Centrifugal Distortion in Asymmetric Top Molecules. III. H_2O, D_2O, and HDO†

D. W. POSENER* AND M. W. P. STRANDBERG
Department of Physics and Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received March 1, 1954)

Structural and potential constants obtained from infrared data are used with the theory of vibration-rotation interaction to obtain rotational and distortion parameters for the molecules H_2O, D_2O, and HDO; transition frequencies calculated using these parameters are compared with those observed in the microwave region, and, in the case of HDO Q-branch lines, a simple relation between the two sets is obtained. The validity of approximation theories as applied to HDO Q-branch transitions is discussed. Methods of analyzing the observed spectrum of HDO are described, and so-called "observed" parameters for this molecule are obtained; the rotational constants are found to be $a=7.0396\pm0.0005\times10^5$ Mc/sec, $b=2.7360\pm0.0005\times10^5$ Mc/sec, $c=1.9186\pm0.0005\times10^5$ Mc/sec, $\kappa=-0.6841\pm0.0002$.

1. INTRODUCTION

THE careful investigation of the infrared spectrum of water by a number of workers[3–7] has led to its rotational spectrum becoming probably the most thoroughly studied of any asymmetric top molecule. Moreover, its equilibrium structure and force constants, through quartic terms, are also known to various degrees of accuracy, from analysis of the vibrational spectrum.

This molecule, familiar to all, and simple enough at first sight, shows many interesting and complicated effects in its spectrum. Not the least of these arises from the fact that the molecule is so light that vibration and rotation cause comparatively large distortion of the equilibrium structure, and this has to be taken into account in any detailed description of the spectrum.

Contributions to the theory of centrifugal distortion in polyatomic molecules have been made by a number of authors,[8–16] but only a very little comparison with experiment has been carried out because most molecules are so heavy that the effects of centrifugal distortion in their spectra are almost negligible. The distortion effects observable in the water spectrum are so large, however, that a detailed check of the theory is possible in this case; the microwave method is particularly suited to such a study because its accurate frequency measurements immediately show up small perturbations (centrifugal distortion is, after all, a high-order effect). The present work is a contribution to such an investigation.

A number of microwave absorption lines due to some isotopic modifications of water have been reported by various workers.[17–24] Many of these transitions were found either by chance or as the result of searching in the general region of the positions predicted from infrared data. Tables[25] of such predictions are particularly useful in the case of HDO, although based on rigid rotor calculations, because distortion effects in adjacent energy levels partially cancel and thus observed a-type Q-branch transitions are found fairly close to the predicted rigid values. Moreover the relative abundance of HDO Q-branch lines in the microwave region makes this isotopic variety a much more useful subject for study than H_2O or D_2O, since more information can be extracted from it. Accordingly,

† Supported in part by the Signal Corps, the Air Materiel Command, and the U. S. Office of Naval Research, and in part by a grant from the Commonwealth Scientific and Industrial Research Organization, Australia. A detailed account is given in reference 1; a preliminary report appeared as reference 2.

* Present address: Division of Electrotechnology, Commonwealth Scientific and Industrial Research Organization, Sydney, Australia.

[1] D. W. Posener, Massachusetts Institute of Technology Research Laboratory of Electronics Technical Report No. 255, May 14, 1953 (unpublished).
[2] D. W. Posener and M. W. P. Strandberg, J. Chem. Phys. **21**, 1401 (1953).
[3] Randall, Dennison, Ginsburg, and Weber, Phys. Rev. **52**, 160 (1937).
[4] Fuson, Randall, and Dennison, Phys. Rev. **56**, 982 (1939).
[5] B. T. Darling and D. M. Dennison, Phys. Rev. **57**, 128 (1940).
[6] H. H. Nielsen, Phys. Rev. **59**, 565 (1941).
[7] G. W. King, J. Chem. Phys. **15**, 85 (1947).
[8] E. B. Wilson, Jr., and J. B. Howard, J. Chem. Phys. 4, 260 (1936); E. B. Wilson, Jr., J. Chem. Phys. 4, 313 (1936); E. B. Wilson, Jr., J. Chem. Phys. 4, 526 (1936); E. B. Wilson, Jr., J. Chem. Phys. **5**, 617 (1937).
[9] W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939).
[10] H. H. Nielsen, Phys. Rev. **60**, 794 (1941); H. H. Nielsen, Phys. Rev. **61**, 540 (1942).
[11] W. H. Shaffer and R. P. Schuman, J. Chem. Phys. **12**, 504 (1944).
[12] R. B. Lawrance and M. W. P. Strandberg, Phys. Rev. **83**, 363 (1951).
[13] R. E. Hillger and M. W. P. Strandberg, Phys. Rev. **83**, 575 (1951).
[14] H. H. Nielsen, Revs. Modern Phys. **23**, 90 (1951).
[15] D. Kivelson and E. B. Wilson, Jr., J. Chem. Phys. **20**, 1575 (1952).
[16] D. Kivelson and E. B. Wilson, Jr., J. Chem. Phys. **21**, 1229 (1953).
[17] C. H. Townes and F. R. Merritt, Phys. Rev. **70**, 558 (1946).
[18] Golden, Wentink, Hillger, and Strandberg, Phys. Rev. **73**, 92 (1948).
[19] Strandberg, Wentink, Hillger, Wannier, and Deutsch, Phys. Rev. **73**, 188 (1948).
[20] M. W. P. Strandberg, J. Chem. Phys. **17**, 901 (1949).
[21] D. W. Posener, Massachusetts Institute of Technology Research Laboratory of Electronics Quarterly Progress Reports: July 15, 1952, p. 28; October 15, 1952, p. 20; January 15, 1953 (unpublished), p. 14.
[22] C. I. Beard and D. R. Bianco, J. Chem. Phys. **20**, 1488 (1952).
[23] Jen, Bianco, and Massey, J. Chem. Phys. **21**, 520 (1953).
[24] Weisbaum, Beers, and Herrmann, Phys. Rev. **90**, 338 (1953); Y. Beers and S. Weisbaum, Phys. Rev. **91**, 1014 (1953); S. Weisbaum and Y. Beers (private communication).
[25] King, Hainer, and Cross, Phys. Rev. **71**, 433 (1947); hereafter referred to as KHC II.

the present work is concerned primarily with the HDO microwave spectrum and its analysis.

An attempt at such an analysis has previously been made,[26] but inadequacy of the then known data prevented it from being very successful. Concurrently with the present work, Weisbaum and Beers have investigated this problem and published a preliminary report;[24] their results will be discussed below.

2. ROTATIONAL ENERGIES OF MOLECULES

Nielsen[10,14] has derived expressions for the energies of the general vibrating-rotating molecule. We wish to express some of his results in terms of the phase choice of KHC I;[27] our notation is similar to that of reference 14, though we have made minor alterations; the details of some of our equations do, however, differ somewhat from those given in the works cited.

We use a central-force coordinate system in which to express the potential energy. Let s_{ij} and s_{ij}^e be the distance and equilibrium distance, respectively, between the i-th and j-th nuclei in the molecule, and let $r_{ij}=s_{ij}-s_{ij}^e$ be the "relative displacement" from equilibrium. The potential energy, through cubic terms, may be written $V=V_0+V_1$, where V_0 is the quadratic term and V_1 the cubic term. For the water-type molecule, numbering the central (oxygen) nucleus "1," and writing r_1, r_2, $r_3\equiv r_{12}$, r_{13}, r_{23}, respectively, we have:

$$V_0=K_{11}(r_1^2+r_2^2)+K_{33}r_3^2+2K_{12}r_1r_2+2K_{13}(r_1+r_2)r_3$$
$$=\tfrac{1}{2}\sum_s\omega_s^2Q_s^2=\tfrac{1}{2}\hbar\sum_s\omega_sq_s^2, \tag{1}$$

where Q_s is the s-th normal coordinate, $\omega_s=2\pi\nu_s=2\pi c\tilde{\nu}_s$ is the sth normal angular frequency, and $q_s=(\omega_s/\hbar)^{\frac{1}{2}}Q_s$. The cubic term is

$$V_1=K_{111}(r_1^3+r_2^3)+K_{112}r_1r_2(r_1+r_2)+K_{113}r_3(r_1^2+r_2^2)$$
$$+K_{133}r_3^2(r_1+r_2)+K_{333}r_3^3+K_{123}r_1r_2r_3$$
$$=\sum_{s\le s'\le s''}k_{ss's''}Q_sQ_{s'}Q_{s''}=\sum_{ss's''}k_{ss's''}q_sq_{s'}q_{s''}. \tag{2}$$

By neglecting effects due to the electronic contribution to the rotational energy,[28] and omitting discussion of degeneracies, Coriolis, and other vibrational effects (which do not interfere with the ground states of the molecules under discussion), the rotational energies, to the second order of perturbation theory, may be obtained as follows.

