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Molecular Structure and the Force Constants of Hydrogen Disulphide

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The molecular configuration of hydrogen disulphide has been discused and C_2–symmetrical structure model has been proposed

The force constants of H_2S_2 have been calculated, by means of a quadratic potential fonction assumed for the same model. 2509, 882, 509 and 202 cm^{-1} symmetrical, and 2577 and 886 cm^{-1} unsymmetrical fundemantal vibration frequencies which were detected both in the IR and R, have been used for the calculation of the force constants.

INTRODUCTION

The structures of the hydrogen peroxide, the sulphure monochloride and the similar molecules such as 1,2 dihalogenoethane have been the object of many experimental works, but little attention has been given to the structure of the hydrogen disulphide.

The simplest molecule similar to H_2S_2, with 0–0 bond as the internal rotation axis, is the hydrogen peroxide. A number of models has been suggested at one time or another for H_2O_2.

Up to now, the investigations of the hydrogen peroxide spectra have not led, due to great experimental difficulties, to an unambigous result as to its structure. These works, however, definitely ruled out some of the proposed models (1), (2). At least two strong Raman shifts are seen in its infrared spectra. This concurrence proves that hydrogen peroxide and the similar molecule such as hydrogen monochloride and hydrogen disulphide cannot have a center of symmetry. In fact if the molecule has a center of symmetry, transition that are allowed for this molecule in the infrared, are forbidden in the Raman spectrum, and conversely, transitions that are allowed in the Raman, are forbidden in the infrared. More explicitly, we may also say, in the infrared, only transitions between states of opposite symmetry with respect to a center of symmetry (İ) can take place ($g \longleftrightarrow u$); whereas, in the Raman effect only transitions between states of the same symmetry with respect to (İ) ($g \longleftrightarrow g$, $u \longleftrightarrow u$) (3), This eliminates definitely both, linear symmetrical model $D_{\infty h}$ and the bent model D_{2h}. Thus, only U and Y shape planar structure models with C_{2h} symmetry and non-planar structure model with C_2 symmetry remain as possibilities to be considered, according to the observed spectroscopic data.

Penney and Sutherland (4) were led to the structure with C_2 symmetry from a theoretical investigation of the electronic strcture of the H_2O_2 like molecule. The essential feature of the argument given is that the electrons of two internal atoms arrange themselves to form the strongest possible bond and in so doing, render the charge density on these atoms unsymmetrical about the 0–0 or S–S axis. It was shown that the interaction of the stable form of this two electronic clouds is the dominant factor in determining the stable form, in which the azimuth, of one half of the molecule with respect to the other is approximately 90° and all other types of interactions are less significant.

Although infrared absoption spectra of the H_2O_2 observed by many investigator may be construed as a suggestion for C_2 model, among of them, it was only Giguère (5) who gave some evidence to this possibility. The same author assigned the band observed at 550 cm^{-1} to the torsional motion ν_4 of the OH groups about 0–0 axis.

From the similarity of the electronic structure, the molecule of sulphure monochloride, S_2Cl_2 may be expected to have the same configuration as that of the hydrogen peroxide. Morino and Misushima (6) have taken the Raman spectrum and measured the dipole moment, to see if the experimental results can be explained on the basis of this model. Observed Raman frequencies can be brought into agreement with the theoretically calculated values for molecular model in which the azimuth of one half of the molecule with respect to the other is assumed to be 90°. Also Palmer's electron diffraction experiment (7) is in good agreement with the results of Morino and Mizushima.

Bernstein and Powling (8) measured the Raman frequencies and the infrared absorptions of S_2Cl_2 and found 104 cm^{-1} which may be due to the torsinoal motion of the SCl groups about the S–S axis and proved the two –planar C_2 –symmetrical structure model of the molecule.

