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## The Infra-Red Spectrum and Molecular Configuration of Hydrogen Persulfide\*

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(Received March 25, 1949)

The infra-red spectrum of hydrogen persulfide has been investigated in the region 1.5 to  $15\mu$ , and vibrational assignments have been made. The perpendicular band at  $2\mu$  has been studied under high resolution and a value for one of the rotational constants has been obtained. The data strongly support a chain structure for hydrogen persulfide and probably exclude *cis*- or *trans*-planar structures, but give no very definite information regarding the azimuthal angle.

### 1. INTRODUCTION

ALTHOUGH the structure of hydrogen peroxide has been the object of much experimental work and speculation,<sup>1</sup> comparatively little attention has been paid to its sulfur analog, hydrogen persulfide. Stevenson and Beach<sup>2</sup> investigated the persulfide by means of electron diffraction and reported the *S-S* distance to be  $2.05 \pm 0.02\text{\AA}$ . Since this distance corresponds closely to the single-bond distance for sulfur,  $2.08\text{\AA}$ ,<sup>3</sup> they concluded that the persulfide molecule had the chain structure with the hydrogens attached to different sulfur atoms. It is reasonable to expect that the structures of hydrogen persulfide and hydrogen peroxide should be similar and that the former molecule should have at least the symmetry  $C_2$ , which is reasonably well established for hydrogen peroxide by the spectroscopic observations of Zumwalt and Giguère,<sup>4</sup> but the angles between the two planes including the heavy atoms and a hydrogen atom may well be somewhat different in the two molecules.

The only previously existing spectroscopic data on hydrogen persulfide are three Raman shifts of 510, 882, and  $2513\text{ cm}^{-1}$ , respectively, obtained on the liquid by Fehér and Baudler.<sup>5</sup> The present work is concerned with an investigation of the infra-red vibration spectrum of this substance and the rotational structure of the first overtone of the *S-H* stretching vibration at  $2\mu$  in an attempt to obtain further information regarding the molecular structure.

### 2. EXPERIMENTAL PROCEDURE

#### Materials and Methods

The hydrogen persulfide used in this investigation was prepared by the procedure detailed by Butler and

Maass.<sup>6</sup> Briefly this method consists of dropping a sodium polysulfide solution into cold, concentrated hydrochloric acid and fractionally distilling under vacuum the mixture of hydrogen polysulfides formed. The colorless redistilled hydrogen persulfide was used immediately for the spectroscopic investigations. Two separate preparations were made and no spectroscopic difference was noted.

Hydrogen persulfide decomposes rapidly in the presence of alkali. To minimize this decomposition, the Pyrex cells were first cleaned in boiling concentrated nitric acid and thoroughly dried. The sodium chloride windows with Koroseal gaskets were then clamped in place, the cell evacuated, and filled with dry hydrogen chloride gas. The hydrogen chloride gas was allowed to remain in the cell for 10-15 minutes before the cell was again evacuated and the hydrogen persulfide introduced.

At  $25^\circ\text{C}$  the vapor pressure of hydrogen persulfide is  $109\text{ mm}$ .<sup>5</sup> With this vapor pressure a path length of  $50\text{ cm}$  was found to be adequate.

#### Prism Instrument

The vibration spectrum was traced from 1.5 to  $15\mu$  with a Beckman IR-2 spectrophotometer which has a resolution of about  $3\text{ cm}^{-1}$  at  $9\mu$ . The wave-length drive and slit control of our instrument are coupled in such a fashion that the intensity of the background is reasonably constant through the region  $4\text{--}13\mu$ , though a noticeable dip occurs in the vicinity of  $9.3\mu$ . A Brown recorder was used to give a continuous plot of intensity *versus* wave-length.

#### Grating Instrument

The  $2\mu$ -band of hydrogen persulfide was also investigated under high dispersion with an automatic recording one-meter grating vacuum spectrograph which has recently been described by Badger, Zumwalt, and Giguère.<sup>7</sup> The spectra were taken in the first order of a replica grating with 7500 lines per inch, using a lead sulfide cell as the photo-sensitive element and a slit width of  $0.05\text{ mm}$ , corresponding to  $0.85\text{ cm}^{-1}$ .