The Hamiltonian is

$$H_R=\tfrac{1}{2}\sum_{gg'}\sigma_{gg'}{}^vP_gP_{g'}$$
$$+\tfrac{1}{4}\sum_{gg'g''g'''}\tau_{gg'g''g'''}P_gP_{g'}P_{g''}P_{g'''}, \tag{3}$$

where

$$\sigma_{gg'}{}^v=(\delta_{gg'}/I_{gg'}{}^e)-\sum_s(v_s+\tfrac{1}{2})b_s{}^{(gg')},$$
$$\tau_{gg'g''g'''}=-\tfrac{1}{2}(1/I_{gg}{}^eI_{g'g'}{}^eI_{g''g''}{}^eI_{g'''g'''}{}^e)$$
$$\times\sum_s(a_s{}^{(gg')}a_s{}^{(g''g''')})/\omega_s^2,$$
$$b_s{}^{(gg')}=(1/I_{gg}{}^eI_{g'g'}{}^e)(\hbar/\omega_s) \tag{4}$$
$$\times[A_{ss}{}^{(gg')}-\sum_{g''}(a_s{}^{(gg'')}a_s{}^{(g'g'')})/I_{g''g''}{}^e$$
$$-4\sum_{s'}\zeta_{ss'}{}^{(g)}\zeta_{ss'}{}^{(g')}\omega_s^2/(\omega_s^2-\omega_{s'}{}^2)$$
$$-3\omega_s\sum_{s'}k_{sss'}a_{s'}{}^{(gg')}/(\hbar\omega_{s'})^{\frac{3}{2}}].$$

Here g, g', etc., stand for x, y, z in the equilibrium principal axis system, $I_{gg'}{}^e$ is an equilibrium moment or product of inertia, P_g is the component of total angular momentum along the g-th axis, the v_s are vibrational quantum numbers defining the vth vibrational state, $\delta_{gg'}$ is the Kronecker delta, and $a_s{}^{(gg')}$, $A_{ss}{}^{(gg')}$, and $\zeta_{ss'}{}^{(g)}$ have been defined elsewhere.[1,14]

Since the $b_s{}^{(gg')}$ are small, we may write

$$I_{gg'}{}^v=1/\sigma_{gg'}{}^v\approx I_{gg}{}^e[\delta_{gg'}+I_{gg}{}^e\sum_s(v_s+\tfrac{1}{2})b_s{}^{(gg')}],$$

from which a useful expression for the inertia defect[5] of a planar molecule can be obtained. With the usual convention $I_{aa}\leqslant I_{bb}\leqslant I_{cc}$, and with

$$\Delta_v=I_{cc}{}^v-I_{aa}{}^v-I_{bb}{}^v, \tag{5}$$

it is easily shown that

$$\Delta_v\approx-\sum_s(v_s+\tfrac{1}{2})(\hbar/\omega_s)\{(a_s{}^{(cc)})^2/I_{cc}{}^e$$
$$-[(a_s{}^{(aa)})^2+(a_s{}^{(ab)})^2]/I_{aa}{}^e$$
$$-[(a_s{}^{(bb)})^2+(a_s{}^{(ab)})^2]/I_{bb}{}^e$$
$$+4\sum_{s'}(\zeta_{ss'}{}^{(c)})^2\omega_s^2/(\omega_s^2-\omega_{s'}{}^2)\}. \tag{6}$$

For the water molecule this approximation is good to a few percent.[1]

In a symmetric top representation, with the phase choice of KHC I, the matrix elements of the Hamiltonian (3) become:

$$(K|H_R|K)=R_0+R_2K^2-D_KK^4,$$
$$(K|H_R|K\pm1)=[g(J,K\pm1)]^{\frac{1}{2}}(2K\pm1)\{\tfrac{1}{2}(B_{yz}{}^v\pm iB_{zx}{}^v)$$
$$+(R_8{}^{(x)}\pm iR_8{}^{(y)})J(J+1)$$
$$+(R_9{}^{(x)}\pm iR_9{}^{(y)})[K^2+(K\pm1)^2]\},$$
$$(K|H_R|K\pm2)=[g(J,K\pm1)g(J,K\pm2)]^{\frac{1}{2}}\{(R_4\pm iR_4')$$
$$-(R_5\pm iR_5')[K^2+(K\pm2)^2]\}, \tag{7}$$
$$(K|H_R|K\pm3)=[g(J,K\pm1)g(J,K\pm2)g(J,K\pm3)]^{\frac{1}{2}}$$
$$\times(2K\pm3)(R_7{}^{(y)}\pm iR_7{}^{(x)}),$$
$$(K|H_R|K\pm4)=[g(J,K\pm1)g(J,K\pm2)g(J,K\pm3)$$
$$\times g(J,K\pm4)]^{\frac{1}{2}}(R_6\pm iR_6'),$$

[26] W. H. Lewis, thesis, Massachusetts Institute of Technology, 1951 (unpublished).
[27] King, Hainer, and Cross, J. Chem. Phys. **11**, 27 (1943); hereafter referred to as KHC I.
[28] B. F. Burke and M. W. P. Strandberg, Phys. Rev. **90**, 303 (1953).

where

$$\begin{aligned} R_0&=\tfrac{1}{2}(B_{xx}{}^v+B_{yy}{}^v)J(J+1)-D_JJ^2(J+1)^2,\\ R_2&=B_{zz}{}^v-\tfrac{1}{2}(B_{xx}{}^v+B_{yy}{}^v)-D_{JK}J(J+1),\\ R_4&=\tfrac{1}{4}(B_{yy}{}^v-B_{xx}{}^v)+\delta_JJ(J+1),\\ R_4'&=\tfrac{1}{2}B_{xy}{}^v+\delta_J'J(J+1), \end{aligned} \tag{8}$$

$$B_{gg'}{}^v=\tfrac{1}{2}\hbar^2\sigma_{gg'}{}^{v(\mathrm{eff})}=\hbar^2/2I_{gg'}{}^{v(\mathrm{eff})}, \tag{9}$$

$$\sigma_{gg'}{}^{v(\mathrm{eff})}=\sigma_{gg'}{}^v-D_{gg'},$$

$$g(J,K\pm1)=J(J+1)-K(K\pm1), \tag{10}$$

and

$$\begin{aligned} D_{xx}&=\beta(\tau_{xxxx}+\tau_{yyyy}-2\tau_{xxyy}+4\tau_{xyxy}\\ &\qquad-12\tau_{yzyz}+8\tau_{zxzx}),\\ D_{yy}&=\beta(\tau_{xxxx}+\tau_{yyyy}-2\tau_{xxyy}+4\tau_{xyxy}\\ &\qquad+8\tau_{yzyz}-12\tau_{zxzx}),\\ D_{zz}&=-\tfrac{3}{4}(D_{xx}+D_{yy})+5\beta(\tau_{yzyz}+\tau_{zxzx}),\\ D_{xy}&=20\beta\tau_{yzzx},\\ D_{yz}&=-5\beta(\tau_{yzxx}-\tau_{yzyy}-2\tau_{xyzx}),\\ D_{zx}&=5\beta(\tau_{zxxx}-\tau_{zxyy}+2\tau_{xyyz}),\\ D_J&=-2\beta^2(3\tau_{xxxx}+3\tau_{yyyy}+2\tau_{xxyy}+4\tau_{xyxy}),\\ D_K&=D_J-16\beta^2(\tau_{zzzz}-\tau_{zzxx}-\tau_{yyzz}-2\tau_{yzyz}-2\tau_{zxzx}),\\ D_{JK}&=-D_J-D_K-16\beta^2\tau_{zzzz},\\ \delta_J&=-4\beta^2(\tau_{xxxx}-\tau_{yyyy}),\\ \delta_J'&=8\beta^2(\tau_{xxxy}+\tau_{yyxy}),\\ R_5&=-2\beta^2(\tau_{xxxx}-\tau_{yyyy}+2\tau_{yyzz}-2\tau_{zzxx}\\ &\qquad+4\tau_{yzyz}-4\tau_{zxzx}),\\ R_5'&=4\beta^2(\tau_{xxxy}+\tau_{yyxy}-2\tau_{zzxy}-4\tau_{yzxz}),\\ R_6&=\beta^2(\tau_{xxxx}+\tau_{yyyy}-2\tau_{xxyy}-4\tau_{xyxy}),\\ R_6'&=-4\beta^2(\tau_{xxxy}-\tau_{yyxy}),\\ R_7{}^{(x)}&=-4\beta^2(\tau_{zxxx}-\tau_{zxyy}-2\tau_{xyyz}),\\ R_7{}^{(y)}&=-4\beta^2(\tau_{zyxx}-\tau_{zyyy}+2\tau_{xyzx}),\\ R_8{}^{(x)}&=4\beta^2(\tau_{yzxx}+3\tau_{yzyy}+2\tau_{xyzx}),\\ R_8{}^{(y)}&=4\beta^2(3\tau_{zxxx}+\tau_{zxyy}+2\tau_{xyyz}),\\ R_9{}^{(x)}&=-R_8{}^{(x)}+8\beta^2\tau_{yzzz},\\ R_9{}^{(y)}&=-R_8{}^{(y)}+8\beta^2\tau_{zxzz}, \end{aligned} \tag{11, 12}$$

in which $\beta=\hbar^2/8$.

