The Infra-Red Spectrum of Hydrogen Peroxide*

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The absorption spectrum of hydrogen peroxide vapor was examined under low dispersion in the range 2–15μ. Four bands were observed at 3590, 2630, 1255, and 877 cm^{-1}. The spectrum of the liquid also was measured between 2 and 21μ; it showed five bands at about 3400, 2780, 1350, 880, and 550 cm^{-1}. The last one, which seems very diffuse, is presumably the torsional oscillation of the OH groups; as such it corresponds to a potential energy barrier of the order of 4 kcal./mole. New assignments are proposed in agreement with the model of Penney and Sutherland. Under high dispersion the second harmonic O—H frequency was found to consist of two identical hybrid bands at 7036.6 and 7041.8 cm^{-1}, of which the rotational constant for the ground state is in perfect agreement with that already found for the third harmonic band. The explanation given previously for the doublet character of the vibrational levels of hydrogen peroxide is further substantiated by the present results. From both vibrational and rotational data the O—H distance in hydrogen peroxide appears to be slightly greater than that in water.

INTRODUCTION

THE molecular configuration of hydrogen peroxide is now well established as the result of theoretical[1] and experimental[2] investigatons; however, the absorption spectrum of this substance has not so far been accounted for satisfactorily. The problem is of great interest because of the question of torsional oscillation or hindered rotation. According to theory, a tetratomic molecule with point-group symmetry C_2 should have six fundamental vibrations, none of them degenerate. In their investigation of the infra-red spectrum of hydrogen peroxide between 2 and 13μ Bailey and Gordon[3] observed four bands in the vapor as well as in the liquid. Because of experimental difficulties they were unable to locate accurately the center of the bands. On the other hand, the Raman spectrum, studied by a number of authors,[4,5,6] seemed also to consist of four bands. These results were interpreted by Bailey and Gordon who made tentative assignments of the observed frequencies (Table I). In a later investigation, however, Fehér[7] could find only three definite frequencies in the Raman spectrum of both hydrogen and deuterium peroxides. From the measured shifts in the isotopic molecule he questioned some of the assignments shown in Table I. Finally an investigation of the fine structure of two photographic bands of hydrogen peroxide[8] did not lead to a unique interpretation of the bands on account of

multiple overlapping. Therefore it seemed desirable to study further the infra-red spectrum of this molecule.

EXPERIMENTAL PROCEDURE

The low dispersion spectra were obtained with a Beckman IR-2 spectrometer. For the region beyond 15μ a special model of this instrument, with potassium bromide optics, was made available by courtesy of the manufacturer. All the spectra were recorded at rather high speed (20 minutes for complete scanning) with the two-second response. The slit width was automatically controlled so as to offset partly the intensity distribution of the Nernst glower. The near coincidence of some of the water bands with those of hydrogen peroxide made it necessary to dry thoroughly the spectrometer case.[9] Because of the low vapor pressure and of the reactivity of hydrogen peroxide, the absorption cells supplied with the instrument could not be used. Instead the liquid was distilled under constant pressure through a 50-cm Pyrex tube, 25-mm diameter, surrounded by a heating jacket to prevent condensation. The windows were silver chloride plates five-mm thick (Harshaw Chemical Company) held against the tube by means of stainless steel collars and Koroseal gaskets. This material was not affected by the hot peroxide vapor except for a slight leaching of the plasticiser which did not seem to affect the measurements. Previous to a run the entire system was cleaned with hot fuming nitric acid and rinsed re-
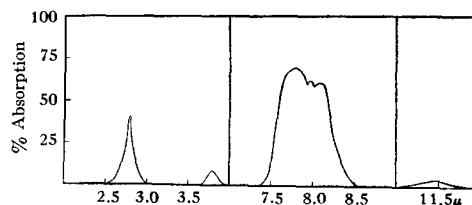
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[1] W. G. Penney and G. B. B. M. Sutherland, Trans. Faraday Soc. 30, 898 (1934); J. Chem. Phys. 2, 492 (1934).

[2] Lu, Hughes, and Giguère, J. Am. Chem. Soc. 63, 1507 (1941).

[3] C. R. Bailey and R. R. Gordon, Trans. Faraday Soc. 34, 1133 (1938).

[4] S. Venkateswaran, Nature 127, 406 (1931); Phil. Mag. 15, 263 (1933).