\* K. H. Butler and O. Maass, *J. Am. Chem. Soc.* **52**, 2184 (1930).

<sup>7</sup> Badger, Zumwalt, and Giguère, *Rev. Sci. Inst.* **19**, 861 (1948).

\* Contribution No. 1264 from the Gates and Crellin Laboratories of Chemistry.

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<sup>1</sup> G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 301.

<sup>2</sup> D. P. Stevenson and J. Y. Beach, *J. Am. Chem. Soc.* **60**, 2872 (1938).

<sup>3</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1942).

<sup>4</sup> L. R. Zumwalt and P. A. Giguère, *J. Chem. Phys.* **9**, 458 (1941).

<sup>5</sup> F. Fehér and M. Baudler, *Zeits. f. Elektrochemie* **47**, 844 (1941).

The instrument was calibrated by observing first and higher orders of visible and near-infra-red argon lines from a sodium vapor lamp containing argon at low pressure. The wave-lengths of these standards were corrected to vacuum. In the case of lines having a sharp maximum it is believed that our wave-length and frequency determinations are accurate to 1 part in 25,000.

### 3. EXPERIMENTAL RESULTS AND INTERPRETATION

#### Vibrational Structure

Traces of the prismatic spectrum from 1 to  $12\mu$  and of the overtone band at  $2\mu$  under high dispersion are shown in Figs. 1 and 2, respectively. The frequencies of the band centers are given in Table I together with the previous Raman data on the liquid and probable assignments. The assignments were made on the assumption of a chain structure, which, as will be shown, is compatible with the observations. Structures resembling formaldehyde or chloramine appear to be excluded by the data.

If hydrogen persulfide has the chain structure with point group symmetry  $C_2$ , the six normal modes in probable order of decreasing frequency may be described as unsymmetrical and symmetrical  $S-H$  vibrations,  $\nu_5(b)$  and  $\nu_1(a)$ ; symmetrical and unsymmetrical bending motions,  $\nu_2(a)$  and  $\nu_6(b)$ ; an  $S-S$  valence vibration  $\nu_3(a)$ ; and a torsional oscillation,  $\nu_4(a)$ . In principle  $\nu_5$  and  $\nu_6$  may both give rise to hybrid bands unless the molecule has higher symmetry than  $C_2$ . The relative intensities of the "parallel" and "perpendicular" components of the hybrid fundamental of  $\nu_5$  should be quite sensitive to the azimuthal angle, but the fundamental of  $\nu_6$  should in any case be expected to have predominantly "parallel" character. The remaining fundamentals must give rise to bands of pure "perpendicular" type. Owing to the relatively large mass of the central atoms, the  $C_2$  model is very nearly a sym-

TABLE I.

Infra-red bands (vapor)		Raman shifts <sup>b</sup> (liquid) $\nu(\text{cm}^{-1})$	Assignment
$\nu(\text{cm}^{-1})$	Relative intensity* (a)		
—	—	510	$\nu_3(a)$
—	—	882	$\nu_2(a)$
886 { 875 897	0.035 } 0.043 }	—	$\nu_6(b)$
—	—	2513	$\nu_1(a)$
2577	0.015	—	predominantly $\nu_5(b)$
3065	0.002	—	$\nu_3 + \nu_5(B)$
3400	0.002	—	$\nu_5 + \nu_6(A)$ or $\nu_2 + \nu_5(B)$
5007.2	0.003	—	$\nu_1 + \nu_5(B)$ and possibly $2\nu_1(A)$

\* The figure given is the apparent absorption coefficient at the maximum of the band defined by the equation  $a = (1/\rho l) \log T_0/T$  and measured under conditions such that the absorption was between 15 and 50 percent. The equivalent path,  $\rho l$ , is expressed in cm atmos. at  $0^\circ\text{C}$ .

metrical rotator for any value of the azimuthal angle, and one might anticipate difficulty in distinguishing bands in which the change in electric moment is parallel to major or intermediate axes of inertia. For a planar *trans*-structure,  $\nu_1$  should be inactive, and  $\nu_5$  active, but for smaller azimuthal angles it is at present not possible to predict their relative activities.

