THE CENTRIFUGAL DISTORTION COEFFICIENTS
OF
THE MOLECULE HYDROGEN DEUTERIUM OXIDE

by

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ABSTRACT

The centrifugal distortion coefficients of hydrogen deuterium oxide (HDO) are calculated, using the known molecular structure and force constants of the molecule H_2O, from theoretical expressions. These coefficients are used in the expression developed by R. E. Hillger for the frequencies of "a" type transitions corrected for centrifugal distortion to estimate the three molecular parameters κ, $\frac{a-c}{2}$, and $\frac{a+c}{2}$ from five known absorption frequencies in the microwave region. The resulting values are $\kappa = -0.67712$, $\frac{a-c}{2} = 8.2340 \text{ cm.}^{-1}$, $\frac{a+c}{2} = 14.457 \text{ cm.}^{-1}$. These values are slightly different from previous values obtained by analysis of a vibration-rotation band in the infrared. Some of the more important "a" type transitions in the microwave region are predicted on the basis of the parameters deduced; these transitions, when found, will allow a further refinement of knowledge concerning the molecule.

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ABSTRACT

Using the known structure and force constants of the molecule H_2O, the equilibrium moments of inertia, normal frequencies and normal coordinates of the molecule hydrogen deuterium oxide (HDO) are calculated. This information is then used to calculate the centrifugal distortion coefficients as given by H. H. Nielsen. These turn out to be:

$$\begin{aligned} D_J &= 3.282 \times 10^{-4} \text{ cm}^{-1} \\ D_{JK} &= 1.140 \times 10^{-3} \\ D_K &= 9.001 \times 10^{-3} \\ \delta_J &= 1.198 \times 10^{-4} \\ R_5 &= -2.836 \times 10^{-4} \\ R_6 &= -7.251 \times 10^{-5} \end{aligned}$$

The centrifugal distortion coefficients are now used in the expression developed by Hillger for "a" type transition frequencies to find the molecular parameters κ and $\frac{a-c}{2}$. The equation used gives corrected "a" type frequency in terms of quantities dependent on the molecular parameters and distortion coefficients. By substituting the measured frequencies of four "a" type transitions in the equation and plotting curves of $\frac{a-c}{2}$ vs. κ, an estimate of these parameters is made.

Similarly, the parameter $\frac{a+c}{2}$ is evaluated by using

the expression for a $\Delta J = +1$ transition and the known frequency. This is checked by calculating the inertial defect $\Delta = I_A + I_B - I_C$ theoretically and comparing it with that resulting from the values deduced previously for the three parameters. Agreement is not very good, but due to the indefinite state of knowledge, it may be improved when better values are known.

The values found for the parameters are $\kappa = -0.67712$, $\frac{a-c}{2} = 8.2340$ cm.$^{-1}$, $\frac{a+c}{2} = 14.457$ cm.$^{-1}$. These are not in serious disagreement with values determined from infrared data, and since they are derived from pure rotational transitions, should predict the rotational spectrum more accurately. Finally, several of the strongest "a" type transition absorption frequencies are predicted using the new values of the parameters with a view to further improvement of knowledge about the molecule.

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INTRODUCTION

Microwave spectroscopy has become a very useful tool of physical research, and its applications are numerous. One of the most important of these applications is in the study of molecular structure, where it supplements and aids in interpreting data obtained by other means, particularly infrared spectroscopy.

The present thesis is concerned with the application of microwave spectroscopy to the study of the molecule hydrogen deuterium oxide. The related molecules H_2O and D_2O have been rather thoroughly studied, and a comparison of the completely asymmetric form HDO with the symmetric forms H_2O and D_2O is of some interest. Since little direct information is available for HDO, the usefulness of a theoretical analysis using information obtained from H_2O and D_2O can also be examined, to a certain extent.

The experimental information available on HDO at the present time is meager, and insufficient to determine accurately the effective rotational constants and structure of the molecule. The data in the microwave region consists of five measured rotational transitions:

Transition	Frequency (mc/sec.)
$2_1 \rightarrow 2_2$	10,278.99

Transition	Frequency (mc/sec.)
$3_0 \rightarrow 3_1$	50,236.90
$4_1 \rightarrow 4_2$	5,702.78
$5_0 \rightarrow 5_1$	22,307.67
$4_{-3} \rightarrow 3_1$	20,460.40

The Stark effect for these transitions has also been evaluated, theoretically and experimentally[1]. Herzberg[2] has analyzed the band at 1.1 μ in the infrared, and obtained approximate values for the rotational constants; these values were used by King, Hainer, and Cross[3] to predict rotational transitions of the molecule. Some of the predicted lines have been found to be fairly accurate, but others are not so good. Accordingly, a reevaluation of the rotational constants using the known rotation spectrum instead of the rotation-vibration spectrum seems desirable. The $4_1 \rightarrow 4_2$ transition was found and identified by P. Sieck of this laboratory while this work was in progress, thus increasing direct information in the microwave region by 25%.