[5] I. Damaschun, Zeits. f. physik. Chemie B16, 81 (1932).

[6] A. Simon and F. Fehér, Z. Elektrochem. 41, 290 (1935).

[7] F. Fehér, Ber. d. d. chem. Ges. 72, 1778 (1939).

[8] L. R. Zumwalt and P. A. Giguère, J. Chem. Phys. 9, 458 (1941).

FIG. 1. Absorption spectrum of hydrogen peroxide vapor. Equivalent path length, 0.5 cm; temperature, 90°C.

[9] P. A. Giguère and R. M. Badger, J. Opt. Soc. Am. 38, 987 (1948).

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peatedly. The decomposition in one operation amounted to less than one percent. Some difficulty was encountered in obtaining the spectrum of the liquid. A film, a few microns thick, was obtained by pressing one drop between highly polished silver chloride plates. Due to the large interface, decomposition invariably set in after a few minutes, and the oxygen formed interfered with the transmission of the sample. The cell had to be refilled periodically and a number of spectra were run for a good check.

The vacuum spectrometer used for the high dispersion investigation of the 1.4μ-band has been described elsewhere.[10] The grating, an échelette replica with 7500 lines to the inch, was used in the first and second orders. Wave-length determinations were based on the higher orders of the red and near infra-red lines of argon as observed in the discharge of an ordinary sodium Lab-arc. The effective slit width was about 0.8 cm⁻¹ in the region covered. The absorption cell, one meter long, was made so as to allow continuous recycling of the vapor through the absorption path.

The hydrogen peroxide was prepared from Becco's 90 percent commercial solution by fractionation at low pressure; its purity was of the order of 99.5 percent.

RESULTS

Vibrational Structure

The spectrum of the vapor at 90°C and 15 mm pressure is shown in Fig. 1. Similar tracings were made at five and ten mm to obtain the "apparent" absorption coefficients α given in Table II. Attempts to operate at higher pressures in order to bring out weak overtones and combination bands were unsuccessful due to increased decomposition of hydrogen peroxide on raising the temperature. The present data are somewhat different from those of Bailey and Gordon both as regards location and relative intensities of the bands. On the other hand the spectrum of the liquid, in Fig. 2, is quite similar to theirs. As a matter of fact there was hardly any difference between their published spectra of the liquid and of the vapor, contrary to what should be expected. This may have been caused by some fogging of the windows due to the action of hydrogen peroxide on rock salt. The band at 18.3μ has not been reproduced here because of the uncertainty as to its exact shape; on account of the low transmission of the sample in that region a higher amplifier gain was required, which re-
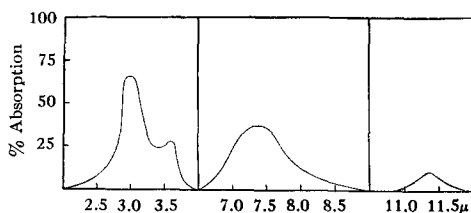

FIG. 2. Absorption spectrum of liquid hydrogen peroxide between two and 15μ.

[10] Badger, Zumwalt, and Giguère, Rev. Sci. Inst. **19**, 861 (1948).

TABLE I. Previous data on infra-red and Raman spectra of hydrogen peroxide.

Vapor (cm⁻¹)	Infra-red Relative intensity	Liquid (cm⁻¹)	Relative intensity	Raman Liquid (cm⁻¹)	Assignment (Bailey and Gordon)	Ref.
870	18	877	33	877	ν_4*	(3–6)
1370	22	1341	87		ν_6	(3)
				1408	ν_3*	(6)
				1435	ν_2	(6)
2870	15	2869	55		ν_1	(3)
3418	59	3418	78	3407	ν_5	(3–6)
10,283.68 10,291.08		9900				(8, 14)

* In this assignment ν_4 corresponds to the vibrational mode designated below (Fig. 3) as ν_3, and vice versa.

TABLE II. Vibrational spectrum of hydrogen peroxide.