In the neighborhood of the  $S-H$  fundamentals only one absorption region was observed with center at  $2577\text{ cm}^{-1}$ , which might include both  $\nu_1$  and  $\nu_5$ . Though no structure was resolvable with the low dispersion employed, the narrowness of the band suggests, however, that it is predominantly of parallel type and should be ascribed chiefly to  $\nu_5(b)$ . The Raman shift of  $2513\text{ cm}^{-1}$  in the liquid is presumably  $\nu_1(a)$ . In the vapor this frequency is probably appreciably greater and not greatly different from  $\nu_6$ . The second harmonic  $S-H$  band appears to have a strong "parallel" type component, as is discussed below, and consequently must be attributed at least in considerable part to  $\nu_1 + \nu_5(B)$ . It may contain traces of  $2\nu_1(A)$  or of absorp-

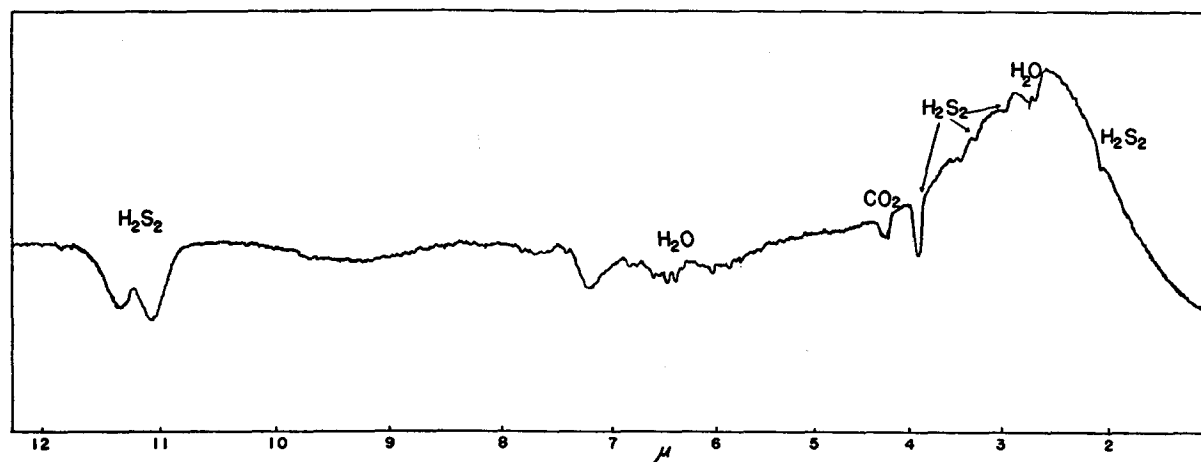


FIG. 1. Prismatic spectrum of hydrogen persulfide; equivalent path length =  $6.2\text{ cm}$  (S.T.P.); temp. =  $25^\circ\text{C}$ . The minima at about  $7.2\mu$  and  $3.3\mu$  are "ghost" bands due to the contamination of a window in the spectrograph.

