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The Band Spectrum of HS

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The absorption spectrum of HS is obtained by passing repeated flashes from a source of continuous background through a discharge tube in which HS radicals are formed from H_2S by pulses of radiofrequency current synchronized to precede immediately the flashes. The spectrograms obtained show only one band at 3237A. The rotational structure indicates that the ground state is an inverted $^2\Pi$, and the excited state a $^2\Sigma$. Because of the strong $\Lambda\Sigma$ coupling in the $^2\Pi$ state the doublet is wide, and since the Boltzmann factor greatly favors $^2\Pi_{3/2}$, only the strongest branch, Q_2, from the $^2\Pi_{1/2}$ state is found. From $^2\Pi_{3/2}$ the $^QP_{21}$ and $^RQ_{21}$ satellite branches as well as P_1, Q_1 and R_1 are found. For the $^2\Pi$ ground state the best values of the constants obtained are $B_0''=9.47$; $D_0''=-0.001$ and $A=-378.6$ cm^{-1}. The constants for the excited $^2\Sigma$ state are $B_0'=8.30$; $D_0'=-0.00078$, and $\gamma=0.32$ cm^{-1}. The origin of the 0,0 band is at 30,659.1 cm^{-1}.

Introduction

THE band spectra for the hydrides of all the elements in the first two rows of the periodic table (except the rare gases) have previously been found with the one exception of HS. By analogy with the known spectrum of OH the stable states of HS can be predicted. The presence of free HS radicals is also indicated by the experiments of Avery and Forbes[1] on the photolysis of H_2S in solution. As these radicals should also exist in the gaseous state, several unsuccessful attempts have been made in the past[2] to excite its emission spectrum, chiefly by discharges through H_2S. We first attempted to excite an emission spectrum of HS by collision of H_2S molecules with resonance excited mercury atoms. No bands caused by HS were found. The reason the spectrum has not been found must be either that the HS radicals react chemically before they radiate, or that their spectrum is masked by that of sulfur. It was found that these difficulties can be avoided by working in absorption using the method described by Oldenberg[3] for studying the OH absorption spectrum.

Experimental

H_2S was made by the reaction of HCl and FeS. The gas was dried with P_2O_5 and $CaCl_2$, and passed into a previously evacuated glass storage reservoir. From here it was flowed continuously during the exposure through the absorption tube and out through the pumps. The pressure was maintained at about 1 mm. The HS molecules were formed in the absorption tube by passing a short pulse of radiofrequency current between two large electrodes above and below the tube. The length of the optical path between the electrodes, where absorption by HS occurred, was 70 cm. As the discharge also formed sulfur vapor that would hide the HS absorption, this had to be removed by flushing the tube completely with H_2S between each flash of the exposure. The duration of the pulse of current was found to be important. Sulfur is chemically stable, and its concentration is proportional to the length of the pulse; HS is relatively short-lived, and its concentration rapidly approaches a limiting value. Thus there must be an optimum duration for the pulse that will produce as much HS as possible without concealing it with sulfur absorption. This was found to be of the order of a hundredth of a second. The mean lifetime of the HS radical must be at most as long as this.

Radiofrequency current was supplied from a power oscillator tube built by Sloan, Thornton and Jenkins.[4] Keying was accomplished by interrupting the d.c. power supply to the filament. The source of continuous background for absorption was the Lyman continuum of a low

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[1] W. H. Avery and G. S. Forbes, J. Am. Chem. Soc. **60**, 1005 (1938).

[2] W. H. Bair, Astrophys. J. **52**, 301 (1920); N. O. Stein, Astrophys. J. **77**, 270 (1933).

[3] O. Oldenberg, J. Chem. Phys. **3**, 266 (1935).

[4] D. H. Sloan, R. L. Thornton and F. A. Jenkins, Rev. Sci. Inst. **6**, 79 (1935).

pressure spark in a quartz capillary. This was used with a 1μf condenser and set off at the desired instant by breaking down a series spark gap with a tickler electrode activated by a Ford ignition coil. To get sufficient resolving power to observe the narrow, rather faint absorption band lines of HS it was necessary to use the new 21-foot, 30,000-line/in. aluminum grating now in the Paschen mounting. The source was bright enough to give a satisfactory exposure in 900 sparks or 5 hours with one spark every 20 seconds. As the position of the spectrum was unknown, a cylindrical lens could not be used to increase the speed of the grating.