Vapor $\nu_{vac.}$ (cm⁻¹)	Infra-red α*	Liquid $\nu_{vac.}$ (cm⁻¹)	Slit width cm⁻¹	Raman† Liquid ν (cm⁻¹)	Assignment
(490)		550(?)			ν_4 (a)
877	0.025	880	6	877 (v.s.)	ν_3 (a)
1255	0.70	1350	6		ν_6 (b)
				1421 (w.)	ν_2 (a)
2630	0.05	2780	10		$\nu_2+\nu_3+\nu_4$ (A)
				3395 (m.)	ν_1 (a)
3590	0.35	3400	13		ν_5 (b)
		4720 (?)			$\nu_5+\nu_6$ (A)
7036.6 7041.8	0.085		0.8		$\nu_1+\nu_5$ (B)
10,283.68 10,291.08		9900			$\begin{cases}2\nu_1+\nu_5 & \text{(B)}\\ \text{or } 3\nu_5 & \text{(B)}\end{cases}$

* $\alpha=(1/pl)\log T_0/T$, with p in atm. and l in cm.
† See reference 7.

sulted in a rather confused recording of the spectrum. Under these conditions, it was not possible to estimate the intensity or the width of that band. The existence of a very weak band at 2.1μ in the liquid is uncertain as it did not show on all tracings.

Assignment of the observed bands with respect to the vibrational modes of the molecule (Fig. 3) was made as follows: The 3590 cm⁻¹ frequency is obviously an O−H stretching vibration as confirmed by its proximity to the corresponding bands in water[11] and by the isotopic shift in deuterium peroxide (Table III). Only one O−H stretching frequency has been observed in all previous spectroscopic investigations of hydrogen peroxide. It has been argued[7] that because of the loose coupling between the two OH groups the symmetric and asymmetric frequencies are accidentally degenerate. Support of this view may be seen in the exact coincidence, to within the accuracy of the measurements, of the Raman and infra-red bands at 3400 cm⁻¹ in the liquid. It is logical to think that the former corresponds to the symmetric, and the latter mostly to the antisymmetric vibration. However, this question can be decided only by a high dispersion study of the spectrum in that region.

[11] Cross, Burnham, and Leighton, J. Am. Chem. Soc. **59**, 1134 (1937).

TABLE III. Isotopic shifts in the Raman spectra of liquid water* and hydrogen peroxide.**

	H_2O ν (cm^{-1})	D_2O ν (cm^{-1})	H_2O_2 ν (cm^{-1})	D_2O_2 ν (cm^{-1})
ν_1	3440	2515	3395	2510
ν_2	1656	1208	1421	1009

* See reference 11.
** See reference 7.

Leaving for the moment the 2630 cm^{-1} band, that at 1255 cm^{-1} is taken as an O−H bending frequency again by comparison with water. Because it occurred in the region of maximum dispersion of the prism instrument its contour was more clearly discernible; thus it appeared to consist of a double maximum at 1280 and 1240 cm^{-1}, the latter being roughly four-fifths as intense as the former. In as much as they are real they must very likely correspond to the P and R branches of the ν_6 band since ν_2 should be rather weak in the infra-red. This is further confirmed by indications, on some of the tracings, of a prominent Q branch as should occur in the case of an oscillating dipole parallel to the top axis. Then the Raman band at 1420 cm^{-1} is the symmetric bending vibration ν_2, as evidenced by the isotopic shift (Table III).

No doubt exists regarding the origin of the 877 cm^{-1} frequency since its remains unchanged in the spectra of both deuterium and hydrogen peroxides. Badger's rule gives 1.48A for the O−O bond length, very nearly the same value as found by electron diffraction.[12] The fact that ν_3 is the strongest Raman band but fairly weak in the infra-red (it was hardly noticeable in the spectrum of the vapor) is further evidence for the C_2 point-group model for hydrogen peroxide.

Lastly, the 550 cm^{-1} band in the liquid is of the right order of magnitude for ν_4, the torsional oscillation; in hydrazine, where the oscillating mass is double, this vibration is believed to occur at 360 cm^{-1}.[13] Certainly the present experimental evidence for the torsional oscillation would not carry much weight by itself were it not for the fact that it allows an unambiguous assignment of the 2780 cm^{-1} band as a combination of $\nu_2+\nu_3+\nu_4$. No satisfactory interpretation had been given previously for the occurrence of that band. Fehér[7] believed that it was due to the O−H vibration shifted to longer wave-length by hydrogen bond formation. The present data render such an explanation untenable for the following reasons: First, the band appears not only in the spectrum of the liquid but in that of the vapor as well, where there is known to be no appreciable association. Second, the frequency shift on going from vapor to liquid has been observed in the fundamental as well as in the second overtone[14] of the O−H frequency

(Table II), and it corresponds to the right magnitude for the energy of hydrogen bonds in hydrogen peroxide, as calculated by other methods.[15] The hypothetical value, 490 cm^{-1}, for ν_4 in the vapor was obtained indirectly from the combination band. Therefore the shift due to molecular association is in the same direction as that of the O−H bending but opposite to that of the O−H stretching vibration, which seems reasonable.

