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An analysis of the 8.5-μ band of D_2O has been made by matching the observed transmission curve (published by Barker and Sleator) with a calculated curve. This was obtained by punched-card techniques developed for analyzing incompletely resolved spectra, in which the relative intensity and position of every line was computed by rigid-rotor theory for various choices of moments of inertia, and the absorption coefficients summed over a suitable "slit width." The band is caused by a transition in which the induced electric moment is parallel to the intermediate axis of inertia. Its center is at 1179 cm^{-1}. The most satisfactory fit was obtained with moments calculated by the empirical equation of Fuson, Randall, and Dennison which applies an isotope effect to the known moments of inertia of H_2O, corrected slightly for the known values of $\Delta = I_C - I_B - I_A$. The reciprocal moments are 15.38, 7.25, and 4.84 cm^{-1} for the ground state, and 16.50, 7.33, and 4.79 cm^{-1} for the upper state (the first deformation vibrational level).

INTRODUCTION

IN a previous paper[1] we have described a method, based on punched-card procedures, of analyzing band spectra of asymmetric rotors. The principle was to calculate the position and absorption coefficient of every line appearing in the band, and to sum the coefficients over appropriate slit widths. Trial-and-error procedures result in the determination of a set of moments for the upper and lower states. It was anticipated that this approach could yield effective moments of inertia even when the band was incompletely resolved.

Even with machine methods, the number of trials needed to determine the seven molecular constants is large. In order to investigate the possibilities of this approach, it has been first tried on the 8.5-μ band of D_2O. No vibrational-rotational bands of D_2O have hitherto been analyzed, so that the determination of moments of inertia in a vibrational state will be of interest in the theory of this molecule. This band is also suitable for an initial approach because the moments of the lower state are known exactly, and those of the upper state can be predicted by an empirical theory. With these constants known at least fairly closely, other questions in such analyses could be studied. For example, the analysis[2] of the pure rotation spectrum of

D_2O has shown that some of the rotational energy levels depart very greatly from those of the rigid rotor, chiefly on account of centrifugal distortion. There is, therefore, a question of whether our procedure is valid as long as it is based on the tables of reduced energy levels of rigid rotors. Another question is whether deviations from Beer's law, on account of the large number of lines of varying absorption coefficient in each slit width, would depend so much on the experimental conditions of source of radiation, slit width and shape, resolving power of the instrument, etc., as to invalidate the procedure.

ROTATIONAL LEVELS OF D₂O

A hitherto unanalyzed, incompletely resolved band of D_2O at 8.5μ has been reported by Barker and Sleator.[3] Unfortunately, the percentage transmissions were not given. However, the positions of the major peaks were measured accurately, and a graph given including subsidiary peaks. The richness of this spectrum in sharply defined peaks suggests that the moments of inertia of the two levels involved might be found by our procedure. Since the theory of distortion of the rigid-rotor levels is not adapted to our procedure, the position of the lines has been calculated on the basis of the rigid-rotor levels of both states. Although the term values of the rotational levels of the lower state are

[1] G. W. King, P. C. Cross, and G. B. Thomas, J. Chem. Phys. **14**, 35 (1946).
[2] N. Fuson, H. M. Randall, and D. M. Dennison, Phys. Rev. **56**, 982 (1939).

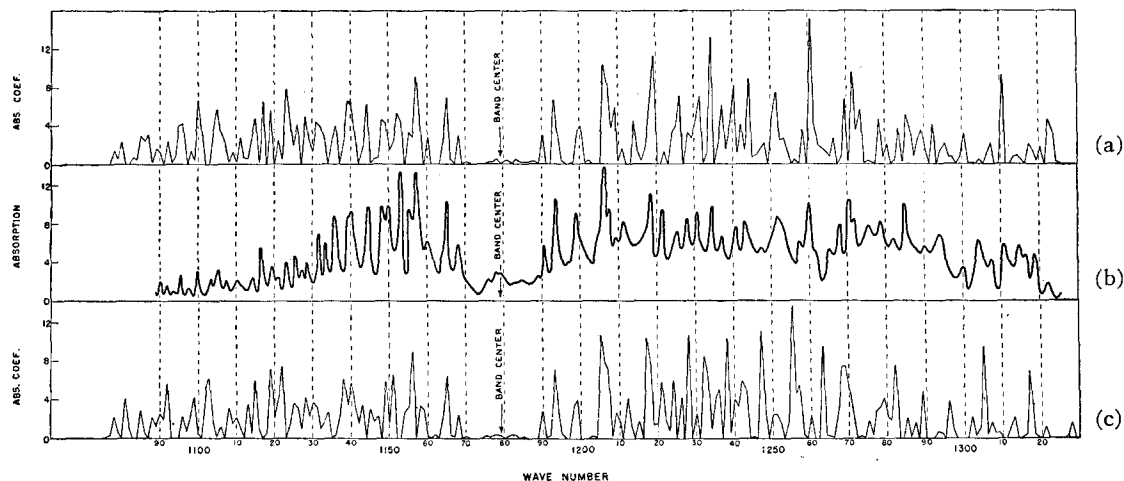[3] E. F. Barker and W. W. Sleator, J. Chem. Phys. **3**, 660 (1935).