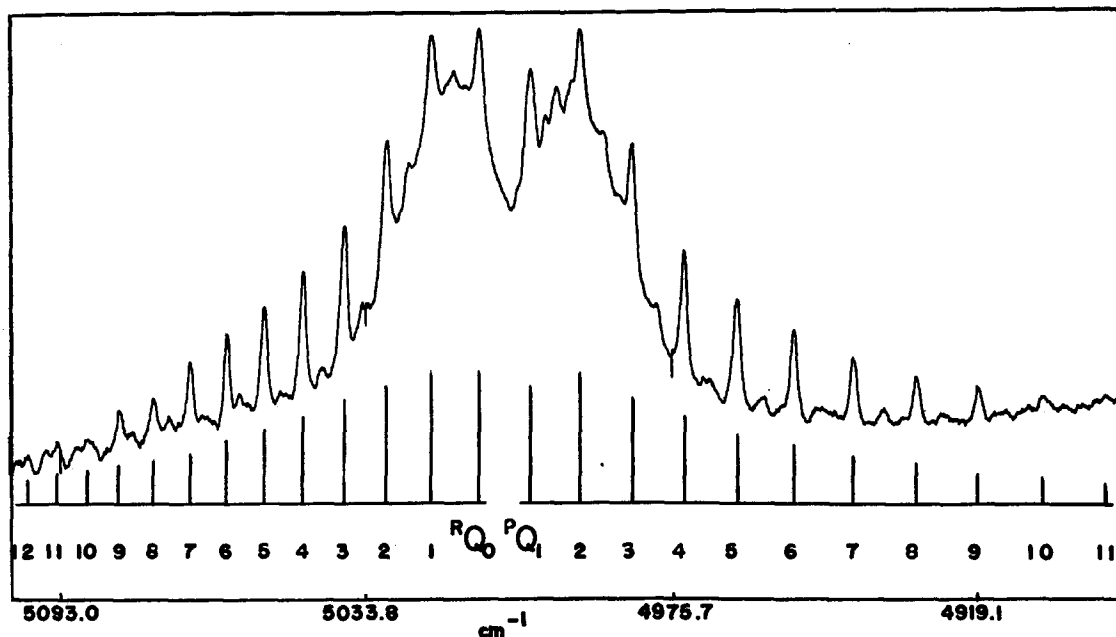


Fig. 2. Rotational structure of the hydrogen persulfide band at  $2\mu$ ; equivalent path length =  $12.4\text{ cm}$  (S.T.P.).

tion from the first excited level of  $\nu_4$ . We regard it as unlikely that  $2\nu_6(A)$  will appear with significant intensity. In the spectra of the non-linear triatomic molecules there is a conspicuous absence of harmonics or combination bands in which the unsymmetrical frequency  $\nu_3$  would occur in an even multiple.

The frequency of the  $S-H$  fundamental differs no more from the frequencies in  $H_2S$  than should be expected from the difference in reduced masses. This indicates that the  $S-H$  distance is not greatly different in the two molecules and is possibly some evidence for the chain structure of the polysulfide.

In the region  $5-15\mu$  only one band of appreciable intensity was found. This moderately strong band at  $886\text{ cm}^{-1}$  has a frequency less than that of  $\nu_2$  in  $H_2S$  by a factor slightly greater than the square root of two. It is rather definitely of the parallel type, and the separation of the maxima in  $P$  and  $R$  branches is that which would be predicted from the calculated moments of inertia which will be discussed below. With the limited resolution employed the failure to observe a  $Q$ -branch is not unexpected since it should be relatively weak because of the large ratio of major to minor moments of inertia and should be "washed out" by the noticeable band convergence. The resolution was adequate to distinguish a perpendicular type structure, had such been present with appreciable intensity. We can, with assurance assign this band to  $\nu_6(b)$ , the unsymmetrical bending vibration of the chain structure. The Raman shift at  $882\text{ cm}^{-1}$  is probably  $\nu_2(a)$ , but the very near equality of  $\nu_6$  and  $\nu_2$  is somewhat surprising and indicates very little interaction between the two  $H-S-S$  bendings.

The frequency of the  $11\mu$ -band, its structure, and the absence of other bands of appreciable intensity in the region  $5-15\mu$  are very good evidence for the chain structure of hydrogen persulfide. A formaldehyde structure would have three bending frequencies, presumably all on the short wave side of  $15\mu$ , and all should be expected to have reasonable intensity in the infra-red. Only one of these fundamentals  $\nu_2(a_1)$ , would have parallel structure, and its frequency might be expected to lie close to that of  $\nu_2$  in  $H_2S$ . In a model of the chloramine type even the analogous vibration would give rise to hybrid bands, and the previous remark regarding frequency would be applicable.

