

Dipole moment of water from Stark measurements of H<sub>2</sub>O, HDO, and D<sub>2</sub>O

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(Received 7 May 1973)

The equilibrium dipole moment of the water molecule has been determined from Stark effect measurements on two H<sub>2</sub>O, one D<sub>2</sub>O, and six HDO rotational transitions. The variation of the dipole moment projection operator with rotational state is taken into account and expressions are given for this operator evaluated in the ground vibrational states of the three isotopes. The value obtained for the equilibrium dipole moment is  $|\mu_x| = 1.8473 \pm 0.0010$  D. The effective dipole moments in the principal axis energy representation are  $|\mu_b(\text{HOH})| = 1.8546 \pm 0.0006$  D,  $|\mu_b(\text{DOD})| = 1.8558 \pm 0.0021$  D and  $|\mu_b(\text{DOH})| = 1.7318 \pm 0.0009$  D,  $|\mu_a(\text{DOH})| = 0.6567 \pm 0.0004$  D.

## INTRODUCTION

The dipole moment of the water molecule has been determined by several authors using methods including Stark effect and bulk dielectric measurements.<sup>1-6</sup> This paper describes the determination of the equilibrium dipole moment for the water molecule using Stark effect measurements on two H<sub>2</sub>O transitions, six HDO transitions, and one D<sub>2</sub>O transition. In a subsequent article the determination of the dipole moment will be described by Dyke and Muentner<sup>7</sup> using a molecular beam method on three H<sub>2</sub>O and three D<sub>2</sub>O rotational levels.

The ability to obtain a single value of the equilibrium dipole moment to a precision consistent with the experimental limits of the Stark measurements is due to the inclusion of electrical distortion in the dipole moment function, the availability of improved eigenvalues and eigenvectors for the molecules considered, improved methods of treating the data, and significantly more accurate Stark effect measurements.

## THEORY

The Hamiltonian for the Stark effect is given by  $H = -\mu \cdot \mathcal{E} = -\mathbf{M} \cdot \mathcal{E}$ , where  $\mu$  is the dipole moment operator,  $\mathcal{E}$  is the electric field, and  $\mathbf{M}$  is the projection of the dipole moment on the space-fixed (field) axis.  $\mathbf{M}$  is expanded through the second order as follows:

$${}^0\mathbf{M} = \sum_{\alpha} ({}^0\mu_{\alpha}) \Phi_{\alpha}, \quad (1)$$

$${}^1\mathbf{M} = \sum_{\alpha} \sum_i ({}^1\partial\mu_{\alpha}/\partial q_i) \mathbf{q}_i \Phi_{\alpha}, \quad (2)$$

$${}^2\mathbf{M} = \sum_{\alpha} \sum_{ij} ({}^2\partial^2\mu_{\alpha}/\partial q_i \partial q_j) \mathbf{q}_i \mathbf{q}_j \Phi_{\alpha}, \quad (3)$$

where the superscript on  $\mathbf{M}$  denotes the order of magnitude in an appropriate expansion parameter  $\lambda$ ,  $\Phi_{\alpha}$  is the direction cosine between the  $\alpha$ -molecular-fixed axis and the space-fixed axis,  $q$  is a dimensionless normal coordinate, and the quantities in parentheses are electric constants of the molecule and for convenience may be given in Debye units ( $10^{-18}$  esu · cm). The equilibrium dipole moment ( ${}^0\mu_{\alpha}$ ), within the restrictions of the Born-Oppenheimer approximation, is independent of isotopic substitution for a given molecule. The geometric representation that we will use in the present study is that shown in Fig. 1. It is to be noted that the permanent dipole lies on the  $x$  axis and is assumed to point in the negative  $x$  direction, and consequently  ${}^0\mu_x$  will be designated as a negative quantity. The phases of the dipole moment derivatives are chosen to be consistent with this convention.