The molecule HDO is an asymmetric rotor, and since it has a component of dipole moment along the axis of least moment of inertia as well as along the intermediate axis, both "a" and "b" type transitions are allowed. The asymmetry of the top causes a splitting of energy levels which are degenerate in the limiting prolate symmetric top case, and between which "a" type transitions are allowed. The small resulting energy differences lead to a number of transitions in the microwave regions (from ~5,000 mc/sec. to ~80,000 mc/sec.).

Centrifugal distortion in such a light molecule as HDO would be expected to be large, and consequently a rigid rotor analysis is useful only as a first approximation. An example of this is the case of the transition $4_{-3} \rightarrow 3_1$, identified by Strandberg[1] at 20,460.40 mc/sec.; the rigid rotor approximation predicts this line at about 33,900 mc/sec.[3]

The expressions given in the literature for energy levels of polyatomic molecules all involve several parameters of the molecule: the reciprocal moments of inertia a, b, and c, and from 5 to 9 terms arising from vibration and centrifugal stretching in the molecule. Nielsen[4] gives the elements of the energy matrix taking centrifugal stretching into account, and Hillger[5] has combined these elements with the rigid rotor analysis of KHC[6] to arrive at a relatively simple expression for "a" type transition frequencies.

Because there are more constants to be evaluated than there are known lines, a unique determination is impossible. Therefore, in the present paper, the centrifugal distortion constants, which are small relative to the reciprocal moments of inertia, will be calculated from data on H_2O and D_2O and used to find reasonably close values for the reciprocal moments of inertia. The results of this operation can then be used to predict more transition frequencies, and when enough of these are found, a complete analysis can be carried out.

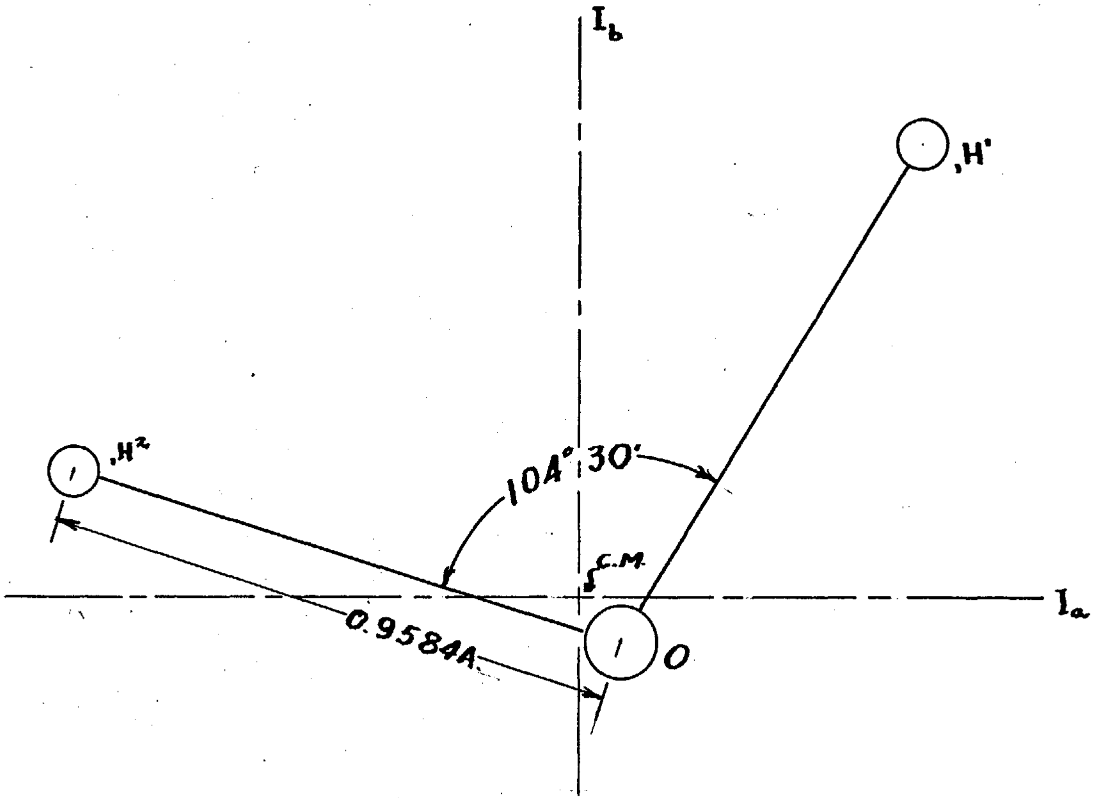

FIGURE I

ASSUMED EQUILIBRIUM STRUCTURE OF HDO

CHAPTER I

THE CENTRIFUGAL DISTORTION COEFFICIENTS OF HDO

Section a. Equilibrium Structure and "Internal Coordinates".

The theoretical values of the centrifugal distortion constants of a molecule are given by Nielsen[4] in terms of the equilibrium moments of inertia, and the normal frequencies and coordinates of vibration. These can be found if the assumption that isotopic substitution makes little difference in the force constants and structure of the molecule is allowed. This assumption has been justified by several workers.