On the basis of this frequency the height V_0 of the barrier restricting free rotation in hydrogen peroxide would be of the order of 4 kcal./mole according to the equation

$$\nu_t = 2n(V_0 A)^{\frac{1}{2}}$$

where n is the symmetry number and A is the rotational constant corresponding to the small moment of inertia of the molecule. Obviously this is only a rough estimate since the shape of the potential energy curve is not very well known.

Rotational Structure of the 1.4 μ-Band

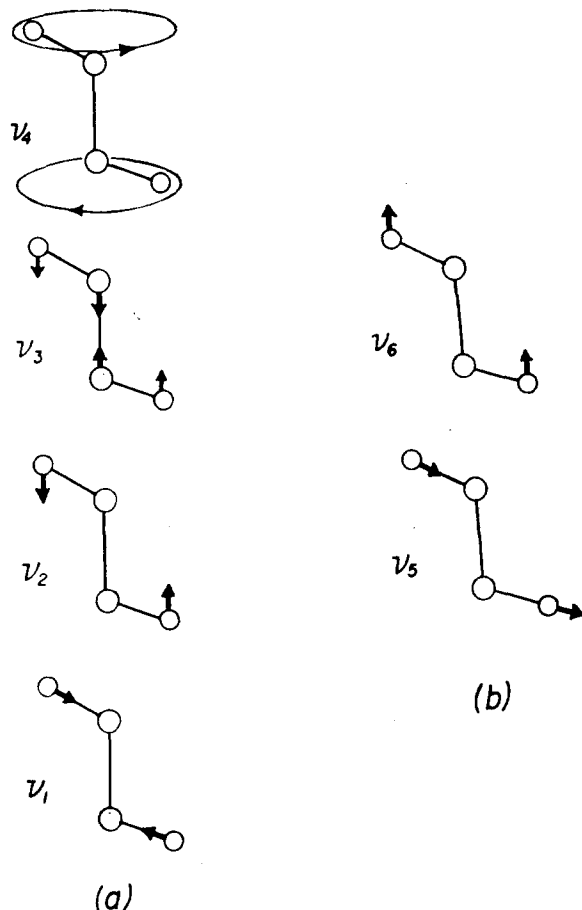As may be seen from Fig. 4, the second harmonic of the O−H vibrations is strikingly similar in appearance

FIG. 3. Normal vibrations of the hydrogen peroxide molecule.

[12] P. A. Giguère and V. Schomaker, J. Am. Chem. Soc. 65, 2025 (1943).
[13] Scott, Oliver, Gross, Hubbard, and Huffman, J. Am. Chem. Soc. 71, 2293 (1949).
[14] P. A. Giguère, Trans. Roy. Soc. (Canada) 3 (III) 35, 1 (1941).
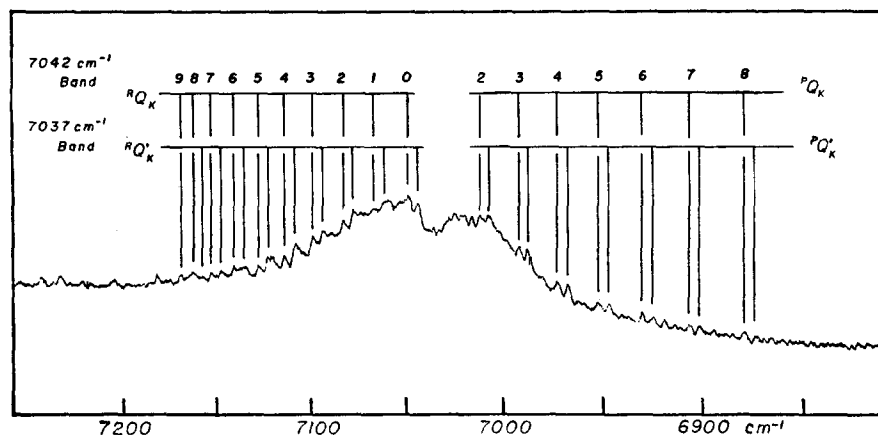[15] L. Pauling, Nature of Chemical Bond (Cornell University Press, Ithaca, New York, 1939).

