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The Asymmetric Rotor. V. An Analysis of the 3.7-μ Band of H_2S by Punched-Card Techniques

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The H_2S band at 3.7μ described by Nielsen and Barker is interpreted as the R branch of band for which the induced moment is parallel to the least axis of inertia; between the ground state with moments of inertia determined by Cross and an upper state with moments 2.8_3, 3.1_0, and $6.0_2\times10^{-40}$ gcm² (reciprocal moments 9.90, 9.04, and 4.65 cm⁻¹, respectively). The band center is 2625 cm⁻¹. Punched-card methods were used to do the following calculations. The relative position and intensities of all the lines in the band are computed by the theory of the rigid rotor, their absorption coefficients α summed over an interval of 0.5 cm⁻¹, or $\frac{1}{5}$ of the slit width to give $\Sigma\alpha$. These are converted to transmissions, $e^{-q\Sigma\alpha}$, where q is an adjustable parameter. The transmissions over a range of 5 intervals are combined with suitable weight factors (1, 2, 4, 2, 1) to give the transmission through a "slit" of finite resolution and half width of 1 cm⁻¹. This computed transmission curve is compared directly with the actual experimental observations. These calculations were made for several estimates of the moments until a satisfactory fit was obtained.

INTRODUCTION

A VERY peculiar band of H_2S has been reported[1] at 3.7μ. We believe we can identify it as half of a fundamental of the asymmetric vibrational frequency ν_σ, where the induced moment is parallel to the least axis of inertia. This is contrary to the interpretation given in reference 1 as a complete band with no Q branch associated with an induced moment parallel to the intermediate axis. We believe it is impossible to identify the recorded curve as a complete band of an asymmetric rotor. Furthermore, there are certain reasonable restrictions on the moments of inertia of H_2S in the infra-red to a range of values which cannot possibly give rise to a complete band of the shape recorded.

RANGE OF MOMENTS

From the combination band at 9911 cm⁻¹ Cross[2] has been able, by accounting for all the lines of a completely resolved spectrogram, to determine the effective moments of inertia of the ground state and of the level $n_\sigma=1$, $n_\pi=3$, $n_\delta=0$. This gives the orders of magnitude of the moments of inertia of H_2S and of their dependence on the three vibrational quantum numbers. These trends in the moments are supported by an approximate analysis of the 2.6-μ band for which the data is also given in reference 1. A complete analysis of this band cannot be given at this time because of the more serious lack of resolution, although the principal features can be accounted for by moments $I_A=2.6_9$, $I_B=3.6_5$, and $I_C=6.0_6\times10^{-40}$ gcm². Fourteen sets of estimates of the moments have been tried, and we feel that the correct values cannot be far from those given.

Thus the moments obtaining in the upper level of the 3.7μ are fairly well prescribed. Furthermore, the three moments are not independent parameters, for Darling and Dennison[3] have shown that although $I_C-I_B-I_A=\Delta$ is not zero (as it would be for a rigid planar molecule), nevertheless it is dependent only on two parameters, $\Delta=k_\delta(n_\delta+\frac{1}{2})-k_\sigma(n_\sigma+\frac{1}{2})$. The coefficient of $n_\pi+\frac{1}{2}$ is extremely small for this type of molecule. Now k_σ and k_δ can be estimated from the fundamental frequencies, giving 0.231 and 0.025, respectively. Conversely, since the moments of two states have been determined exactly by Cross, these coefficients can be evaluated empirically as 0.314 and 0.040, respectively. The difference between these pairs of values is caused by the fact that the frequencies we have used in the expression for Δ given by Darling and Dennison were

[1] H. H. Nielsen and E. F. Barker, Phys. Rev. **37**, 727 (1931). The absorption curve in this paper has been redrawn in Fig. 1. A. D. Sprague and H. H. Nielsen, J. Chem. Phys. **5**, 85 (1937), state that this band was re-measured, with the same results as given in the first paper. This problem has recently been discussed with Professor Nielsen. The absence of absorption in the "P" and "Q" region has again been asserted by R. H. Noble and H. H. Nielsen, Paper Z9 of the programme of the New York Meeting of the American Physical Society, January, 1947.

[2] P. C. Cross, Phys. Rev. **46**, 536 (1934); *ibid.* **47**, 7 (1935); J. Chem. Phys. **5**, 370 (1937); P. C. Cross and B. L. Crawford, Jr., *ibid.* **5**, 371 (1937) and **5**, 621 (1937).

[3] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).

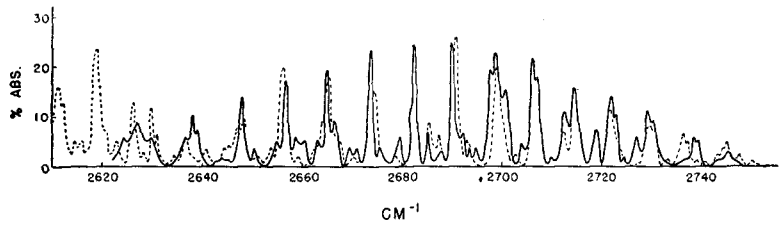

FIG. 1.

not corrected to equilibrium values, since band centers and anharmonicities are not yet known for H_2S.