Assuming the H_2O equilibrium structure for HDO, then, (figure 1), the equilibrium moments of inertia are found to be:

$$\begin{aligned} I_a &= 1.212 \times 10^{-40}\,\text{gm-cm}^2 &&= I_{zz}^{(e)} \\ I_b &= 3.071 &&= I_{xx}^{(e)} \\ I_c &= 4.283 &&= I_{yy}^{(e)} \end{aligned}$$

The axis I_b makes an angle of $21^\circ 8'$ with the dipole axis (bisector of $\angle$-HOD) and the axis I_c is perpendicular to the plane of the molecule. The assignment of x-, y-, and z-axes is on the basis of the I^r representation of KHC, the most appropriate in view of the fact that $\kappa = \frac{2b-a-c}{a-c}$ is in the neighborhood of -0.7, and "a" type transitions will be our major interest.

The equilibrium positions of the atoms in these coordinates are then:

$$x_1^0 = -0.7481 \times 10^{-8} \text{ cm.}$$
$$z_1^0 = 0.5661$$
$$x_2^0 = -0.2018$$
$$z_2^0 = -0.8473$$
$$x_3^0 = 0.0725$$
$$z_3^0 = 0.0710$$
$$y_1^0 = y_2^0 = y_3^0 = 0,$$

where the H, D, and O atoms are numbered 1, 2, and 3 respectively.

The force constants given by Herzberg[7] are in terms of "internal" coordinates or Q_i. These coordinates represent changes of interatomic distances as follows: Q_1 is the change in the distance O-D, Q_2 the change in the distance O-H, and Q_3 the change in distance D-H. Since there are $3N-6 = 3$ normal frequencies of vibration, these coordinates have the advantage of reducing the secular determinant to minimum order automatically.

By applying the conditions:

$$\sum_i m_i \alpha_i = 0, \qquad \alpha = x,\ y,\ z$$

and $\sum_i m_i (\alpha_i^0 \delta\beta_i - \beta_i^0 \delta\alpha_i) = 0, \quad \alpha, \beta = x,\ y,\ z,\ \alpha \neq \beta$

that is, that the center of mass remain at rest, and that there is no rotation of the molecule, along with the relations (for small amplitude)

$$Q_1 = (\delta x_2 - \delta x_3) \operatorname{Cos} \gamma_1 + (\delta z_3 - \delta z_2) \sin \gamma_1$$
$$Q_2 = (\delta x_3 - \delta x_1) \operatorname{Cos} \gamma_2 + (\delta z_3 - \delta z_1) \sin \gamma_2$$
$$Q_3 = (\delta x_2 - \delta x_1)$$

the transformation from Cartesian displacement coordinates $\delta x_i, \delta y_i, \delta z_i$ to the coordinates Q_i is found to be (in matrix form):

$$\begin{bmatrix} \delta x_1 \\ \delta x_2 \\ \delta x_3 \\ \delta z_1 \\ \delta z_2 \\ \delta z_3 \end{bmatrix} = \begin{bmatrix} -0.3562 & -1.154 & 0.4616 \\ -0.5867 & -0.3503 & 0.4594 \\ 0.0963 & 0.1668 & -0.0869 \\ -0.6218 & -0.1768 & 0.8787 \\ -0.7109 & 0.1339 & -0.1942 \\ 0.1287 & -0.0057 & -0.0309 \end{bmatrix} \begin{bmatrix} Q_1 \\ Q_2 \\ Q_3 \end{bmatrix}$$

$$\delta y_i = 0, \quad i = 1, 2, 3.$$

The δx_i, δy_i, δz_i represent small displacements from the equilibrium positions x_i^o, y_i^o, z_i^o.

Writing the kinetic energy as

$$2T = \sum_i m_i (\delta\dot{x}_i)^2 + (\delta\dot{y}_i)^2 + (\delta\dot{z}_i)^2 =$$
$$\sum_{i,j} b_{ij} \dot{Q}_i \dot{Q}_j, \quad \text{with } b_{ij} = b_{ji},$$

the b_{ij} are

$b_{11} = 4.387 \times 10^{-24}$gm. $\qquad b_{12} = 1.520$

$b_{22} = 3.115 \qquad b_{13} = -1.957$

$b_{33} = 2.707 \qquad b_{23} = -2.042$

Herzberg[7] gives for the potential energy:

$$2V = \sum_{i,j} a_{ij} Q_i Q_j, \quad a_{ij} = a_{ji}$$

in which

$$a_{11} = a_{22} = 9.568 \times 10^5 \text{ dynes/cm.}$$
$$a_{33} = 2.037 \times 10^5$$
$$a_{12} = 1.048 \times 10^5$$
$$a_{13} = a_{23} = -1.535 \times 10^5$$

Section b. Normal Frequencies and Normal Coordinates.

The secular determinant for the normal frequencies is:

$$\begin{vmatrix} b_{11}\lambda_i - a_{11} & b_{12}\lambda_i - a_{12} & b_{13}\lambda_i - a_{13} \\ b_{12}\lambda_i - a_{12} & b_{22}\lambda_i - a_{22} & b_{23}\lambda_i - a_{23} \\ b_{13}\lambda_i - a_{13} & b_{23}\lambda_i - a_{23} & b_{33}\lambda_i - a_{33} \end{vmatrix} = 0$$

where $\lambda_i = 4\pi^2 c^2 \omega_i^2$.