The switches for the radiofrequency and source were mounted on two shafts driven by a synchronous motor at 300 and 3 r.p.m., respectively, with a 100 : 1 reduction gear between them. Each circuit had two switches in series, one on each shaft, so that each received a short impulse every 20 seconds. The timing was regulated by the angle between the switches for the two different circuits. On all the plates the time between the end of the discharge and the spark was kept less than a thousandth of a second. No optical shutter was needed to keep the emission spectrum out of the spectrograph, as no such spectrum is known. A schematic diagram of the apparatus is shown in Fig. 1.

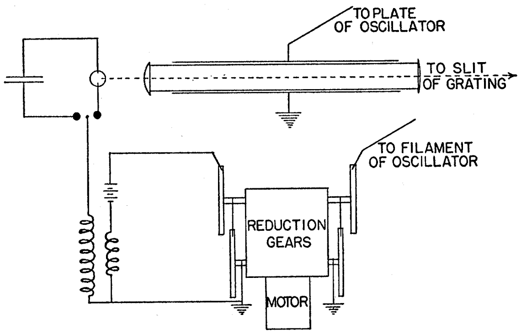

FIG. 1. Schematic diagram of apparatus.

ANALYSIS

The only new band appearing on the plates had its strongest head at 3237A, and was degraded toward long wave-lengths. The wide spacing of the lines made it at once recognizable as a hydride band. Since in homologous series of molecules the corresponding electronic frequencies generally decrease with increasing mass, it was suspected that the observed band was the HS band analogous to the OH band at 3064A. Accordingly, it should represent a transition from an inverted $^2\Pi$ normal state to an excited $^2\Sigma$ state.[5] With this assumption, it was possible to predict the constants of the two states fairly accurately, and the analysis of the band structure confirmed these predictions so well that there remained no doubt as to the correctness of this interpretation.

The value of $B''=h/8\pi^2I''c$ was predicted by interpolation between the values of r_e for the ground states of the hydrides PH and HCl lying on either side of HS in the second row of the periodic table.[6] Thus we obtained $B''=9.43$, as compared with the value 9.47 finally resulting from the analysis. An approximate value of B' could then be obtained by finding the difference $B'-B''$ from the second differences in the easily recognizable branches P_1, Q_1 and $^QP_{21}$. The combination principle was then used to identify the branches R_1, in which there is considerable blending because it forms the head, and $^RQ_{21}$, which is partly superimposed on other stronger lines. Thus the five strongest branches of the sub-band $^2\Sigma\leftarrow{}^2\Pi_{3/2}$ were identified, and the results are represented in Table I as well as in the Fortrat diagram of Fig. 2.

Two features in which the structure apparently differed radically from that of the corresponding OH band were at first puzzling. The first was the apparent absence of the other sub-band $^2\Sigma\leftarrow{}^2\Pi_{1/2}$, and the second was the very large intensity of the satellite branches $^QP_{21}$ and $^RQ_{21}$ as compared to those in OH. However, it was soon apparent that both of these were a consequence of the much stronger spin-orbit coupling in HS. The coupling coefficient A, which determines the splitting between $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, can be estimated from the splitting in the normal ^3P state of the sulfur atom.[7] The separation $^3P_0-{}^3P_2$ in S is -572 cm$^{-1}=-3a/2$. Assuming the ratio $A/a=0.97$ as found in HCl$^+$,

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[5] W. Jevons, *Report on Band-Spectra of Diatomic Molecules* (University Press, Cambridge, 1932), p. 164.

[6] R. Mecke, Zeits. f. Elektrochem. **36**, 581 (1930).

[7] R. S. Mulliken, Rev. Mod. Phys. **4**, 1 (1932); R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, 1932), p. 397.

one obtains $A=-370$ cm^{-1}, in close agreement with the value -378.6 resulting from our analysis.

Since the temperature of the absorbing molecules in our experiment, as shown from the rotational intensity distribution, is not far above room temperature, the Boltzmann factor favors the lower $^2\Pi_{3/2}$ state by a factor of about 6 with the doublet separation given above. Hence the $^2\Sigma\leftarrow{}^2\Pi_{1/2}$ sub-band is expected to be very faint. From the predicted A it was possible to identify the head and a few lines of the strongest branch, Q_2, of this sub-band, as shown in Table I and Fig. 2.