FIG. 1. The middle curve is replotted from the table and curve given by Barker and Sleator (reference 3). The upper curve is based on the calculated moments, columns 2 and 7 of Table I. The adjusted moments in columns 3 and 8 give practically the same curve. The lower curve is calculated from the upper-state moments in column 5. The vertical scale is arbitrary in all cases.

known, they were not used because the corrections applied to upper and lower states largely cancel. Furthermore, the important lines in this band arise from levels of low K_{-1} (or τ) value where the amount of distortion is small in any case. For the lower state the effective reciprocal moments chosen by Fuson, Dennison, and Randall were used, namely 15.38, 7.25, and 4.83 cm^{-1} (corresponding to moments 1.820, 3.860, and 5.794$\times$10^{-40} gcm^2). For the upper state, the formulas given by these authors for computing the isotope effect on the anharmonicity coefficients in the known expressions for the moments of inertia of H_2O were used. The predicted reciprocal moments for the first deformation vibrational level, the upper state of the 8.5-μ band, are accordingly 16.50, 7.33, and 4.77 cm^{-1} (corresponding to moments 1.696, 3.818, and 5.867$\times$10^{-40} gcm^2).

RESULTS

With these constants, the procedure described in reference 1 was followed, with arbitrary band center. The absorption coefficients were summed over various slit widths. A slit width of 1 cm^{-1} was found to be appropriate, and the sums of the absorption coefficients over this interval were plotted for several choices of moments of inertia of the upper state. The calculations were done for transition probabilities appropriate to

both a- and b-type bands, where the induced moment is parallel to the axis of the least and intermediate moment of inertia, respectively. There is no doubt this is a b-type band. Because numerical values of the percent transmission are not available, further determination of slit width and shape to fit the experimental curve better were not made. Investigation of this point for other bands of this general structure indicate that the relative intensities would not be modified seriously by such considerations.

The experimental curve is shown in Fig. 1(b). This was drawn from the table of position of the principal peaks and careful measurement of the curve given by Barker and Sleator. The curve for the moments based on the isotope effect on H_2O moments (given above and in columns 2 and 7 of Table I) is shown in Fig. 1(a). It agrees surprisingly well with the experimental, considering the fact that deviations from the rigid rotor and from Beer's law were not incorporated. By superposition of the calculated and observed curve the band center was located at 1179 cm^{-1}.

In order to test the sensitivity of the calculated curve to changes in the moment, other moments (given in Table I) were tried. The set in column 4 was one of the early approximations and gave a curve with some of the features of the experimental curve (especially in the center),

but the agreement was by no means as satisfactory as that of Fig. 1(a).

During the course of this work, Dickey and Nielsen[4] reported the re-measurement of this band with a grating, and gave effective moments for the upper state listed in column 5 of Table I. Naturally, these moments were tried by our procedure. The resulting curve is given in Fig. 1(c). The over-all agreement is not as good as with the predicted moments of column 7. We believe the reason for the disagreement of the moments in column 5 is that, although those moments were obtained from a better resolved spectrum, they were based only on levels of low J. Our experience in analyzing these spectra is that moments based on the low levels, although easy to calculate, are subject to large errors, and that better approximations to effective moments can be made on the basis of lines involving high J values, or as in the procedure used here, on all the lines involved. The reason is that the term values for low J have one or two less significant figures than those of high J. For example, the peaks in the center of the band can be fitted by any of the moments in Table I equally well. It could be argued that this is offset by distortion increasing with J. However, we can define the effective moments as those fitting the lowest τ levels at all J values, and since the peaks in this type of spectrum arise from these levels (chiefly because they have large Boltzmann factors), the moments derived by our analysis are effective moments, defined as forming a framework of rigid-rotor levels to which could be added the elaborations of centrifugal and vibrational interactions.

Subsequently Dickey and Nielsen changed[5] the moments given in the original abstract to values close to ours (Table I, column 6). The higher value of c does not fit the data quite as well as that in column 7, but the data available to us is possibly not suitable for making a decision. There is, however, another criterion which has to be met. Darling and Dennison[6] have shown that in molecules of this type the

discrepancy Δ in moments of inertia, which would be zero if the molecule was rigid, can be expressed as

$$\Delta = I_C - I_B - I_A$$
$$= (h/\pi^2 c)[\omega_3^2(\omega_2(\omega_3^2 - \omega_2^2))^{-1}(n_2 + \tfrac{1}{2})$$
$$- \omega_2^2(\omega_3(\omega_3^2 - \omega_2^2))^{-1}(n_3 + \tfrac{1}{2})], \quad (1)$$

where ω_2 and ω_3 are the vibrational frequencies at zero-point energy, which for D_2O are 1210.25 and 2883.79 cm^{-1}, respectively. Thus, it is possible to calculate Δ for any vibrational level of D_2O precisely.