The normal coordinates can be found in a straightforward manner as the solution of a matrix problem: given two matrices $B = [b_{ij}]$ and $A = [a_{ij}]$, to find a transformation K such that $\tilde{K}BK = E$, and $\tilde{K}AK = \Lambda = [\lambda_i \delta_{ij}]$. Essentially this is the finding of a linear transformation $Q_i = \sum_j k_{ij}\eta_j$ such that $2T = \sum_{ij} b_{ij}\dot{Q}_i\dot{Q}_j = \sum_i \dot{\eta}_i^2$ and simultaneously $2V = \sum_{ij} a_{ij}Q_iQ_j = \sum_i \lambda_i\eta_i^2$ where the η_i are the desired normal coordinates. By applying the transformation from Cartesian coordinates to the Q_i given above, the δx_i, δy_i, and δz_i can be found in terms of the normal coordinates.

When the proper congruent transformation K is found, the normal frequencies of vibration are found to be:

$$\omega_1 = 2823 \text{ cm.}$$
$$\omega_2 = 1456 \text{ cm.}$$
$$\omega_3 = 3884 \text{ cm.},$$

and the matrix giving the transformation from Cartesian to normal coordinates is:

$$\begin{bmatrix} \delta x_1 \\ \delta x_2 \\ \delta x_3 \\ \delta z_1 \\ \delta z_2 \\ \delta z_3 \end{bmatrix} = 10^{12} x \begin{bmatrix} 0.0434 & -0.2804 & -0.6408 \\ 0.1504 & -0.2777 & 0.0064 \\ -0.0234 & 0.0526 & 0.0794 \\ -0.0188 & -0.5341 & 0.3868 \\ 0.4921 & 0.1232 & 0.0210 \\ -0.0608 & 0.0181 & -0.0270 \end{bmatrix} \begin{bmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \end{bmatrix}$$

The first three rows are the l_{is} of Nielsen, and the last three are the n_{is}; all the m_{is} are zero (the subscript σ is dropped since there is no degeneracy).

An examination of the matrix shows that the vibration frequency ω_1 is associated with a vibration primarily of the deuterium atom, roughly along the line O-D. The frequency ω_2 is that of a bending vibration of the molecule, the H and D moving in opposite directions; ω_3 is the frequency of vibration of the hydrogen atom approximately along the line O-H. The frequencies of the fundamentals of HDO given by Herzberg[7] are $\nu_1 = 2719$ cm.$^{-1}$, $\nu_2 = 1402$ cm.$^{-1}$, $\nu_3 = 3620$ cm.$^{-1}$, which must be corrected for anharmonicity, so there is no great discrepancy here.

Section c. Centrifugal Distortion Coefficients.

This information can now be used to calculate the centrifugal distortion coefficients. The constants $a_{s\sigma}$, $b_{s\sigma} \ldots f_{s\sigma}$ simplify considerably in a planar molecule:

$$a_s = 2\sum_i M_i z_i^o n_{is}$$

$$b_s = a_s + c_s$$

$$c_s = 2\sum_i M_i x_i^o l_{is}$$

$$d_s = e_s = 0 \text{ for all } s;$$

$$f_s = \sum_i M_i (x_i^o n_{is} - z_i^o l_{is})$$

where M_i = mass of i-th atom (grams)

x_i^o, z_i^o = equilibrium position of i-th atom (cm.)

and $\delta x_i = \sum_s l_{is} \eta_s$, $\delta z_i = \sum_s n_{is} \eta_s$ (δx_i in cm., η_s in $gm^{\frac{1}{2}}$-cm.)

These quantities turn out to be:

$a_1 = -3.054 \times 10^{-20}$ $c_1 = -0.4018$
$a_2 = -1.642$ $c_2 = 1.280$
$a_3 = 0.5116$ $c_3 = 1.902$

$b_1 = -3.456$ $f_1 = -0.8549$
$b_2 = -0.3623$ $f_2 = 1.241$
$b_3 = 2.413$ $f_3 = -1.026$

When these values are substituted in the expressions for the distortion coefficients, which are too long to present here, the distortion coefficients are found to be (in $cm.^{-1}$):

TABLE I

Centrifugal Distortion Coefficients of HDO

$D_J = 3.282 \times 10^{-4}$

$D_{JK} = 1.140 \times 10^{-3}$

$D_K = 9.001 \times 10^{-3}$

$\delta_J = 1.198 \times 10^{-4}$

$R_5 = -2.836 \times 10^{-4}$

$R_6 = -7.251 \times 10^{-5}$

These coefficients are rather large, as they are for H_2O, but the fact that coefficients computed in this way give good agreement with experiment for several other molecules (e.g. HDS) lends hope that these will be useful in interpreting experimental data.

CHAPTER II

THE MOLECULAR PARAMETERS OF HDO

Section a. Estimate of κ and $(\frac{a-c}{2})$.