The effective reciprocal moments $B_{gg}{}^v$ are usually denoted by a, b, and c, and ordered so that $a\leqslant b\leqslant c$. "Off-diagonal" terms may appear in molecules of low symmetry, e.g., HDO. For the latter molecule, in a I^r representation, the $b_s{}^{(zx)}$ are nonvanishing, and a $B_{zx}{}^v$ exists; then the first term of the Hamiltonian is not a sum of squares, but can be made so by a simple rotation of axes (which also mixes up the τ's of the second term).[1,8]

Following the notation of KHC I, we can rewrite certain terms in the rotational matrix (7) thus:

$$\begin{aligned} R_0&=\tfrac{1}{2}(a+c)J(J+1)+\tfrac{1}{2}(a-c)FJ(J+1)\\ &\qquad-D_J{}^2(J+1)^2,\\ R_2&=\tfrac{1}{2}(a-c)(G-F)-D_{JK}J(J+1),\\ R_4&=\tfrac{1}{4}(a-c)H+\delta_JJ(J+1), \end{aligned} \tag{13}$$

where, for a I^r representation, $F=\frac{1}{2}(\kappa-1)$, $G-F=-\frac{1}{2}(\kappa-3)$, $H=-\frac{1}{2}(\kappa+1)$, and $\kappa=(2b-a-c)/(a-c)$.

For the particular case of HDO in a I^r representation, after transforming the $B_{gg'}{}^v$ to principal axes, it is convenient to write

$$H_R=\tfrac{1}{2}(a+c)J(J+1)-D_JJ^2(J+1)^2+\tfrac{1}{2}(a-c)E, \tag{14}$$

where E is the *reduced energy matrix* with elements

$$\begin{aligned} E_{K\,K}&=FJ(J+1)\\ &\quad+[(G-F)-D_{JK}J(J+1)]K^2-D_KK^4,\\ E_{K\,K\pm1}&=\pm i[g(J,K\pm1)]^{\frac{1}{2}}(2K\pm1)\{\tfrac{5}{2}R_7{}^{(x)}\\ &\quad+R_8{}^{(y)}J(J+1)+R_9{}^{(y)}[K^2+(K\pm1)^2]\},\\ E_{K\,K\pm2}&=[g(J,K\pm1)g(J,K\pm2)]^{\frac{1}{2}}\{\tfrac{1}{2}H+\delta_JJ(J+1)\\ &\quad-R_5[K^2+(K\pm2)^2]\},\\ E_{K\,K\pm3}&=\pm i[g(J,K\pm1)g(J,K\pm2)\\ &\quad\times g(J,K\pm3)]^{\frac{1}{2}}(2K\pm3)R_7{}^{(x)},\\ E_{K\,K\pm4}&=[g(J,K\pm1)g(J,K\pm2)\\ &\quad\times g(J,K\pm3)g(J,K\pm4)]^{\frac{1}{2}}R_6, \end{aligned} \tag{15}$$

in which D_{JK}, D_K, δ_J, R_5, R_6, $R_7{}^{(x)}$, $R_8{}^{(y)}$, and $R_9{}^{(y)}$ now stand for the original distortion constants divided by $\frac{1}{2}(a-c)$; they are the *reduced distortion constants*. The above result is equally applicable to H_2O and D_2O, but the vanishing of $R_7{}^{(x)}$, $R_8{}^{(y)}$, and $R_9{}^{(y)}$ for these molecules very considerably simplifies computational problems.

It is apparent that the major complexity of the problem lies in the reduced energy matrix. This can be transformed to a basis of Wang functions, using the transformation X of KHC I in the usual manner. In the presence of $(K|K\pm1)$ and $(K|K\pm3)$ elements, the resulting matrix can now be factored into two submatrices only, corresponding to symmetric (+) and antisymmetric (−) Wang functions, and these submatrices are of order $J+1$ and J, respectively; they

take the forms

$$(+)=\begin{pmatrix} H_{00} & H_{01} & H_{02} & H_{03} & H_{04} & 0 & 0 & \cdots & \cdots \\ H_{10} & H_{11}^{+} & H_{12}^{+} & H_{13}^{+} & H_{14} & H_{15} & 0 & \cdots & \cdots \\ H_{20} & H_{21}^{+} & H_{22}^{+} & H_{23} & H_{24} & H_{25} & H_{26} & \cdots & \cdots \\ H_{30} & H_{31}^{+} & H_{32} & H_{33} & H_{34} & H_{35} & H_{36} & \cdots & \cdots \\ H_{40} & H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & H_{46} & \cdots & \cdots \\ 0 & H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & H_{56} & \cdots & \cdots \\ 0 & 0 & H_{62} & H_{63} & H_{64} & H_{65} & H_{66} & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix},$$

$$(-)=\begin{pmatrix} H_{11}^{-} & H_{12}^{-} & H_{13}^{-} & H_{14} & H_{15} & 0 & \cdots & \cdots \\ H_{21}^{-} & H_{22}^{-} & H_{23} & H_{24} & H_{25} & H_{26} & \cdots & \cdots \\ H_{31}^{-} & H_{32} & H_{33} & H_{34} & H_{35} & H_{36} & \cdots & \cdots \\ H_{41} & H_{42} & H_{43} & H_{44} & H_{45} & H_{46} & \cdots & \cdots \\ H_{51} & H_{52} & H_{53} & H_{54} & H_{55} & H_{56} & \cdots & \cdots \\ 0 & H_{62} & H_{63} & H_{64} & H_{65} & H_{66} & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \end{pmatrix}, \quad (16)$$

where

$$H_{0\,K}=2^{\frac{1}{2}}E_{0\,K}, \quad (K=1,2,3,4)$$
$$H_{K\,K'}{}^{\pm}=E_{K\,K'}\pm E_{-K\,K'}, \quad (17)$$

and otherwise

$$H_{K\,K'}=E_{K\,K'}.$$

Here

$$E_{-K\,-K-1}=E_{K\,K+1}, \qquad E_{-K\,-K+1}=E_{K\,K-1},$$
$$E_{K+1\,K}=-E_{K\,K+1}, \qquad E_{K+3\,K}=-E_{K\,K+3}, \quad (18)$$

etc.

Although these matrices may present a formidable appearance for large J values, they can be handled, for computation purposes, by an extension of the continued-fraction method described by KHC I for the rigid rotor case; a detailed account of the procedure is given in Appendix D of reference 1.[29]

3. THEORETICAL PARAMETERS

Our "theoretical" computations are based on the following geometrical model of the water molecule:[30] $r_{OH}=0.9584\times10^{-8}$ cm, $\angle HOH=104°27'$. For atomic masses we take $m(H)=1.67341233\times10^{-24}$ g, $m(D)=3.34428232\times10^{-24}$ g, $m(O^{16})=26.55872000\times10^{-24}$ g. As fundamental constants we use[31] $c=2.9979\times10^{10}$ cm/sec, $h=6.62363\times10^{-27}$ erg sec. On the assumption that the equilibrium geometry and the potential constants are invariant to isotopic substitution, the latter constants may be obtained from infrared data;[5,32] using the normal "frequencies" (in cm^{-1}): H_2O, $\bar{\nu}_1=3825.32$, $\bar{\nu}_2=1653.91$, $\bar{\nu}_3=3935.59$; D_2O, $\bar{\nu}_1=2758.06$, $\bar{\nu}_2=1210.25$, $\bar{\nu}_3=2883.79$, we obtain (in dyne/cm$\times10^5$) $K_{11}=9.04949641$, $K_{12}=0.52397791$, $K_{13}=-1.20497839$, $K_{33}=2.04835571$. Reference 5 also gives the cubic constants for H_2O (in cm^{-1}), $\alpha_1=-322$, $\alpha_2=-47$, $\alpha_3=1$, $\alpha_4=216$, $\alpha_5=-909$, $\alpha_6=160$; these are related to our $k_{ss's''}$ according to $k_{111}=hc\alpha_1$, $k_{112}=k_{121}=k_{211}=-hc\alpha_3/3$, $k_{122}=k_{212}=k_{221}=hc\alpha_4/3$, $k_{133}=k_{313}=k_{331}=hc\alpha_5/3$, $k_{233}=k_{323}=k_{332}=-hc\alpha_6/3$, $k_{222}=-hc\alpha_2$; from them we get (in dyne/cm$^2\times10^{12}$) $K_{111}=-84.56753212$, $K_{112}=57.47345798$, $K_{113}=-35.92925361$, $K_{133}=24.61366648$, $K_{333}=-2.51799700$, $K_{123}=-96.56701865$.

