

The Infrared Absorption Spectra of H₂S, HDS and D₂S

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The Infrared Absorption Spectra of H_2S , HDS and D_2S

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The infrared spectra of H_2S , HDS and D_2S have been examined up to $15\ \mu$ with a monochromating prism spectrometer, and the results compared with the Raman spectra. The fundamental frequencies have been assigned with reasonable certainty, and a calculation has been made of the frequencies corresponding to infinitesimal amplitude. The cruder methods of the vibrational-rotational spectrum suggest a vertical angle of 110° , as compared with 92° obtained previously from a rotational analysis.

THERE have been many investigations of the infrared absorption spectrum of hydrogen sulphide.¹⁻⁷ The possible presence of impurities has led to the postulation of bands which do not exist,^{1, 2, 4} and to the denial of others which are really there.^{3, 5} We have re-examined the spectra of this compound and its deuterium isotopes between 1 and $15\ \mu$ with a monochromating prism spectrometer.

The weakness of absorption throughout the spectrum has increased the difficulties of observation and interpretation; and although finality is not claimed, we think we have presented at least a concordant account of the three isotopic molecules, while we have stressed in what follows the uncertainties which would justify further investigation.

¹ W. W. Coblentz, Pub. Carnegie Inst., No. 35, pp. 52 and 178 (1902).

² A. H. Rollefson, Phys. Rev. **34**, 604 (1929).

³ H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931).

⁴ W. Mischke, Zeits. f. Physik **67**, 106 (1931).

⁵ H. H. Nielsen and A. D. Sprague, Phys. Rev. **37**, 1183 (1931).

⁶ A. D. Sprague and H. H. Nielsen, Phys. Rev. **43**, 375 (1933).

⁷ P. C. Cross, Phys. Rev. **47**, 7 (1935).

EXPERIMENTAL

1. Apparatus

The general arrangement has been fully described,⁸ the only important modifications being the replacement of the Downing galvanometer by a photo-relay using a Zernicke and a Moll galvanometer, and the fitting of the absorption cells and thermopile with potassium bromide end-plates. We would emphasize the need for great care in the calibration of a prism spectrometer, particularly in the use of the unresolved maxima of atmospheric CO_2 bands, since the position of these changes considerably with the percentage of carbon dioxide present. In our experience the use of two absorption cells, one evacuated and the other containing the gas under examination, seems to be essential. The omission of this precaution inevitably leads to the inclusion of false absorption regions, and to a good deal of imaginary resolution.

A preliminary run was made with the rocksalt prism, and the located regions of absorption were then more closely examined with the appropriate

⁸ A. B. D. Cassie and C. R. Bailey, Proc. Roy. Soc. **A132**, 252 (1931).

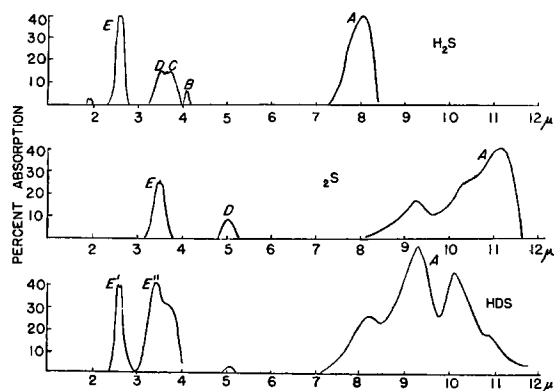


FIG. 1. The infrared spectra of H_2S , D_2S and HDS .

prism of quartz, fluorite, or rocksalt. Readings were taken at intervals of approximately 0.02μ in order to have full advantage of the available resolution. The slit widths used and the spectral interval included are as already given.⁹ Corrections were made for the temperature of setting and of observing, and for the error in setting at minimum deviation. The absorption cell length was 45 cm.

