c) Ref. 34. d) Ref. 35. e) Ref. 15. f) Ref. 7.

computer system at the Computer Center of the University of Tokyo. The calculation made it possible to assign the observed Raman and infrared bands to individual rotational isomers and to determine a consistent set of force constants of halogenoalkanes. Structural parameters and symmetry coordinates used in the calculation and a final set of the force constants will be reported in a separate paper.[33]

The force constants of halogenoalkanes were determined in the following way. The force constants associated with a methyl or methylene group which is not bound directly to a halogen atom were assumed to be the same as those for the paraffin molecules.[32] The force constants associated with the halogen atom, including those of the methyl or methylene group adjacent to the halogen atom, were refined in the least-squares adjustment. The initial values for the chlorine part were transferred from the result by Snyder and Schachtschneider.[14] The initial values for the bromine and iodine parts were estimated from the corresponding values of the chlorine part. Some of the halogenoalkane force constants including those which were unestimable from the observed frequencies were assumed to be the same values as those for the corresponding paraffin force constants.

Table 1 shows the procedure of the least-squares calculation. The calculation began with the simplest halogenoalkanes in the extended form, and then the molecules to be treated were extended to the longer halogenoalkanes and the non-extended forms. In the force constant refinement, we also used the observed frequencies of the deuterated derivatives of 1-bromopropane,[15] 1-halogenopentanes,[34] 1,3-dihalogenopropanes,[35] and 1,4-dihalogenobutanes.[34] A total of 23 force constants associated with the chlorine part were determined from 336 Raman and infrared frequencies of 21 forms of 5 molecular species, 21 force constants associated with the bromine part from 419 frequencies of 29 forms of 7 molecular species, and 23 force constants associated with the iodine part from 242 frequencies of 16 forms of 4 molecular species.

The normal vibration calculation of fluoroalkanes was also carried out in the same way as the other halogenoalkanes on the basis of the experimental data by Crowder and Mao.[7] The procedure of the least-squares calculation of fluoroalkanes is also included in Table 1. A total of 22 force constants associated with the fluorine part were determined from 100 Raman and infrared frequencies of 10 forms of 3 molecular species.

## Results

Figures 1—16 show the Raman and infrared spectra in the gaseous, liquid, glassy, and crystalline states. The observed frequencies and the vibrational assignments based on the calculated potential-energy distributions are listed in Tables 2—7. The observed spectra were analyzed with reference to the results of the normal coordinate treatment. The values of enthalpy differences obtained from the intensity variation of the Raman bands with temperature are given in Figs. 17 and 18.

In the following subsections, the rotational isomerism of the individual halogenopropane and halogenobutane molecules is described.

*1-Halogenopropanes.* These molecules have two possible rotational isomers, T and G, as given in Table 1 of Part I of this series.[27] The observed Raman and infrared spectra and the calculated frequencies are compared in Figs. 7 and 8. These figures show that the T form exists in the crystalline state of 1-chloro-, 1-bromo-, and 1-iodopropanes and the T and G forms coexist in the glassy, liquid, and gaseous states.

The individual rotational isomers of each molecule are discriminated from each other by the Raman key bands of the liquid state, their frequencies being given in parentheses: T form (364 and 723 $cm^{-1}$) and G form (292, 424, 648, and 787 $cm^{-1}$) of 1-chloropropane, T form (311 and 648 $cm^{-1}$) and G form (274, 402, 563, and 777 $cm^{-1}$) of 1-bromopropane, and T form (288 and 593 $cm^{-1}$) and G form (390, 503, and 763 $cm^{-1}$) of 1-iodopropane. These Raman bands were used for the determination of the enthalpy difference between the T and G forms of each molecule. Figure 17 shows the obtained results of the enthalpy differences in the liquid state. As is evidently seen in Fig. 17, the G form is slightly more stable than the T form for any of 1-chloro-, 1-bromo-, and 1-iodopropanes in the liquid state.

The enthalpy difference in the gaseous state of 1-chloropropane was also determined. The $\Delta H_{G-T}$ value of $15\pm30$ cal/mol and $-210\pm100$ cal/mol were obtained from the pairs of the Raman bands at 663 and 745 $cm^{-1}$ and at 793 and 745 $cm^{-1}$, respectively. Thus, the G form is as stable as or slightly more stable than the T form in gaseous 1-chloropropane.

*1-Halogenobutanes.* These molecules have five possible isomers, TT, TG, GT, GG, and GG′,[27] where the first and second conformation symbols in each isomer designation are those for the CC–CC and CC–CX axes,

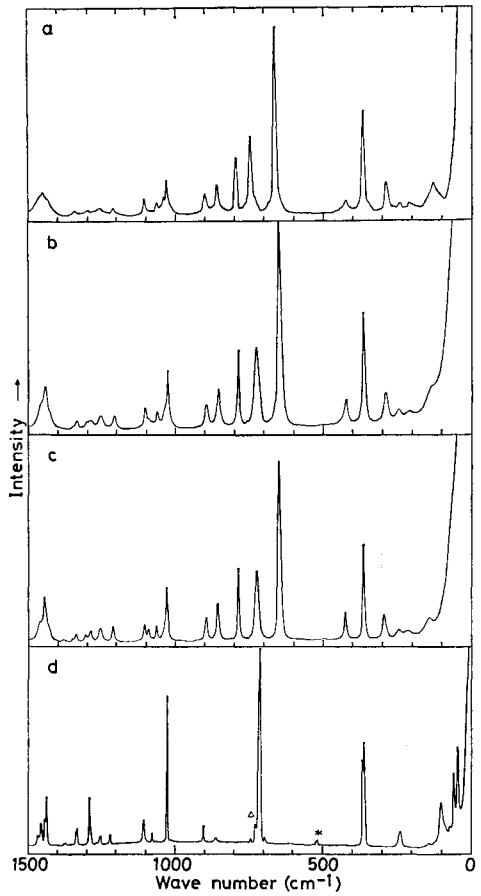


Fig. 1. Raman spectra of 1-chloropropane.
a: Gas (23 °C), b: liquid (23 °C), c: liquid (−100 °C), d: crystal (liquid nitrogen temperature). Following symbols are used in Figs. 1—16. *: Emission line of $Ar^+$, △: origin unknown, ×: impurity.

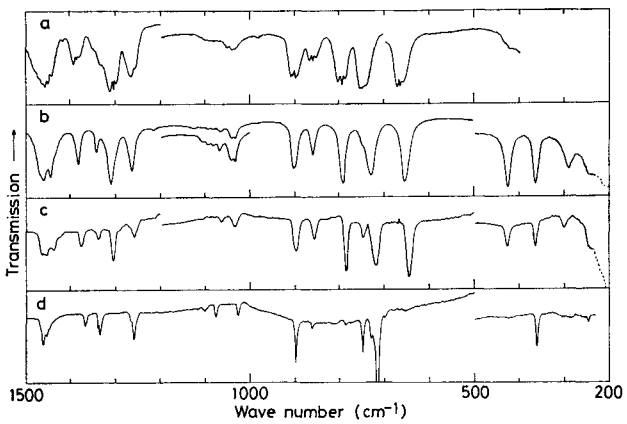


Fig. 2. Infrared spectra of 1-chloropropane.
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.

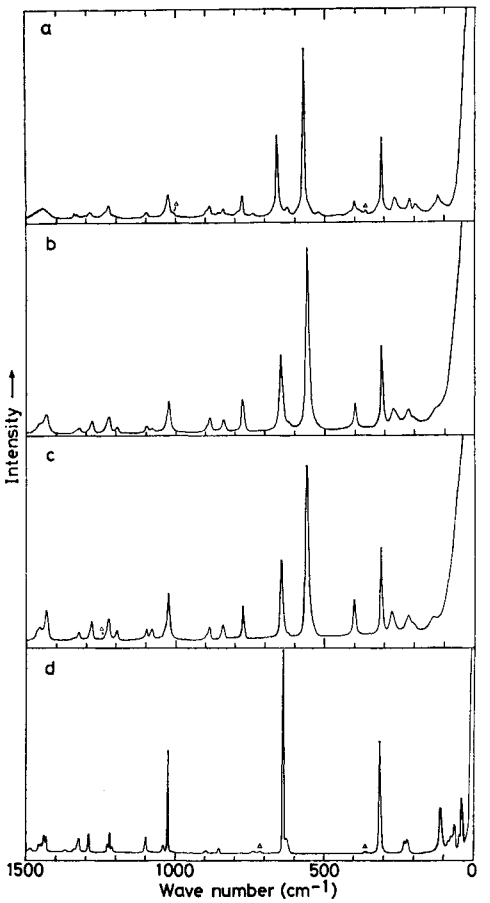


Fig. 3. Raman spectra of 1-bromopropane.
a: Gas (23 °C), b: liquid (23 °C), c: liquid (−90 °C), d: crystal (liquid nitrogen temperature).
The symbol is explained in the caption of Fig. 1.

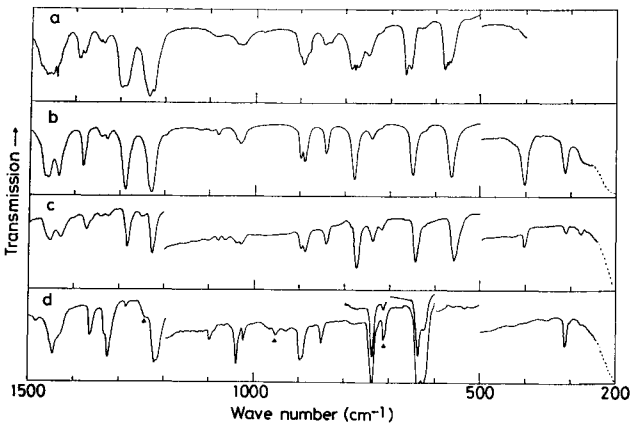


Fig. 4. Infrared spectra of 1-bromopropane.
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.
The symbol is explained in the caption of Fig. 1.

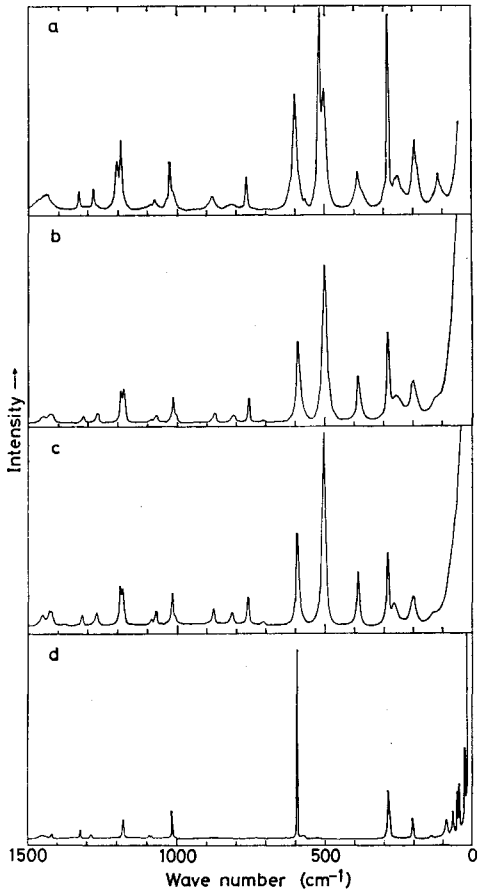


Fig. 5. Raman spectra of 1-iodopropane.
a: Gas (23 °C), b: liquid (23 °C), c: liquid (−80 °C), d: crystal (liquid nitrogen temperature).