In applying the distortion coefficients found above to the observed transitions, the most useful expression for energy levels, or rather transition frequencies, is that developed by Hillger[5] for "a" type transitions:

$$\nu_{J_{K_{-1}}} = \nu_r \Big[1 + 2KJ(J+1)\frac{\delta_J}{H} + (K-1)J(J+1)\frac{D_{JK}}{G-F} + \frac{2}{3}K(K^2+2)\left(\frac{D_K}{G-F} - \frac{2R_5}{H}\right) + \begin{cases} 16\left(\frac{G-F}{H^2}\right)R_6 - 4D_K \ (K \text{ even}) \Big] \\ 64\left(\frac{G-F}{H^2}\right)R_6 - 2D_K \ (K \text{ odd}) \Big] \end{cases}$$

Here ν_r is the transition frequency predicted by the rigid rotor approximation of KHC, $\nu_r = (\frac{a-c}{2})\,\Delta E(\kappa)$, where a, b, and c are the reciprocal moments of inertia in cm^{-1} or mc/sec., $a \geq b \geq c$, and κ, the asymmetry parameter, is $\frac{2b - a - c}{a - c}$.

$\Delta E(\kappa)$ is the difference in (reduced) energy between the two states involved in the transition. Briefly, the states are designated by a quantum number J, and two symmetry and state indices K_{-1} and K_1. K_{-1} is the component of J along the symmetry axis in the limiting case of the prolate symmetric rotor, and K_1 is the same component in the limiting oblate symmetric rotor. K_{-1} and K_1 run from 0 to J. Thus a state is specified by $J_{K_{-1}K_1}$. In another notation, if $\tau = (K_{-1} - K_1)$, the levels can be identified as J_τ, $\tau = -J \ldots 0 \ldots J$. Thus there are $2J + 1$ levels for every J, which in the limiting cases of the symmetric top possess degeneracy, so that they reduce to $J + 1$ terms. The selection rules for "a" type transitions are: $\Delta J = 0, \Delta K_{-1} = 0$, $\Delta K_1 = -1$, i.e. $\Delta\tau = +1$. Then the levels $2_{2,1} = 2_1$ and $2_{2,0} = 2_2$ give rise to the transition $2_1 \rightarrow 2_2$, etc. Four of the five known transitions are "a" type.

The total energy of a rigid rotor in state J_τ is $W^J_\tau = (\frac{a + c}{2}) J(J + 1) + (\frac{a - c}{2}) E^J_\tau(\kappa)$. The values of $E(\kappa)$ are given by KHC in a table, and can be calculated for values of κ not listed there from explicit formulae or as roots of a secular determinant. For "a" type transitions $\Delta E(\kappa) = (E^J_{\tau+1} - E^J_\tau)$.

In the expression given above for the corrected "a" type transition frequency, K means K_{-1}, which is the same for both levels, and the distortion coefficients are dimensionless quantities obtained by dividing those given previously by $\frac{a-c}{2}$. The quantities F, G, and H are scale factors, which in the I^r identification are:
$F = +\frac{1}{2}(\kappa - 1)$, $G = 1$, $H = -\frac{1}{2}(\kappa + 1)$.

It is seen that the expression can be written

$$\nu_{J_{K_{-1}}} = \left(\frac{a-c}{2}\right) \Delta E(\kappa) \left[1 - \frac{\delta}{\frac{a-c}{2}}\right];$$

rearrangement gives $\frac{a-c}{2} = \frac{\nu_J}{\Delta E(\kappa)} + \delta$, with δ calculated in cm^{-1} or mc/sec. Because of the dependence of F, G, and H on κ, both quantities on the right are functions of κ.

If, for each transition frequency ν_γ a curve of $\frac{a-c}{2}$ vs. κ were plotted, and if the distortion correction δ were exactly correct, the curves for the 4 "a" transitions would all be tangent or cross at one point, and this would give the correct values of the parameters. Now, the quantities are known roughly as $\kappa = -0.685$, $\frac{a-c}{2} = 8.495$ cm^{-1}. A preliminary sketch shows the curves crossing in the neighborhood of $\kappa = -0.6775$, and points were therefore calculated at intervals of $\Delta\kappa = 0.0005$ from $\kappa = -0.6790$ to $\kappa = -0.6760$; the result is shown in figure 2.

As can be seen from this figure, the lines do not all cross at the same point. Pairs having different J but the same K_{-1} are almost parallel, from which it appears that the slope is mostly a function of K_{-1}. If it is assumed that the distortion coefficients are almost correct, the probable value of κ is somewhere in the parallelogram enclosed by the four lines. If the average values are taken, $\kappa = -0.67712$ and $\frac{a-c}{2} = 8.2340$ cm^{-1}.