Here, as in the sequel, parameters are frequently quoted to significant figures far in excess of the accuracy warranted by the data (for example, the cubic potential constants are known to perhaps one significant figure only). However, it appears to be undesirable to attempt to work only to estimated accuracies since this may easily lead to a rounding-off errors. Accordingly, we quote here the actual numbers used in our computations.

A detailed listing of intermediate quantities is given in reference 1. Here we record only those parameters which enter directly into the rotational matrix; Table I shows these (in a I^r representation).

TABLE I. "Theoretical" parameters. (a) Before principal axis transformation. (b) After principal axis transformation.

	H_2O	D_2O	HDO (a)	HDO (b)
	Effective rotation constants (Mc/sec$\times10^5$)			
a	8.3172247	4.6128487	6.97845341	6.97876766
b	4.3413336	2.1741669	2.72550273	2.72522145
c	2.7779216	1.4504848	1.91859173	1.91863695
$d=B_{zx}{}^0$	0	0	−0.03262965	0
	Inertia defect (g cm$^2\times10^{-40}$)			
Δ_0	0.07609087	0.10381619	0.08676075	0.08676075
	Asymmetry parameter			
κ	−0.43552032	−0.54231577	−0.68105413	−0.68120013
	Distortion constants (Mc/sec)			
D_J	28.92348858	7.45681896	9.01676826	9.14172899
D_K	729.36580935	225.00743493	279.94933771	287.08933921
D_{JK}	−112.71978845	−32.66381366	41.47209724	36.81321390
δ_J	14.00262952	3.46850038	3.24683339	3.33311881
R_5	31.16163450	8.12053047	9.03150455	−7.87718656
R_6	−3.05588799	−0.69525362	−0.54839883	−0.57220390
$R_7{}^{(x)}$	0	0	3.05952301	3.11603472
$R_8{}^{(y)}$	0	0	−8.00882857	−9.19943988
$R_9{}^{(y)}$	0	0	50.81694501	49.91730954

[29] For an effectively similar treatment in the case of vanishing $(K|K\pm1)$ and $(K|K\pm3)$ matrix elements, see also B. L. Crawford, Jr., and P. C. Cross, J. Chem. Phys. 5, 621 (1937).

[30] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 489.

[31] J. A. Bearden and H. M. Watts, Phys. Rev. 81, 73 (1951).

[32] W. H. Shaffer and R. R. Newton, J. Chem. Phys. 10, 405 (1942).

TABLE II. H_2O microwave absorption lines.

Transition	Observed	Frequency (Mc/sec) KHC II	RDGW[a]	"Theoretical" (this work)
$2_{20}\rightarrow3_{13}$	...	184 000	182 000	187 471
$5_{23}\rightarrow6_{16}$	22 235.22±0.05	23 380	20 400	24 588

[a] See reference 3.

4. MICROWAVE SPECTRUM OF H_2O

The K-band "radar water line" at 22 235 Mc/sec,[17,18] because of the $5_{23}\rightarrow6_{16}$ transition of H_2O, has been observed by a number of workers, and is the only microwave line known to belong to this molecule.

Examination of the KHC II tables shows that no other H_2O lines are likely to be found below about 180 000 Mc/sec ($2_{20}\rightarrow3_{13}$ transition); the difficulties of working in this region, however, make it desirable that a better prediction be available before searching is carried out. The one known H_2O line does not give us enough information to improve our knowledge—the KHC II tables, based on $\kappa=-0.436426$, predict it at the rigid rotor frequency of 23 400 Mc/sec, some 1000 Mc/sec too high, and the term values of reference 3 show it at 20 400 Mc/sec, so it is apparent that better parameters are needed. The present work shows no better agreement with experiment; with the parameters of Table I our calculations give the results shown in Table II.

We will show in Sec. 6 that we can expect the "theoretical" parameters to give a good estimate of the distortion, so it is interesting to compare our calculated energy levels with those of RDGW,[3] as in Table III; here the "distortion correction" is the total energy (as shown) minus the calculated rigid rotor energy.

There is little else we can say about H_2O at present, but it is hoped that eventually better values of the parameters will be deducible from the results of investigations of other isotopic modifications.

5. MICROWAVE SPECTRUM OF D_2O

The $2_{20}\rightarrow3_{13}$ and $5_{32}\rightarrow4_{41}$ transitions of D_2O were found in the course of a general search,[21] though only the first of these was identified; both lines were subsequently reported independently.[22] Their frequencies, together with those calculated from the parameters of Table I, are shown in Table IV.

TABLE III. H_2O energy levels.

Level	RDGW[a] Energy (Mc/sec ×10⁶)	RDGW[a] Distortion correction (Mc/sec ×10⁶)	This work Energy (Mc/sec ×10⁶)	This work Distortion correction (Mc/sec ×10⁶)
2_{20}	4.080100	−0.004800	4.066769	−0.008787
3_{13}	4.262100	−0.001500	4.254240	0.001449
5_{23}	13.386000	−0.026382	13.352540	−0.040304
6_{16}	13.407000	−0.015000	13.377127	0.025789

[a] See reference 3.

In the FRD work, distortion corrections were obtained semiclassically; in Table V we compare the distortion corrections calculated here with those given by FRD.

It is expected that additional useful work can be done on D_2O. Two weak lines in the water spectrum have been observed[23] at 30 182.57±0.1 and 30 778.62 ±0.1 Mc/sec, and these are as yet unidentified. In the next section we investigate probable HDO transitions, and find none in this region, though these calculations are not conclusive. Thus there is a good chance that these two lines may be due to D_2O.

6. MICROWAVE SPECTRUM OF HDO

A. Introduction

Until recently there has been little infrared work carried out on HDO because of the difficulty of untangling its lines from those of H_2O and D_2O. From one such infrared analysis, however, KHC II deduced $\kappa=-0.685$, from which they constructed their rigid rotor tables of expected HDO microwave transitions.

TABLE IV. D_2O microwave absorption lines.

Transition	Observed	Frequency (Mc/sec) FRD[a]	"Theoretical"[b]
$2_{20}\rightarrow3_{13}$	10 919.39±0.05[b] 10 919.8 ±0.1[c]	7500	10 670
$5_{32}\rightarrow4_{41}$	10 947.13±0.05[b] 10 947.4 ±0.1[c]	16 000	17 472

[a] The KHC II tables give rigid rotor term values taken from FRD (reference 4); in Tables IV and V we quote the FRD "corrected" levels.
[b] This work.
[c] Reference 22.

Previous to this publication, the only microwave line of HDO known was the $5_{33}\rightarrow5_{32}$ transition.[17,19] On the basis of these tables, however, Strandberg[20] located the $2_{21}\rightarrow2_{20}$, $3_{22}\rightarrow3_{21}$, and $4_{14}\rightarrow3_{21}$ lines, and estimated $\kappa=-0.696$.

Three other lines were then found by workers in this Laboratory[33]; the $4_{32}\rightarrow4_{31}$ line, the $7_{44}\rightarrow7_{43}$ line, and an unidentified line at 26 880 Mc/sec. During the present investigations the latter was found to have been originally discovered by McAfee[34] who assigned it to a D_2O transition; it is the conclusion of this work that it is the $6_{24}\rightarrow7_{17}$ transition of HDO.

Concurrently with the present work, Weisbaum and Beers[24] discovered a number of lines in the S-band region, and identified the transitions $6_{43}\rightarrow6_{42}$, $9_{55}\rightarrow9_{54}$, $12_{67}\rightarrow12_{66}$, and $4_{22}\rightarrow5_{05}$; we were advised of these investigations privately, though the final identity of

[33] Microwave Spectroscopy Laboratory, Research Laboratory of Electronics, Massachusetts Institute of Technology (unpublished work).
[34] K. B. McAfee, Jr., Doctoral thesis, Harvard, 1949 (unpublished).

the lines was not reasonably certain until a late stage in the present work.