The weak bands at  $3065\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$  may reasonably be assigned to combinations of a  $S-H$  valence vibration with the  $S-S$  valence frequency,  $\nu_3(a)$ , and with one of the bending frequencies, respectively. The Raman shift in the liquid at  $510\text{ cm}^{-1}$  must certainly be ascribed to the  $S-S$  vibration, and the frequency in the vapor is probably not significantly different.

The fundamental of the twisting frequency,  $\nu_4(a)$  should be expected to lie well below the limit of the region available to rock salt optics. A search for this fundamental would be worth while since its intensity would give some information regarding the angle between the  $H-S-S$  planes. Its presence in the infra-red spectrum would exclude the possibility of a planar, *cis*-structure for hydrogen persulfide, which possibly cannot be completely ruled out by our present observations.

Structure of the Overtone Band at  $2\mu$ 

Although the absorption region at  $5007.2\text{ cm}^{-1}$  shows rather strong and well-resolved  $^PQ$ - and  $^RQ$ -branches the distribution of intensity is not that to be expected in a band of pure perpendicular type. The strong concentration of absorption in the unresolved background immediately to both sides of the band center indicates the presence of a fairly strong parallel type component which can result only from  $\nu_1 + \nu_5(B)$ . We believe that the most probable explanation of this band is that it is a truly hybrid structure similar to the third harmonic band of hydrogen peroxide<sup>4</sup> and is due almost entirely to the transition just mentioned. Some weak maxima lying between the intense  $^PQ$ - and  $^RQ$ -branches may conceivably be due to a weak and nearly coincident  $2\nu_1(A)$ , or to absorption from the first excited level of  $\nu_4$ . If this explanation is correct the planar *cis*-structure for hydrogen persulfide is of course excluded because of the hybrid structure of the band. Furthermore, the relatively greater intensity of the perpendicular component of the band as compared with both overtone hydrogen peroxide bands<sup>4,8</sup> suggests that the azimuthal angle may be slightly larger in the persulfide than in the peroxide. It is of particular interest that the persulfide absorption shows no indication of the doubling found in both overtone bands of the OH frequency in hydrogen peroxide, and attributed by Zumwalt and Giguère to a double minimum in the torsional potential.

The frequencies of the principal maxima of the  $2\mu$ -band are given in Table II, together with rotational constants for the upper and lower states. In Table III are given approximate moments of inertia and rotational constants calculated for  $C_2$  models for hydrogen persulfide with several azimuthal angles.

The moment of inertia about the axis of symmetry is given by the expression:

$$I_s = 2m_H p^2 + 2m_S a^2/4 \quad (1)$$

and the remaining moments of inertia by the expression:

$$I_{1,2} = 2m_H[(n-m)^2 + p^2 \sin^2(\varphi + \alpha)] + 2m_S[m^2 + (a^2/4) \sin^2\varphi] \quad (2)$$

when  $\varphi$  is given the two complementary values given by the relation below. Quantities entering into these equations are defined as follows:

$$\begin{aligned} n &= b \sin\beta \cos\theta \\ m &= m_H n / (m_H + m_S) \\ p^2 &= [(a/2) + b \cos\beta]^2 + (b \sin\beta \sin\theta)^2 \\ \alpha &= \tan^{-1}[(b \sin\beta \sin\theta) / (b \cos\beta + a/2)] \\ \varphi &= -\frac{1}{2} \tan^{-1}[\sin 2\alpha / (\cos 2\alpha + m_S a^2 / 4m_H p^2)] \end{aligned}$$

where  $a$  is the  $S-S$  distance,  $b$  the  $S-H$  distance,  $\beta$  the angle between the  $S-H$  bond and the projection of the  $S-S$  bond,  $2\theta$  the azimuthal angle, or angle

TABLE II. Principal maxima in the hydrogen persulfide band at  $5007.1\text{ cm}^{-1}$ .