It is next necessary to obtain the dipole moment function to second order in the representation in which the vibration-rotation Hamiltonian is vibrationally diagonal to second order. It is most convenient to use the contact transformation method to obtain this result. If  $S'$  is the transformation function which diagonalizes the Hamiltonian to second order, then matrix elements of the dipole moment function in this representation (the  $\dagger$  representation) are given as

$${}^0\mathbf{M}_{ij}^{\dagger} = {}^0\mathbf{M} \delta_{ij}, \quad (4)$$

$${}^1\mathbf{M}_{ij}^{\dagger} = {}^1\mathbf{M}_{ij}, \quad (5)$$

$${}^2\mathbf{M}_{ij}^{\dagger} = {}^2\mathbf{M}_{ij} + \{ {}^1\mathbf{H}_{im}, {}^1\mathbf{M}_{mj} \}_{R \in im} + \{ {}^1\mathbf{M}_{im}, {}^1\mathbf{H}_{mj} \}_{R \in jm} + [ {}^1\mathbf{H}_{ij}, {}^0\mathbf{M} ]_{R \in ij}, \quad (6)$$

where we follow the notation of Rothman and

TABLE I. Dipole derivative constants for the water molecule given in Debye units ( $10^{-18}$  esu · cm).

$\alpha$	HOH		DOH <sup>a</sup>		DOD <sup>a</sup>	
	$b$	$a$	$b$	$a$	$b$	$a$
$^1(\partial\mu_\alpha/\partial q_1)$	-0.0216	0	0.0050	-0.058	-0.024	0
$^1(\partial\mu_\alpha/\partial q_2)$	0.161	0	0.120	0.107	0.137	0
$^1(\partial\mu_\alpha/\partial q_3)$	0	0.0950	-0.0401	0.0611	0	0.0868

<sup>a</sup>Constants for DOH and DOD are calculated from observed values for HOH. See Ref. 10.

Clough<sup>8</sup> in which  $\{, \}$  and  $[, ]_R$  indicate rotational anticommutators and commutators, respectively.

$^1H_{ij}$  is the matrix element of the vibration-rotation Hamiltonian in the principal axis, harmonic oscil-

lator representation and  $\epsilon_{ij} \equiv 1/({}^0H_{ii} - {}^0H_{jj})$  (for  $i=j$ ,  $\epsilon_{ij} \equiv 0$ ). For the numerical constants needed in the calculations, force constants were derived from the work of Benedict *et al.*<sup>9</sup> Unfortunately, unambiguous values for  $^2(\partial^2\mu_\alpha/\partial q_i^2)$  which contribute directly to the coefficient of  $\Phi_\alpha$  in  $^2M$ ,

$$\langle 000 | {}^2(\partial^2\mu_\alpha/\partial q_i^2) \mathbf{q}_i^2 | 000 \rangle = \frac{1}{2} {}^2(\partial^2\mu_\alpha/\partial q_i^2),$$

are not available for water and this contribution has necessarily been neglected. Using the constants of Table I, the dipole moment projection operators for the ground vibrational states of the three isotopic species as a function of the direction cosine and angular momentum operators are

HOH:

$$^0M = {}^0\mu_x \Phi_b,$$

$$^1M = 0,$$

$$\begin{aligned} ^2M = & -0.0067 \Phi_b + 1.06 \times 10^{-4} \{\Phi_b, P_b^2\} - 3.34 \times 10^{-6} \{\Phi_b, P_c^2\} \\ & - 4.05 \times 10^{-4} \{\Phi_b, P_a^2\} - 3.34 \times 10^{-5} \{\Phi_c, (P_b P_c + P_c P_b)\} \\ & + 6.69 \times 10^{-5} \{\Phi_a, (P_a P_b + P_b P_a)\}; \end{aligned} \quad (7)$$

DOH:

$$^0M = {}^0\mu_x \cos\phi_0 \Phi_b + {}^0\mu_x \sin\phi_0 \Phi_a,$$

$$^1M = 0,$$

$$\begin{aligned} ^2M = & -0.0088 \Phi_b + 1.78 \times 10^{-5} \{\Phi_b, P_b^2\} - 9.13 \times 10^{-5} \{\Phi_b, P_c^2\} \\ & - 9.53 \times 10^{-5} \{\Phi_b, P_a^2\} + 5.85 \times 10^{-5} \{\Phi_b, (P_a P_b + P_b P_a)\} \\ & - 1.44 \times 10^{-5} \{\Phi_c, (P_b P_c + P_c P_b)\} + 3.66 \times 10^{-4} \{\Phi_c, (P_c P_a + P_a P_c)\} \\ & + 0.0067 \Phi_a + 6.70 \times 10^{-5} \{\Phi_a, P_b^2\} + 2.34 \times 10^{-4} \{\Phi_a, P_c^2\} \\ & - 5.21 \times 10^{-4} \{\Phi_a, P_a^2\} + 1.18 \times 10^{-4} \{\Phi_a, (P_a P_b + P_b P_a)\}; \end{aligned} \quad (8)$$