We have now observed the $8_{45}\rightarrow 8_{44}$, $10_{56}\rightarrow 10_{55}$, and $11_{57}\rightarrow 11_{56}$ transitions.

The $8_{45}\rightarrow 8_{44}$ line has been independently reported,[23] and these workers also conclude from the Stark effect that the 26 880-Mc/sec line is to be assigned to the HDO $6_{24}\rightarrow 7_{17}$ transition.

The present state of experimental knowledge of the HDO microwave spectrum is summarized in Table VI.

B. "Theoretical" Frequencies

In principal, transition frequencies may be calculated by diagonalization of the rotational matrix to find the appropriate energy levels, then taking differences. We call this "exact" calculation, though in practice it may involve finding characteristic values by numerical approximation method; in our computations we have used sufficient significant figures to get within the experimental error.

TABLE V. D_2O energy levels.

Level	FRD Energy (Mc/sec $\times 10^6$)	FRD Distortion correction	This work Energy (Mc/sec $\times 10^6$)	This work Distortion correction
2_{20}	2.2193	0	2.2184	−0.003049
3_{13}	2.2268	−0.009000	2.2291	−0.000694
4_{41}	8.0641	−0.001200	8.0665	−0.049868
5_{32}	8.0481	−0.026400	8.0490	−0.016747

As indicated in Sec. 3, the main problem is the determination of the "reduced energies"; unless otherwise stated, the following discussion will be in terms of "reduced" parameters.

In the original assumption that $(K|K\pm 1)$ and $(K|K\pm 3)$ matrix elements could be safely neglected, we carried out some "exact" calculations for Q-branch transitions, using the appropriate constants of column a of Table I. With $\nu^0(J_K)$ and $\nu(J_K)$ the observed and calculated frequencies, the results are shown in Table VII.

It is noticed that the differences (last column of Table VII) increase in an apparently fairly regular manner within each K family; a significant relationship is obtained by simply taking the ratios $r(J_K)=\nu(J_K)/\nu^0(J_K)$, which are substantially constant (to about five significant figures) for a given value of K. If we use r_K to denote the average of $r(J_K)$, for different J but the same K, we find, for $r=2$, 3, 4, 5, 6, that $r_K=1.00937$, 1.02013, 1.03163, 1.04242, 1.05445, respectively, and that $r_6/r_4=1.02212$, $r_4/r_2=1.02205$, $r_5/r_3=1.02185$, or, $r_K/r_{K-2}=1.0220$, approximately. (The values of r_K/r_{K-1} are less consistent.)

At the time of these calculations, only the identities and frequencies of the lines 2_2, 3_2, 4_3, 5_3, 7_4, 8_4 had been definitely established. Assuming the ratio r_K/r_{K-2} (i.e., r_4/r_2) was significant, we predicted the 6_4, 9_5, and 12_6 lines at 2394.2, 3045.1, and 2961.2 Mc/sec, respectively. The agreement with the then tentatively reported frequencies of these lines appeared so good that we extended the predictions to the 6_3, 10_5, and 11_5 lines,

TABLE VI. HDO observed microwave absorption lines.

Transition	Frequency (Mc/sec)	Reference
	Q-branch transitions	
$2_{21}\rightarrow 2_{20}$	10 278.99	20
$3_{22}\rightarrow 3_{21}$	50 236.90	20
$3_{31}\rightarrow 3_{30}$	824.64±0.05	24[a]
$4_{32}\rightarrow 4_{31}$	5702.78	33
$5_{33}\rightarrow 5_{32}$	22 309 ±5	17
	22 307.67±0.05	19
$6_{43}\rightarrow 6_{42}$	2394.56±0.05	24[a]
$7_{44}\rightarrow 7_{43}$	8576.89	33
	8577.7 ±0.1	This work
$8_{45}\rightarrow 8_{44}$	24 884.77±0.05	This work
	24 884.85±0.1	23
$9_{55}\rightarrow 9_{54}$	3044.71±0.10	24[a]
$10_{56}\rightarrow 10_{55}$	8836.95±0.1	This work
$11_{57}\rightarrow 11_{56}$	22 581.1 ±0.2	This work
$12_{67}\rightarrow 12_{66}$	2961 ±1	24[a]
	P- and R-branch transitions	
$4_{14}\rightarrow 3_{21}$	20 460.40	20
$4_{22}\rightarrow 5_{05}$	2887.4 ±0.1	24[a]
$6_{24}\rightarrow 7_{17}$	26 880.44	34
	26 880.38±0.05	This work[b]
	26 880.47±0.1	23

[a] This table quotes the latest reported measured values (see reference 24), which were not available to us at the time our work was carried out. The $3_{22}\rightarrow 3_{21}$ line was discovered subsequently, and is included here for completeness.

[b] Our identification of this transition is based partly on Stark (see reference 21) and Zeeman (see reference 28) effect data, and partly on the results of analysis of the remainder of the spectrum (see below).

TABLE VII. HDO Q-branch "theoretical" frequencies (1).

Transition[a] J_K	Frequency (Mc/sec) Observed[b] $\nu^0(J_K)$	Calculated $\nu(J_K)$	$\nu^0(J_K)-\nu(J_K)$
2_2	10 278.99	10 375.742	−96.752
3_2	50 236.90	50 705.828	−468.928
4_3	5702.78	5817.548	−114.768
5_3	22 307.67	22 756.857	−449.187
6_3	...	65 714.268	...
6_4	2394.6	2470.073	−75.473
7_4	8577.7	8849.329	−271.629
8_4	24 884.77	25 673.369	−788.599
9_5	3044.7	3174.077	−129.377
10_5	8836.95	9211.967	−375.017
11_5	22 581.1	23 536.847	−955.747
12_6	2961	3122.212	−161.212

[a] Here and in the sequel we will usually use J_K to denote the Q-branch transition J_{K-1}, $\kappa_1\rightarrow J_{K-1}$, $\kappa_1{}_{-1}$, with K standing for K_{-1}, the index denoting the K value of the limiting prolate symmetric rotor.

[b] "Observed" frequencies listed here are those actually used in computations, before the later measurements of Table VI were available.

thus:

6_3, 64 417 Mc/sec;
10_5, 8836 Mc/sec;
11_5, 22 577 Mc/sec.

A search for the latter two lines subsequently showed them at 8837 and 22 581 Mc/sec, respectively.

We may also "extrapolate" similarly to predict the 1_1 line at 80 743 Mc/sec, but the prediction is probably not quite so accurate here because the dependence on the distortion constants is less complicated functionally.

This simple "extrapolation method" of predicting Q-branch frequencies of HDO therefore seems to be quite reliable. It appears to have the significance that the major contribution to $\nu^0(J_K)-\nu(J_K)$ comes from variations in $\frac{1}{2}(a-c)$ and κ. This is reasonable since the transition frequencies are most sensitive to small percentage variations in the effective moments, and these in turn depend partly on the anharmonic potential constants (which are not known accurately); moreover, the distortion constants should be fairly reliable because the harmonic portion of the potential is known accurately.

Thus we conclude tentatively that the "theoretical" distortion corrections are good approximations to the true corrections.

The foregoing calculations have neglected the effects of $(K|K\pm1)$ and $(K|K\pm3)$ matrix elements. The major contribution from these arises from the off-diagonal moment I_{zx}^0; its removal by a principal axis transformation leads to the parameters of column b, Table I, which provide the frequencies $\nu^t(J_K)$ of Table VIII. In this tabulation, $\nu(J_K)$ denotes frequencies computed on a similar basis to those of Table VII, i.e., with $R_7^{(x)}$, $R_8^{(y)}$, and $R_9^{(y)}$ set equal to zero; the last column, $\nu^c(J_K)=\nu^t(J_K)-\nu(J_K)$, lists the correction frequencies due to the 1- and 3-off matrix elements.

Relations between the r_K now no longer hold so nicely as before, either for $\nu(J_K)/\nu^0(J_K)$ or $\nu^t(J_K)/\nu^0(J_K)$; this fact seems to be due to some large error appearing in the original I_{zx}^0. However, the magnitude of the $\nu^c(J_K)$ shows that the effects of $R_7^{(x)}$, $R_8^{(y)}$, and $R_9^{(y)}$ certainly cannot be neglected. We note that the energy level contributions, due to these parameters, arise mainly from the $(K|K\pm1)$ elements [particularly the terms in $R_9^{(y)}$—as may be expected from Table I], and increase with K; for the 12_6 levels the correction is some $-15\,000$ Mc/sec—about 0.5 cm^{-1}, which is of sufficient magnitude to interest the infrared spectroscopists.