$K$	$^PQ(K)$ ( $\text{cm}^{-1}$ )	$^RQ(K)$ ( $\text{cm}^{-1}$ )	$\frac{^RQ(K) - ^PQ(K)}{4K}$	$\frac{^RQ(K-1) - ^PQ(K+1)}{4K}$
0		5012.0		
1	5002.3	21.0	4.67	4.80
2	4992.8	29.5	4.59	4.73
3	83.2	37.6	4.53	4.60
4	73.4	45.6	4.51	4.64
5	63.4	52.9	4.48	4.64
6	52.8	60.3	4.48	4.63
7	41.8	67.3	4.48	4.65
8	30.1	74.6	4.51	4.64
9	18.7	81.1	4.51	4.66
10	6.8	87.1	4.51	4.62
11	4896.2	93.0	4.47	
12		99.4		

## Rotational Constants

$$\begin{aligned} (A' - B') &= 4.50\text{ cm}^{-1} \\ (A'' - B'') &= 4.64\text{ cm}^{-1} \end{aligned}$$

between  $H-S-S$  planes, and  $m_H$  and  $m_S$  are the masses of the hydrogen and sulfur atoms.

In making the calculations,  $a$  was given the electron diffraction value,  $2.05\text{ \AA}$ . For reasons given above the  $H-S$  distance was taken to be  $1.334\text{ \AA}$  and the  $H-S-S$  angle was assumed to be  $92^\circ 16'$ , the apex angle in  $\text{H}_2\text{S}$ .

The small moment of inertia varies roughly as the square of the  $S-H$  distance, which is not known exactly. It is very insensitive to the  $S-S$  distance, the  $H-S-S$  angle and to the azimuthal angle. A change of  $0.01\text{ \AA}$  in the  $S-H$  distance produces a greater effect than a change of  $180^\circ$  in the azimuthal angle. Consequently it is evident that no very definite conclusion regarding the azimuthal angle can be drawn from the rotational spacing of the  $2\mu$ -band. Though the agreement is best for an azimuthal angle of about  $90^\circ$  it must be regarded as satisfactory for any angle.

The general appearance of the band is compatible with the angle mentioned. None of the  $^PQ$ - or  $^RQ$ -branches are missing near the band center nor do they show evidence of splitting, and the minimum at the center may be attributed largely to the presence of the parallel type band component rather than to asymmetry. The hydrogen persulfide molecule becomes a symmetrical top when the azimuthal angle is very close to  $90^\circ$  but it is not very unsymmetrical even for the two extremes of this angle. The angle could consequently deviate rather greatly from  $90^\circ$  without having a significant effect upon the appearance of the band.

TABLE III. Moments of inertia and rotational constants for hydrogen persulfide model.

Azimuthal angles ( $2\theta$ )	Moments of inertia ( $\text{g cm}^2 \times 10^{40}$ )			Rotational constants ( $\text{cm}^{-1}$ )	
	$I_1$	$I_s$	$I_2$	$B$	$(A-B)$
$0^\circ$	5.76	115	121	0.24	4.62
$60^\circ$	5.75	116	120	0.24	4.63
$140^\circ$	5.72	120	116	0.24	4.65
$180^\circ$	5.72	121	115	0.24	4.65

<sup>8</sup> P. A. Giguère (to be published).

It should be noted, however, that the rotational constant shows that the  $S-S-H$  angles must be near to  $90^\circ$  unless the  $S-H$  distance is abnormally long. This fact offers very strong support for the chain structure, since such angles are rather improbable for any other structure.

#### 4. CONCLUSION

As has been shown, the character of the hydrogen persulfide spectrum offers very strong support for a chain structure of the molecule, but gives no very direct information regarding the azimuthal angle, though the apparent hybrid character of the  $2\mu$ -over-

tone band makes the *cis*-planar model quite improbable. The significant differences between the overtone  $S-H$  band and the  $O-H$  overtones of hydrogen peroxide are probably related to differences in the angle in these two molecules. It is hoped that a study of the fundamental of  $\nu_4$ , the twisting vibration, may be made in the near future. The presence of this band in the infra-red spectrum would definitely exclude the *cis*-planar form. If the molecule has neither planar form the double minimum in the torsional potential would probably give rise to a detectable doubling of this band which would possibly permit an estimate to be made of the azimuthal angle.