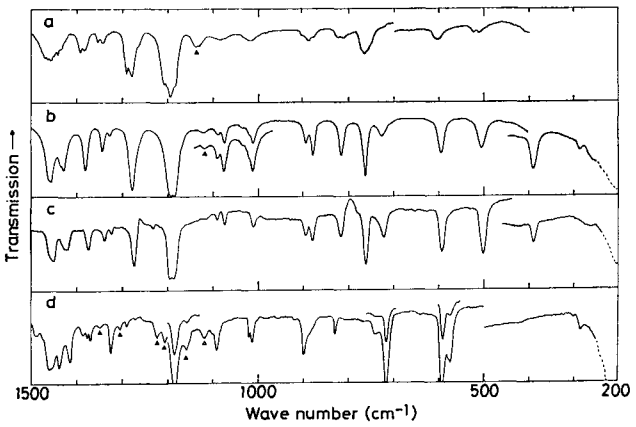


Fig. 6. Infrared spectra of 1-iodopropane.
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.
The symbol is explained in the caption of Fig. 1.

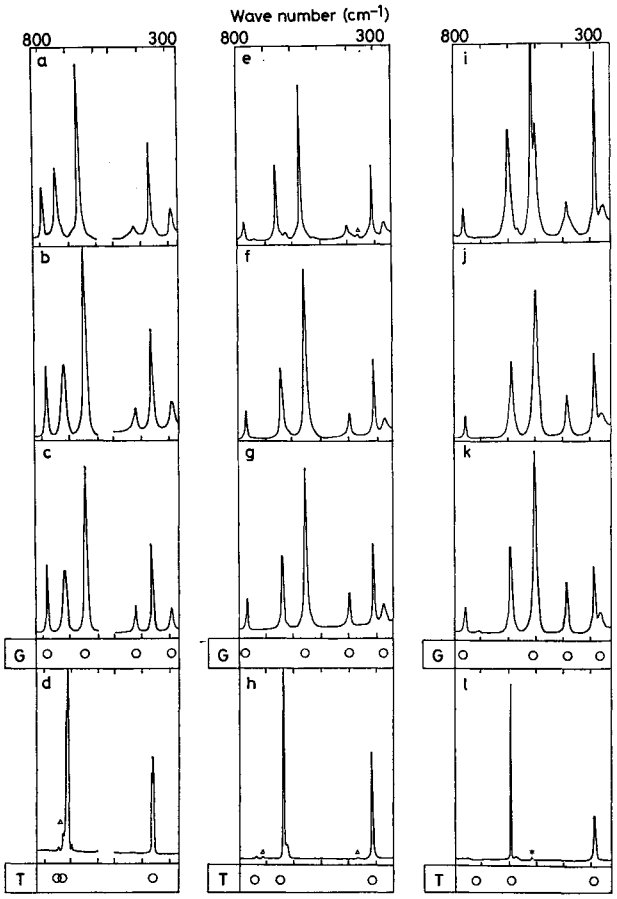


Fig. 7. Comparison between the Raman spectra and the calculated frequencies of 1-halogenopropanes.
1-Chloropropane,
a: gas (23 °C), b: liquid (23 °C), c: liquid (−100 °C), d: crystal (liquid nitrogen temperature).
1-Bromopropane,
e: gas (23 °C), f: liquid (23 °C), g: liquid (−90 °C), h: crystal (liquid nitrogen temperature).
1-Iodopropane,
i: gas (23 °C), j: liquid (23 °C), k: liquid (−80 °C), l: crystal (liquid nitrogen temperature).
The symbols are explained in the caption of Fig. 1.

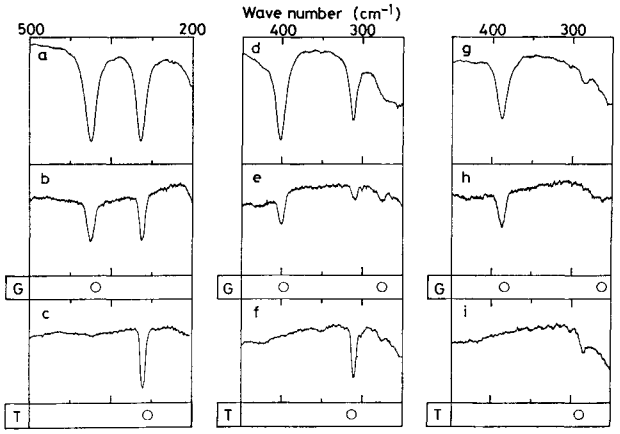


Fig. 8. Comparison between the infrared spectra and the calculated frequencies of 1-halogenopropanes.
1-Chloropropane,
a: liquid (room temperature), b: glass, c: crystal.
1-Bromopropane,
d: liquid (room temperature), e: glass, f: crystal.
1-Iodopropane,
g: liquid (room temperature), h: glass, i: crystal.

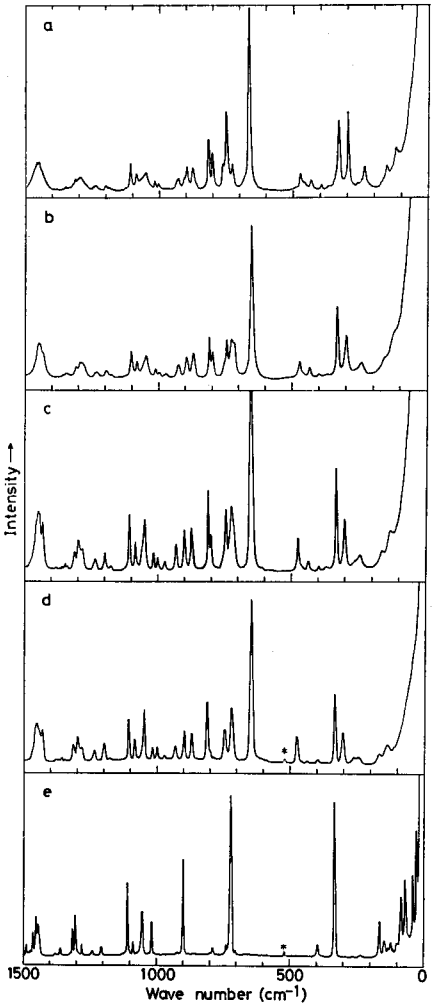


Fig. 9. Raman spectra of 1-chlorobutane.
a: Gas (23 °C), b: liquid (23 °C), c: liquid (−90 °C), d: glass (liquid nitrogen temperature), e: crystal (liquid nitrogen temperature).
The symbol is explained in the caption of Fig. 1.

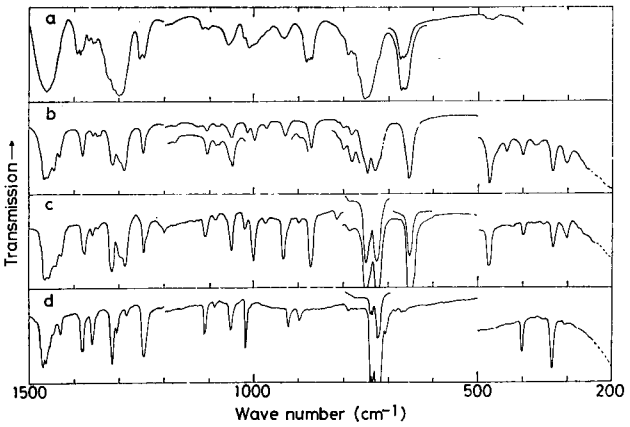


Fig. 10. Infrared spectra of 1-chlorobutane.
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.

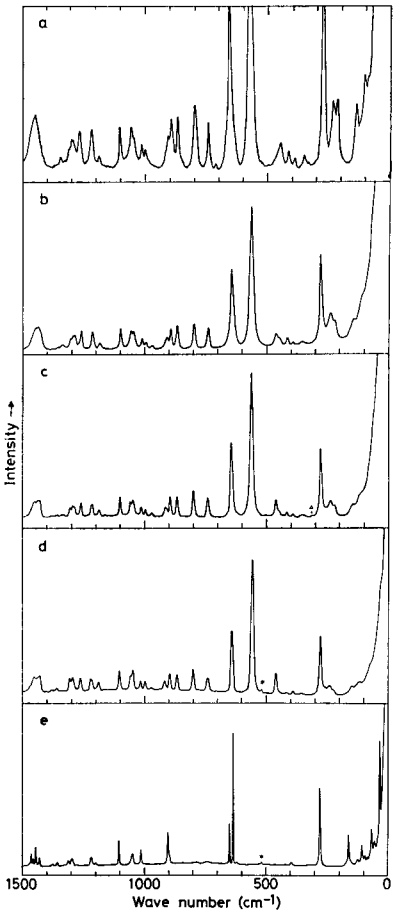


Fig. 11. Raman spectra of 1-bromobutane.
a: Gas (23 °C), b: liquid (23 °C), c: liquid (−90 °C), d: glass (liquid nitrogen temperature), e: crystal (liquid nitrogen temperature).
The symbols are explained in the caption of Fig. 1.

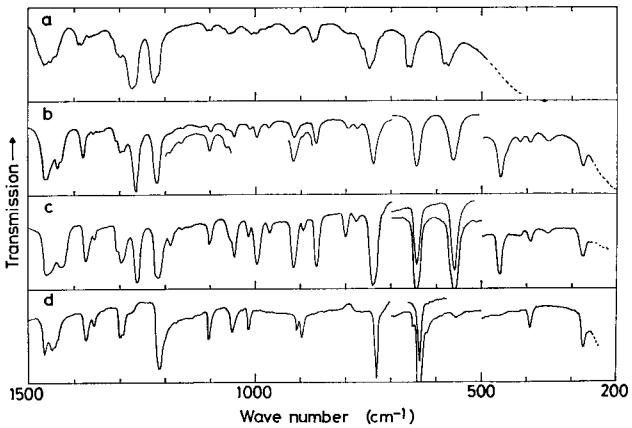


Fig. 12. Infrared spectra of 1-bromobutane.
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.

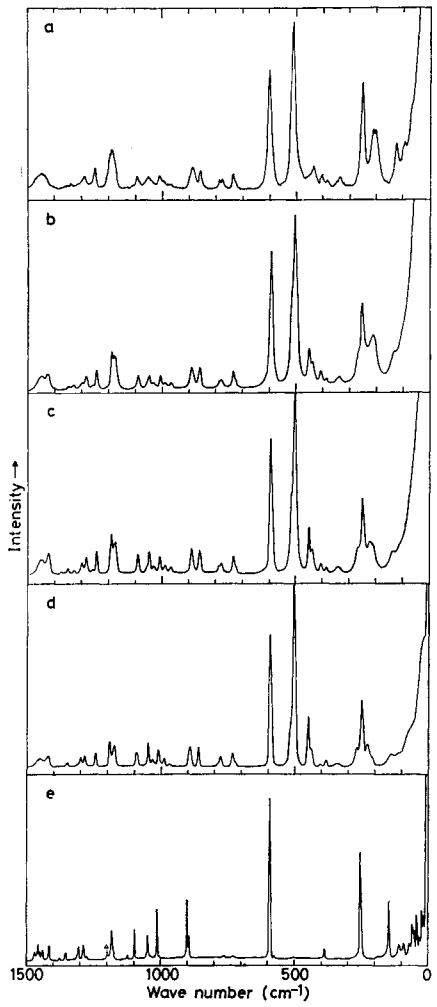


Fig. 13. Raman spectra of 1-iodobutane.
a: Gas (42 °C), b: liquid (23 °C), c: liquid (−95 °C), d: glass (liquid nitrogen temperature), e: crystal (liquid nitrogen temperature).
The symbol is explained in the caption of Fig. 1.