Including 1- and 3-off matrix elements, "theoretical" frequencies for the three P- and R-branch transitions of Table VI are shown in Table IX; we cannot yet draw any useful conclusions from these results.

TABLE VIII. HDO Q-branch "theoretical" frequencies (2).

Transition	Calculated frequency (Mc/sec) $\nu(J_K)$	$\nu^t(J_K)$	$\nu^c(J_K)$
2_2	10 369.484	10 369.413	−0.071
3_2	50 670.284	50 670.692	0.408
4_3	5812.013	5811.893	−0.116
5_3	22 727.785	22 729.495	1.710
6_4	2466.454	2466.551	0.097
7_4	8830.310	8835.272	4.962
8_4	25 599.113	25 611.148	12.035
9_5	3163.981	3167.166	3.185
10_5	9168.512	9182.991	14.479
11_5	23 394.123	23 426.396	32.273
12_6	3099.340	3114.354	15.014

C. Approximate Calculations

A much simpler method of calculating Q-branch transitions between K-doublet levels can be obtained by expanding the matrices to first order in the distortion parameters;[13,15] we refer to the method as the HSKW formula, for short, and use the following notation. Let

$$\begin{aligned}\Delta^{(1)}(J_K)=&2KJ(J+1)\delta_J/H\\&+(K-1)J(J+1)D_{JK}/(G-F)\\&-(4/3)K(K^2+2)R_5/H\\&+(2/3)K(K-1)(2K-1)D_K/(G-F)\\&+(8/3)K(K^2-1)(G-F)R_6/H^2\end{aligned}\quad(19)$$

be the first-order approximation to the (reduced) distortion correction. Then, to first order, the transition frequency is given by

$$\nu^{(1)}(J_K)=\nu^R(J_K)[1+\Delta^{(1)}(J_K)],\quad(20)$$

where $\nu^R(J_K)$ is the calculated rigid rotor frequency. This is, in effect, the HSKW formula in terms of reduced distortion constants.

The HSKW formula is not claimed to be anything more than a first order approximation; we will show its limitations for the case of HDO, where the distortion effects are large, and where the approximation cannot be expected to agree perfectly with the exact calculation.

Since (19) neglects 1- and 3-off matrix elements, it is fair to compare $\nu^{(1)}(J_K)$, as calculated by (20), with $\nu(J_K)$ of Table VIII. In Table X we show $\nu^{(1)}(J_K)$, together with the "exact" calculated distortion correction $\nu^d(J_K)=\nu(J_K)-\nu^R(J_K)$, the difference $\nu(J_K)-\nu^{(1)}(J_K)$, and the percentage difference $p=100\times[\nu(J_K)-\nu^{(1)}(J_K)]/\nu^d(J_K)$. It is clear that for the "theoretical" parameters, at least, the agreement be-

TABLE IX. HDO P- and R-branch "theoretical" frequencies.

Transition	Frequency (Mc/sec) Observed	Calculated
$4_{14}\rightarrow3_{21}$	20 460.40	−13 397.134
$4_{22}\rightarrow5_{05}$	2888	10 761.553
$6_{24}\rightarrow7_{17}$	26 880.38	27 811.867

tween the exact and HSKW methods is quite good for low J and K, but cannot be pushed too far.

D. Methods of Analysis of the Spectrum

It is apparent that we must first analyze the Q-branch spectrum; only two parameters $\frac{1}{2}(a+c)$ and D_J are then needed to account for other transitions.

In our attempt to analyze the microwave spectrum of HDO so as to obtain "true" molecular constants we have been guided by the behavior of the "theoretical" (infrared) parameters. For example, it is apparent from our discussion of these that the HSKW formula should agree with "exact" calculations to a few percent; *it is our experience that, in the fitting process, the "theoretical" distortion parameters cannot be varied by more than a few percent without giving rise to serious discrepancies between the HSKW approximation and "exact" calculations* (even though the distortion corrections remain substantially constant as required by the extrapolation method).

We have tried several methods of obtaining a "fit," always using the "exact" calculations to check our results. In these, we have assumed the $\nu^c(J_K)$, as given in Table VIII, to be constant, and have made allowance for them, thus attempting to fit the seven parameters $x_i=\frac{1}{2}(a-c)$, κ, D_{JK}, D_K, δ_J, R_5, and R_6.

(a) *Variation of all parameters*

Assuming a fit can be obtained by making only small changes in the parameters x_i, we may write

$$\nu^0(J_K)-\nu^c(J_K)=\nu(J_K)+\Delta\nu(J_K), \tag{21}$$

and

$$\Delta\nu(J_K)=\sum_i \frac{\partial\nu(J_K)}{\partial x_i}\Delta x_i. \tag{22}$$

The $\partial\nu/\partial x_i$ are readily calculable to sufficient accuracy. Solution of this set of simultaneous equations for the Δx_i, and iteration of the process, gives results which do not converge and which show large discrepancies between the $\nu(J_K)$ and $\nu^{(1)}(J_K)$. Similar difficulties arise when the $\nu^c(J_K)$ are neglected. It thus appears that close agreement cannot be obtained with seven parameters.

(b) *Variation of $\frac{1}{2}(a-c)$, κ, only*

Keeping the "theoretical" distortion parameters constant [though modifying the reduced parameters with change of $\frac{1}{2}(a-c)$], we can simplify the method (a) by varying only $\frac{1}{2}(a-c)$ and κ, using a least squares reduction of the equations. This gives frequency differences of the order of one percent of the distortion corrections, and is the method finally used.

If we were to follow the Hillger and Strandberg method,[13,26] we would now use the HSKW formula to vary the distortion parameters so as to improve the fit.

TABLE X. HDO Q-branch "theoretical" frequencies (3).

Transition J_K	Frequency (Mc/sec) $\nu^{(1)}(J_K)$	$\nu^d(J_K)$	$\nu(J_K)-\nu^{(1)}(J_K)$	p
2_2	10 369.603	−50.026	−0.119	0.24
3_2	50 671.812	−322.733	−1.529	0.47
4_3	5812.112	−79.667	−0.099	0.12
5_3	22 727.744	−390.265	0.041	−0.011
6_4	2466.391	−71.639	0.063	−0.088
7_4	8829.172	−311.383	1.138	−0.37
8_4	25 588.117	−1082.154	10.996	−1.02
9_5	3161.580	−197.722	2.401	−1.21
10_5	9158.796	−676.855	9.716	−1.44
11_5	23 345.677	−2008.58	48.446	−2.41
12_6	3091.899	−369.063	7.441	−2.02

As in method (a), however, we find that any such attempts—when checked by "exact" calculations—are doomed to failure.

The same difficulties were experienced when 1- and 3-off matrix elements were completely neglected.

(c) *Variation of $\frac{1}{2}(a-c)$, κ, keeping $\Delta^{(1)}(J_K)$ constant*

This method involves small changes in the "fundamental" distortion parameters, since $\Delta^{(1)}(J_K)$ is a function of $\frac{1}{2}(a-c)$ and κ. It does not seem to be much more satisfactory than (b), though it does give somewhat better agreement between $\nu(J_K)$ and $\nu^{(1)}(J_K)$. However, although the "theoretical" percentage differences p of Table X are small, there does not appear to be any reason why the true ones should be exactly the same magnitude—convenient though this might be.

As a result of these investigations we conclude that it is not possible to get a "perfect" fit with seven parameters. The next approximation, inclusion of $(K|K\pm1)$ and $(K|K\pm3)$ matrix elements, gives little better results; we believe this is due to considerable error in the $\nu^c(J_K)$ and/or neglect of other approximations, e.g., in the vibrational diagonalization of the energy matrix. Unfortunately, there seems to be no convenient way of varying the $\nu^c(J_K)$ so as to be able to consider them adjustable in the fitting process; in principal, this can be done by making small changes in the three additional parameters $R_7^{(x)}$, $R_8^{(y)}$, and $R_9^{(y)}$, and calculating the effect on the ν's; since we have been unable to find a simple way of doing this, it is apparent that a considerable amount of labor would be involved.

At this stage, then, we have to be satisfied with agreement to a few percent of the distortion corrections. Method (a) does not give this since the changes in the magnitude of the parameters which are required to force a fit become too large for the method to be valid. Methods (b) and (c) do give reasonable agreement, though there is little to decide between the two. We arbitrarily choose method (b), because it involves variation only of the effective moments, whose "theo-

TABLE XI. HDO Q-branch frequencies (4).