2. Preparation of the gases

H_2S was prepared by three different methods: (i) by warming calcium sulphide with a saturated solution of magnesium chloride; the gas was then bubbled through water and baryta solution and over P_2O_5 ; it was then liquefied by solid CO_2 and fractionated; (ii) by passing H_2S into a suspension of magnesium oxide in water, and gently warming the resulting $\text{Mg}(\text{HS})_2$; the gas so obtained was washed and dried as before; (iii) as a check, a sample was prepared from aluminum sulphide: an apparatus was devised which could be swept out with dry, CO_2 -free air and evacuated; water was dropped onto Al_2S_3 from within the apparatus and the resulting H_2S passed over baked calcium chloride and P_2O_5 , and collected in a trap from which it could be fractionated; the sample so prepared was found to be free from CO_2 . It was found that neither KHS nor baryta saturated with H_2S removed CO_2 completely.

D_2S was first obtained by method (iii) above, with 99.2 percent D_2O . Additional Al_2S_3 was introduced as a drying agent. Curve (a) (Fig. 2) shows that the sample contained HDS , probably

⁹ C. R. Bailey, A. B. D. Cassie and W. R. Angus, Proc. Roy. Soc. **A130**, 134 (1930).

derived from the calcium chloride and Al_2S_3 . The former was therefore discarded, and the latter baked in vacuum before use, when curve (b) (Fig. 2) was obtained: it will be seen that although the amount of HDS was considerably reduced, complete elimination was not effected.

HDS was obtained by mixing equal volumes of H_2S and D_2S , and allowing the mixture to come to equilibrium.

EXPERIMENTAL RESULTS

A general comparison of the three spectra is given in Fig. 1, from which a rough measure of the relative intensities can be made. The adjusted percentage absorptions of Figs. 2–4 should not be used for that purpose.

H_2S

Band A: 8.089μ ; 1236 cm^{-1} (rocksalt); Fig. 2. There has been much discussion as to the existence of this band, but we have found it in all samples of H_2S , and all doubt is removed by the appearance of the corresponding isotopic bands. Although a good deal of the rotational structure is revealed, there is no evidence of separation into *P* and *R* branches, and the band is altogether different in appearance from the corresponding

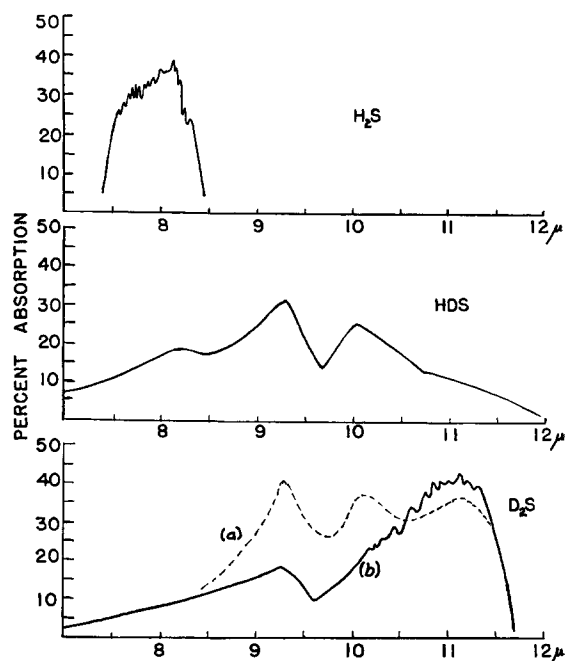


FIG. 2. ω_2 or band *A*.

fundamentals of D_2O and H_2O . It is just possible that the band may be overlaid by a difference tone. A number of the most prominent lines show a separation of the order of 7 cm^{-1} .

Band B: $4.127\text{ }\mu$; 2423 cm^{-1} (fluorite). This band of low intensity is probably real and different from that located at $4.25\text{ }\mu$ by Coblenz,¹ Rollefson,² and Mischke,⁴ which is most likely due to CO_2 .

Bands C and D: $3.8\text{ }\mu$; (fluorite) Fig. 3. In this region there are peaks at $3.91\text{ }\mu$ (2558 cm^{-1}), $3.70\text{ }\mu$ (2703 cm^{-1}), and $3.435\text{ }\mu$ (2911 cm^{-1}). The separation between 3.70 and $3.43\text{ }\mu$ is 208 cm^{-1} , and is much too large to enable these peaks to be considered as a doublet: we therefore conclude that $3.70\text{ }\mu$ consists of the unresolved Q and R branches of a band, C , whose P branch is at $3.91\text{ }\mu$. The line (-7) of Nielsen and Barker's Curve C^3 may perhaps be the weak Q branch.