The expression for Δ, with the two experimentally determined coefficients, thus enables us to calculate Δ for every vibrational state, and get a relation between I_C, I_B, and I_A, thus reducing the number of unknown parameters to two. This is of value not only in reducing the labor of the trial-and-error method, but of restricting the range of moments so that the appearance of the bands of a given molecule in the infra-red must fall into certain general types.

METHOD

The interpretation of the 3.7-μ band is based on a method[4] of analyzing partially resolved infra-red spectra by taking into account all possible transitions, for a suitable range of possible values of the moments of inertia. The elaborate and extensive calculations are done by International Business Machine punched-card machines. In this stochastic method a series of estimates of these moments of inertia are made, from which all the rotational energy levels of both states are computed by means of the table[5] of the reduced energy levels (of the rigid rotor) for the chosen degree of asymmetry. From these the positions, ν, and absorption coefficients, α, of all lines are calculated, the latter based on the transition probabilities[6] of the asymmetric rotor and Boltzmann factors. Each line in the spectrum is represented by a card bearing its position and absorption coefficient.

The cards, i.e., lines, are arranged in increasing wave number ν, and α summed over various intervals corresponding to slit widths. A series of slit widths 0.5, 1, $2\cdots$cm^{-1} are first tried, to find the order of magnitude of the one corresponding to the experimental data. Deviations from Beer's law can be allowed for in part by further elaborations made feasible by having the calculations on punched-cards. The absorption coefficients α are summed again over a fraction of the approximate slit width, and summary cards bearing $\sum\alpha$ prepared. Next transmissions, $e^{-q\sum\alpha}$, for each interval are obtained for each summation $\sum\alpha$ for several values of q, which is an unknown parameter involving the square of the induced dipole moment and the number of molecules in the path length. This was done by collation with a master set bearing x, $e^{-1.0x}$, $e^{-0.9x}\cdots e^{-0.1x}$, and a suitable shift of decimal point. The calculated total transmission (at approximately the experimental conditions of slit shape and width) at a given frequency, is calculated by adding to the transmission of the small interval at that frequency the transmissions of neighboring intervals on each side multiplied by weight factors, whose rate of decrease describes the slit shape and

TABLE I. Summary of constants of H_2S. The 3.7-μ band is between the ground state (000) whose constants were determined by Cross and the upper state (100). The constants for the (130) state found by Cross are given in the last column for comparison. Here I_A, I_B, and I_C are the moments of inertia in units of 10^{-40} gcm^2, with discrepancy $\Delta=I_C-I_A-I_B$; a, b, c are the corresponding reciprocal moments in units of cm^{-1}, with asymmetry $\kappa=(2b-a-c)/(a-c)$.

	State 000	100	130
I_A	2.693	2.82_7	2.824
I_B	3.096	3.09_6	3.340
I_C	5.926	6.01_9	6.261
Δ	0.137	0.097	0.097
a	10.393	9.90	9.910
b	9.040	9.04	8.379
c	4.723	4.65	4.470
κ	0.523	0.673	0.437

[4] G. W. King, P. C. Cross, and G. B. Thomas, J. Chem. Phys. **14**, 35 (1946).

[5] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27 (1943). This table of reduced energy levels has been extended to $J=11$ and 12, and now covers all the important levels appearing in this type of band.

[6] P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 210 (1944). By extrapolating the wings of the more important sub-branches, the small contribution of $J=13$ and 14 levels to the extreme ends of the bands were incorporated.

width. A few trials determine a "slit width and shape" equivalent to that obtaining in the experimental work, and also determine q. The small interval over which the α's were summed was 0.5 cm^{-1}, and the weighting factors were 1, 2, 4, 2, 1, so that the half-width was 1 cm^{-1}. A value of $q=0.053$ matched the height of most of the principal peaks. If the amount of gas in the light path had been measured, this value of q would have determined the magnitude of the induced dipole in this transition.

In this way a calculated transmission curve can be made and compared numerically with the observed percentage transmission. Successive estimates of the moments of inertia are made until a satisfactory fit with experiment is achieved.

RESULTS

It was found that the experimental curve of the 3.7-μ band of Nielsen and Barker can be reproduced quite well as the R branch of a band with induced moment parallel to the least axis of inertia, between the ground state with moments given by Cross,[2] and a vibrational state (100) with moments given in Table I. Curves for neighboring values of the moments were computed and give detectably poorer fits to the experimental data. On the basis of these, we estimate the uncertainties in a, b, and c are 0.03, 0.05, and 0.01 cm^{-1}, respectively. The band center is 2625 cm^{-1}.

DISCUSSION

The solid line in Fig. 1 is the experimental data given by Nielsen and Barker. The dotted curve is the calculated transmission curve obtained with the above moments, where it does not agree exactly with the experimental. The worst agreement is at the low wave number end, but this is where the observed absorption becomes zero instead of rising to the P branch, as predicted by the dotted curve.

It is our experience that the moments cannot be determined very accurately in this type of band in the absence of the absorption curve for the P branch, so that it did not seem worth while to try to fit the minor peaks in Fig. 1 any better. There seems to be no theoretical reason for the non-observance of the P branch. We hope to examine this infra-red band experimentally with a different type of spectrometer.