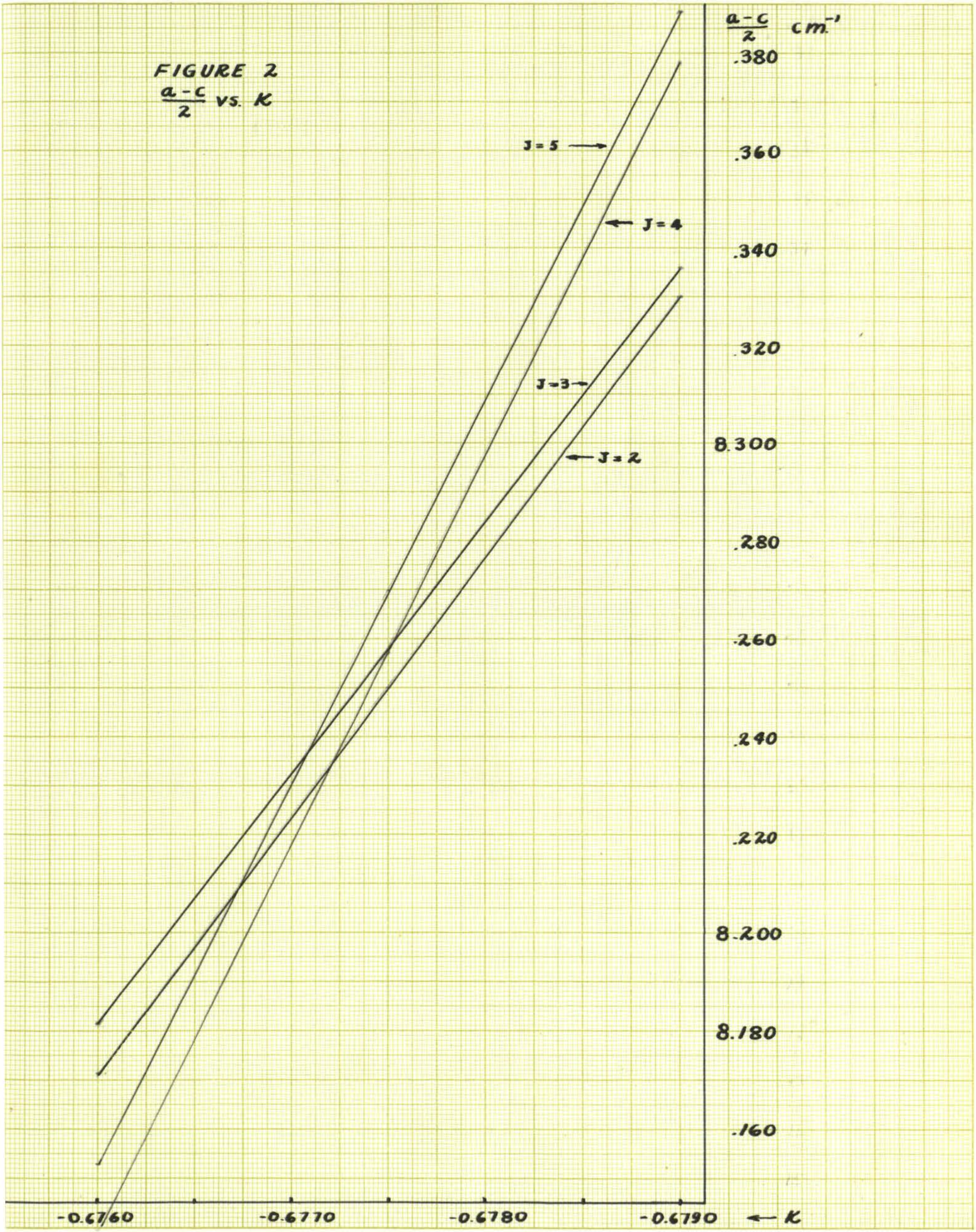
FIGURE 2
$\frac{a-c}{2}$ vs. K
$\frac{a-c}{2}$ cm^{-1}
.380
.360
.340
.320
8.300
.280
.260
.240
.220
8.200
8.180
.160
J = 5
J = 4
J = 3
J = 2
-0.6760
-0.6770
-0.6780
-0.6790
← K

It seemed desirable, at first, to attempt adjustment of distortion coefficients, once values of the parameters were selected. However, this did not prove feasible. The values of R_6 and D_K are the most critical, since they contribute most to the distortion correction. However, changing R_6 will move the curves parallel to themselves and cannot be used to bring $J = 2$ and $J = 3$ or $J = 4$ and $J = 5$ together. This is almost true for D_K, since the K-dependent term containing D_K is quite small.

Another possible scheme is to use an expression very nearly equivalent, which is found by rearrangement and a slight simplification, as pointed out by Hillger:

$$\nu = \nu_r \left[(1 - r \ ) + J(J+1)(AK + B) + K^2(K - 2)^2(CK + D) \right]$$

Lawrance[8] developed and applied the similar form

$\nu = \nu_r \left[1 - (X_J + X_{JK}K)J(J+1) - (X_K + X_{KK}K)K^2 \right]$ which has the advantage of having as many constants as there are known lines. The constants have been determined, but are probably not reliable, becuase the largest term by far is the K-dependent term $(X_K + X_{KK}K)$, and only two values of K, 2 and 3, are involved in the four transitions. The formula gives exact corrections, as it should, for the four known lines, but for the transition $7_0 \rightarrow 7_1$ with $K = 4$ the correction is over 11%, which is much higher than that predicted using the distortion coefficients.

It might be well at this point to look at the results provided by the theoretical coefficients, with $\kappa = -0.67712$ and $\frac{a-c}{2} = 8.2340$ cm.$^{-1}$.