Band E: $2.636\text{ }\mu$; 3764 cm^{-1} (quartz); Fig. 4. The contour shows the presence of P , Q , and R branches in agreement with the complete resolution obtained by Nielsen and Barker.³

Band F: $1.94\text{ }\mu$; 5155 cm^{-1} (quartz). The band was not resolved, but has been shown to be a doublet by Sprague and Nielsen,⁶ whose value for the center is 5130 cm^{-1} .

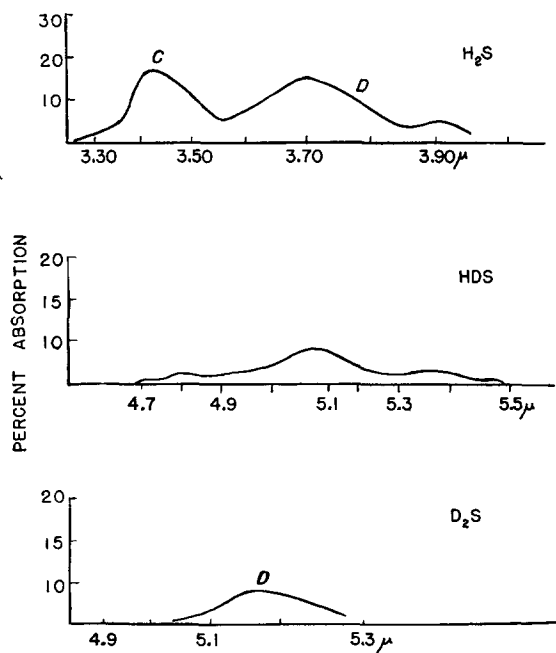


FIG. 3. Bands C and D.

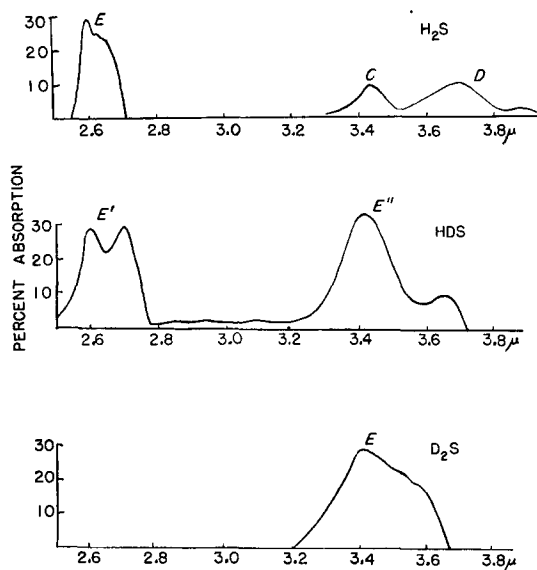


FIG. 4. Band E.

D_2S

Band A: $11.14\text{ }\mu$; 898 cm^{-1} (rocksalt); Fig. 2 (b). The band is similar in structure to Band A of H_2S ; there is some faint evidence of rotational structure, but a spacing of 3.5 cm^{-1} corresponding to the 7 cm^{-1} is hardly within the limits of resolution of our spectrometer.

Band C: $5.155\text{ }\mu$; 1940 cm^{-1} (fluorite); Fig. 3. The band was extremely weak, but has the one-sided appearance often associated with the presence of a Q branch.

Band E: $3.57\text{ }\mu$; 2798 cm^{-1} (quartz); Fig. 4. The band resembles that of H_2S , but again no resolution was obtained.