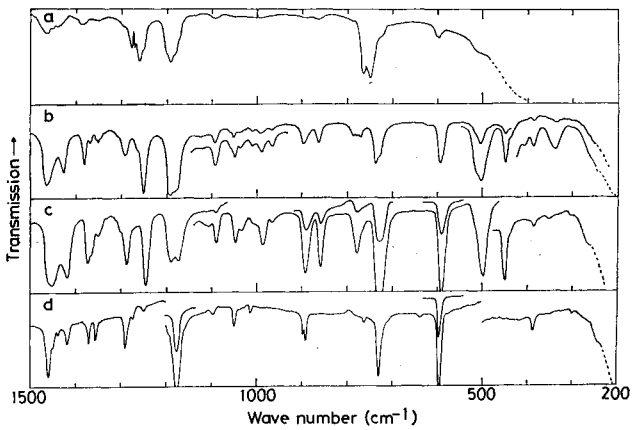


Fig. 14. Infrared spectra of 1-iodobutane.
a: Gas (room temperature), b: liquid (room temperature), c: glass, d: crystal.

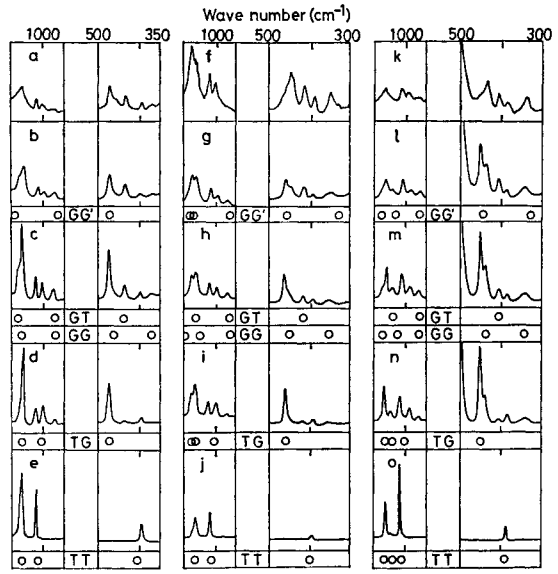


Fig. 15. Comparison between the Raman spectra and the calculated frequencies of 1-halogenobutanes.
1-Chlorobutane,
a: gas (23 °C), b: liquid (23 °C), c: liquid (−90 °C), d, glass (liquid nitrogen temperature), e: crystal (liquid nitrogen temperature).
1-Bromobutane,
f: gas (23 °C), g: liquid (23 °C), h: liquid (−90 °C), i: glass (liquid nitrogen temperature), j: crystal (liquid nitrogen temperature).
1-Iodobutane,
k: gas (42 °C), l: liquid (23 °C), m: liquid (−95 °C), n: glass (liquid nitrogen temperature), o: crystal (liquid nitrogen temperature).

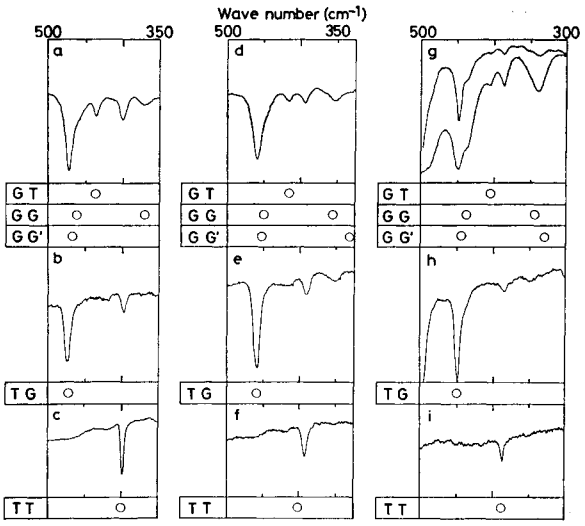


Fig. 16. Comparison between the infrared spectra and the calculated frequencies of 1-halogenobutanes.
1-Chlorobutane,
a: liquid (room temperature), b: glass, c: crystal.
1-Bromobutane,
d: liquid (room temperature), e: glass, f: crystal.
1-Iodobutane,
g: liquid (room temperature), h: glass, i: crystal.

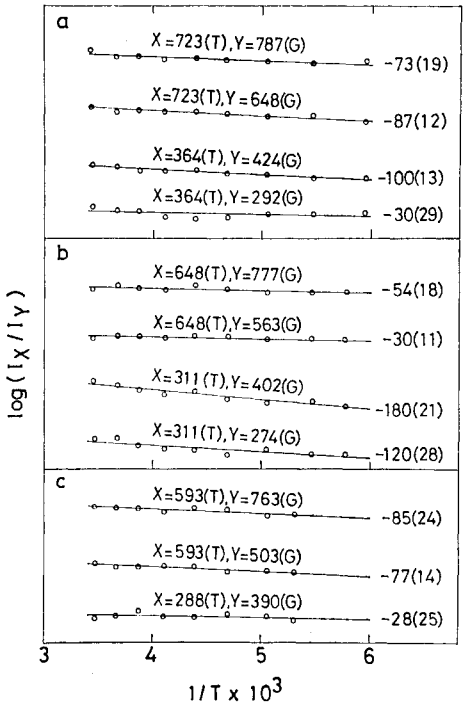


Fig. 17. Enthalpy differences between the T and G forms of 1-halogenopropanes.
a: 1-Chloropropane, b: 1-bromopropane, c: 1-iodopropane.
X and Y denote the band pairs ($cm^{-1}$). The values of $\Delta H_{G-T}$ (cal/mol) are given on the right side of the straight lines. The standard deviations obtained by the method of least-squares are also given in parentheses.

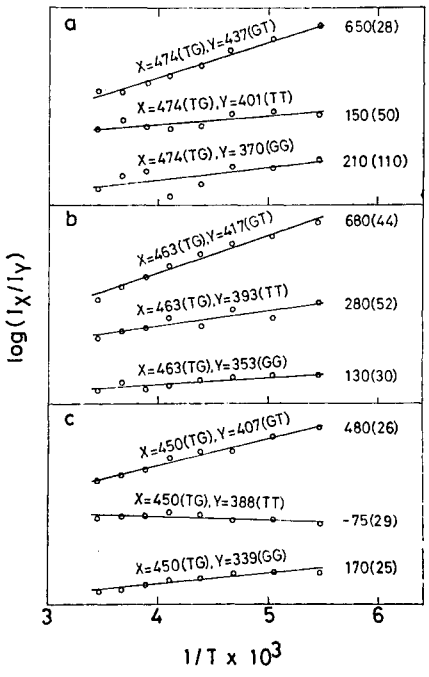


Fig. 18. Enthalpy differences among the TT, TG, GT, and GG forms of 1-halogenobutanes.
a: 1-Chlorobutane, b: 1-bromobutane, c: 1-iodobutane.
X and Y denote the band pairs ($cm^{-1}$). The values of $\Delta H_{Y-X}$ (cal/mol) are given on the right side of the straight lines. The standard deviations obtained by the method of least-squares are also given in parentheses.

respectively. The observed Raman and infrared spectra and the calculated frequencies are compared in Figs. 15 and 16.

For 1-chlorobutane (see Figs. 15a—e and 16a—c), the spectra in the crystalline state show that only the TT form exists. The Raman band at 397 $cm^{-1}$ and the infrared band at 400 $cm^{-1}$ persisting in the crystalline state can be explained only by the existence of the TT form. In the glassy, liquid, and gaseous states, the observed spectra are explained by the coexistence of the TT, TG, GT, and GG forms. The Raman band at 476 $cm^{-1}$ and the infrared band at 474 $cm^{-1}$ in the glassy state, whose intensities relative to those of other bands increase in going from the liquid state to the glassy state, can be explained only by the existence of the TG form. The Raman band at 437 $cm^{-1}$ and the infrared band at 436 $cm^{-1}$ observed in the liquid state are assigned to the GT form, while the Raman bands at 458 (a shoulder of the 474 $cm^{-1}$ band) and 370 $cm^{-1}$ and the infrared bands at 458 (a shoulder of the 473 $cm^{-1}$ band) and 370 $cm^{-1}$ in the liquid state are assigned to the GG form.

For 1-bromobutane (see Figs. 15f—j and 16d—f), the comparison between the observed spectra and the calculated frequencies indicates that the TT form exist in the crystalline state. The Raman band at 397 $cm^{-1}$ and the infrared band at 394 $cm^{-1}$ are assigned only to the TT form. The glassy-, liquid-, and gaseous-state spectra show the coexistence of the TT, TG, GT, and GG forms in these states. The Raman band at 462 $cm^{-1}$ and the infrared band at 459 $cm^{-1}$ in the glassy state, whose intensities are enhanced as compared with those of the liquid state at room temperature, are assigned only to the TG form. The existence of the GT form is confirmed by the Raman and infrared bands at 417 $cm^{-1}$ in the liquid state, and the existence of the GG form is also clear from the observation of the Raman bands at 448 (a shoulder of the 463 $cm^{-1}$ band) and 353 $cm^{-1}$ and the infrared bands at 445 (a shoulder of the 459 $cm^{-1}$ band) and 352 $cm^{-1}$ in the liquid state. In the gaseous state, the Raman spectral pattern around 450 $cm^{-1}$ is different from that in the liquid state. The existence of the TG and GG forms is, however, confirmed definitely by the observation of the Raman bands at 1000 and 350 $cm^{-1}$, respectively.

For 1-iodobutane (see Figs. 15k—o and 16g—i), the spectra of the crystalline state are explained by the existence of the TT form and those of the glassy, liquid, and gaseous states by the coexistence of the TT, TG, GT, and GG forms similarly to the cases of 1-chloro- and 1-bromobutanes. The Raman band at 389 $cm^{-1}$ and the infrared band at 387 $cm^{-1}$ in the crystalline state are assigned only to the TT form and the Raman band at 452 $cm^{-1}$ and the infrared band at 449 $cm^{-1}$ in the glassy state only to the TG form. The Raman band at 407 $cm^{-1}$ and the infrared band at 406 $cm^{-1}$ in the liquid state indicate the existence of the GT form and the Raman bands at 438 (a shoulder of the 450