Stevenson and Beach (9) who investigated the hydrogen disulphide by means of the electron diffraction, reported the S–S distance to be 2,05 A. This distance corresponds closely to the single bond distance for sulphur atoms. Whereas the double bond covalent radious of S is reported to be 0,90 A (10). By eliminating the possibility of double bond between the sulphur atoms in the hydrogen disulphide, it is concluded that the H_2S_2 has a chain structure and the hydrogens are attached to different sulphurs.

The first spectroscopic data on hydrogen disulphide are the three Raman shifts obtained for the liquid by Fehér and Baudler (11) and Fehér, Lane and Winkhaus (12). The only existing infrared spectroscopic data for the gas phase, was concerned with the rotational structure of the first overtone of the S–H stretcching vibration which has been observed in the vicinty 5000 cm^{-1}. Thus valuble information about H_2S_2 in especially about its moment of inertia has been given by Wilson and Badger (13) however this investigation was not sufficient to propose a definit structural model for the molecule.

The recent infrared spectra of heydrogen disulphide (14) is taken in the solid phase at liquid-air teperature. In this work, the torsional vibration (ν_4) around S–S bond, has been detected through the combination of the ν_4 with the unsymmetrical bending vibration ν_6. The calculated value for this fundamental vibration which is the only oscillation that can be used to prove the possibility of C_2 configuration of H_2S_2, is found to be 202 cm^{-1}

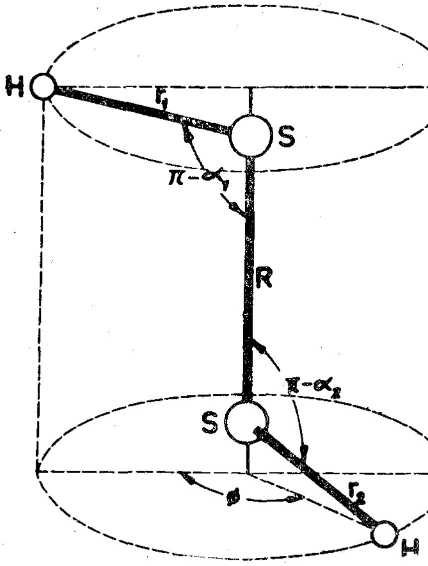

Fig. 1.

It may be concluded, therefore that H_2S_2, S_2Cl_2 and H_2O_2 should have the similar configurations, that is the first should have the same symmetry as that of the latters.

FORCE CONSTANTS IN THE HYDROGEN DISULPHIDE

The skeleton and the normal vibrations of hydrogen disulphide are shown in Fig. 1. and Fig. 2., respectively

The four-atom molecule which has the chain structure with point group syymmetry C_2 can have six normal modes which may be described as: the symmetrical S–H vibration ν_1 (a), the unsymmetrical S–H vibration υ_5 (b), The symmetrical S–H bending vibration υ_2 (a), the unsymmetrical S–H bending vibration υ_6 (b), the S–S valence vibration υ_3 (a) and lastly the torsional oscillation υ_4 (a).

The observed infrared fundemental vibrations and the comcombination bands (13), (14), all of which are used for calcula-

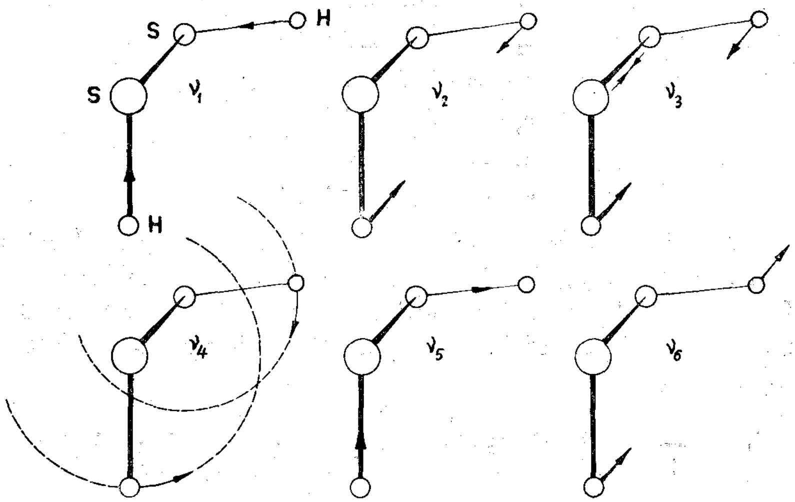

Fig. 2. Normal vibrations of the hydrogen disulphide

ting the fundamental frequencies are listed in Table 1. together with the Raman shifts (12).