HDS

Band A: $9.28\text{ }\mu$; 1078 cm^{-1} (rocksalt); Fig. 2. The shape of the band serves to emphasize the difficulties in the interpretation of the spectra. Two peaks are observed at 1078 and 988 cm^{-1} . The separation between them is some 90 cm^{-1} , a not unlikely value for a P - R spacing in HDS; but the total frequency range included in the band is some 340 cm^{-1} against 180 for H_2S and 135 for D_2S . We are faced with the absence or extreme weakness of a P branch in the latter substances, or alternatively the appearance of a new band in HDS. The determination below of the force constant k_3 makes it certain that the three peaks 1236 , 898 , and 1078 cm^{-1} correspond in the three

substances. Since HDS is asymmetric, ω_2 for this molecule should possess a small component of change of electric moment along the least axis of inertia, and the band should therefore show a weak Q branch, and it is tempting to find in the sharper character of the peak at 1078 cm^{-1} some faint evidence for its existence.

Band C at $5\text{ }\mu$: (fluorite); Fig. 3. There is a much extended region of weak absorption from 4.5 to $6.0\text{ }\mu$, with peaks in the neighborhood of 4.7 and $5.1\text{ }\mu$.

Band E': $3.5\text{ }\mu$: (quartz); Fig. 4. The peak at 2721 cm^{-1} is probably due to H_2S , and that at 2938 cm^{-1} to D_2S and HDS (see assignments).

Band E'': $2.7\text{ }\mu$: (quartz); Fig. 4. The peaks at 3724 and 3849 cm^{-1} are probably both due to HDS and to H_2S .

THEORETICAL

A very striking and complete analysis of the band at 9911 cm^{-1} has been carried out by Cross⁷ from measurements in the photographic infrared. The bond angle in the normal state was found to be $92^\circ 20'$, while for water vapor the corresponding value is $105^\circ 6'$.¹⁰ It is difficult to predict qualitatively the effect upon the vertical angle of the exchange of sulphur for oxygen: the distance of the hydrogen atom from the central atom increases from 0.97 to 1.34 \AA so that lessened interaction between the extreme hydrogen atoms would favor closer approach to the theoretical valence angle for p - s binding of 90° ; on the other hand the electronic structure of the sulphur atom tends to make the angular rigidity less.

An investigation of a purely vibrational spectrum will not yield results of the same high order as those obtained by Cross, but for the purpose of comparison with heavier molecules whose rotational structure cannot as yet be unravelled, it is interesting to enquire what accuracy may be expected when the number of approximations is reduced as far as possible. We therefore propose to apply the potential energy expression used by Van Vleck and Cross in their consideration of the water vapor molecule.¹¹ For this purpose we require an estimate of the mechanical frequencies ν_i associated with infinitesimal amplitudes; and

we now proceed to an attempted assignment of frequencies.

ASSIGNMENTS

We will adopt the conventional numbering of Dennison, in which ν_3 is the asymmetrical frequency, ν_1 the short wave and ν_2 the long wave symmetrical frequencies. The limiting angle above which the axis of least inertia is perpendicular to the symmetry axis is $88^\circ 16'$ for H_2S , and for D_2S is $86^\circ 38'$: hence we may expect ν_3 to have a more or less well developed Q branch. A , the smallest moment of inertia, is about $0.9B$, whereas for water, $A=0.5B$; and from Dennison's curves¹² we see that this Q branch will be much weaker in H_2S than in H_2O . This may account for our inability to resolve the band. For H_2S we therefore take 2632 cm^{-1} as ω_3 . The peak at 2911 cm^{-1} gives a force constant of some 4.9×10^5 dynes per cm which seems to be too high to allow this band to count as an H_2S fundamental, although the possibility should not be overlooked. We have to confess that we can offer no reasonable assignment for it, and since it appears in all samples of the gas we do not think it can be ascribed to an impurity. ω_1 is found in the Raman spectrum of the gas at 2615 cm^{-1} .¹³ ω_2 we must place at $8\text{ }\mu$, although the peculiar structure of the band again makes it difficult to determine the center exactly: a comparison of our own and Rollefson's curve² suggests 1236 cm^{-1} as the most reasonable value, and the data for the isotopic molecules are in agreement. 2432 cm^{-1} is then $2\omega_2$, and since 3794 cm^{-1} has a Q branch it must be $\omega_3 + \omega_2$. As far as one can say from our own work and that of Sprague and Nielsen⁶ the band at $1.9\text{ }\mu$ has no Q branch and may be $2\omega_1$, rather than $\omega_1 + \omega_3$. Weizel¹⁴ has shown for H_2O that even overtones of ω_3 are not to be expected, and we may probably transfer his reasoning to this case. 9911 cm^{-1} ($\omega_3 + 3\omega_1$) and $10,100\text{ cm}^{-1}$ ($3\omega_3 + \omega_1$) have already been assigned by Cross.⁷

