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The transitions described above appear to be relatively simple from this point of view. In an extreme type of disorder the configurations may be uniformly distributed in space, but the most extreme case is one of free or nearly free rotation in space in which case con-

figurations of rotational oscillation are no longer significant. It is doubtful that a precise determination of the rotational behavior of BaCO_3 or SrCO_3 can be made by means of x-ray diffraction studies if the transition forms are disordered.

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Rotational Absorption Spectrum of HDO*

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The 2_2-2_1 , 3_0-3_1 , $4_{-3}-3_1$, and the 5_0-5_1 rotational absorption transitions of HDO have been observed and identified on the basis of their Stark effect. By comparing the theoretical and experimental Stark shift, the dipole moment for all these transitions has been measured as 1.84 ± 0.01 . The effective HOD angle is also determined as $104^\circ \pm 30'$ and the parameter of asymmetry, κ , as about -0.696 . The line breadth $\Delta\nu$ at one atmosphere is $0.38 \pm 0.04 \text{ cm}^{-1}$. None of these quantities is in disagreement with independent determinations.

INTRODUCTION

THE intermediate heavy water molecule, HDO, has not been studied as fruitfully as have the H_2O and D_2O isotopic forms. The pure rotational spectrum of the intermediate molecule observed in the infra-red is, of course, hopelessly complicated by absorption due to the inevitable H_2O and D_2O impurities. However, King, Hainer, and Cross¹ (KHC) have reanalyzed existing vibration-rotation data and on the basis of a rigid rotor model have published a table of expected absorption frequencies in the microwave region.

One might expect that little could be said about the HDO molecule if these absorption frequencies were measured since, for example, centrifugal distortion of the energy levels would obscure any relation between the absorption frequencies and the molecular structure. It is inevitable that with a molecule as complicated as HDO, an asymmetric top, those rotational energy levels having magnitudes of several hundred wave numbers may not be calculated exactly from measured energy-level differences of the order of one wave number.

On the other hand, such measurements are of value in determining the usefulness of a rigid rotor analysis of infra-red data, and in supplementing infra-red data used in assigning term values. Stark effect measurements also provide additional structure data in the case of HDO, as we shall show below. A study of the absorption due to HDO in the microwave region can thus be of use, although application of the data is certainly more limited than in the case of a linear or a symmetric top molecule.

EXPERIMENTAL MEASUREMENTS

The sweep spectroscope and frequency standard used in these measurements have been described elsewhere.² Since KHC have pointed out that centrifugal distortion effects cancel out rather well in $\Delta J=0$ transitions, these transitions were first studied. The 5_0-5_1 ** line at 22307.67 Mc/sec has been reported by Townes and Merritt,³ and by us.⁴ To obtain a more accurate analysis the Stark effect for this transition was remeasured, and two other transitions, the 2_1-2_2 and the 3_0-3_1 were also measured at 10,278.99 Mc/sec and 50,236.90 Mc/sec, respectively. The Stark measurements on these lines enable positive identification to be made.

INTERPRETATION RESULTS

The theoretical Stark effect may be calculated for these transitions to compare with the observed perturbation. For perturbation energies ($\mu \cdot E$, where μ is the electric dipole moment, E is the electric field) much less than the energy difference between the asymmetric-top term values, the Stark effect is a second-order perturbation. The problem is one of calculating the quantum mechanical matrix elements of the direction cosines of the molecule-fixed axes to the space-fixed electric field axis. Induced polarization may generally be ignored as Golden and Wilson⁵ have shown. Fortunately, necessary direction-cosine matrix elements have been tabu-

² Strandberg, Wentink, and Kyhl, *Phys. Rev.* **75**, 270 (1949).

** The $J\tau$ notation will be used. J is the total angular momentum quantum number, and τ is a running index over the energy levels within the given J group.

³ C. H. Townes and F. R. Merritt, *Phys. Rev.* **70**, 558 (1946).