Table 1

Gas (IR) cm^{-1}	Liquid (R) cm^{-1}	Soild (IR) cm^{-1}	Assignement
....	509	501) 518)	ν_3
875) 897)	....	....	ν_6
....	882.	....	ν_2
....	....	1070	$\nu_6+\nu_4$
2577	....	....	ν_5
....	2509	....	ν_1
3065	....	....	$\nu_3+\nu_5$
3400	....	....	$\nu_5+\nu_6$
5007	....	....	$\nu_1+\nu_5$

The six fundamental frequencies are calculated according to the data which are given in Table. 1, and the value of these frequencies are tabulated below:

$$\nu_1 = 2509\ \text{cm}^{-1}$$
$$\nu_2 = 882\ \text{cm}^{-1}$$
$$\nu_3 = 509\ \text{cm}^{-1}$$
$$\nu_4 = 202\ \text{cm}^{-1}$$
$$\nu_5 = 2577\ \text{cm}^{-1}$$
$$\nu_6 = 886\ \text{cm}^{-1}$$

A quadratic potential fonction has been assumed by Morino and Mizushima (6) for the S_2Cl_2 molecule of C_2 symmetry. This fonction has been used to evaluate the force constants in the molecule. In the cas of H_2S_2 this potential fonction can be written as,

$$V = \frac{1}{2} k_{S-S} (\Delta R)^2 + \frac{1}{2} k_{S-H} [(\Delta r_1)^2 (\Delta r_2)^2] - k'_{S-H}. (\Delta r_1) (\Delta r_2)$$

$$+ \frac{1}{2} \delta r_0^2 (\Delta\alpha_1)^2 (\Delta\alpha_2)^2 - \delta' r_0^2 (\Delta\alpha_1) (\Delta\alpha_2) + \gamma r_0^2 (\Delta\Phi)^2$$

The symbols which are used in the fonction, have the following meaning: ΔR, Δr_1, Δr_2 are the changes in the S–S and the two S–H distances, r_0 being the equilibrium S–H distance, $\Delta\alpha_1$, and $\Delta\alpha_2$ are the changes in the angle between the S–H bonds and the extension of the S–S bond,and $\Delta\Phi$, the change in azimuthal angle. k, δ and γ are the force costants for the squared terms, and k′ and δ' are those for the crossed terms.

The secular equation which has been derived from the potential fonction may be factored into two equation, one corresponding to the symmetrical and the other to the unsymmetrical vibrations (Appendix).

As the unsymmetrical vibrations ν_5 and ν_6 have been determined directly and precisely in the gas infrared spectrum of hydrogen disulphide, the following quatities are obtained from secular equation (B),

$$k_{S-H} + k'_{S-H} = 3{,}77\ 10^5\ \text{dynes/cm}$$
$$\delta_{SSH} + \delta'_{SSH} = 1{,}20\ 10^5\ \text{dynes/cm}$$

The solution of the secular equation corresponding to the symmetrical vibrations are less accurate than that of the second

(B), on account of the υ_1, υ_2, and υ_3 which were detected in the Raman spectrum in the liquid phase, on one hand, υ_4 was calculated by means of combination band observed in the solid on the other hand.

The following quantities are obtained from the first secular equation (A):

$$k_{S-S} = 2{,}53\ 10^5 \text{ dynes/cm}$$
$$k_{S-H} - k'_{S-H} = 3{,}62\ 10^5 \text{ dynes/cm}$$
$$\delta_{SSH} - \delta'_{SSH} = 0{,}70\ 10^5 \text{ dynes/cm.}$$
$$\gamma = 0{,}1\ 10^5 \text{ dynes/cm.}$$

The quantities which have been found by solving the two equations were used to calculate the force constants listed in Table. II.