TABLE 2. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 1-CHLOROPROPANE

| Observed frequency ($cm^{-1}$)[a] | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | Crystal | | |
| R | IR | R | IR | IR | R | IR | |
| | 1464 S, sh | | 1464 S, sh | 1463 M | 1465 VW | 1463 M | $CH_2$ scis |
| 1452 W, b | 1457 S<br>1450 S, sh | 1458 W, sh | 1457 S | 1453 M | 1453 W | 1455 M<br>1448 W, sh | $CH_3$ op-d-deform<br>$CH_3$ ip-d-deform |
| | 1441 M, sh | 1443 M | 1442 S | 1438 M | 1441 W, sh<br>1434 M | 1443 W, sh | $CH_2$ scis (T) |
| | | 1431 VW,sh* | 1436 M, sh | 1425 VW, sh | | | $CH_2$ scis (G) |
| | 1395 M<br>1388 M<br>1383 M, sh | 1382 VW | 1381 M | 1378 M | 1372 VW | 1375 W, sh<br>1372 W | $CH_3$ s-deform |
| | 1352 W, sh | 1347 VW, sh | 1352 VW, sh | | | | $CH_2$ wag (G) |
| 1343 VW | 1335 M, sh | 1337 W | 1339 M | 1339 M | 1336 VW<br>1332 VW | 1343 W<br>1338 M | $CH_2$ wag (T) |
| 1304 VW | 1315 S<br>1307 S<br>1300 S | 1305 VW, sh | 1306 S | 1307 M | | | $CH_2$ wag (G) |
| | | 1288 VW | 1300 M, sh | 1295 VW, sh | 1288 M<br>1284 VW, sh | | $CH_2$ twist (T) |
| 1259 VW | 1266 S<br>1258 M, sh | 1256 W | 1266 M, sh<br>1260 S | 1266 W, sh<br>1261 M | 1262 VW, sh<br>1254 VW | 1268 VW, sh<br>1262 M | $CH_2$ wag (T)<br>$CH_2$ twist (G) |
| 1212 VW | | 1217 VW, sh<br>1209 W | 1211 VW | 1215 VW | 1220 VW | | $CH_2$ twist (T)<br>$CH_2$ twist (G) |
| 1108 W | 1098 VW, b | 1104 W<br>1090 VW, sh | 1103 VW<br>1090 VW | 1105 VW | 1104 W | 1104 VW | CC stretch (T)<br>CC stretch (G) |
| 1079 VW | 1068 VW, sh | | 1078 VW | 1080 VW | 1078 VW | 1079 W | $CH_3$ op-rook (T) |
| 1067 W | | 1063 W | 1063 W | 1065 W | | | CC stretch (G) |
| 1042 W, sh | 1051 W | 1038 W, sh | 1038 W | 1035 M | | | $CH_3$ op-rock (G) |
| 1032 M | 1038 W | 1027 M | 1030 W | | 1028 VS | 1029 W | CC stretch (T) |
| 899 W | 908 S<br>903 S, sh | 899 W, sh* | 899 S | 897 S | 904 W | 898 S | $CH_3$ ip-rock (T) |
| | 898 S | 895 W | 895 S, sh | | | | $CH_3$ ip-rock (G) |
| | | | | | 861 VW | 863 VW | $CH_2$ rock (T) |
| 857 M | 866 M<br>859 M<br>852 M, sh | 856 W | 856 M | 857 M | | | $CH_2$ rock (G) |
| 793 S | 802 S<br>793 S<br>787 S | 787 S | 789 VS | 786 VS | | | $CH_2$ rock (G) |
| | | | 746 W, sh | 748 M | 745 VW | 748 S | $CH_2$ rock (T) |
| | | | | | 728 VW | 730 VW, sh | Origin unknown |
| 745 S | 748 S, b | 723 S | 727 S | 720 S | 717 S, sh<br>712 VS | 715 VS | CCl stretch (T) |
| | | | | | 698 VW | | $^{13}$CCl stretch (T)? |
| 663 VS | 671 S<br>665 S<br>658 S | 648 VS | 651 VS | 645 VS | | | CCl stretch (G) |
| 422 VW | | 424 W | 425 VW | 425 VW | | | CCC deform (G) |
| 364 S | | 364 S | 365 VW | 362 VW | 367 S, sh<br>361 S | 361 VW | CCC deform (T) |
| 288 M | | 292 M | 291 VW | 296 VW | | | CCCl deform (G) |
| 242 VW | | 248 W | 246 VW | 245 VW | 241 W | 245 VW | CCCl deform (T) |
| 207 VW | | 214 VW | | | | | $CH_3$ torsion (G) |
| 130 W | | 140 VW | | | 145 W | | CC torsion (T, G) |

Table 2. Continued

| Observed frequency ($cm^{-1}$)[a] | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | Crystal | | |
| R | IR | R | IR | IR | R | IR | |
| | | | | | 103 S<br>88 W, sh<br>74 W<br>59 S<br>47 S | | Lattice vibrations |

a) VS: Very strong, S: strong, M: medium, W: weak, VW: very weak, b: broad, sh: shoulder. The broadness of the band shapes in the gaseous state does not always allow us to correlate the individual bands in the liquid state to those in the gaseous state. Only approximate correlations are made in such cases and in other cases of similar situations. The bands denoted with * were observed in the liquid-state Raman spectra at lower temperature. b) For the notation and definition of the local symmetry coordinates, see Ref. 36. According to the results of the normal coordinate treatment,[33] the $CH_3$ rocking, $CH_2$ rocking, $CH_2$ twisting, and CC stretching coordinates are highly coupled to yield complicated vibrational modes. The listed assignments are thus only approximate ones.

Table 3. Observed frequencies and vibrational assignments of 1-bromopropane

| Observed frequency ($cm^{-1}$)[a] | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | Crystal | | |
| R | IR | R | IR | IR | R | IR | |
| | | | | | 1485 VW | 1484 VW | Overtone or combination? |
| | 1464 S | | 1464 S | | | 1463 W, sh | $CH_2$ scis |
| 1452 VW, sh | 1451 S | 1458 VW, sh | 1458 S | 1453 M | 1457 VW<br>1450 VW | 1458 M, sh<br>1446 S | $CH_3$ op-d-deform<br>$CH_3$ ip-d-deform |
| 1443 W | 1443 M, sh | 1436 W | 1435 S | 1428 M | 1438 W<br>1432 W | 1440 M, sh<br>1433 W, sh | $CH_2$ scis |
| 1387 VW | 1393 M<br>1383 M | 1381 VW* | 1382 S | 1375 M<br>1363 W, sh | 1365 VW | 1368 M | $CH_3$ s-deform (G)<br>$CH_3$ s-deform (T) |
| 1338 VW | 1348 VW | 1336 VW, sh | 1343 VW | 1342 VW | | | $CH_2$ wag (G) |
| 1331 VW | 1340 VW | 1326 VW | 1330 W | 1327 VW | 1335 VW, sh<br>1321 W | 1336 M, sh<br>1327 S | $CH_2$ wag (T) |
| 1288 VW | 1296 S<br>1288 S | 1290 VW, sh<br>1283 VW | 1287 VS | 1283 S | 1289 W | 1291 VW | $CH_2$ twist (T)<br>$CH_2$ twist (G) |
| | | | | 1253 VW | | 1245 VW, sh | Origin unknown |
| 1233 VW, sh | 1235 VS | 1233 VW, sh | 1233 VS, sh | 1226 VS | | | $CH_2$ wag (G) |
| 1226 W | 1227 VS | 1226 W | 1228 VS | | 1226 VW<br>1219 W | 1222 S<br>1218 S | $CH_2$ wag (T) |
| | | 1213 VW* | | | 1211 VW | | $CH_2$ twist (T) |
| 1200 VW | | 1198 VW | 1200 W | | | | $CH_2$ twist (G) |
| 1099 VW | 1085 W, b | 1100 VW | 1099 VW | 1102 VW | 1099 W | 1099 W | CC stretch (T) |
| | | 1081 VW | 1082 VW | 1080 VW | | | CC stretch (G) |
| | | | | 1065 W | | | $CH_3$ ip-rock (G) |
| | | 1041 VW,sh* | 1042 W, sh | 1040 W | 1039 W | 1039 M | $CH_3$ op-rock (T) |
| 1027 W | 1033 W, b | 1031 W, sh | 1032 M | 1029 W | | | $CH_3$ op-rock (G) |
| | | 1025 M | 1025 W, sh | | 1025 S | 1025 W | CC stretch (T) |
| 1008 VW, sh | | | | | | | Origin unknown |
| | | | | | | 953 VW | Origin unknown |
| 896 VW, sh | 903 W, sh<br>895 M | 896 VW, sh | 897 M | 896 M | 895 VW | 898 M<br>894 M, sh | $CH_3$ ip-rock (T) |
| 887 VW | 883 W, sh | 886 W | 888 M | 888 M | | | CC stretch (G) |
| 856 VW | 848 W | 850 VW, sh | 841 M | 842 M | 852 VW | 851 W | $CH_2$ rock (T) |
| 840 VW | 836 W | 840 W | | | | | $CH_2$ rock (G) |

TABLE 3. CONTINUED

| Observed frequency ($cm^{-1}$)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | Crystal | | Assignment[b] |
| R | IR | R | IR | IR | R | IR | |
| 792 VW, sh<br>778 W | 788 M<br>780 M<br>773 M | 777 M | 778 S | 774 VS | | | $CH_2$ rock (G) |
| 742 VW | 752 W | | 740 W | 738 M | 736 VW | 738 VS | $CH_2$ rock (T) |
| | | | | 720 VW | 714 VW | 714 W | Origin unknown |
| 660 S | 666 S<br>657 S | 648 S | 648 S | 644 VS | 638 VS | 637 VS | CBr stretch (T) |
| 627 W | 630 W, b | 620 VW, sh | 620 VW, sh | | 625 VW, sh | 623 VW, sh | $2\times313$ $cm^{-1}$ or $^{13}$CBr stretch (T)? |
| 572 VS | 580 S<br>573 S<br>567 S | 563 VS | 563 VS | 559 VS | | | CBr stretch (G) |
| 523 VW | | | | | | | Origin unknown |
| 401 W | | 402 M | 401 VW | 402 VW | | | CCC deform (G) |
| 363 VW | | | | | 363 VW | | Origin unknown |
| 311 S | | 311 S | 312 VW | 311 VW | 313 S | 311 VW | CCC deform (T) |
| 268 W | | 274 W | 273 VW | 277 VW | | | CCBr deform (G) |
| | | | | | 232 W | | $CH_3$ torsion (T) |
| 217 W | | 224 W | | | 222 W | | CCBr deform (T) |
| 198 VW | | 205 VW, sh | | | | | $CH_3$ torsion (G) |
| 122 W | | 133 W | | | | | CC torsion (T) |
| | | | | | 115 W, sh<br>111 M<br>86 W, sh<br>77 W, sh<br>65 M<br>48 W, sh<br>39 M | | Lattice vibrations |

a), b) See a) and b), respectively, of Table 2.

TABLE 4. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 1-IODOPROPANE

| Observed frequency ($cm^{-1}$)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | Crystal | | Assignment[b] |
| R | IR | R | IR | IR | R | IR | |
| | | | | | | 1488 W | 591+898 $cm^{-1}$? |
| | | 1469 VW, sh* | 1460 S | | | 1473 W, sh | $CH_2$ scis |
| | 1458 M<br>1443 W, sh | 1455 W | 1456 S | 1452 M | 1460 VW<br>1454 VW<br>1448 VW<br>1443 VW | 1460 S<br>1451 S<br>1438 S | $CH_3$ op-d-deform<br>$CH_3$ ip-d-deform |
| 1435 W, b | | 1433 W | 1435 M, sh | 1423 M | | | $CH_2$ scis (G) |
| | | 1427 W | 1428 S | | 1418 VW | 1415 S | $CH_2$ scis (T) |
| 1383 VW | 1392 M<br>1383 M | 1378 VW | 1380 S | 1376 M | 1375 VW<br>1367 VW | 1386 W<br>1376 W<br>1370 W | $CH_3$ s-deform |
| | | | | | | 1349 VW | Origin unknown |
| | 1354 W<br>1343 W | 1338 VW, sh* | 1344 M | 1340 W | | | $CH_2$ wag (G) |
| 1332 W | | 1323 W | 1328 W | 1325 VW | 1324 W | 1325 M | $CH_2$ wag (T) |
| | | | | | | 1304 VW | Origin unknown |
| 1282 W | 1291 S<br>1279 S | 1285 VW, sh*<br>1273 W | 1279 S | 1275 S | 1286 VW | 1289 VW | $CH_2$ twist (T)<br>$CH_2$ twist (G) |
| | | | | | | 1212 VW | Origin unknown |
| | | | | | | 1206 VW | Origin unknown |