⁴ Strandberg *et al.*, *Phys. Rev.* **73**, 188 (1948).

⁵ S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.* **16**, 669 (1948).

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¹ King, Hainer, and Cross, *Phys. Rev.* **71**, 433 (1947).

lated by CHK⁶ in the form of line strengths, for various degrees of asymmetry of the molecule. They have also outlined a convenient method for calculating these matrix elements for any asymmetry. Some arithmetical juggling is necessary to recover the direction cosines themselves from the line strengths tabulated by CHK, since the line strengths are the sums of the squares of the direction-cosine matrix elements over the magnetic quantum numbers and the three space directions. The term values in the presence of an electric field are given by conventional perturbation theory^{7,8}

$$W_{J,\tau} = W^{(0)}_{J,\tau} + W^{(2)}_{J,\tau} \text{ ergs,} \quad (1a)$$

where $W^{(2)}_{J,\tau}$ is the second-order correction to the unperturbed energy $W^{(0)}_{J,\tau}$ and is calculated as

$$W^{(2)}_{J,\tau} = E^2 \sum'_{J',\tau'} \frac{\mu_g^2 |\Phi_{z,g}(J, \tau; J', \tau')|^2}{W^{(0)}_{J,\tau} - W^{(0)}_{J',\tau'}} R \text{ ergs,} \quad (1b)$$

where $|\Phi_{z,g}(J, \tau; J', \tau')|^2$ is the line strength for the transition $J, \tau \rightarrow J', \tau'$ for a field along the space-fixed axis, z , interacting with a dipole moment along the molecule-fixed axis, g ; this quantity is given in the CHK tables; μ_g^2 is the square of the component of the electric dipole moment along the molecule-fixed axis g ;

$$R = \frac{M^2}{J^*(J^*+1)(2J^*+1)}, \quad |M| \leq J^* = J \text{ if } J = J'$$

or

$$R = \frac{J^{*2} - M^2}{J^*(4J^{*2} - 1)}, \quad |M| \leq J^* - 1 \text{ where } J^* = J \text{ if } J = J' + 1 \\ \text{or } J^* = J' \text{ if } J = J' - 1$$

The primed summation indicates that the term $J', \tau' = J, \tau$ is omitted.

The paper of Golden and Wilson⁵ gives an identical formulation of this solution in addition to a more general discussion of the problem for the case of degeneracy, a situation which has no bearing on the present problem.

The calculations themselves are straightforward. We have used three-point interpolation in the CHK tables for the line strengths. Three-place logarithmic interpolation was used for cases where the line strength varied rapidly with the asymmetry coefficient, κ . (κ is defined as $(2b-a-c)/(a-c)$ where a , b , and c are the maximum, intermediate, and minimum reciprocal moments of inertia.)

Interpolation seemed unsatisfactory for the line strength of the 5_0-5_1 , and the $4_{-3}-3_1$ transitions, so we have calculated these two direction-cosine matrix elements exactly by using the method of CHK.⁶ KHC have investigated interpolation errors in the paper¹ and the operation seems justified in the other cases.

For HDO we have used $\kappa = -.685$, $(a-c)/2 = 8.495 \text{ cm}^{-1}$ and $(a+c)/2 = 14.88 \text{ cm}^{-1}$, the latter two parameters being one-half the difference and the sum of the extreme reciprocal moments of HDO. These parameters were deduced from the KHC paper.¹ The term value differences $W^{(0)}_{J,\tau} - W^{(0)}_{J',\tau'}$ must be calculated by using a rigid rotor model with the above parameters. In general the most important term is the one with the smallest energy difference in the denominator, and this usually corresponds to the transition frequency measured in the microwave region. Since this energy difference is therefore known very accurately, the major term in the above summation is thus known to an accuracy limited only by the validity of the interpolation of the line strength. The other terms essentially form a small correction factor so that rigid rotor term values are sufficiently accurate for use in their denominator. Hence we do not calculate the rigid rotor Stark effect as given in the Golden and Wilson tables,⁵ but the Stark effect based on rigid rotor wave functions and corrected for centrifugal distortion.