FIG. 4. High dispersion structure of the overtone bands of hydrogen peroxide at 1.4μ. Equivalent path length, 2.7 cm.

to the third harmonic; it shows a doublet structure with the two components of about equal intensity and a separation very closely two-thirds of that found in the latter case.

Considered separately neither of these harmonic bands could be given a unique interpretation. But if it is assumed, as is most probable, that their great resemblance is not a pure accident, then they should be explained similarly. Granted this, a number of otherwise plausible interpretations can be eliminated. Judging from the width of the bands and the relative weakness of the P and R branches, the over-all intensity distribution in both cases is more nearly that to be expected of a parallel type rather than a perpendicular type band. Consequently both bands are primarily due to vibrational transitions in which the upper level is unsymmetrical. In the third harmonic band both the parallel type and the weaker perpendicular type structures center on the same origin and clearly belong to one and the same hybrid band doublet. Therefore this band must be assigned to one of the two possible transitions, $3\nu_5$ (B) or $2\nu_1+\nu_5$ (B). Since the two doublet components have essentially equal intensity it seems highly improbable that they could originate respectively from these two vibrational levels. Indeed, if the intensities were equalized by "borrowing" then the interaction would cause a much larger doublet separation than is observed. At any rate the hybrid band $\nu_1+\nu_5$ (B) is definitely the only possibility in the 1.4μ-region; both $2\nu_1$ and $2\nu_5$ would be purely perpendicular. Thus the present results provide additional support of the explanation previously given for the doublet character, namely that it arises from the presence of a double minimum in the torsional oscillation potential.

The average value of the frequencies obtained from measurements on three different tracings are listed in Table IV together with the calculated rotational constants; the nomenclature used is the same as that of Zumwalt and Giguère.[8] Using these rotational constants the position of the Q branches were calculated and from these, in turn, the center of the two bands were found to occur at 7036.6 and 7041.8 cm^{-1}, respectively. The accu-

racy of these determinations is somewhat inferior to those in the photographic infra-red because of the limited resolving power of the replica grating. In that connection it should be mentioned at this point that the published microphotometer trace of the 0.927μ-band of hydrogen peroxide shows far less detail than was easily visible on the original photographic plates.

The number of P and R branches measured in the 1.4μ-band is too limited to make an accurate estimate of $X_{02}{}^0$ the rotational convergence constant; but if one takes the same value as obtained from the third harmonic band, the rotational constant for the ground state $X_{01}{}^0$ is in perfect agreement for the two bands. Furthermore the constants for the various vibrational levels show a systematic trend which is strong evidence for the significance of the analyses.

It is interesting to compare the above rotational constants with those corresponding to calculated moments of inertia of the hydrogen peroxide molecule. These quantities are related as follows:

$$X_{01}{}^0 = A_0 - \tfrac{1}{2}(B_0 + C_0); \quad X_{10}{}^0 = \tfrac{1}{2}(B_0 + C_0),$$

where

$$A_0 = h/8\pi^2 c I_{A^0}; \quad B_0 = h/8\pi^2 c I_{B^0};$$

$$C_0 = h/8\pi^2 c I_{C^0}; \quad A_0 \gg B_0 \simeq C_0.$$

Using a set of equations derived for the hydrogen persulfide molecule[16] the calculations were done for various values of ϕ the azimuthal angle, and the following structural data: 1.48A for the O—O distance, 0.98A for the O—H distance, both from the corresponding vibrational frequencies reported above (Badger's rule), and 102° for the H—O—O angle, a decrease of some 3° from the apex angle in H_2O to account for the reduced repulsion of the hydrogen atoms. As could be expected the rotational constant $X_{10}{}^0$ corresponding to the harmonic mean of the two large moments of inertia, $2I_{B^0}I_{C^0}/(I_{B^0}+I_{C^0})$, is very insensitive to changes of the azimuthal angle (cf. Table V); on the other hand the constant $X_{01}{}^0$, which depends mainly on the small

[16] M. K. Wilson and R. M. Badger, J. Chem. Phys. **17**, 1232 (1950).

TABLE IV. Frequency of principal maxima in the 1.4μ-band of hydrogen peroxide.