J_K	$\nu^t(J_K)$ (Mc/sec)	$\nu^0(J_K)-\nu^t(J_K)$ (Mc/sec)	$\nu^d(J_K)$ (Mc/sec)	p	$\nu^D(J_K)$ (Mc/sec)	P
2_2	10 275.660	3.330	−50.099	−2.2	−50.170	−6.6
3_2	50 232.692	4.208	−322.636	−1.4	−322.228	−1.3
4_3	5701.757	1.023	−79.600	−3.3	−79.716	−1.3
5_3	22 307.350	0.320	−388.924	−2.8	−387.214	−0.083
6_4	2395.019	−0.419	−71.277	−4.2	−71.180	0.59
7_4	8582.081	−4.381	−308.872	−3.8	−303.910	1.4
8_4	24 865.250	19.520	−1096.841	−1.5	−1084.806	−1.8
9_5	3041.952	2.748	−196.823	−4.2	−193.638	−1.4
10_5	8829.125	7.825	−666.128	−4.8	−651.649	−1.2
11_5	22 538.263	42.837	−1972.977	−5.4	−1940.704	−2.2
12_6	2961.394	−0.394	−360.668	−5.9	−345.654	0.11

retical" accuracy is more liable to suspicion because of their dependence on the anharmonic potential constants.

E. Results of Analysis of the Spectrum

Starting from Table VIII, but omitting the data on the 10_5 and 11_5 lines (which were not then known), a least squares solution for $\Delta[\frac{1}{2}(a-c)]$ and $\Delta\kappa$ was obtained from the nine equations of the form of (22), leading to the following "observed" HDO parameters: $\frac{1}{2}(a-c)=2.55544755\times10^5$ Mc/sec, $\kappa=-0.68410904$, $D_{JK}=1.44057795\times10^{-4}$, $D_K=11.23440546\times10^{-4}$, $\delta_J=0.13043190\times10^{-4}$, $R_5=-0.30825076\times10^{-4}$, and $R_6=-0.02239153\times10^{-4}$. From these we get the $\nu(J_K)$ (as in Table VII), which give, with the $\nu^c(J_K)$ of Table VIII, the $\nu^t(J_K)=\nu(J_K)+\nu^c(J_K)$ of Table XI. Here also p and $\nu^d(J_K)$ have the same meaning as in Table X, while $\nu^D(J_K)=\nu^t(J_K)-\nu^R(J_K)$ is the total distortion correction, and $P=100\times[\nu^t(J_K)-\nu^t(J_K)]/\nu^D(J_K)$ is the percentage discrepancy (referred to the total distortion) between observed and calculated frequencies.

The worst (percentage) discrepancy occurs for the 2_2 line, which also has the least distortion; we believe this is a result of the least squares analysis, which weights this line the least.

Although P for the 11_5 line (which was not included in the analysis) is of the same order of magnitude as for the other lines, the actual frequency difference, 42 Mc/sec, between calculated and observed frequencies is much larger than we would expect from consideration of the extrapolation method discussed earlier; by keeping $\Delta^{(1)}(J_K)$ constant—method (b) of the preceeding sub-section—the difference is reduced to only about 3 Mc/sec, but the fit on the 8_4 line becomes worse (about 25 Mc/sec), and the over-all picture is about the same.

TABLE XII. HDO "observed" rotation-distortion constants.

$\frac{1}{2}(a+c)$	4.48416164 ×10⁵ Mc/sec	δ_J	3.33311881 Mc/sec
$\frac{1}{2}(a-c)$	2.55544755 ×10⁵ Mc/sec	R_5	−7.87718656 Mc/sec
κ	−0.68410904	R_6	−0.57220390 Mc/sec
D_J	11.56583333 Mc/sec	$R_7^{(x)}$	3.11603472 Mc/sec
D_{JK}	36.81321390 Mc/sec	$R_8^{(y)}$	−8.19943988 Mc/sec
D_K	287.08933921 Mc/sec	$R_9^{(y)}$	49.91730954 Mc/sec

It is interesting to refer to Table X and note how small changes in $\Delta^{(1)}(J_K)$, because of the variation of $\frac{1}{2}(a-c)$ and κ, markedly affect p, even though $\nu^d(J_K)$ is almost the same in the two cases.

We believe the general agreement shown in Table XI is as good as one can get using the present methods. Slight improvement might be obtained by now feeding in the 10_5 and 11_5 data, but this will not lead to any significant change in our final results.

With the Q-branch spectrum "solved," it is a simple matter to analyze the P- and R-branch lines. Since we have concluded that the "theoretical" distortion constants are good approximations to the true ones, we ought to get fairly consistent values of $\frac{1}{2}(a+c)$ from the $|\Delta J|=1$ transitions on the assumption that D_J is also good. With the value of D_J given in column b of Table I, the three lines of Table VI give an average $\frac{1}{2}(a+c)$ of $(4.4827\pm0.0020)\times10^5$ Mc/sec, which is apparently good to about four significant figures (we take this to be a measure of just how reliable our major parameters are). This average value gives the following frequencies: $4_{14}\rightarrow3_{21}$, 21 058.871 Mc/sec; $4_{22}\rightarrow5_{05}$, 2740.896 Mc/sec; $6_{24}\rightarrow7_{17}$, 28 133.594 Mc/sec. Although the agreement cannot be described as excellent, it is a great improvement on Table IX, and argues for some consistency in our work, as well as providing support for the identification of the 26 880-Mc/sec line. It shows that the distortion constants are fairly good, and that reasonable correlation with experiment can be obtained by changes in the effective moments alone.

Further improvement is obtained if we allow D_J to vary; a least squares solution for $\frac{1}{2}(a+c)$ and D_J gives 4.48416164×10^5 and 11.56583333 Mc/sec, respectively, from which the calculated frequencies now become $4_{14}\rightarrow3_{21}$, 20 515.856 Mc/sec; $4_{22}\rightarrow5_{05}$, 2983.326 Mc/sec; $6_{24}\rightarrow7_{17}$, 26 843.995 Mc/sec. The differences between observed and calculated frequencies are now −55.456 Mc/sec, −95.326 Mc/sec, and 36.385 Mc/sec, respectively.

Since these results are obtained in a very straightforward manner, the agreement must be regarded as quite good, even though we have had to change D_J by some 25 percent.

Table XII summarizes the results of the foregoing analysis of the HDO microwave spectrum, the distortion constants quoted being the "fundamental" values.

From $\frac{1}{2}(a+c)$, $\frac{1}{2}(a-c)$, and κ, the effective moments and reciprocal moments of inertia are easily obtained and are shown in Table XIII.

There is less than one percent difference between "theoretical" and "observed" values, and this change in three parameters, together with a comparatively large variation in D_J, has been all we have introduced to get a reasonably good fit to the spectrum.

Some rotational energy levels, calculated from the constants of Table XII, are shown in Table XIV. The effects of $(K|K\pm1)$ and $(K|K\pm3)$ matrix elements have not been taken into account exactly here, though

in some cases the corresponding "theoretical" energy corrections have been included.

Using Table XIV, some of the $|\Delta J|=1$ transitions expected from KHC II have been calculated, and are shown in Table XV. Attempts to observe the $7_{07}\rightarrow 6_{24}$ line, in the vicinity of 12 200 Mc/sec, have so far been unsuccessful.

F. Discussion of Results

Although the agreement between observed and finally calculated $|\Delta J|=1$ transitions is considered good, the large change we had to make in D_J is inconsistent with our assumption that the "theoretical" distortion constants are very close to the true ones. But it is apparent that the parameters entering into the Q-branch frequencies must be known more accurately before we can draw precise conclusions about $\frac{1}{2}(a+c)$ and D_J; the values we get for these two constants are therefore to be regarded as containing the lumped errors of the other parameters, and this has to be born in mind when examining the results of Table XIII.

TABLE XIII. HDO effective moments and reciprocal moments of inertia.

	Theoretical	Observed
a	6.97876766×10^{5} Mc/sec	7.03960919×10^{5} Mc/sec
b	2.72522145×10^{5} Mc/sec	2.73595687×10^{5} Mc/sec
c	1.91863695×10^{5} Mc/sec	1.92871409×10^{5} Mc/sec
I_a	1.20206397×10^{-40} g cm^2	1.19167485×10^{-40} g cm^2
I_b	3.07825449×10^{-40} g cm^2	3.06617597×10^{-40} g cm^2
I_c	4.37233588×10^{-40} g cm^2	4.34949132×10^{-40} g cm^2
Δ	0.09201742×10^{-40} g cm^2	0.09164050×10^{-40} g cm^2

We would like to have Q-branch parameters that are good enough to calculate "exactly" frequencies which will agree with observations to within something like 1 Mc/sec, if not better. Any such agreement obtained by the use of approximation methods (e.g., the HSKW method) must be checked by "exact" calculations, otherwise the constants obtained cannot be considered the true molecular parameters, but are merely constants in a semiempirical formula. We believe that the results obtained by Weisbaum *et al.*[24] should be described in the latter manner.