DOD:

$$^0M = {}^0\mu_x \Phi_b,$$

$$^1M = 0,$$

$$\begin{aligned} ^2M = & -0.0052 \Phi_b + 5.33 \times 10^{-5} \{\Phi_b, P_b^2\} + 8.40 \times 10^{-7} \{\Phi_b, P_c^2\} \\ & - 2.25 \times 10^{-4} \{\Phi_b, P_a^2\} - 2.21 \times 10^{-5} \{\Phi_c, (P_b P_c + P_c P_b)\} \\ & + 4.07 \times 10^{-5} \{\Phi_a, (P_a P_b + P_b P_a)\}. \end{aligned} \quad (9)$$

Using these expressions and the rotational constants in a principal axis representation for HOH, DOH, and DOD<sup>11</sup> obtained from an analysis using all available microwave data and some infrared data, line strengths were calculated in the energy representation. These line strengths were then used to obtain the Stark shifts as a function of  $M^2$ ,  $\mathcal{E}^2$ , and  ${}^0\mu_\alpha^0$ , where  $M$  is the projection of the total angular momentum along the space-fixed axis. Using the usual second order perturbation treatment,<sup>12</sup> we obtain

$${}^{2+4}E = \mathcal{E}^2 \sum_\alpha {}^0\mu_\alpha^2 ({}_0\gamma_\alpha + {}_2\gamma_\alpha M^2), \quad (10)$$

where  ${}_n\gamma_\alpha$  is the coefficient of  $M^n$  and includes the higher order contributions to the dipole moment and  $\alpha$  runs over the directions in the principal axis molecular coordinate system. For HOH and DOD there is a contribution to  ${}^{2+4}E$  only when  $\alpha = b$  and for DOH when  $\alpha = a, b$ . It is useful to write this expression in terms of the rotation angle to principal axes as follows

$${}^{2+4}E = {}^0\mu_x^2 \mathcal{E}^2 \{ {}_0\gamma_a \sin^2\phi_0 + {}_2\gamma_a \sin^2\phi_0 M^2 \\ + {}_0\gamma_b \cos^2\phi_0 + {}_2\gamma_b \cos^2\phi_0 M^2 \} \quad (11)$$

or in a more useful form as

$${}^{2+4}E = {}^0\mu_x^2 \mathcal{E}^2 \{ ({}_0\gamma_b + {}_2\gamma_b M^2) \\ + \sin^2\phi_0 [({}_0\gamma_a - {}_0\gamma_b) + ({}_2\gamma_a - {}_2\gamma_b) M^2] \} \quad (12)$$

since

$${}^0\mu_a = {}^0\mu_x \sin\phi_0, \quad {}^0\mu_b = {}^0\mu_x \cos\phi_0,$$

and

$$\sin^2\phi_0 + \cos^2\phi_0 = 1.$$

This result for the Stark energy shift of a rotational energy level includes the effect of electrical and mechanical distortion through fourth order.

There are two other fourth order effects which must be considered in the analysis of the Stark effect for a molecule such as water. One is the consideration of higher order terms in the perturbation treatment of the Stark calculations. It can be shown that the contribution from a fourth order treatment will have the form

$${}^4E = {}^0\mu_x \mathcal{E}^4 ({}_0\Delta + {}_2\Delta M^2 + {}_4\Delta M^4). \quad (13)$$

Although in principle it is possible to obtain the coefficients from an analysis of the Stark shifts, this has not been possible from our results due to

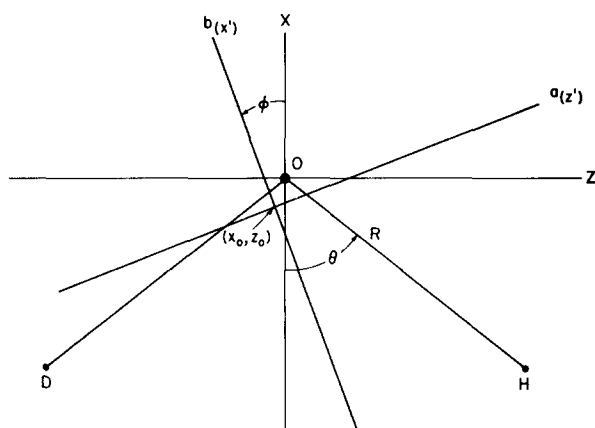


FIG. 1. Coordinate systems for the water molecule. The coordinates of the center of mass with respect to the origin at the oxygen atom are given as  $x_0$  and  $z_0$  in angstroms. The primed coordinate system is the principle axis system and the rotation angle from the unprimed system is  $\phi$ . The  $I'$  system is used where  $a \leftrightarrow z'$ ,  $b \leftrightarrow x'$ , and  $c \leftrightarrow y'$ . The phase for a positive change in the normal coordinates is chosen as  $q_1$ : DO stretch, OH stretch;  $q_2$ : increase in the band angle;  $q_3$ : DO contraction, OH stretch. Data are  $R = 0.9573412$  Å;  $\theta = 52.28026^\circ$ , and