TABLE 4. CONTINUED

| Observed frequency ($cm^{-1}$)[a] | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | Crystal | | |
| R | IR | R | IR | IR | R | IR | |
| 1202 M | 1208 S<br>1195 VS | 1194 M | 1195 VS | 1194 VS | | | $CH_2$ wag (G) |
| 1189 M | 1185 VS, sh | 1184 M | 1185 VS | 1186 VS | 1182 W | 1185 VS | $CH_2$ wag (T), $CH_2$ twist (T) |
| | | | | | | 1158 W, sh | Origin unknown |
| | 1133 W | | 1121 VW | | | 1117 W | Origin unknown |
| 1089 VW<br>1076 W | 1083 W, b | 1088 VW<br>1073 W | 1089 VW<br>1075 W | 1090 VW<br>1075 W | 1092 VW<br>1087 VW | 1090 M | CC stretch (T)<br>CC stretch (G) |
| 1035 VW, sh | | 1032 VW, sh | 1036 VW, sh | | | | $CH_3$ op-rock (G) |
| 1024 M<br>1013 W, sh | 1016 W, b | 1019 M<br>1011 W, sh | 1020 W, sh<br>1012 M | 1010 W | 1016 W<br>1011 VW | 1020 W<br>1013 W | CC strech (T)<br>$CH_3$ op-rock (T), CC stretch (G) |
| 895 VW, sh<br>880 W | 888 M | 894 VW, sh<br>879 W | 895 M<br>880 M | 895 M<br>880 M | 898 VW | 898 M<br>880 W, sh | $CH_3$ ip-rock (T)<br>$CH_3$ ip-rock (G) |
| | 823 W, sh | 828 VW, sh | | | 828 VW | 829 W | $CH_2$ rock (T) |
| 817 VW | 812 W | 816 VW | 816 M | 817 M | | | $CH_2$ rock (G) |
| 765 W | 765 M | 763 M | 764 S | 762 S | | | $CH_2$ rock (G) |
| | | 711 VW | 726 W | 722 M | 724 VW | 716 VS | $CH_2$ rock (T) |
| 602 S | 603 W | 593 S | 594 M | 593 S | 594 VS | 591 VS | CI stretch (T) |
| | | | | | 578 VW | 575 W | $^{13}$CI stretch (T) |
| 518 VS<br>503 S | 523 W<br>512 W | 503 VS | 503 M | 500 S | | | CI stretch (G) |
| 388 W | | 390 M | 388 VW | 388 VW | | | CCC deform (G) |
| 285 VS | | 288 S | 285 VW | 270 VW | 286 S | 285 VW | CCC deform (T) |
| 256 W | | 263 W | 263 VW | | | | CCI deform (G) |
| | | | | | 240 VW | | $CH_3$ torsion (T) |
| 197 M | | 203 M | | | 206 M | | CCI deform (T) |
| 189 W, sh | | | | | | | $CH_3$ torsion (G) |
| 116 W | | 130 VW | | | 144 VW | | CC torsion (T) |
| | | | | | 116 VW<br>91 M<br>69 M<br>53 S<br>46 S<br>28 S | | Lattice vibrations |

a), b) See a) and b), respectively, of Table 2.

$cm^{-1}$ band) and 339 $cm^{-1}$ and the infrared bands at 438 (a shoulder of the 449 $cm^{-1}$ band) and 339 $cm^{-1}$ indicate the existence of the GG form. In the gaseous state, a trend similar to the case of 1-bromobutane is observed in the Raman spectral pattern around 440 $cm^{-1}$. The existence of the TG and GG forms is confirmed by the observation of the Raman bands at 995 and 337 $cm^{-1}$, respectively.

It is not probable that the GG′ form of 1-bromobutane exists, since no bands are observed in the gaseous, liquid, or glassy state around its characteristic frequency of 331 $cm^{-1}$. The distance between the terminal methyl group and the bromine atom seems to be too short for the GG′ form to be stable. Thus, it is also improbable that the GG′ form of 1-chloro- or 1-iodobutane exists, although its existence is uncertain from the normal coordinate analysis because of the coincidence of the frequencies of the GG′ and other forms.

As has been described above, the key bands for the individual isomers of each molecule in the skeletal deformation region have become clear. These key bands were used for the determination of the enthalpy differences among the isomers in the liquid state. Figure 18 shows the obtained results of the enthalpy differences.

For 1-chlorobutane, the intensity ratios of the Raman bands at 370 (GG form) and 474 $cm^{-1}$ (TG form), those at 401 (TT form) and 474 $cm^{-1}$, and those at 437 (GT form) and 474 $cm^{-1}$ gave the enthalpy differences, $\Delta H_{GG-TG}=210\pm110$ cal/mol, $\Delta H_{TT-TG}=150\pm50$ cal/

Table 5. Observed frequencies and vibrational assignments of 1-chlorobutane

| Observed frequency ($cm^{-1}$)[a] | | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | | Crystal | | |
| R | IR | R | IR | R | IR | R | IR | |
| | | 1480 VW, sh | 1476 M, sh | 1483 VW, sh | 1474 M, sh | 1488 W | 1486 VW | $CH_2$ scis |
| | | 1468 M, sh* | 1467 VS | 1468 W, sh | 1465 S | 1477 VW<br>1471 VW | 1475 M, sh<br>1469 S | $CH_3$ op-d-deform, $CH_2$ scis |
| 1454 M, b | 1460 VS, b | 1458 M* | 1460 VS | 1454 M | 1456 S | 1462 W<br>1451 M | 1462 S<br>1454 M, sh | $CH_2$ scis, $CH_3$ op-d-deform |
| | | 1447 M | 1446 S | 1443 M | 1442 M, sh | 1444 M | 1447 W, sh | $CH_3$ ip-d-deform |
| | | 1434 W, sh | 1433 M | 1432 M | 1428 M, sh | 1438 W, sh | 1432 W | $CH_2$ scis |
| | 1393 M<br>1387 M | 1383 VW | 1383 M | 1380 VW | 1377 M | 1378 VW | 1383 M | $CH_3$ s-deform |
| | 1368 W | 1369 VW | | 1370 VW | | | | $CH_2$ wag (TG) |
| | 1359 W | 1358 VW | 1360 VW | 1360 VW | 1359 W | 1360 VW | 1362 M | $CH_2$ wag (TT, GG) |
| 1348 VW | 1352 W<br>1340 W, sh | 1346 VW | 1349 VW<br>1344 W | 1346 VW | 1348 VW | | | $CH_2$ wag (GT)<br>$CH_2$ wag (GG, GT) |
| | 1322 M, sh | | 1319 M, sh | | | | | $CH_2$ wag (TG) |
| 1313 W, sh | 1312 S, sh | 1311 W | 1316 M | 1315 W | 1315 S | 1324 VW<br>1314 W | 1316 S<br>1307 W | $CH_2$ wag (TT, GG) |
| 1297 W | 1300 VS | 1300 W | 1302 M, sh | 1299 W | 1298 M, sh | 1303 M | | $CH_2$ twist (TT, TG) |
| | | 1285 W, sh | 1291 S | 1284 VW | 1285 S | | | $CH_2$ wag (TG), $CH_2$ twist (GT) |
| | | | | | | 1280 VW | 1284 VW | $CH_2$ twist (TT) |
| 1250 VW | 1253 M<br>1244 M | 1242 VW, sh | 1248 M | 1242 VW, sh | 1245 M | 1240 VW | 1246 S | $CH_2$ wag (TT), $CH_2$ twist (GT) |
| 1238 VW | | 1234 VW | 1234 VW, sh | 1236 W | 1237 W, sh | | | $CH_2$ twist (TG) |
| 1228 VW | | 1230 VW, sh | | | | | | $CH_2$ twist (GG) |
| | | | | | | 1205 W | 1208 VW | $CH_2$ twist (TT) |
| 1198 W | 1195 VW | 1198 VW | 1200 VW | 1199 W | 1200 W | | | $CH_2$ twist (TG) |
| | | | 1190 VW | | | | | $CH_2$ twist (GT) |
| | | 1178 VW, sh | 1178 VW | 1178 VW | | | | $CH_2$ twist (GG) |
| 1107 W | 1113 W<br>1102 W | 1107 W | 1106 W | 1108 M | 1106 W | 1109 S<br>1100 VW | 1109 M | CC stretch (TT, TG, GT) |
| 1085 W | | 1084 W | 1085 VW | 1086 W | 1083 VW | 1087 W | 1088 VW | $CH_2$ rock (TT), $CH_3$ ip-rock (TG), CC stretch (GT) |
| | | | 1080 VW | | | | | $CH_3$ op-rock (GG) |
| 1064 W, sh | 1057 W | 1058 W, sh | 1058 VW, sh | | | | | CC stretch (GG, GT) |
| 1050 W | 1050 W, sh | 1050 W | 1051 W | 1049 M | 1048 M | 1052 M | 1052 M | CC stretch (TT, TG) |
| 1017 VW | 1023 W, sh | 1015 VW | 1017 W | 1018 W | 1017 W | 1017 M | 1018 M | CC stretch (TT) |
| 1000 VW | 1010 W | 998 VW | 1000 W | 1000 W | 999 M | | | CC stretch (TG) |
| 976 VW | 972 W, sh | 972 VW | 973 VW | 973 VW | 972 VW | | | $CH_3$ ip-rock (GG), $CH_3$ op-rock (GT) |
| 929 VW | 934 W | 932 VW, sh | 932 W | 932 W | 931 M | | | $CH_2$ rock (TG) |
| | | 927 W | | | 922 VW, sh | 920 VW | 924 W | $CH_3$ op-rock (TT), $CH_2$ rock (GG, GT) |
| 897 W | | 896 W | 898 VW | 899 W | 897 VW | 900 S | 898 W | $CH_3$ ip-rock (TT, GT) |
| 876 W | 882 M<br>877 M<br>872 M | 872 W | 875 M | 872 W | 870 S | | | $CH_3$ op-rock (TG), $CH_2$ rock (GG) |
| 813 M | | 811 M | 812 VW | 813 M | 812 VW | | | $CH_2$ rock (TG) |
| 800 M | | 800 W | 801 VW | 803 VW, sh | 804 VW, sh | | | CC stretch (GG), $CH_2$ rock (GT) |
| | 790 M | | 783 W | 786 VW | 783 VW | 788 VW | 787 VW | $CH_2$ rock (TT) |
| 761 W | 767 M, sh | 755 VW, sh | 757 M, sh | | | | | $CH_2$ rock (GG, TT) |
| | 753 VS | 746 M | 747 S | 746 W | 747 VS | | | $CH_2$ rock (TG) |
| | | | | | 738 M, sh | 743 VW<br>738 VW | 740 S<br>736 S | $CH_2$ rock (TT) |

Table 5. Continued

| Observed frequency ($cm^{-1}$)[a] | | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | | Crystal | | |
| R | IR | R | IR | R | IR | R | IR | |
| 748 S | 743 VS | 727 M | 730 S | 721 M | 723 VS | 725 S<br>718 VS | 722 VS | CCl stretch (TT) |
| 726 W | 722 M, sh | 718 M, sh | 718 M, sh | | | | | CCl stretch (GT) |
| 665 VS | 671 S<br>663 S | 653 VS | 653 VS | 647 VS | 650 VS | | | CCl stretch (TG, GG) |
| 473 W | | 474 W | 473 VW | 476 W | 474 VW | | | CCC deform (TG) |
| 459 VW, sh | | 458 VW, sh | 458 VW, sh | | | | | CCC deform (GG) |
| 434 VW | | 437 VW | 436 VW | 438 VW | | | | CCC deform (GT) |
| 397 VW | | 401 VW | 399 VW | 398 VW | 398 VW | 397 W | 400 VW | CCC deform (TT) |
| 370 VW | | 370 VW | 370 VW | 370 VW | | | | CCC deform (GG) |
| 332 S | | 334 S | 333 VW | 334 S | 332 VW | 333 VS | 334 VW | CCC deform (TT) |
| 298 S | | 302 M | 300 VW | 305 W | 302 VW | | | CCCl deform (TG), CCC deform (GT) |
| 262 VW | | 265 VW, sh | | 266 VW | | | | CCC deform (TG), CCCl deform (GT) |
| 238 VW | | 243 VW | | 247 VW | | | | CCCl deform (GG) |
| | | | | | | 237 VW | | $CH_3$ torsion (TT) |
| 154 VW | | 161 VW | | 170 VW | | 166 M | | CCCl deform (TT) |
| | | | | | | 148 W | | |
| 120 VW | | 125 VW | | 139 W | | 133 VW | | |
| | | | | | | 124 W | | |
| | | | | | | 100 VW | | Torsions (TT) and |
| | | | | | | 85 M | | lattice vibrations |
| | | | | | | 69 S | | |
| | | | | | | 41 S | | |
| | | | | | | 28 S | | |

a), b) See a) and b), respectively, of Table 2.