TABLE II

Transition	ν^*_r	$\nu^*_{corrected}$	$\nu^*_{observed}$	% error
$2_1 \rightarrow 2_2$	10,437.19	10,283.97	10,278.99	0.05
$3_0 \rightarrow 3_1$	51,050.34	50,213.53	50,236.90	−0.05
$4_1 \rightarrow 4_2$	5,982.94	5,707.39	5,702.78	0.08
$5_0 \rightarrow 5_1$	23,462.97	22,290.82	22,307.67	−0.08

* megacycles per second

The error of prediction in any of these lines is not so great as to make it difficult to find on a microwave spectroscope. If the distortion coefficients are nearly correct, further lines of different J and K should be predictable with slightly less accuracy, but still close enough to make them easy to find. The lines most needed for further refinement are those with K values of 1, 4, 5, and J's of 1, 6, 7.

Section b. Estimate of $(\frac{a+c}{2})$.

The third important molecular parameter to be found is $\frac{a+c}{2}$. This can be evaluated directly because a $\Delta J = -1$ transition is known, the $4_{-3} \rightarrow 3_1$ transition. The secular determinants for each level give quadratic equations for the roots, and the expressions for the levels can be written quite easily. Each expression is of the form

$$W = \frac{a + c}{2} J(J + 1) + \frac{a - c}{2} E\,(\kappa, \text{ distortion terms}),$$

and the transition frequency is $\nu = -8\,\frac{a + c}{2} + \frac{a - c}{2}\,\Delta E$, which upon substitution can be solved for $\frac{a + c}{2}$. The result is $\frac{a + c}{2} = 14.457$ cm.$^{-1}$; however, $\frac{a - c}{2}\,\Delta E$ is very large compared to the transition frequency, so that the value is not critically dependent on transition frequency.

Another way of evaluating $\frac{a + c}{2}$ is to make use of the inertial defect of a planar molecule. It can be shown that in a planar molecule a relation $\Delta = I_a + I_b - I_c$ exists such that Δ is independent of anharmonic force constants to the second approximation. Hillger^5 has derived the relationship for HDS, and for HDO the derivation is the same, except for identification of axes. It starts with Nielsen's expressions for effective reciprocal moments of inertia in a vibrational state:

$$X_v = X_e - x_o - \sum_s x_s(v_s + g_{s/2})$$
$$Y_v = Y_e - y_o - \sum_s y_s(v_s + g_{s/2})$$
$$Z_v = Z_e - z_o - \sum_s z_s(v_s + g_{s/2})$$

where $X_v = b$, $Y_v = c$, $Z_v = a$, and $X_e = h/8\ {}^2cI^{(e)}_{xx}$, $Y_e = h/8\ {}^2cI^{(e)}_{yy}$, $Z_e = h/8\ {}^2cI^{(e)}_{zz}$. The quantities x_o, x_s, etc. are rather long expressions involving the equilibrium moments of inertia, normal coordinates and frequencies of vibration, and the force constants associated with cubic terms in the potential energy. x_o, y_o, and z_o are quite small even in comparison with x_s, y_s, and z_s and can be neglected. v_s is the integral quantum number of the vibrational state s, and g_s depends on the degeneracy of state s. Since there is no degeneracy, $g_s = 1$, and in the ground state considered here, $v_s = 0$. The moments of inertia can be solved for by inverting the expressions for a, b, and c. They are dependent, among other things, on the anharmonic force constants; but when they are combined to find $\Delta = I_a + I_b - I_c$, the anharmonic constants disappear because $a_s + c_s - b_s = 0$. The expression for Δ turns out to be:

$$\Delta = h/8\pi^2 c \sum_s \frac{1}{\omega_s}\Big[2\Big(\frac{b_s^2}{I_{yy}^{(e)}} - \frac{a_s^2+f_s^2}{I_{xx}^{(e)}} - \frac{c_s^2+f_s^2}{I_{zz}^{(e)}}\Big)$$

$$+\sum_{s'}{}' \Big[\sum_i M_i(n_{is}l_{is'} - n_{is'}l_{is})\Big]^2 \frac{5\omega_s^2 - \omega_{s'}^2}{\omega_s^2 - \omega_{s'}^2}\Big]$$

where the quantities have all been previously defined. The result is $\Delta = -0.0578 \times 10^{-40}$ gm-cm^2.

The relation $I_a + I_b - I_c = -.0578 \times 10^{-40}$ combined with $\frac{a-c}{2} = 8.2340$ cm^{-1} and $\kappa = -0.67712$, gives enough information to find $\frac{a+c}{2}$, since there are three unknowns, a, b, and c. The value of $\frac{a+c}{2}$ obtained in this way is $\frac{a+c}{2} = 14.636$ cm^{-1} which differs from that obtained previously by about 1.2 percent. The agreement can be made much better if it is assumed that the 4_{-3} level is higher than the 3_1 level: in that case $\frac{a+c}{2} = 14.627$ cm.$^{-1}$ from the energy difference equation. A decision between the two cases can be made only by reference to further data, and this data is provided by the Stark effect.