D_2S . We assign 898 cm^{-1} to ω_2 , 1940 cm^{-1} , to ω_3 , and 2793 cm^{-1} to $\omega_3 + \omega_2$. The only reference we have been able to find to the Raman spectrum occurs in an authors' abstract of a paper presented last year to the Vienna Academy;¹⁵ as far

¹⁰ R. Mecke, *Zeits. f. Physik* **81**, 313 (1933).

¹¹ J. H. Van Vleck and P. Cross, *J. Chem. Phys.* **1**, 357 (1933).

¹² D. M. Dennison, *Rev. Mod. Phys.* **3**, 280 (1931).

¹³ S. Bhagavantam, *Nature* **126**, 502 (1930).

¹⁴ W. Weizel, *Zeits. f. Physik* **88**, 214 (1934).

¹⁵ A. Dadiou and H. Kopper, *Nature* **136**, 235 (1935).

TABLE I. *Proposed assignment of Raman and infrared bands of H₂S, HDS, and D₂S.*

	H ₂ S (cm ⁻¹)	HDS (cm ⁻¹)	D ₂ S (cm ⁻¹)
ω_2	1236	1078	898
ω_1	2615	(1910) calc.	1906
ω_3	2632	(2619) calc.	1940
$2\omega_2$	2423	2110	—
$\omega_3 + \omega_2$	3794	3724	2798
$\omega_1 + \omega_2$	—	2938	—
$2\omega_1$	5155	3849	—
$3\omega_1 + \omega_3$	9911	—	—
$3\omega_3 + \omega_1$	10100	—	—
?	2911	—	—
	—	988	—

as we can say, the paper has not yet been published. The mixture of H₂S and D₂S gives lines at 1880 and 2585 cm⁻¹. These are certainly the values for the liquid state, and we find for D₂O and H₂O that the percentage change in frequency in passing from the liquid to the gaseous state is the same for both molecules. Hence we may assume that the change in D₂S is of the same order as in H₂S, and take the calculated gaseous frequency 1906 cm⁻¹ as ω_1 .

HDS. The peculiar double nature of ω_2 has already been described, and the additional possibilities discussed should be borne in mind. For the purposes of approximate calculation of ω_3 and ω_1 , we may use the valence force expression derived by Lechner¹⁶ for the asymmetrical triatomic molecule. The somewhat complicated expression is a cubic for the frequencies, and on inserting the values $K_{\text{H}_2\text{S}} = 3.92$, $K_{\text{D}_2\text{S}} = 4.09$, and $d(=2k_3 \text{ as determined below}) = 0.47 \times 10^5$ dynes/cm, together with the observed frequency $\omega_2 = 1078$ cm⁻¹, we find $\omega_3 = 2619$ and $\omega_1 = 1910$ cm⁻¹ in agreement with the values calculated for the gas from Dadiou and Kopper's results. We may thus assume that the weak, extended region of absorption at 5 μ contains ω_1 of HDS together with ω_3 of D₂S. 3.5 μ (band D') contains ω_3 of H₂S, ω_3 of HDS, and $\omega_1 + \omega_2$ of HDS at 2938 cm⁻¹. Band D'' at 2.64 μ contains $2\omega_1$ and $\omega_3 + \omega_2$ of HDS, with $\omega_3 + \omega_2$ of H₂S. There are indications of $2\omega_2$ for HDS at 4.8 μ .

The above conclusions are summarized in Table I.

¹⁶ F. Lechner, Wien. Ber. **141**, 291 (1932).