The unexpectedly large intensities of the satellite branches is now a necessary consequence of the large value of A for HS. The parameter $Y=A/B$ appearing in the intensity formulas[8] is -40 in our case, compared to -7.5 for OH. The observed relative intensities of all of the branches are in good agreement with the theoretical equations for this value of Y.

CONSTANTS

The electron configurations of the two states here involved are $3p\sigma^2\ 3p\pi^3\ {}^2\Pi$ and $3p\sigma\ 3p\pi^4\ {}^2\Sigma$. Since these only differ in the λ value of one electron, the Π and Σ states must stand approximately in the relation of pure precession to each other.other.[9, 10] This simplifies the calculation of constants.

For the $^2\Sigma$ state, the rotational terms are given by

$$F(J)=B_v^*K(K+1)+D_v^*K^2(K+1)^2 \\ +\tfrac{1}{2}\gamma[J(J+1)-K(K+1)-S(S+1)], \quad (1)$$

where

$$B_v^*=B_v-q$$

and

$$q=\frac{2B_v^2l(l+1)}{\nu(\Pi,\Sigma)}. \quad (2)$$

Calculation of q shows that within the experimental error it is negligible, so we may take $B_v^*=B_v$. The spin doubling constant γ may be evaluated directly from the separations $Q_1(K)-{}^QP_{21}(K)=\gamma(K+\frac{1}{2})$. We find $\gamma=0.32$, as compared to the value 0.41 calculated on the assumption of pure precession. That this value is reasonable is seen from comparison with those for the corresponding $^2\Sigma$ states in other hydrides.[10]

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[8] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928); L. T. Earls, Phys. Rev. **48**, 423 (1935).

[9] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

[10] R. S. Mulliken and R. Christy, Phys. Rev. **38**, 87 (1931).

TABLE I. *Strongest branches of the band* $^2\Sigma\leftarrow{}^2\Pi$.

	R_1 BRANCH			Q_1 BRANCH			P_1 BRANCH		
J	λ	I		λ	I		λ	I	
1.5	3237.099	1*	30882.97	3240.666	7*	30849.00	3242.412	5	30832.37
2.5	3236.765	8*	30886.16	3242.002	5	30836.27	3245.480	6*	30803.23
3.5	3236.600	6*	30887.74	3243.548	5	30821.57	3248.791	5	30771.83
4.5	3236.600	6*	30887.74	3245.304	5	30804.90	3252.294	5	30738.69
5.5	3236.867	8*	30885.19	3247.284	4	30786.11	3256.010	4	30703.61
6.5	3237.269	1	30881.36	3249.465	4	30765.45	3259.928	4	30666.71
7.5	3237.994	1	30874.44	3251.871	5	30742.69	3264.080	3	30627.70
8.5	3238.916	0	30865.65	3254.513	3	30717.74	3268.432	1	30586.92
9.5	3240.092	0	30854.45						

	$^RQ_{21}$ BRANCH			$^QP_{21}$ BRANCH			Q_2 BRANCH		
J	λ	I		λ	I		λ	I	
0.5							3279.780	0	30481.10
1.5				3240.666	7*	30849.00	3279.258	4	30485.95
2.5	3236.867	8*	30885.19	3242.055	4	30835.77	3279.121	4*	30487.22
3.5	3236.600	8*	30886.16	3243.664	4	30820.47	3279.121	4*	30487.22
4.5	3236.600	8*	30886.16	3245.480	6*	30803.23	3279.413	5	30484.51
5.5	3237.099	1*	30882.97	3247.459	2	30784.45	3279.908	2	30479.91
6.5	3237.580	2	30878.39	3249.703	00	30763.20	3280.698	1	30472.57
7.5	3238.294	1	30871.58	3252.119	00	30740.35			

* Indicates blend with another identified line.