The present work has shown that such desirable Q-branch parameters are unachievable if only the seven quantities $\frac{1}{2}(a-c)$, κ, D_{JK}, D_K, δ_J, R_5, and R_6 are considered. Remaining discrepancies turn out to be of the order of magnitude of the corrections introduced by taking $R_7^{(x)}$, $R_8^{(y)}$, and $R_9^{(y)}$ into account, but inclusion of these corrections still leaves much to be desired. The assumption of the essential correctness of the "theoretical" distortion parameters leads one to expect that only small changes in $R_7^{(x)}$, $R_8^{(y)}$, and $R_9^{(y)}$ should be tolerated, and it is unlikely that such small changes would lead to significant differences in the corrections $\nu^c(J_K)$. Thus it is probable that either our theories and/or calculations involving $R_7^{(x)}$, $R_8^{(y)}$, and $R_9^{(y)}$ are incorrect, or that we must look elsewhere to improve our results; this means examination of higher terms in the vibration-rotation theory, e.g., terms in the Hamiltonian of the order of $\mathbf{P}^6$, where $\mathbf{P}$ is an angular mo-

TABLE XIV. HDO rotational energies.

Level	Energy (Mc/sec$\times10^6$) Rigid W^R	Nonrigid W^N	Distortion W^N-W^R
2_{21}	3.282311	3.276432	−0.005879
2_{20}	3.292637	3.286708	−0.005929
3_{22}	4.681712	4.673735	−0.007977
3_{21}	4.732267	4.723968	−0.008299
4_{14}	4.707305	4.703452	−0.003853
4_{22}	6.684485	6.671355	−0.013130
4_{32}	8.925689	8.890918	−0.034771
4_{31}	8.931471	8.896619	−0.034852
5_{05}	6.682430	6.674338	−0.008092
5_{24}	8.848938	8.834291	−0.014648
5_{23}	9.163016	9.141062	−0.021954
5_{33}	11.285626	11.241421	−0.044205
5_{32}	11.308320	11.263728	−0.044592
6_{06}	9.225386	9.210664	−0.014722
6_{24}	12.169757	12.133066	−0.036691
6_{33}	14.186789	14.127912	−0.058877
6_{43}	17.392922	17.272528	−0.120394
6_{42}	17.395389	17.274923	−0.120466
7_{07}	12.145962	12.120853	−0.025109
7_{17}	12.184437	12.159910	−0.024527
7_{16}	14.288870	14.245622	−0.043248
7_{35}	17.429084	17.349701	−0.079383
7_{44}	20.707197	20.561306	−0.145891
7_{43}	20.716083	20.569888	−0.146195
8_{45}	24.504725	24.324235	−0.180490
8_{44}	24.530675	24.349100	−0.181575
8_{53}	28.685244	28.376901	−0.308343
9_{46}	28.786442	28.560607	−0.225835
9_{55}	32.950146	32.584549	−0.365597
9_{54}	32.953382	32.587591	−0.365791
10_{56}	37.702535	37.268638	−0.433897
10_{55}	37.712015	37.277468	−0.434547
11_{57}	42.944157	42.424541	−0.519616
11_{56}	42.968636	42.447079	−0.521557
12_{67}	53.721091	52.829222	−0.891869
12_{66}	53.724398	52.832183	−0.892215

TABLE XV. HDO predicted P- and R-branch frequencies.

Transition	Frequency (Mc/sec)
$7_{07}\rightarrow6_{24}$	12 198
$5_{24}\rightarrow4_{31}$	62 447
$5_{23}\rightarrow6_{06}$	69 602
$6_{42}\rightarrow7_{35}$	74 778
$6_{33}\rightarrow7_{16}$	117 710
$8_{53}\rightarrow9_{46}$	183 710

TABLE XVI. HDO parameters.

Rotation-distortion constants					
$\frac{1}{2}(a+c)$	4.484	$\pm 0.002 \times 10^5$ Mc/sec	δ_J	3.333	± 0.005 Mc/sec
$\frac{1}{2}(a-c)$	2.555	$\pm 0.005 \times 10^5$ Mc/sec	R_5	−7.877	± 0.010 Mc/sec
κ	−0.684	±0.00002	R_6	−0.572	± 0.005 Mc/sec
D_J	9.1	±1.5 Mc/sec	$R_7^{(x)}$	3.12	± 0.05 Mc/sec
D_{JK}	36.8	±0.5 Mc/sec	$R_8^{(y)}$	−8.20	± 0.05 Mc/sec
D_K	287	±5 Mc/sec	$R_9^{(y)}$	50.0	± 0.5 Mc/sec

Effective moments and reciprocal moments of inertia	
a	$7.0396 \pm 0.0005 \times 10^5$ Mc/sec
b	$2.7360 \pm 0.0005 \times 10^5$ Mc/sec
c	$1.9186 \pm 0.0005 \times 10^5$ Mc/sec
I_a	$1.1917 \pm 0.0005 \times 10^{-40}$ g cm^2
I_b	$3.0662 \pm 0.0005 \times 10^{-40}$ g cm^2
I_c	$4.3495 \pm 0.0005 \times 10^{-40}$ g cm^2

mentum operator. Rough calculations, based on orders of magnitude, indicate that such terms probably will be negligible for the present work, but one cannot be conclusive about this without going into considerable detail.

It is our opinion that any improvement in the present results will have to be obtained with the aid of a high-speed digital computer to set up exactly and solve equations of the type of (22). Notwithstanding the conclusions of the previous paragraph, it may still be possible to get a satisfactory solutions by including variations of $R_7^{(x)}$, $R_8^{(y)}$, and $R_9^{(y)}$, the corresponding $\partial\nu/\partial x_i$ being obtained by computer diagonalization of the complete matrices; this possibility ought to be considered early in any extension of this work, since even small changes in the $\nu^c(J_K)$ could conceivably bring about a neat fit—the transition frequencies are much more sensitive to changes in certain parameters (e.g., κ) than in others.

The good agreement we get for $|\Delta J| = 1$ transitions gives some confidence in our final results. However, it must be pointed out that the consistency vanishes if the 26 880-Mc/sec line is not the $6_{24} \rightarrow 7_{17}$ transition, or if the 2888-Mc/sec line is actually the $5_{05} \rightarrow 4_{22}$ transition. Our information[24] is that the latter is the $4_{22} \rightarrow 5_{05}$ line, though we are not aware of any evidence (e.g., Stark data) to show the relative positions of the levels.

To conclude this sub-section, we give in Table XVI what we consider to be reasonable HDO parameters; these are obtained by rounding off the constants of Tables XII and XIII; the accuracies indicated have been estimated by us on the basis of our experience with the problem.

7. CONCLUSION

By analysis of the microwave rotational spectrum of HDO we have obtained approximate values of the molecular parameters which are in fairly good agreement with the theoretically calculated constants. The "theoretical" values, derived from infrared data on H_2O and D_2O, together with some observed microwave frequencies enabled us to calculate HDO Q-branch frequencies with rather unexpected accuracy; it must be considered very gratifying that we can do this in view of the rather tortuous calculations that have had to be carried out in going from one isotopic molecule to another.

Distortion effects in this type of molecule have been found to be large, so large that to get detailed agreement between theory and observation (in the microwave region) one must use higher approximations in the theory than had previously been considered necessary. Our results are by no means final, and possible methods of improving them have been indicated.

During preparation of this paper several other authors have reported infrared[35] and microwave[36] work on the water molecule, and comparison with the present account be of interest when detailed descriptions are published.

8. ACKNOWLEDGMENTS

The authors are grateful to Dr. Y. Beers and Dr. S. Weisbaum for making available to us their results prior to publication; to J. D. Kierstead who assisted with the experimental work; and to Miss H. Paul who carried out some of the computations.

One of us (D.W.P.) would like to acknowledge a grant from the Commonwealth Scientific and Industrial Research Organization, Australia.

[35] Benedict, Gailar, and Plyler, J. Chem. Phys. **21**, 1301 (1953); Benedict, Gailar, and Plyler, J. Chem. Phys. **21**, 1302 (1953).

[36] W. Gordy, J. Chim. Phys. **50** (9), C114 (1953); Duke University Report No. 3, Aug. 1, 1953, to Nov. 1, 1953 (unpublished)