DETERMINATION OF THE FORCE CONSTANTS

The significance of the force constants will be seen from the potential energy expression used by Van Vleck and Cross:¹¹

$$V = \frac{1}{2}[k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + 2k_3 r_1^0 (\Delta \gamma)^2] + k_{12} \Delta r_1 \Delta r_2 + 2^{\frac{1}{2}} k_{13} r_1^0 (\Delta r_1 \Delta \gamma + \Delta r_2 \Delta \gamma). \quad (1)$$

On the assumption $r_1^0 = r_2^0$, and $k_1 = k_2$, the solution of the secular equation yields

$$(a_{11} - a_{12})\lambda^3 - k_1 + k_{12} = 0, \quad (2)$$

$$[(a_{11} + a_{12})\lambda_1, \lambda^2 - k_1 - k_{12}][a_{33}\lambda_1, \lambda^2 - k_3] - 2[a_{13}\lambda^2 - k_{13}]^2 = 0.$$

The coefficients a_{ij} are not given explicitly in the original. They have therefore been deduced and recorded for various values of the vertical angle, γ (Table II). If m and M are the relative atomic masses of H and S, respectively,

$$\mu = m(m+M)/(2m+M), \quad \mu_3 = m^2/(2m+M).$$

Since the coefficients are all of dimensions $[M]^{\frac{1}{2}}$, we may write $\lambda^2 = 4\pi^2 c^2 \nu^2 = 5.863 \times 10^{-2} \nu^2$, and thus obtain the k 's in dynes per cm.

The frequency equations apply to the corrected frequencies, ν_i , and not to the observed frequencies, ω_i . We have therefore adopted an expression of the type

$$E_{000} = X_1 V_1 + X_2 V_2 + X_3 V_3 + X_{11} V_1^2 + X_{22} V_2^2 + X_{33} V_3^2 + X_{12} V_1 V_2 + X_{23} V_2 V_3 + X_{31} V_3 V_1, \quad (3)$$

where $V_i = (n_i + \frac{1}{2})$, and have attempted a solution from the observed data. We have, for example, $\omega_{100} = E_{100} - E_{000}$ when E is expressed in cm⁻¹, and the values of X_i give the required frequencies ν_i : unfortunately only eight bands can be located and assigned with reasonable certainty for H₂S, and it has been necessary to calculate X_{12} from the D₂S spectrum on the assumption that the anharmonic constants in the

TABLE II.

a_{ij}	H ₂ S			D ₂ S		
	92°20'	105°	110°	92°20'	105°	110°
$a_{11} = a_{22} = \mu - \mu_3^2 \sin^2 \gamma / 2(\mu - \mu_3 \cos \gamma)$	0.971	0.971	0.971	1.886	1.886	1.884
$a_{12} = -\mu_3 \cos \gamma$.001	.008	.010	0.008	0.032	0.043
$a_{13} = a_{33} = (1/2 \sqrt{2}) \mu_3 \sin \gamma$.010	.010	.010	.039	.038	.037
$a_{33} = \frac{1}{4}(\mu + \mu_3 \cos \gamma)$.242	.240	.240	.473	.465	.462

two molecules show the same ratio (determinable from the reduced masses) as is found for the fundamentals,¹⁷ e.g., $(\omega_2/\omega_2^*)^2 = 1.87$. The results for H₂S are $X_1 = 2719$, $X_2 = 1294$, $X_3 = 2749$, $X_{11} = -37$, $X_{22} = -24$, $X_{33} = -11$, $X_{12} = +57$, $X_{23} = -74$, $X_{31} = -114$, and for D₂S, $X_1 = 1961$, $X_2 = 929$, $X_3 = 2003$, $X_{11} = -20$, $X_{22} = -13$, $X_{33} = -6$, $X_{12} = 30$, $X_{23} = -40$, $X_{31} = -62$, all in cm^{-1} . The high positive value for X_{12} is in accordance with the other observed data: furthermore we can now apply Teller's relationship¹⁷ between the symmetrical frequency ν_1 for the two molecules H₂S and D₂S and thus make an estimate of the vertical angle, γ . We have $(\nu_1/\nu_1^*)^2 = D(S+2H \sin^2 \gamma/2)/H(S+2D \sin^2 \gamma/2)$ where H, D, and S are the atomic masses of the respective atoms, and hence from $(2719/1969)^2$ we have $\gamma = 110^\circ$. This value is considerably greater than that of $92^\circ 20'$ deduced by Cross⁷ from the rotational structure of the band at 9911 cm^{-1} , but as will be seen below, it furnishes better agreement among the force constants in the vibrational spectrum, and on the whole one would expect the vertical angle for H₂S to be certainly not less than that of the water molecule, which is 105° .