Table 6. Observed frequencies and vibrational assignments of 1-bromobutane

| Observed frequency ($cm^{-1}$)[a] | | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | | Crystal | | |
| R | IR | R | IR | R | IR | R | IR | |
| | | 1488 VW* | 1473 W, sh | 1488 VW, sh | | 1478 VW | | $CH_2$ scis |
| | 1465 M | 1465 W, sh* | 1466 S | 1468 W, sh | 1462 S | 1462 W | 1466 M | $CH_3$ op-d-deform, $CH_2$ scis |
| 1453 M, sh | | 1456 W, sh* | 1458 S, sh | | | 1454 VW | 1448 M | $CH_2$ scis |
| | 1452 M, sh | | | | | | | |
| 1448 M | | 1448 M | 1452 M, sh | 1448 M | | 1443 W | 1442 M | $CH_3$ ip-d-deform |
| | 1442 M, sh | 1438 M | 1437 S | | | | | $CH_2$ scis |
| | | 1429 W, sh | 1430 M, sh | 1427 M | 1430 S | 1433 VW<br>1428 W | 1435 W, sh | $CH_2$ scis |
| | 1390 W<br>1386 W | 1381 VW | 1382 M | 1378 VW | 1378 M | 1376 VW | 1375 M | $CH_3$ s-deform |
| | 1368 VW | | 1370 VW, sh | | 1368 M, sh | | | $CH_2$ wag (TG) |
| 1363 VW | | 1357 VW | 1360 VW | 1356 VW | 1358 W | 1356 VW | 1358 W | $CH_2$ wag (TT) |
| | | | 1355 VW | | | | | $CH_2$ wag (GG) |
| | | | 1347 VW | | | | | $CH_2$ wag (GT) |
| 1343 VW | | 1337 VW | 1340 VW | | | | | $CH_2$ wag (GG, GT) |
| 1308 W, sh | 1307 M, sh | 1305 W | 1308 W, sh | 1305 W | 1308 M, sh | 1312 W | | $CH_2$ twist (TT,TG) |
| 1295 W | 1300 M | 1295 W | 1299 M | 1294 W | 1298 M | 1300 W<br>1296 W | 1299 M<br>1293 M | $CH_2$ wag (TT, TG) |
| | 1297 M | 1288 W | 1293 M | | 1292 M, sh | | | $CH_2$ twist (GG, GT) |
| 1267 M | 1272 VS | 1262 M | 1267 VS | 1273 VW | | 1275 VW<br>1270 VW | 1277 VW | $CH_2$ twist (TT) |
| | | | | 1261 W | 1263 VS | | | $CH_2$ twist (TG, GG, GT) |

Table 6. Continued

| Observed frequency ($cm^{-1}$)[a] | | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | | Crystal | | |
| R | IR | R | IR | R | IR | R | IR | |
| 1217 M | 1224 VS<br>1217 S, sh | 1220 W, sh*<br>1215 M | 1219 VS | 1218 W | 1222 VS<br>1217 VS | 1217 W<br>1209 VW, sh | 1213 S | $CH_2$ wag (TG, GG, GT)<br>$CH_2$ wag (TT) |
| | | | | 1198 VW | 1203 W, sh | 1199 VW | | $CH_2$ rock (TT) |
| 1189 VW | | 1186 VW | 1189 VW | 1187 W | 1189 W | | | $CH_2$ twist (TG, GT) |
| 1155 VW | | 1160 VW | 1164 VW | 1162 VW | 1164 VW | | | $CH_2$ twist (GG) |
| 1103 M | 1107 W<br>1100 W | 1100 M | 1100 W | 1101 M | 1103 W | 1104 M | 1104 M | CC stretch (TT, GT) |
| | | | | | 1100 W, sh | | | CC stretch (TG) |
| | 1074 VW, sh | | | 1080 VW | | | | CC stretch (GT) |
| | | | 1064 VW | | | | | $CH_3$ op-rock (GG) |
| 1060 M | 1057 W | 1057 M | 1053 VW, sh | 1056 W, sh | 1056 W, sh | 1056 W, sh | 1051 M | CC stretch (TT), $CH_3$ ip-rock (TG) |
| 1048 W, sh | 1048 W, sh | 1048 M | 1048 W | 1046 M | 1047 M | 1047 W | | $CH_2$ twist (TT), CC stretch (TG, GT) |
| 1013 W | 1022 VW, sh<br>1008 W | 1013 W | 1014 VW | 1014 W | 1016 W | 1013 W | 1016 W | CC stretch (TT) |
| 1000 VW | 997 W | 997 VW | 996 W | 996 W | 997 S | | | CC stretch (TG) |
| 973 VW, sh | | 972 VW | 970 VW | 969 VW | 970 W | | | $CH_3$ ip-rock (GG), $CH_3$ op-rock (GT) |
| 915 VW, sh | 918 W | 915 VW, sh | 915 W | 913 W | 916 S | | | $CH_2$ rock (TG, GG) |
| 907 W, sh | | 907 W | | | | | 908 W | $CH_3$ op-rock (TT), $CH_2$ rock (GT) |
| 896 M | | 893 M | 895 VW | 893 W | 895 W | 902 M<br>897 W, sh | 898 W | $CH_3$ ip-rock (TT) |
| 869 M | 873 W<br>868 W | 868 M | 867 M | 864 W | 865 S | | | $CH_3$ op-rock (TG), $CH_2$ rock (GG), $CH_3$ ip-rock (GT) |
| 800 S | 800 W | 799 M | 797 W | 801 M | 801 W | | | $CH_2$ rock (TG), CC stretch (GG) |
| | 783 W | 777 VW* | 777 W | 775 VW | 778 W | 776 VW | | $CH_2$ rock (TT, GT) |
| 743 M | 764 W, sh<br>748 S | 740 M | 742 S | 740 W | 740 VS | | | $CH_2$ rock (TG, GG, GT) |
| | 738 M, sh | | 732 M, sh | | 733 VS | 741 VW | 733 VS | $CH_2$ rock (TT) |
| 658 VS | 664 M<br>657 M | 643 S | 646 S | 640 S | 642 VS | 649 M<br>636 VS | 650 VW, sh<br>637 VS | CBr stretch (TT, GT) |
| | | | | | 621 VW | 620 VW | 620 W, sh | $^{13}$CBr stretch (TT)? |
| 576 VS | 582 M<br>574 M | 562 VS | 564 S | 558 VS | 558 VS | | | CBr stretch (TG, GG) |
| 456 VW, sh | | 463 W | 459 VW | 462 M | 459 VW | | | CCC deform (TG) |
| 448 W | | 448 VW, sh | 445 VW, sh | 448 VW, sh | 444 VW, sh | | | CCC deform (GG) |
| 415 VW | | 417 VW | 417 VW | 419 VW | 417 VW | | | CCC deform (GT) |
| 390 VW | | 393 VW | 393 VW | 392 VW | 392 VW | 397 VW | 394 VW | CCC deform (TT) |
| 350 VW | | 353 VW | 352 VW | 355 VW | 352 VW | | | CCC deform (GG) |
| 276 VS | | 279 S | 277 VW | 278 S | 275 VW | 280 S | 274 VW | CCC deform (TT, GT), CCBr deform (TG) |
| | | | | 267 W, sh | | | | CCC deform (TG) |
| 232 S | | 238 M | | 242 W | | | | CCBr deform (GT) |
| 215 S | | 224 M, sh | | 227 VW, sh | | | | $CH_3$ torsion |
| 138 M | | 143 W | | 153 VW | | 162 M | | CCBr deform (TT) |
| 105 W | | 115 VW | | 122 VW | | 125 VW | | CC torsion |
| | | | | | | 108 W<br>93 VW<br>84 VW<br>67 M<br>57 W<br>42 VW, sh<br>36 S | | Torsion (TT) and lattice vibrations |

a), b) See a) and b), respectively, of Table 2.