Trouble was encountered in calculating the 3_1 Stark perturbation for there are two near terms; one is the 3_0 , the other is the 4_{-3} level. The 3_0-3_1 energy denominator is immediately calculated from the observed absorption frequency, but the $4_{-3}-3_1$ energy term is known rather inaccurately and is listed by KHC¹ as 1.13 cm^{-1} . We therefore brought into the calculations at this point a frequency ν_{34} to stand for the expected $4_{-3}-3_1$ absorption frequency, and carried the calculations through with this additional unknown. The other unknowns are the static dipole moment μ , and the angle δ between the dipole moment and the molecule-fixed principal axis of the intermediate moment of inertia. The resulting Stark shift in the 3_0-3_1 absorption may then be given in the form

$$\Delta\nu = \left(\frac{\mu E}{hc}\right)^2 10^4 \left\{ \sin^2 \delta (A + BM^2) + \cos^2 \delta \left[\frac{C(16 - M^2)}{\nu_{34}} + D + FM^2 \right] \right\} \text{ Mc/sec.,} \quad (2)$$

where A , B , C , D , and F are constants calculable by the procedure outlined above, and E is the electric field in kilovolts/cm, h is Planck's constant and c is the speed of light.

The observed Stark shift was measured to have the form

$$\Delta\nu = (0.577 + 0.087M^2)E^2 \text{ Mc/sec.} \quad (3)$$

If the predicted ratio of the M -dependent and M -independent term in Eq. (2) is set equal to the observed ratio in Eq. (3), we obtain ν_{34} in terms of A , B , C , D , F , and δ . The angle is known approximately as $20^\circ 30'$,¹ and to this approximation a value for ν_{34} may be calculated. This procedure was carried out roughly and gave a value of $20,000 \text{ Mc/sec}$ or $.67 \text{ cm}^{-1}$ for this frequency,

⁶ Cross, Hainer, and King, *J. Chem. Phys.* **12**, 210 (1944).

⁷ See reference 5.

⁸ E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, London, 1935).

TABLE I. Theoretical and experimental Stark shift.

2_1-2_2	$\Delta\nu_{\text{theor.}} = \left(\frac{\mu E}{hc}\right)^2 \{\sin^2\delta(64.50M^2 + .01506) + \cos^2\delta(.00709M^2 + .2163)\}$ $\Delta\nu_{\text{obs.}} = (.0545 + 2.36M^2)E^2$
3_0-3_1	$\Delta\nu_{\text{theor.}} = \left(\frac{\mu E}{hc}\right)^2 \{\sin^2\delta(3.178M^2 + .3052) + \cos^2\delta[(.1280 + .2880\kappa)M^2 - 4.608\kappa - .987]\}$ $\Delta\nu_{\text{obs.}} = (.577 + .087M^2)E^2$
$4_{-3}-3_1$	$\Delta\nu_{\text{theor.}} = \left(\frac{\mu E}{hc}\right)^2 \{\sin^2\delta(1.607M^2 - .1461) + \cos^2\delta[(.2184 + .5760\kappa)M^2 - 2.159 - 9.216\kappa]\}$ $\Delta\nu_{\text{obs.}} = 1.056E^2$
5_0-5_1	$\Delta\nu_{\text{theor.}} = \left(\frac{\mu E}{hc}\right)^2 \{\sin^2\delta(2.636M^2 + .0135) + \cos^2\delta(.00621M^2 - .1093)\}$ $\Delta\nu_{\text{obs.}} = (-.027 + .0950M^2)E^2$

$\Delta\nu$ in Mc/sec.
 μ is the electric dipole moment in e.s.u. cm
 h is Planck's constant in erg sec.
 c is speed of light in cm/sec.