That the mechanical frequencies so deduced cannot be far from true may be seen by solving a simplified valence force system for the two molecules.¹⁸ Without a knowledge of the force constants we can construct a cubic in the frequencies for the vertical angle:

$$\frac{p_1^2 p_2^2}{p_3^2} \cdot \frac{x^3}{1 + (2m/M)} - (p_1^2 + p_2^2 + p_3^2)x + 2p_3^2 \left(1 + \frac{m}{M}\right) = 0; \quad (4)$$

where $x = 1 + (2m/M) \sin^2 \alpha$, α being the semi-vertical angle, and $p_i = 2\pi\nu_i c$. On insertion of the frequencies deduced for infinitesimal amplitude, we find for H₂S that 2α is $111^\circ 26'$, and for D₂S that 2α is $111^\circ 30'$. The uncorrected frequencies give no such measure of agreement, the value for H₂S being 102° and for D₂S, 119° .

We may note in passing that the expression deduced by Rosenthal¹⁹ for the vibrational effect

¹⁷ E. Teller, Det kgl. Danske Videnskabernes Selskab (1934).

¹⁸ C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. A137, 622 (1932).

¹⁹ J. E. Rosenthal, Phys. Rev. 45, 426 (1934).

TABLE III. The force constants for H₂S and D₂S (in dynes/cm $\times 10^{-5}$).

	$k_1 - k_{12}$	$k_1 + k_{12}$	k_3	k_{13}
$92^\circ 20'$ H ₂ S	4.29	4.21	0.238	0.04
D ₂ S	4.40	4.27	0.239	0.04
110° H ₂ S	4.26	4.25	0.236	0.04
D ₂ S	4.33	4.34	0.234	0.04

in ω_2 , the asymmetric vibration, is incorrect. As given it is

$$\omega_3^*/\omega_3 = [1 - 2k\mu(\sin^2 \alpha + \mu \cos^2 \alpha)^{-1}], \quad (5)$$

where $k = \frac{1}{2}\Delta m(m + \Delta m)^{-1}$; $\mu = M/(2m + M)$; and 2α is the vertical angle. If the term on the left is squared, one obtains results of the right order. Miss Rosenthal's formula for the ratio of the two symmetric frequencies is useful: we have

$$(\omega_1^*/\omega_1)(\omega_2^*/\omega_2) = (1 - 2k\mu)^{\frac{1}{2}}(1 - 2k)^{\frac{1}{2}}. \quad (6)$$

Inserting $\nu_1 = 2719$, $\nu_2 = 1294$, and $\nu_1^* = 1961$, we have $\nu_2^* = 925$ compared with $\nu_2^* = 929 \text{ cm}^{-1}$ observed, and so obtain a good check on our assignments and observations.

THE FORCE CONSTANTS

We have solved the frequency Eq. (2) using the calculated values of γ for H₂S and D₂S. On comparison with H₂O it now seems fairly certain that the potential energy curves of a polyatomic molecule do not correspond sufficiently closely with those of the isotopic molecule to enable them to be used to give highly accurate values of the vertical angle, and in fact no reasonable solution for this angle can be obtained on the assumption that the force constants are the same for the two molecules. We have therefore examined the Van Vleck and Cross relationship for certain values of the angle, and summarize those for $92^\circ 20'$ and 110° in Table III.