	^PQ_K	^RQ_K	$\dfrac{^RQ_K - {}^PQ_K}{4K}$	$\dfrac{^RQ_{(K-1)} - {}^PQ_{(K+1)}}{4K}$
0		7050.6		
0'		7045.8		
1		7068		
1'		7063		
2	7014.1	7084.3	8.77	9.37
2'	7009.3	7078.7	8.67	9.37
3	6993.3	7099.9	8.88	9.26
3'	6988.3	7094.7	8.87	9.13
4	6973.2	7114.6	8.84	9.19
4'	6968.2	7109.1	8.74	9.19
5	6952.8	7128.8	8.80	9.18
5'	6947.7	7123.3	8.78	9.18
6	6930.9	7142.4	8.81	9.17
6'	6925.5	7135.8	8.76	9.16
7	6908.6	7154.7	8.79	
7'	6903.5	7149.2	8.77	
8	6880	7164.2		
8'	6875	7158.8		

Rotational constants for the various vibrational levels.
$X_{02}{}^0 = -0.0008_5{}^*$ cm^{-1} $X_{01}{}^0 = 9.23 = 9.23_1{}^*$ cm^{-1}.
$(X_{02}{}^2 = -0.0008_5$ cm$^{-1})$ $X_{01}{}^2 = 8.83$ cm^{-1}
$X_{02}{}^3 = -0.0008_6{}^*$ cm^{-1} $X_{01}{}^3 = 8.66_8{}^*$ cm^{-1}

* From the third harmonic band.

TABLE V. Calculated moments of inertia and rotational constants for the hydrogen peroxide molecule.

Azimuthal angle	Moments of inertia (g cm^2 $\times 10^{40}$) I_A	I_B	I_C	Rotational constants (cm^{-1}) $X_{10}{}^0$	$X_{01}{}^0$
0°	2.89	32.0	35.0	0.83$_5$	8.83
45°	2.88	32.5	34.6	0.83	8.88
90°	2.83	33.6	33.7	0.83	9.03
135°	2.78	34.7	32.8	0.83	9.21
180°	2.76	35.1	32.4	0.83	9.29

moment of inertia, increases by about five percent from the *cis*- to the *trans*-configuration. However, this quantity cannot give any definite information about the azimuthal angle because it also varies as the square of the O—H distance, which is not known accurately from other sources. Calculations show that if this latter parameter is given the same value, 0.957A, as in H$_2$O, then the rotational constant $X_{01}{}^0$ becomes greater than the spectroscopic value for the ground state, even in the extreme case of a *cis*-model. Therefore the O—H distance in hydrogen peroxide is probably slightly greater than that in water.

The doublet character is certainly the most remarkable feature of these hybrid bands. In particular, the fact that the doublet splitting in the second and in the third harmonics are almost exactly in the ratio two to three is significant. In other molecules where inversion doubling has been observed so far the magnitude of splitting usually shows a strong dependence on the vibrational level.[17] It appears, from the configuration of hydrogen peroxide, that its normal vibrations are not

considerably affected by internal rotation in the molecule, except, of course, ν_4. The situation here is intermediate between pure inversion doubling, as in ammonia, and torsional oscillation, as in methanol. Because the potential energy curve hindering free rotation of the OH groups contains two maxima of unequal height the energy levels first go over into those of an oscillator of greater amplitude, above the lower barrier, then into those of a rotator. A further difference in the case of hydrogen peroxide is the existence of two distinguishable isomeric forms as shown in the crystal structure of the addition compound CO(NH$_2$)$_2$:H$_2$O$_2$.[2]

The shape of the potential energy curve restricting free rotation in molecules such as hydrogen peroxide and hydrazine will depend on the cause of the hindering potential. According to the quantum mechanical calculations of Penney and Sutherland[1] this arises mostly from the directional properties of the central bond with steric repulsion and ion or dipole interactions contributing only slightly. In this connection it is surprising that the overtone band of hydrogen persulfide shows no sign of doubling under the same dispersion.[16] The use of a lead sulfide cell in the vacuum spectrometer prevented extension of the present investigation beyond 2.7μ. It is hoped that the fundamental frequencies of hydrogen peroxide will be studied soon under high dispersion in order to provide more information on the phenomenon of internal rotation. In particular, it would be interesting to know the equilibrium position of the OH groups and the height of the potential barriers restricting free rotation. Further study of the torsional oscillation is also desirable although it would no doubt involve considerable experimental difficulties.

ACKNOWLEDGMENT

[17] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).