TABLE 7. OBSERVED FREQUENCIES AND VIBRATIONAL ASSIGNMENTS OF 1-IODOBUTANE

| Observed frequency ($cm^{-1}$)[a] | | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | | Crystal | | |
| R | IR | R | IR | R | IR | R | IR | |
| | | | 1474 W, sh | 1481 VW | | 1470 VW | | $CH_2$ scis |
| | 1465 VW, sh | 1466 VW* | 1463 S | 1465 VW, sh | 1458 VS, sh | 1457 W | 1459 S | $CH_3$ op-d-deform, $CH_2$ scis |
| | 1460 W | 1453 W, sh* | 1457 S, sh | 1452 W | 1451 VS | 1452 VW | 1450 M, sh | $CH_2$ scis |
| 1448 W, b | 1452 W, sh | 1446 W | 1445 M, sh | | | 1441 VW | 1438 VW | $CH_3$ ip-d-deform |
| | 1437 W, sh | 1429 W | 1431 M, sh | 1430 W, sh | | | | $CH_2$ scis |
| | | 1423 W, sh* | 1425 M, sh | 1424 W | | | | $CH_2$ scis |
| | | | 1419 M | | 1419 S | 1417 W | 1419 W | $CH_2$ scis |
| | 1384 W | 1379 VW | 1380 M | 1377 VW | 1373 S | 1377 VW<br>1372 VW | 1371 W | $CH_3$ s-deform |
| | | 1368 VW | 1367 W | 1366 VW | 1365 M, sh | | | $CH_2$ wag (TG) |
| 1355 VW | 1352 VW | 1353 VW | 1354 W, sh | 1353 VW | 1353 W | 1354 VW | 1356 W | $CH_2$ wag (TT, GG) |
| | | | 1350 W | | | | | $CH_2$ wag (GT) |
| 1339 VW | | 1343 VW<br>1333 VW | 1343 W, sh<br>1336 VW, sh | 1343 VW<br>1332 VW | 1333 VW, sh | | | $CH_2$ wag (GG)<br>$CH_2$ wag (GT) |
| | | 1303 VW | 1306 VW, sh | 1302 W | 1304 W, sh | 1308 W | | $CH_2$ twist (TT, TG) |
| | 1298 VW, sh | | 1295 W, sh | | | | | $CH_2$ wag (TG) |
| 1289 VW | | 1288 W | 1290 W | 1287 W | 1288 S | 1290 W<br>1276 VW | 1289 M<br>1274 VW | $CH_2$ wag (TT) |
| | 1278 M<br>1271 M, sh | | | 1272 VW | 1272 W, sh | | | $CH_2$ twist (GG) |
| | 1261 M | 1263 VW | 1264 W, sh | 1263 VW | | | | $CH_2$ twist (GT) |
| 1250 W | 1252 M, sh | 1248 W | 1250 VS | 1247 W | 1246 VS | | 1250 VW | $CH_2$ twist (TT, TG, GG, GT) |
| | | | | | | 1201 VW | | Origin unknwn |
| 1193 M, sh | 1203 M, sh<br>1193 M | 1191 M | 1192 VS | 1192 W | 1190 M | | | $CH_2$ wag (TG, GG) |
| 1185 M | 1183 M, sh | 1183 M | 1183 VS, sh | 1182 W, sh | | 1187 W, sh<br>1183 W | | $CH_2$ wag (TT, GT) |
| | | 1175 M, sh | 1175 VS, sh | 1176 W | 1173 M | 1178 VW | 1175 VS | $CH_2$ rock (TT), $CH_2$ twist (GT) |
| | | 1153 VW, sh* | | 1157 VW | 1153 W, sh | | | $CH_3$ ip-rock (TG) |
| | | | 1122 VW | | | | | CC stretch (GG) |
| 1095 W | 1094 VW | 1093 W | 1093 W | 1093 W | 1089 VW | 1098 W | 1095 VW | CC stretch(TT,TG) |
| | | 1089 VW, sh | | 1091 W, sh | | | | CC stretch (GT) |
| | | 1059 VW, sh | 1058 VW, sh | | | | | $CH_3$ op-rock (GG) |
| 1050 W | | 1049 W | 1050 VW | 1050 W | 1047 VW | 1050 W | 1049 W | CC stretch (TT, TG) |
| | | 1037 VW | 1039 VW, sh | | | | | $CH_3$ ip-rock (GT) |
| | | 1032 VW, sh | 1032 VW, sh | 1036 VW | 1035 VW, sh | 1034 VW<br>1024 VW | 1029 VW | $CH_2$ twist (TT, TG) |
| 1010 W | | 1008 W | 1011 VW | 1013 W | 1008 VW, sh | 1014 M<br>1006 VW | 1013 VW | CC stretch (TT) |
| 995 VW | | 990 VW | 991 VW | 990 VW | 987 W | | | CC stretch (TG) |
| 970 VW | | 968 VW | 968 VW | 970 VW | 966 VW, sh | | | $CH_3$ ip-rock (GG), $CH_3$ op-rock (GT) |
| 889 W | 898 VW | 896 W, sh | 896 W | 895 W, sh | 893 W | | | $CH_2$ rock (TG, GT) |
| | | 889 W | 891 VW, sh | 892 W | | 901 M<br>895 W | 898 W<br>892 M | $CH_3$ ip-rock (TT), $CH_3$ op-rock (TT) |
| | | 886 W, sh | | | | | | $CH_2$ rock (GG) |
| 860 W | 870 VW<br>863 VW | 861 W | 863 W | 861 W | 859 W | | | $CH_3$ op-rock (TG), $CH_2$ rock (GG) |
| 786 W | 790 VW, sh | 786 VW | 787 W | 792 VW, sh | 788 VW, sh | | | CC stretch (GG) |
| 778 W | | 779 VW | 779 W | 781 VW | 778 W | | | $CH_2$ rock (TG, GT) |
| | 765 VS<br>759 VS, sh<br>750 VS | | 772 W | 763 VW | 765 VW, sh | 764 VW | 762 VW | $CH_2$ rock (TT) |

TABLE 7. CONTINUED

| Observed frequency ($cm^{-1}$)[a] | | | | | | | | Assignment[b] |
|---|---|---|---|---|---|---|---|---|
| Gas | | Liquid | | Glass | | Crystal | | |
| R | IR | R | IR | R | IR | R | IR | |
| 736 W | | 736 W | 735 M | 735 W | 728 M | | | $CH_2$ rock (TG, GG) |
| 728 VW, sh | 724 W, sh | 728 W, sh | 726 M, sh | 723 VW, sh | | 731 VW | 730 S | $CH_2$ rock (TT, GT) |
| 601 S | 600 W | 593 S | 592 M | 593 S | 590 M | 595 S<br>592 VS<br>589 S | 596 VS | CI stretch(TT, GT) |
| | | | | | | 577 VW | | $^{13}$CI stretch (TT)? |
| | | 515 S, sh | 518 VW, sh | 517 M, sh | 520 VW, sh | | | CI stretch (GG) |
| 511 VS | | 506 VS | 504 W | 503 VS | 500 W | | | CI stretch (TG) |
| 453 VW, sh | | 450 M | 449 VW | 452 M | 449 VW | | | CCC deform (TG) |
| 436 VW | | 438 W, sh | 438 VW, sh | 442 W, sh | 435 VW | | | CCC deform (GG) |
| 408 VW | | 407 W | 406 VW | 407 VW | | | | CCC deform (GT) |
| 385 VW | | 388 VW | 387 VW | 386 VW | 384 VW | 389 VW | 387 VW | CCC deform (TT) |
| 337 W | | 339 VW | 339 VW | 341 VW | 348 VW | | | CCC deform (GG) |
| | | 267 M, sh | 268 VW | 270 W | 267 VW | | | CCC deform (TG, GT) |
| 251 S | | 251 S | 247 VW | 250 M | | 256 S | 245 VW | CCC deform (TT), $CH_3$ torsion (TG) |
| | | 231 M, sh | | 230 W | | | | $CH_3$ torsion (TT) |
| | | 223 M, sh* | | | | | | $CH_3$ torsion (GG) |
| 213 M | | 212 M | | 213 VW, sh | | | | CCI deform (TG, GT) |
| 203 M | | | | | | | | CCI deform (GG) |
| | | 190 W, sh* | | 188 VW | | | | $CH_3$ torsion (GT) |
| 127 M | | 132 W | | 141 W | | 149 M | | CCI deform (TT), CC torsion (TT) |
| 96 W | | 110 VW | | 114 VW | | 112 W | | Torsions and lattice vibrations |
| | | | | | | 95 W | | |
| 70 VW | | | | 75 VW | | 74 W | | |
| | | | | | | 60 W | | |
| | | | | | | 55 W | | |
| | | | | | | 45 M | | |
| | | | | | | 34 VW | | |
| | | | | | | 25 M | | |
| | | | | | | 20 W | | |

a), b) See a) and b), respectively, of Table 2.

TABLE 8. ROTATIONAL ISOMERS OF 1-HALOGENOPROPANES AND 1-HALOGENOBUTANES

| | Gas | | | | Liquid | | | | Glass | | | | Crystal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3CH_2CH_2F$[a] | | T | G | | | —— | | | | T | G | | G |
| $CH_3CH_2CH_2Cl$ | | T | G | | | T | G | | | T | G | | T |
| $CH_3CH_2CH_2Br$ | | T | G | | | T | G | | | T | G | | T |
| $CH_3CH_2CH_2I$ | | T | G | | | T | G | | | T | G | | T |
| $CH_3CH_2CH_2CH_2F$[b] | | —— | | | TT | TG | GT | GG | | —— | | | TG |
| $CH_3CH_2CH_2CH_2Cl$ | TT | TG | GT | GG | TT | TG | GT | GG | TT | TG | GT | TT | TT |
| $CH_3CH_2CH_2CH_2Br$ | TT | TG | GT | GG | TT | TG | GT | GG | TT | TG | GT | GG | TT |
| $CH_3CH_2CH_2CH_2I$ | TT | TG | GT | GG | TT | TG | GT | GG | TT | TG | GT | GG | TT |

a) Refs. 7 and 19. b) Ref. 7.

mol, and $\Delta H_{GT-TG}=650\pm28$ cal/mol, respectively. The relatively large error is estimated for the $\Delta H_{GG-TG}$ value because of the very weak intensity of the band at 370 $cm^{-1}$. Thus, the stability of the rotational isomers in the liquid state is in the order of TG, TT, GG, and GT, with the TG form being the most stable.

For 1-bromobutane, the intensity ratios of the Raman bands at 353 (GG form) and 463 $cm^{-1}$ (TG form), those at 393 (TT form) and 463 $cm^{-1}$, and those at 417 (GT form) and 463 $cm^{-1}$ gave the enthalpy differences, $\Delta H_{GG-TG}=130\pm30$ cal/mol, $\Delta H_{TT-TG}=280\pm52$ cal/mol, and $\Delta H_{GT-TG}=680\pm44$ cal/mol, respective-

ly. In the liquid state, the stability of the rotational isomers is in the order of TG, GG, TT, and GT.

For 1-iodobutane, the enthalpy differences, $\Delta H_{GG-TG}$ $=170\pm25$ cal/mol, $\Delta H_{TT-TG}=-75\pm29$ cal/mol, and $\Delta H_{GT-TG}=480\pm26$ cal/mol were obtained from the pairs of the Raman bands at 339 (GG form) and 450 $cm^{-1}$ (TG form), those at 388 (TT form) and 450 $cm^{-1}$, and those at 407 (GT form) and 450 $cm^{-1}$, respectively. Thus, the stability of the rotational isomers in the liquid state is in the order of TT, TG, GG, and GT.

*Comparison with Previous Results.* Table 8 shows the rotational isomers of 1-halogenopropanes and 1-halogenobutanes existing in the various states, including those of 1-fluoropropane and 1-fluorobutane reported by Crowder and Mao.[7] In the crystalline state, 1-fluoropropane takes the G form and 1-fluorobutane takes the TG form, in contrast with other 1-halogenopropanes and 1-halogenobutanes.

Many investigations[2-6,8-18,20] indicated for 1-chloro-, 1-bromo-, and 1-iodopropanes that the T form exists in the crystalline state and the T and G forms coexist in the glassy, liquid, and gaseous states. These conclusions have been further confirmed by the present normal vibration calculation of these compounds in conjunction with longer halogenoalkanes.

The quite different values of the enthalpy differences were reported by many authors[4-6,10,11,18-20] for 1-halogenopropanes. Tanabe and Saëki[17] discussed this problem and obtained their values of the enthalpy differences by the absolute-intensity method and the temperature-variation method applied to the infrared spectra of the liquid state. The values by the latter method were $\Delta H_{G-T}=-140$ cal/mol for 1-chloropropane, $\Delta H_{G-T}=220$ cal/mol for 1-bromopropane, and $\Delta H_{G-T}=580$ cal/mol for 1-iodopropane. However, the present results show that the G form is more stable than the T form by about 100 cal/mol for these three compounds in common in the liquid state. Tanabe and Saëki mentioned that the good air-tightness of the high temperature cell allowed the experiment at temperatures higher than the boiling point of 1-chloro- or 1-bromopropane. This implies that the enthalpy differences obtained are those at pressures higher than 1 atm. The disagreement between their and our values is ascribed, at least in part, to the above fact. As for gaseous 1-fluoropropane, the $\Delta H_{G-T}$ value of $-50\pm30$ cal/mol was obtained by the microwave measurement.[19]

There has been disagreement concerning the assignment of the $CH_2$ twisting bands of 1-halogenopropanes. Snyder and Schachtschneider[14] assigned the 1292 $cm^{-1}$ band of 1-chloropropane to the *trans* $CH_2$ twisting mode on the basis of the normal vibration calculation of many kinds of chloroalkanes and Hayashi *et al.*[15] assigned the 1288 $cm^{-1}$ band of 1-bromopropane to the *trans* $CH_2$ twisting mode. These assignments agree with those by Brown and Sheppard[9] and Komaki *et al.*[11] On the other hand, Tanabe and Saëki[17] had doubts of these assignments from the viewpoint that the twisting frequencies of the $CH_2$ group (adjacent to $CH_3$) in 1-halogenopropanes should be lower than that of propane, 1278 $cm^{-1}$, and that the twisting frequency of the $CH_2$ group (adjacent to $CH_3$) should be lower than the wagging frequency of the $CH_2$ group (adjacent to halogen) in the *trans* form. Thus, they assigned the 1256, 1200, and 1180 $cm^{-1}$ bands of 1-chloro, 1-bromo-, and 1-iodopropanes, respectively, to the *trans* $CH_2$ twisting mode. In the present study, however, the Raman band of 1-chloropropane at 1288 $cm^{-1}$, the Raman and infrared bands of 1-bromopropane at 1289 and 1291 $cm^{-1}$, respectively, and the Raman and infrared bands of 1-iodopropane at 1286 and 1289 $cm^{-1}$, respectively, all of which are definitely observed in the crystalline state (see Figs. 1—6), are assigned consistently to the *trans* $CH_2$ twisting mode on the basis of our normal vibration calculation including the data of longer halogenoalkanes. Tanabe and Saëki did not assign these bands to any vibration of the T form of 1-halogenopropanes. Also, their grounds for interpreting the spectra are not appropriate, since it is generally acceptable that the twisting frequency of the $CH_2$ group (adjacent to $CH_3$) can be higher than the twisting frequency of a single isolated $CH_2$ group in propane owing to the vibrational coupling between the two $CH_2$ twisting modes in 1-halogenopropanes, and that it can be higher than the wagging frequency of the $CH_2$ group (adjacent to halogen) owing to the mass effect by the halogen atom. The situation is almost the same for the *gauche* twisting frequencies.