E is field strength in kilovolts/cm
 M is the magnetic quantum number
 κ is the parameter of asymmetry.

instead of 34,000 Mc/sec or 1.13 cm^{-1} as predicted by the rigid rotor approximation. The only absorption in water mixtures which we have found in this region is one at 20,460.40 Mc/sec.

It was then evident that the calculation should be carried out with ν_{34} taken as 20,460.40 Mc/sec; and that the theoretical Stark pattern for the 20,460.40 Mc/sec absorption should be computed on the basis of its being a $4_{-3}-3_1$ transition to check this identification with the observed Stark pattern.

The observed Stark splitting was so good even with an estimated value for δ that we assumed the 20,460.40 Mc/sec to be due to the $4_{-3}-3_1$ transition in HDO.

We may now look at the complete picture on the basis of this tentative identification to expose any inconsistencies. Since the rigid rotor predicted frequencies are so close to the observed frequencies for $\Delta J=0$ transition, it may be assumed that centrifugal distortion in the two levels involved in each case is approximately the same. In any case, for an approximation using rigid rotor wave functions both levels must be described geometrically by the single angle parameter δ , which we shall call δ_J . Since we have four J states involved, in the transitions, $J=2 \rightarrow 2$, $3 \rightarrow 3$, $3 \rightarrow 4$, and $5 \rightarrow 5$, there are only four values of δ_J which need be carried throughout the calculations. It must be remembered that from this point of view δ_J is essentially only a parameter which may or may not be related simply to a physical angle in the molecule, but it is the "effective" value of this angle for the transitions $J=2 \rightarrow 2$, $3 \rightarrow 3$, $3 \rightarrow 4$, $5 \rightarrow 5$, etc.

To be entirely consistent the direction-cosine matrix elements will vary with δ , since they are a function of κ alone and it may be shown that in HDO

$$d\kappa \cong -.0043d\delta_J$$

with $d\delta_J$ in degrees. For a variation of δ by one degree, κ will change by .6 percent and for all matrix elements except for the $4_{-3}-3_1$ term the corresponding change

in the matrix elements will be no more than one-fifth of this, or about 0.1 percent. Only the $4_{-3}-3_1$ matrix element was therefore entered explicitly into the calculation as

$$|\Phi_{20}|^2 = (-.4954 - .1158)(16 - M^2);$$

this expression is in error by .3 percent at $\kappa = -.8$, and $-.6$ with no error at $\kappa = -.7$.

The theoretical Stark effect may then be written as in Table I. The experimentally observed Stark shifts are also listed in Table I. By imposing the condition that the ratio of the M -dependent to M -independent coefficients in both the observed and calculated Stark formulae be equal, δ_2 and δ_5 may be determined uniquely. With values of δ so determined, the dipole moment may be obtained by using the condition that both the observed and calculated Stark formulae have the same magnitude. The μ 's and δ 's so determined are listed in Table II.

The 3_0-3_1 and $4_{-3}-3_1$ transitions must be handled differently since κ , δ , and μ enter explicitly into the Stark effect of these two transitions. The situation is under-determined, and so no explicit values for those parameters may be obtained. It would naturally be desirable to have κ_J and δ_J for these two transitions turn out to be identical since the 3_1 term participates in both. However, as we have indicated above, δ_J must be considered only a parameter, or an effective angle in a rigid-rotor Stark-effect calculation. Also it would be well to have μ close to the value determined from the $J=2$ and $J=5$ transitions. Knowing the desired solutions then, one particular solution is: $\mu_{33}=1.85$, $\mu_{34}=1.83$, $\delta_{33}=19^\circ 50'$, and $\kappa = -.696$. This solution seems satisfactory from a physical point of view, and no further discussion of data reduction need be given.