Although the absolute value for k_1 must not be taken too literally, nevertheless it is significant that the larger value for γ tends to remove the discrepancies between H₂S and D₂S, and between $k_1 - k_{12}$ and $k_1 + k_{12}$. For HDS, with $a_{33} = 0.632$ for 110° , the uncorrected frequency 1078 cm^{-1} gives k_3 as approximately 0.216×10^5 dynes per cm as compared with 0.219 for H₂S and 0.218 for D₂S. It is interesting to record approximate

values for k_1 in the series H_2O , H_2S , and H_2Se : with uncorrected data these are 7.8, 4.0, and 3.2×10^5 dynes/cm.

For the sake of completeness we will remark that Végard²⁰ from an x-ray analysis gave a rectilinear structure for H_2S , at least in the solid. It is noteworthy that the observed frequencies give reasonable force constants if introduced into equations for a rectilinear model: the peculiar shape of the long wave fundamental would then have to be explained by invoking the presence of an unresolved Q branch; while all observed bands other than ω_2 and ω_3 must be interpreted as combination tones involving an inactive frequency. The only band in H_2S which cannot be so assigned is $2\omega_2$ at 2423 cm^{-1} , but the last point, together with the irregular nature of the rotational lines in the band at 2.6μ resolved by Nielsen and Barker,³ is sufficient to exclude the rectilinear structure.

While this paper was in preparation, Nielsen

and Nielsen²¹ published a brief note as a preliminary account of similar work. They confirm the existence of the long wave band at 8.0μ for H_2S , and the corresponding bands for D_2S and HDS . They do not appear to have located the fundamental ω_3 for D_2S ; in its place they give a band at 4.55μ and relate it to ω_3 of H_2S . This wave-length corresponds to a force constant of some 5.2×10^5 dynes/cm, and hence the frequency is much too high. The strong peak in HDS at 988 cm^{-1} also seems to have escaped observation. The following comparative table is given by Nielsen and Nielsen:

H_2S	HDS	D_2S
1.9μ	2.1μ	—
2.65	3.15	3.65μ
3.70	4.1	4.55
7.9	9.0	10.8

We wish to express our acknowledgments to Professor F. G. Donnan, F.R.S., for his continued interest in our work.

²¹ A. H. Nielsen and H. H. Nielsen, *J. Chem. Phys.* **4**, 229 (1936).

²⁰ L. Végard, *Nature* **126**, 916 (1930).

The Rate of Thermal Decomposition of Deuterium Iodide

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The partition functions for deuterium iodide have been calculated at temperatures from 300 to 1500°K . Constants were calculated for an equation to give the value of the free energy function at any temperature within this range. A similar calculation was made for D_2 using the data of Johnston and Long. Combining these with the data for the other molecules involved, the equilibrium constant for the decomposition of deuterium iodide and for the exchange reaction was calculated. These results can be differentiated and integrated to give values for ΔH° , ΔC_p and ΔS° . The

equilibrium constant for the reaction $\text{H}_2 + 2\text{DI} \rightleftharpoons \text{D}_2 + 2\text{HI}$ has been plotted against the temperature from 300 to 1500°K . The equilibrium constant for the reaction $\text{DI} \rightleftharpoons \frac{1}{2}\text{D}_2 + \frac{1}{2}\text{I}_2$ has been calculated. The rate of thermal decomposition of deuterium iodide was measured between 660 and 719°K . The experimental ratio of the rate constants for the reactions $\text{HI} \rightarrow \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2$ and $\text{DI} \rightarrow \frac{1}{2}\text{D}_2 + \frac{1}{2}\text{I}_2$ has been compared with the theoretical value of Wheeler, Topley and Eyring. Contrary to their expectations, it was found to be lower than the theoretical value.

THE effect on the rate of several chemical reactions produced by substituting deuterium for hydrogen has been studied by various investigators.¹ Because of the simple homogeneous and bimolecular character of the thermal decomposition of hydrogen iodide, the corre-

sponding reaction with deuterium appears to be one of the most important reactions to study at the present time, since theoretical calculations can be made for this case with some certainty. We have therefore studied the rate of thermal decomposition of deuterium iodide between 660 and 719°K .

Since the reverse reaction also occurs, the rate of decomposition of hydrogen iodide depends

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¹ For a review of the subject, see Urey and Teal, *Rev. Mod. Phys.* **7**, 34 (1935).