$$\Delta = 0.2245(n_2 + \tfrac{1}{2}) - 0.016(n_3 + \tfrac{1}{2}). \quad (2)$$

For the ground state, the calculated Δ is 0.105 whereas the value corresponding to moments used by Fuson, Randall, and Dennison is 0.115. For the upper state, Δ should be 0.329, whereas the moments calculated by the empirical isotope effect equations give 0.353. These discrepancies are caused by the fact that the isotope effect is applied to the equations expressing the reciprocal moments as linear functions of the vibrational quantum number, which are not algebraically equivalent to those for the moments themselves, and hence of Δ. A more exact derivation of the

TABLE I. Summary of constants investigated for D_2O: The moments of inertia are I_A, I_B, and I_C in units of 10^{-40} gcm^2, with discrepancy $\Delta = I_C - I_B - I_A$, calculated with a value of $h/8\pi^2 c = 27.9865 \times 10^{-40}$ from the corresponding reciprocal moments a, b, c in cm^{-1}, of asymmetry $\kappa = (2b - a - c)/(a - c)$. Column 2 gives the effective moments of the ground state of D_2O, calculated in reference 2 from the isotope effect on those of H_2O. Column 7 gives moments similarly calculated for the first deformation vibrational level, which determine a curve (Fig. 1(a)) in good agreement with the observed (Fig. 1(b)). Column 4 gives trial moments used to show the sensitivity of the calculated curve to choice of moments. Column 5 gives moments first suggested by Dickey and Nielsen, reference 4, and results in Fig. 1(c). Column 6 gives the revised moments of Dickey and Nielsen. Columns 3 and 8 are the calculated moments revised to fit the theoretical values of Δ. They result in a curve indistinguishable from Fig. 1(a) (at this resolution).

| | Ground state | | Upper state | | | | |
(1)	F.R.D.[a] (2)	Adj. (3)	Trial (4)	D & N[b] (5)	D & N[c] (6)	Reference 2 (7)	Final (8)
I_A	1.820	1.820	1.696	1.730	1.685	1.696	1.696
I_B	3.860	3.860	3.635	3.830	3.807	3.818	3.818
I_C	5.794	5.784	5.867	5.95	5.775	5.867	5.843
Δ	0.114	0.104	0.536	0.390	0.283	0.353	0.329
a	15.38	15.38	16.50	16.18	16.61	16.50	16.50
b	7.25	7.25	7.70	7.31	7.35	7.33	7.33
c	4.83	4.84	4.77	4.70	4.85	4.77	4.79
κ	−0.541	−0.543	−0.5	−0.545	−0.575	−0.564	−0.566

[a] Reference 2.
[b] Reference 4.
[c] Reference 5.

[4] F. P. Dickey and H. H. Nielsen, Chicago Meeting of the American Physical Society, June 1946.
[5] F. P. Dickey and H. H. Nielsen, Phys. Rev. 70, 109 (1946).
[6] B. T. Darling and D. M. Dennison, Phys. Rev. 57, 128 (1940).

moments of D_2O from those of H_2O could be made by working out the equations of Darling and Dennison, but the data at hand do not warrant this.

The value of Δ for the upper state is brought into agreement with (2) if $c = 4.79$ cm^{-1}. This is within the sensitivity of our method (at the resolution of the data), and the curve with this value of c is only very slightly different from Fig. 1(a). Thus, we believe the best values of the moments of D_2O in the upper state are those given in the last column of Table I.

It is of interest to point out that essentially the whole of this band can be accounted for by levels up to $J = 12$ showing that the basic tables of reduced energy and line strengths[7] on which the calculations are constructed are adequate for bands of this type of molecule.

CONCLUSIONS

The agreement of the calculated curve, Fig. 1(a), with the observed, Fig. 1(b), shows that the effective moments of D_2O in the 8.5-μ band

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[7] G. W. King, R. M. Hainer, and P. C. Cross, J. Chem. Phys. **11**, 27 (1943); P. C. Cross, R. M. Hainer, and G. W. King, J. Chem. Phys. **12**, 210 (1944). Values of $E(\kappa)$ for $J = 11$ and 12 are about to be published.

are close to the values given in the last column of Table I. The curves for slightly different moments, such as those in columns 4 and 5, are substantially different.

Although we have not yet worked out an objective criterion of "goodness of fit," on the basis of "topological" features, such as number and relative magnitude of the peaks, we estimate the possible error in a, b, and c (reciprocal moments) as 0.1, 0.05, and 0.02 cm^{-1}, respectively.

The agreement shows that the moments of D_2O in its upper vibrational states can probably be calculated with sufficient accuracy from the isotope effect on those of H_2O.

This investigation also shows that the incompletely resolved spectra can be analyzed by computing the position and intensity of every line present, and summing the absorption over a "slit width" which in turn can be deduced from the experimental curve.

Because of the lack of numerical values of the transmission in the data used, further attempts to match the observed curve were postponed until further experimental data for this band becomes available.