Many studies[4-9,14,16,21-26] have been made on the rotational isomerism of 1-halogenobutanes. Ukaji and Bonham[26a] proposed for 1-chlorobutane an isomer distribution of 37% TG, 24% GG′, 17% GG, 11% TT, and 11% GT in the gaseous state and Momany *et al.*[26b] proposed for 1-bromobutane 36% TT, 24% TG, 24% GT, and 16% GG in the gaseous state by the electron-diffraction method. Snyder and Schachtschneider[14] concluded for 1-chlorobutane that the TT form exists in the crystalline state and the TT and TG forms coexist in the glassy state on the basis of the comparison of the crystalline- and glassy-state spectra and of the normal coordinate analysis. Crowder and Ali[8a] interpreted the spectra of 1-iodobutane, taking into account only two among various isomers, the TT and TG forms. In the present study, it has been also found that the GT and GG forms of each of 1-halogenobutanes exist in the gaseous, liquid, and glassy states in addition to the TT and TG forms. However, the existence of the GG′ form was not identified in any state of these compounds. The skeletal deformation vibrations of 1-chlorobutane[22] and 1-bromobutane[22,23] were discussed in relation to the identification of existing rotational isomers. The results of these studies, however, do not agree with ours.

Studies concerning the relative stability of the isomers of 1-halogenobutanes have not yet been fully made. So far, only the apparent enthalpy difference between the mixture of the TT and GT forms and that of the TG and GG forms has been determined from the C–Br stretching bands of 1-bromobutane by the infrared and Raman methods,[5,6] and the relative stabilities of the *trans* and *gauche* conformations about the CC–CX and CC–CCX axes have been estimated by the electron-diffraction method.[26] In the present study, it has been possible to determine the enthalpy differences among the

individual isomers of 1-chloro-, 1-bromo-, and 1-iodobutanes, as the key bands in the skeletal deformation region have been clarified.

## Discussion

Several consistent trends have been observed for 1-halogenopropanes and 1-halogenobutanes. (1) The forms existing in the various states are same for all the compounds except 1-fluoroalkanes (Table 8). (2) The enthalpy difference $\Delta H_{G-T}$ in the liquid state is about $-100$ cal/mol for 1-halogenopropanes studied in this work in common. For 1-halogenobutanes in the liquid state, the GT form is the least stable and the TG form is the most stable with an exception that the TT form of 1-iodobutane is slightly more stable than the TG form (Figs. 17 and 18). (3) The force constants of the halogen part[33] show a systematic trend in their values.

The diagonal force constants of the CCX skeletal deformation for different halogen atoms are about the same and the frequency shifts are mainly due to the difference in the masses of halogen atoms. Together with the similarity of the relative stabilities of the rotational isomers, this is one of the principal reasons for the similarity of the spectral patterns. Thus, the skeletal deformation region of 1-halogenobutanes has good key bands for discriminating the individual isomers. In particular, the bands in the 300—500 $cm^{-1}$ region of 1-halogenobutanes are explicit examples, since these bands are associated predominantly with the CCC skeletal deformation (see Tables 5—7) and the frequency shift due to the mass difference is smaller than that for 1-halogenopropanes. In the study of the longer halogenoalkanes,[34] the key bands in the skeletal deformation region are efficiently used together with those in the skeletal stretching and $CH_2$ rocking regions.

It is noticed for the halogenoalkane molecules studied in this work except 1-iodobutane that the most stable isomer in the liquid or glassy state does not exist in the crystalline state. This is reasonably understood by considering that the T or TT form is less stable than the G or TG form by only 100—300 cal/mol in the liquid state and the intermolecular forces favoring the T or TT form in crystal may well overwhelm the intramolecular forces favoring the G or TG form.

Care must be taken in the interpretation of the Raman spectra in the gaseous state on the analogy of that in the liquid state. An apparent band or shoulder observed only in the gaseous-state Raman spectra can be that due to some rotational isomer which is not identified in the liquid-state spectra, part of the rotational contour of the vibrational band, or a hot band. The relative peak intensities of the bands belonging to the same isomer can also be different from those in the liquid state. Such examples are found in the Raman spectra of 1-iodopropane. The C–I stretching band of the G form is observed as doublet at 518 and 503 $cm^{-1}$. This doublet may be the contour of the B-type vibration since the corresponding infrared band is also observed as the B-type doublet. The relative peak intensities of the 602 and 285 $cm^{-1}$ bands, both assigned to the T form, in the gaseous-state spectrum are significantly different from those in the liquid-state spectrum. In the cases of 1-bromo- and 1-iodobutanes, the relative intensities of the Raman bands in the gaseous state at 448 and 456 $cm^{-1}$ and at 436 and 453 $cm^{-1}$, respectively, are different from those in the liquid state.

As has been shown in the present work, the skeletal deformation vibrations are useful for the determination of the enthalpy differences because of the relatively few overlapping bands due to different isomers. The measurement of the Raman spectra in this region is more effective for this purpose than that of the infrared spectra. Experiments of the temperature dependence of Raman intensities, especially at lower temperatures, can be performed without much difficulty, but the measurement of infrared intensities is difficult because of the interference by infrared emissions from the sample and the reference experimental apparatus.

## References

1) Part VI: H. Matsuura, M. Kono, H. Iizuka, Y. Ogawa, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 2272 (1977).
2) S. Mizushima, Y. Morino, and S. Nakamura, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **37**, 205 (1940).
3) G. Radinger and H. Wittek, *Z. Phys. Chem.*, **B45**, 329 (1940).
4) J. Goubeau and H. Pajenkamp, *Acta Phys. Austriaca*, **3**, 283 (1949).
5) T. Yoshino and H. J. Bernstein, *Can. J. Chem.*, **35**, 339 (1957).
6) M. W. Anderson, J. A. Taylor, and C. T. Walker, *J. Chem. Phys.*, **64**, 2695 (1976).
7) a) G. A. Crowder and H.-K. Mao, *J. Mol. Structure*, **16**, 165 (1973); b) G. A. Crowder and H.-K. Mao, *ibid.*, **18**, 33 (1973); c) G. A. Crowder and H.-K. Mao, *ibid.*, **23**, 161 (1974).
8) a) G. A. Crowder and S. Ali, *J. Mol. Structure*, **25**, 377 (1975); b) G. A. Crowder and S. Ali, *ibid.*, **30**, 181 (1976).
9) a) J. K. Brown and N. Sheppard, *Discuss. Faraday Soc.*, **9**, 144 (1950); b) J. K. Brown and N. Sheppard, *Trans. Faraday Soc.*, **50**, 535 (1954); c) J. K. Brown and N. Sheppard, *ibid.*, **50**, 1164 (1954).
10) Y. A. Pentin and V. M. Tatevskii, *Dokl. Akad. Nauk. SSSR*, **108**, 290 (1956); Y. A. Pentin, V. M. Tatevskii, and V. A. Pozdyshev, *Fiz. Sbornik L'vov. Univ.*, **1957**, 300; *Chem. Abstr.*, **55**, 21797c (1961).
11) C. Komaki, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, *Bull. Chem. Soc. Jpn.*, **28**, 330 (1955).
12) N. T. McDevitt, A. L. Rozek, F. F. Bentley, and A. D. Davidson, *J. Chem. Phys.*, **42**, 1173 (1965).
13) K. Radcliffe and J. L. Wood, *Trans. Faraday Soc.*, **62**, 1678 (1966).
14) R. G. Snyder and J. H. Schachtschneider, *J. Mol. Spectrosc.*, **30**, 290 (1969).
15) M. Hayashi, K. Ohno, and H. Murata, *Bull. Chem. Soc. Jpn.*, **46**, 2332 (1973).
16) A. J. Barnes, H. E. Hallam, J. D. R. Howells, and G. F. Scrimshaw, *J. Chem. Soc., Faraday Trans. 2*, **69**, 738 (1973).
17) K. Tanabe and S. Saëki, *J. Mol. Structure*, **27**, 79 (1975).
18) T. N. Sarachman, *J. Chem. Phys.*, **39**, 469 (1963).
19) E. Hirota, *J. Chem. Phys.*, **37**, 283 (1962).
20) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958).

21) L. Kohovec and K. W. F. Kohlrausch, *Z. Phys. Chem.*, **B48**, 7 (1940/41).
22) T. Fujiyama, *Bull. Chem. Soc. Jpn.*, **44**, 1194 (1971); T. Fujiyama, *ibid.*, **45**, 3016 (1972).
23) R. Schröder, H. Böhlig, J. Fruwert, and G. Geiseler, *J. Mol. Structure*, **41**, 37 (1977).
24) F. F. Bentley, N. T. McDevitt, and A. L. Rozek, *Spectrochim. Acta*, **20**, 105 (1964).
25) H. Goetz and S. Domin, *Z. Anal. Chem.*, **246**, 302 (1969).
26) a) T. Ukaji and R. A. Bonham, *J. Am. Chem. Soc.*, **84**, 3631 (1962); b) F. A. Momany, R. A. Bonham, and W. H. McCoy, *ibid.*, **85**, 3077 (1963).
27) Part I: T. Shimanouchi, Y. Ogawa, M. Ohta, H. Matsuura, and I. Harada, *Bull. Chem. Soc. Jpn.*, **49**, 2999 (1976).
28) Part II: I. Harada, H. Takeuchi, M. Sakakibara, H. Matsuura, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 102 (1977).
29) Part III: M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 111 (1977).
30) Part IV: M. Ohta, Y. Ogawa, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 380 (1977).
31) Part V: Y. Ogawa, M. Ohta, M. Sakakibara, H. Matsuura, I. Harada, and T. Shimanouchi, *Bull. Chem. Soc. Jpn.*, **50**, 650 (1977).
32) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, *J. Phys. Chem. Ref. Data*, to be published.
33) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, to be published.
34) Part VIII: S. Imazeki, Y. Ogawa, M. Sakakibara, H. Matsuura, I. Harada, M. Tasumi, and T. Shimanouchi, to be published.
35) J. Thorbjørnsrud, O. H. Ellestad, P. Klaboe, and T. Torgrimsen, *J. Mol. Structure*, **15**, 61 (1973).
36) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies," Consolidated Vol. I, U. S. Govt. Printing Office, No. C13.48 : 39 (1972).