## The Vibrational Spectra of Molecules and Complex Ions in Crystals. II. Benzene\*†

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(Received March 28, 1949)

The infra-red spectrum of crystalline benzene has been studied at  $-12^\circ\text{C}$ ,  $-65^\circ\text{C}$  and  $-170^\circ\text{C}$  as well as the liquid at  $28^\circ\text{C}$ . The lines are extremely sharp, the mean line width for fundamentals being  $7\text{ cm}^{-1}$  in the crystal. In three cases, it is less than the spectral slit width. All out-of-plane degenerate modes are split by about  $10\text{ cm}^{-1}$ . Selection rules are obeyed and agree with the reported x-ray structure. All ungerade fundamentals are observed directly, some for the first time. Fifty-two combination bands are observed. The frequency assignments of Ingold *et al.* are confirmed except for the  $B_{2u}$  species. Evidence is cited for re-assigning  $\nu_{14}$  from  $1648\text{ cm}^{-1}$  to  $1310\text{ cm}^{-1}$  and  $\nu_{15}$  from  $1110\text{ cm}^{-1}$  to  $1150\text{ cm}^{-1}$ . Ingold's isotopic data does not conflict with this change. Combination frequencies involving torsional lattice modes are apparently observed at  $-170^\circ\text{C}$ .

### I. INTRODUCTION

THE study of the infra-red and Raman spectra of crystals is a potentially powerful but as yet little used tool in the determination of molecular and crystal structure. In the first paper in this series<sup>1</sup> it was shown that in the harmonic approximation the spectrum of the crystalline solid (Raman or infra-red) should consist of only a relatively small number of extremely sharp lines, and that in this approximation the simple selection rules suggested by Halford<sup>2</sup> are correct. It was further pointed out that, particularly in the case of molecular crystals, this state of affairs should be most nearly approached at low temperatures.

The utility of the crystal in studying molecular vibrations arises, as has been pointed out by Halford,<sup>2</sup> from the fact that the crystalline field produces a new set of selection rules which are, in general, less strict than for the vapor. Some of the previously forbidden vibrations may become allowed, but their frequencies

will be shifted very little, if at all. In addition, the fact that the lines are usually very sharp, particularly at low temperatures, may be of considerable importance in dealing with a spectrum as complicated as that of benzene. The polarization properties of the lines may supply further information.

The determination of the normal vibrations of the benzene molecule has been the subject of a long series of investigations.<sup>3</sup>

The most successful attack has been the comprehensive study by Ingold and co-workers,<sup>4</sup> utilizing the infra-red and Raman spectra of benzene and five deuterio-benzenes, together with the Redlich-Teller frequency product rule. Their frequency assignments appear to be largely correct.

Several attempts have been made to calculate the benzene frequencies from an assumed potential function.<sup>5-8</sup> In particular, Miller and Crawford have calcu-

\* The work reported here was supported in part by the ONR under Contract N6ori-88, Task 1.

† Based on a thesis submitted by Robert D. Mair in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Brown University.

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<sup>1</sup> D. F. Hornig, *J. Chem. Phys.* **16**, 1063 (1948). Hereafter called I.

<sup>2</sup> R. S. Halford, *J. Chem. Phys.* **14**, 8 (1946).

<sup>3</sup> See G. Herzberg, *Infra-Red and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 362.

<sup>4</sup> C. K. Ingold *et al.*, Parts I-VIII, *J. Chem. Soc.*, 912-987 (1936); Part IX, *ibid.*, 1210 (1936); Part X, *ibid.*, 1728 (1937); Parts XI-XXI, *ibid.*, 222-333 (1946). Hereafter designated simply by the part number.

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<sup>6</sup> K. W. F. Kohlrausch, *Zeits. f. physik. Chemie* **308**, 305 (1935).

<sup>7</sup> R. C. Lord and D. H. Andrews, *J. Phys. Chem.* **41**, 149 (1937).

<sup>8</sup> W. G. Penney and J. Duchesne, *Bull. Soc. Roy. Sci., Liege* **11**, 514 (1939).