There are two possibilities: either the 4_{-3} level lies between the 3_0 and 3_1 levels, or it lies above the 3_1 level. In the former case, the agreement of theoretical Stark effect with experiment for both the $4_{-3} \rightarrow 3_1$ and $3_0 \rightarrow 3_1$ transitions has been shown by Strandberg[1] to be quite good. In the $4_{-3} \rightarrow 3_1$ transition M-dependent terms of the expression for frequency shift accidentally cancel each other, making the shift independent of M, and this is observed to be the case experimentally. On the other hand, if it is assumed that the 4_{-3} level lies above the other two, some of the terms of the Stark perturbation change sign, and the formula for frequency shift no longer calls for M-independence. Again, with this assumption the $3_0 \rightarrow 3_1$ Stark effect comes out too small. Therefore, the conclusion is that the 4_{-3} level lies between the 3_0 and 3_1 levels.

If the value 14.457 cm.$^{-1}$ is taken, $\Delta \simeq -0.11 \times 10^{-40}$ gm.-cm^2. The agreement with theory is not very good, but since the value of $\frac{a+c}{2}$ depends almost entirely on $\frac{a-c}{2}$

with so little dependence on κ and the transition frequency, and since small changes of the two parameters can bring Δ into better agreement, the disagreement is not a serious objection. Δ at least is of the same order of magnitude, and even more important, has the right sign. If more $\Delta J = \pm 1$ transitions are found, a better value of $\frac{a + c}{2}$ may be determined.

CONCLUSION

Section a. Summary of Results.

It is interesting to compare the molecular parameters deduced in this thesis with those previously found. A table of comparison follows:

TABLE III

Comparison of Present and Previous

Molecular Parameters of HDO

Parameter	Previous Values	Present Value
κ	-0.685 g.s. H	-0.67712
	-0.630 e.s. H	
	-0.696 S	
$\frac{a+c}{2}$ (cm.$^{-1}$)	14.879 g.s. H	14.457
	14.345 e.s. H	
$\frac{a-c}{2}$ (cm.$^{-1}$)	8.498 g.s. H	8.2340
	8.168 e.s. H	
Δ (gm.-cm.^{2})	-0.098×10^{-40} g.s. H	-0.113×10^{-40}
	-0.242×10^{-40} e.s. H	

g.s. = ground state e.s. = excited state

H = Herzberg[2] S = Strandberg[1]

The values deduced in the present paper are not in serious disagreement with those previously reported; and they are deduced from pure rotational transitions, whereas the former values appear as linear combinations of small differences between large numbers. The values of Herzberg were not corrected for centrifugal distortion, which can make a difference of a few percent in the rotational constants and a much larger difference in predicted transition frequencies. The small change of κ has a negligible effect on the theoretical Stark effect as given by Strandberg, particularly since the angle δ which enters the calculations is also subject to adjustment.

If the anharmonic force constants of HDO are found by further infrared measurements, they can be used in a theoretical treatment to calculate the effective moments of inertia in an excited rotational state and thus provide a direct comparison of theory with experiment; or, conversely, assuming theory to be exactly correct, the equilibrium moments may be found and from this the departure, if any, of HDO structure from H_2O structure investigated.

Section b. Prediction of Absorption Frequencies

The principle use of the molecular parameters derived here is in the prediction of further transition frequencies which can be used to refine the values and eventually, when enough are known, to get a complete set of experimental distortion coefficients. These distortion coefficients cannot be used to gain further information, since the desired fundamental quantities are hopelessly entangled in their formulae, but they can be used to check theory and provide a guide to its reexamination.

Consequently, as a final step in this thesis, some of the more important transition frequencies are predicted. If the preceding work has been done successfully, these predictions should represent a considerable improvement, in some cases at least, over previous predictions, and make the finding of the transitions easier.

TABLE IV

Some Absorption Frequencies of HDO in the Microwave Region

Transition	ν^*_{KHC}	ν^*_{r}	ν^*_{corr}	α(cm^{-1} x 10^{-6})
$1_0 \rightarrow 1_1$	80,340	79,698	79,529	1590
$6_{-1} \rightarrow 6_0$	67,750	67,930	64,218	199
$6_1 \rightarrow 6_2$	3,000	2,613	2,542	0.34
$7_0 \rightarrow 7_1$	9,893	9,406	9,087	2.2
$8_{-1} \rightarrow 8_0$	28,180	27,431	26,281	8.2
$9_{-2} \rightarrow 9_{-1}$	69,550	68,366	64,892	20.6

* megacycles per second

In Table IV, ν_{KHC} is the frequency predicted by KHC[3]. ν_r is the rigid rotor frequency on the basis of parameters deduced in this thesis, and ν_{corr} is the frequency corrected for centrifugal distortion. The reduced energies $E(\kappa)$ for each level except the $J = 1$ levels were calculated from the reduced energy matrices by the method of continued fractions (KHC[6]), as interpolation from the tables did not give satisfactory results where energy differences were small.

No transitions with $\Delta J = \pm 1$ were predicted, since these transitions are unnecessary in improving $\frac{a - c}{2}$ and κ; the value of $\frac{a + c}{2}$ can be refined, when $\frac{a - c}{2}$ is better known, from the $4_{-3} \rightarrow 3_1$ transition, and then used to predict $\Delta J = \pm 1$ lines.

The absorption coefficient α is that given by KHC[3], revised for a line width $\Delta\nu = 0.3$ cm^{-1} and corrected to the new frequency. The lines given are the strongest lines in the microwave frequency range.

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