Table II

Force constants of H_2S_2 (dynes/cm). 10^{-5}

k_{S-H}	3,69	(k_1)
k'_{S-H}	0,07	(k_1')
k_{S-S}	2,53	(k)
δ_{SSH}	0,95	(δ)
δ'_{SSH}	0,25	(δ')
γ	0,1	

The only force constant reported for hydrogen disulphide until now is the k_{S-S} (11). Fehér was used his own Raman shift of 510 cm^{-1} and calculated this constant as to be 2,512 .10^5 dynes/cm. This value is in good agreement with the results of the present work.

APPENDIX

The secular equations corresponding to the symmetrical vibration (A) and the unsymmetrical vibration (B) can be written in the following form:

$$(A)\quad \begin{vmatrix} Ak-\lambda^2 & E(k_1-k'_1) & F\,(\delta-\delta')r^2_0 & O \\ 2Ek & B(k_1-k'_1)-\lambda^2 & G\,(\delta-\delta')r_0{}^2 & 2H\gamma \\ 2Fk & G(k_1-k'_1) & C\,(\delta-\delta')r_0{}^2-\lambda^2 & 2K\gamma \\ O & H(k_1-k'_1) & K\,(\delta-\delta')r_0{}^2 & D\gamma-\lambda^2 \end{vmatrix} = O$$

$$(B)\quad \begin{vmatrix} B(k_1+k'_1)-\lambda^2 & G\,(\delta+\delta')r_0{}^2 \\ G(k_1+k'_1) & C\,(\delta+\delta')r_0{}^2-\lambda^2 \end{vmatrix} = O$$

wehere

$$A = \frac{2}{M} \qquad E = -\frac{\cos \alpha_0}{M}$$

$$B = \frac{1}{M} + \frac{1}{M} = \frac{1}{\mu} \qquad F = \frac{\sin \alpha_0}{M\ r_0}$$

$$C = \frac{1}{M_1}\left(\frac{2}{R^2{}_0} + \frac{2\ \cos\alpha_0}{R_0 r_0} + \frac{1}{r_0{}^2}\frac{M}{\mu}\right) \qquad G = \frac{\sin \alpha_0}{MR_0}$$

$$D = \frac{2\sin\alpha_0}{M}\left(\frac{\cos^2\alpha_0}{R_0} + \frac{M}{\mu r_0{}^2} + \frac{2\cos\alpha_0}{R_0 r_0}\right) \qquad H = \frac{\cos\alpha_0 \sin^2\alpha_0}{MR_0}$$

$$K = \frac{\sin\alpha_0}{M}\left(\frac{2\cos\alpha_0}{R_0{}^2} + \frac{\cos^2\alpha_0 + 1}{R_0 r_0}\right)$$

$\lambda/2\pi$: normal frequency,

M : Mass of sulphur atom,

M_1 : Mass of hydrogen atom,

R_0 : Equilibrium distace between two sulphur atoms (2,05 A)

r_0 : Equilibrium distance between sulphure and hydrogen atoms (1,334 A)

$\pi-\alpha_0$: Angle S–S–H (92° 16')

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ÖZET

Hidrojen disülfidin spektroskopik verilere göre molekül yapısının münakaşası yapıldı ve iki düzemli,zincirsel C_2 simetrisine sahip bir molekül olması gerektiği sonucuna varıldı.

H_2S_2 molekülünün 2509, 822, 509 ve 202 cm^{-1} frekanslarındaki simetrik titreşimleri ile 2577 ve 886 cm^{-1} frekanslarındaki antisimetrik titreşimleri İnfrared ve Raman spectrumlarında gözlenen fondamental ve kombinezonlardan faydalanarak bulundu. Teklif edilen modele uygun bir potansoiyel fonsiyon kullanılarak, bu moleküle ait kuvvet sabitleri hesaplandı.

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