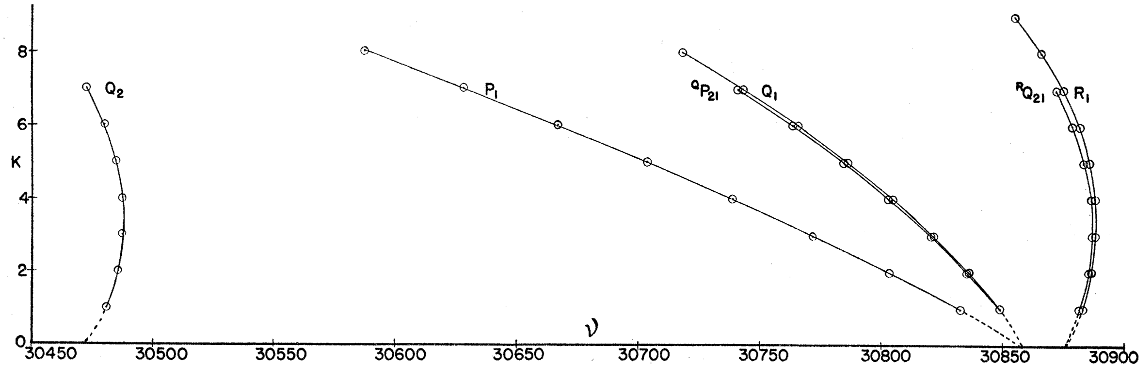

FIG. 2. Fortrat diagram.

To find the values of B_0' and D_0', we have treated the Δ_2F' values obtained from $R(J)-P(J)$ by the usual least-squares method. The results are $B_0'=8.30$ cm^{-1} and $D_0'=-0.00078$ cm^{-1}.

The determination of the constants of the $^2\Pi$ normal state presented more difficulty. This results chiefly from the fact that in the $^2\Sigma \leftarrow {}^2\Pi_{1/2}$ sub-band only one branch, Q_2, is observed, and this yields only one component, T_c, of the Λ-doublets. Since the doubling is largest in $^2\Pi_{1/2}$, it must be taken into account in evaluating the constants.

Since the value of A/B_v is large, it is possible to represent the rotational terms of this $^2\Pi$ state by the case *a* formula

$$F(J)=\text{Const.}+B_v^*J(J+1)+D_v^*J^2(J+1)^2, \quad (3)$$

where $B_v^*=B_v\pm B_v^2/A$ represents an effective value of B_v for the particular sub-state. The plus and minus signs refer to $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, respectively. To evaluate B_0^* and D_0^*, the terms T_{1c} were first obtained by subtracting the frequencies of the Q_1 and $^QP_{21}$ lines from the calculated $^2\Sigma$ terms, the terms T_{1d} by subtracting the P_1 lines, and the terms T_{2c} by subtracting the Q_2 lines. From the average of the T_{1c} and T_{1d} levels the constants obtained are $B_0^*(^2\Pi_{3/2})=9.231$ and $D_0^*=-0.00025$ and from the T_{2c} levels, $B_0^*(^2\Pi_{1/2})=9.567$ and $D_0^*=-0.0023$. The value of $B_0^*(^2\Pi_{1/2})$ is now subject to correction for the effect of the Λ-doubling.

For large negative values of A/B_v, expansion of the general energy expression for $^2\Pi$ states intermediate between case *a* and case *b* gives the following equations for the Λ-doubling:[10]

$$\Delta T_{1cd}=-(p/y^2+2q/y)(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+\tfrac{3}{2}), \quad (4)$$

$$\Delta T_{2cd}=p(J+\tfrac{1}{2}). \quad (5)$$

For the $^2\Pi_{3/2}$ state, Eq. (4) gives a very small doubling for low values of J. Experimentally it is only slightly greater than the error of measurement, but as far as can be determined it has the correct sign and magnitude, and follows the theoretical curve. For the $^2\Pi_{1/2}$ state we have no experimental value of ΔT_{2cd}, but it is necessary to know the magnitude of p to obtain the correct value of $B_0^*(^2\Pi_{1/2})$. Assuming pure precession, one obtains $p=0.46$, but this is probably somewhat too large, as in the analogous cases of OH and HCl$^+$. The observed value of $\gamma=0.32$ should be a better approximation to the true value of p. From this in Eq. (5), it is possible to calculate the average of the terms T_{2c} and T_{2d} in $^2\Pi_{1/2}$.