Incidental to the observation on the 3_0-3_1 HDO absorption we have also measured the half-line breadth at half intensity, $\Delta\nu$, as $.010 \pm .001 \text{ cm}^{-1}$ at 20 mm pressure. This extrapolates to a line breadth at one atmos-

TABLE II. Deduced molecular parameters.

	μ	δ
2_1-2_2	$1.84 \pm 1\%$	$20^\circ 57' \pm 1\%$
$3_0-3_1^*$	1.85	$19^\circ 50'$
$4_{-3}-3_1^*$	1.83	$19^\circ 50'$
5_0-5_1	$1.83 \pm 2\%$	$20^\circ 44' \pm 2\%$

* For $\kappa = -.696$.

phere of $.38 \pm .04 \text{ cm}^{-1}$. Townes and Merritt³ have published a value of $.27 \pm .05 \text{ cm}^{-1}$ for the 5_0-5_1 line breadth extrapolated to one atmosphere pressure. The two measurements agree rather well.

SUMMARY

For four different transitions of low J the static dipole moment of HDO is seen to be a constant $1.84 \pm .01$. Centrifugal distortion makes no radical change in the electric moment between the $J=2$ to $J=5$ states. The angle between the moment of inertia ellipsoid and the symmetry axis δ apparently undergoes no radical change, and may be determined as $20^\circ 30' \pm 30'$; the value of the HOD angle is then $104^\circ \pm 30'$. The value of δ is in good agreement with the determination of this angle from the rigid rotor parameters as given by KHC.¹ Further, the asymmetry parameter may be shown to be about $-.696$ from the Stark data. This value of κ is also in agreement with the KHC determination. It should be noted that though a value of κ had to be known before the Stark data could be reduced, this value needed to be known only roughly. It might be best to say that Stark effect observations are capable of giving information on molecular structure which at least checks otherwise determined knowledge, and beyond that it gives information for a particular pair of rotational states instead of an average value over a number of rotational states. It may be seen from the above identification of the $4_{-3}-3_1$ transition that the

Stark effect is also a very useful tool to aid in assigning transition term values.⁹

We have previously published similar observations on the Stark effect for the $5_{-1}-6_{-5}$ transition in H_2O .¹⁰ In this case the dipole moment proved to be about 5 percent higher than 1.84 debye, the measured result for HDO. A value of 1.84 debye is generally given for the dipole moment of H_2O and D_2O as measured from the temperature dependence of the polarization.¹¹ It has been pointed out to us by E. B. Wilson, Jr. that the dipole moment is of interest to correlate experimental and theoretical studies of the line shape and intensity in this transition.

Van Vleck¹² has shown that if a value of the dipole moment of 1.84 debye is used and the line breadth parameter is adjusted to fit the observed line shape, the calculated peak absorption for the $5_{-1}-6_{-5}$ absorption in H_2O is low by about 20 percent. If the moment observed in microwave Stark measurement for this transition is used, the discrepancy is reduced to 10 percent and the agreement of theory with experiment is markedly enhanced. Van Vleck mentions other effects which could also contribute to this discrepancy, so that for the present one can only say that these absorption studies are not in disagreement with the high dipole moment determined from the Stark effect.

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⁹ For similar use of the Stark effect for transition identification in SO_2 , see Dailey, Golden, and Wilson, Phys. Rev. **72**, 871 (1947). Previously the author has suggested (Phys. Rev. **74**, 1245 (1948)) that the 20,460.40 Mc/sec absorption might be due to D_2O . The argument, though not incorrect, is not so conclusive as the interlocking evidence presented here to assign it to the $4_{-3}-3_1$ transition in HDO.

¹⁰ Golden, Wentink, Hillger, and Strandberg, Phys. Rev. **73**, 92 (1948).

¹¹ See, for instance, Technical Report II, "Tables of Dipole Moments," Laboratory for Insulation Research, M.I.T.

¹² J. H. Van Vleck, Phys. Rev. **71**, 425 (1947).