Treating these average values in the usual way, we then find $B_0^*(^2\Pi_{1/2})=9.60$ and $D_0^*(^2\Pi_{1/2})=-0.0025$. That this B_0^* is very nearly right is shown by calculating B_0 independently from $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ from the equation

$$B_v^*=B_v\pm B_v^2/A+\tfrac{1}{2}q\pm(p+2q)B_v/2A.$$

Taking the value $A=-378.6$ obtained below, we find $B_0=9.47$ and 9.37 from $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, respectively. The former of these is adopted as the correct value, since it involves experimental data only. The average value $D_0=-0.0014$ is probably correct only as to order of magnitude.

The magnitude of the spin doubling and the origin of the bands remain to be found. The electronic splitting of the $^2\Pi$ state may be found from the extrapolation to $K=0$ of the differences $T_2(K)-T_1(K)$. Theoretically this should give

$$\Delta T_{12}(0)=A-B+B^2/A-o-\tfrac{1}{2}p,$$

where

$$o=-\frac{1}{4}\frac{A^2l(l+1)}{\nu(\Pi,\Sigma)}=-2.34\text{ cm}^{-1}.$$

This gives $A=-378.9\text{ cm}^{-1}$. A better value of A and of ν_0 may be found from the following considerations. If $T(J)=T_0+F(J)$ then

$$\begin{aligned}
Q_1&=T_0'+F_1'(J)-[T_0''+F_{1c}''(J)],\\
P_1&=T_0'+F_1'(J-1)-[T_0''+F_{1d}''(J)],\\
\nu_0&=\tfrac{1}{2}\{Q_1-F_1'(J)+F_{1c}''J\\
&\qquad\qquad+P_1-F_1'(J-1)+F_{1d}''J\},\\
Q_2&=T_0'+F_2'(J)-[T_0''+F_{2c}''(J)],\\
\nu_0&=Q_2-F_2'(J)+F_{2c}''(J).
\end{aligned}$$

From these relations A is found to be -378.6 cm^{-1} and $\nu_0=30659.1$ cm^{-1}. The data are not sufficiently accurate or complete to permit any estimate of the system origin ν_e.

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On the Magnetic Scattering of Neutrons

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In this paper there is contained a full elaboration of two previously published short notes on the subject of magnetic scattering of neutrons together with a comprehensive treatment of certain sides of this problem which have already received some attention from other authors. After presenting the state of the problem in the introduction and discussing in detail our reasons for the choice of an interaction function between neutrons and electrons, and the nonmagnetic interaction between neutrons and nuclei, the various possible cases of coherent and incoherent scattering and depolarization phenomena are treated. Later applications to the theory of ferromagnetic scattering are kept in mind. The general expression for the cross section due to magnetic interaction is obtained and applied to various classes of phenomena (scattering by free, rigidly aligned, and coupled magnetic ions). The influence of the elastic form-factor is treated quantitatively with the aid of a simple model for the current distribution in the ion. Finally a series of performed or suggested experiments is discussed mainly from the point of view whether they will permit theoretical interpretation. Arrangements are described which will allow one to obtain a reliable value for the neutron's magnetic moment and also give insight into the magnetic constitution of the scatterer (ion or crystal) which will exceed the knowledge obtainable from macroscopic magnetic experiments.

I. INTRODUCTION

SOMETIME ago it was suggested[1] that a magnetic moment of the neutron should manifest itself in the scattering of slow neutrons from paramagnetic substances. The magnetic scattering should in some instances be several times as great as the total nuclear scattering if, for the neutron, a magnetic moment of two nuclear magnetons is assumed. This magnetic scattering could therefore be easily isolated by comparing the scattering cross section of the same atoms in different chemical combinations which show a varying magnetic susceptibility. It could also be separated from nuclear scattering by studying the angular distribution of the particles scattered from a single paramagnetic compound. This is due to the fact that magnetic scattering is, under practical conditions, strongly favored in the forward direction, whereas the nuclear scattering is isotropic. If the neutron moment is of the order of magnitude of a nuclear magneton the paramagnetic scattering provides a direct and simple method for its quantitative determination.

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[1] O. Halpern and M. H. Johnson, Phys. Rev. **51**, 992; **52**, 52 (1937).