	$x_0$	$z_0$	$\phi$
HOH	-0.0655487	0	0
DOH	-0.0930725	-0.0400709	21.05735°
DOD	-0.1178299	0	0.

the high correlation among the constants. Consequently, we have used calculated values for these coefficients. The most convenient expression for this calculation has been given by Kirchhoff,<sup>13</sup> as

$${}^4E_i = \sum_n \epsilon_{in} \left| \sum_m {}^1H_{im} {}^1H_{mn} \epsilon_{im} \right|^2 - {}^2E_i \sum_m |{}^1H_{im} \epsilon_{im}|^2, \quad (14)$$

where  ${}^2E_i$  is the result obtained from second order perturbation treatment,

$${}^2E_i = \sum_m |{}^1H_{im}|^2 \epsilon_{im}, \quad (15)$$

and the  ${}^1H_{im}$  are the matrix elements in the energy representation for the perturbation  $\mathbf{H} = -\boldsymbol{\mu} \cdot \boldsymbol{\mathcal{E}}$ .

The other effect that must be considered is the energy shift due to the polarizability of the molecule. This effect has the functional dependence

$${}^4E(\text{pol}) = ({}_0\Gamma(\text{pol}) + {}_2\Gamma(\text{pol}) M^2) \mathcal{E}^2 \quad (16)$$

and may be evaluated from the expression

$${}^4E(\text{pol}) = -\frac{1}{2} \mathcal{E}^2 \sum_{\alpha} (p_{\alpha\alpha} \Phi_{\alpha} \Phi_{\alpha}). \quad (17)$$

Diagonal elements of the polarizability tensor have been calculated for HOH by Liebmann and Moskowitz<sup>14</sup> and we have adopted the following polarizability constants:  $p_{aa} = 1.651$ ,  $p_{bb} = 1.452$ , and  $p_{cc} = 1.226$  ( $10^{-24}$  cm<sup>3</sup>). With these values the maximum correction to the observed frequency shifts is 4 kHz for the HOH transitions, 0.4 kHz for the DOD transition, and ignoring the off-diagonal element of the polarizability ( $p_{ab}$ ) 2 kHz for the DOH transitions. For the precision of our experimental data, these corrections are not significant.

## ANALYSIS AND RESULTS

The experimental details of the measurements have been discussed at length by Beers and Klein<sup>15</sup> for the data taken by them. The Stark shifts for the 22 GHz HOH line ( $6_{1,6} \rightarrow 5_{2,3}$ ) were kindly provided by Kirchhoff.<sup>16</sup> The values for the electric fields for the latter data were readjusted using the constants obtained by Muentert<sup>17</sup> for the Stark shifts on the OCS molecule to be consistent with the field determination for the other transitions. In all cases calculated fourth order corrections and experimental corrections were applied to the data before the least square analysis.

The analysis of the microwave Stark effect data has been carried out using the method of least squares. Each observed Stark shift has been appropriately weighted based on the error of the particular measurements and provides an input data point to the least squares analysis. The data for the several rotational transitions, two for HOH, six for DOH, and one for DOD, have been treated in several ways. In Method I, the analysis has been made as a function of  $\mathcal{E}^2$  and  $M^2 \mathcal{E}^2$  to obtain quanti-

ties  ${}_0\Gamma$  and  ${}_2\Gamma$  in the expression for the Stark shift,

$$\nu = \nu_0 + {}_0\Gamma \mathcal{E}^2 + {}_2\Gamma M^2 \mathcal{E}^2, \quad (18)$$

where

$${}_0\Gamma = {}^0\mu_x^2({}_0\gamma_b + \sin^2\phi_0({}_0\gamma_a - {}_0\gamma_b))$$

and

$${}_2\Gamma = {}^0\mu_x^2({}_2\gamma_b + \sin^2\phi_0({}_2\gamma_a - {}_2\gamma_b)). \quad (19)$$

Values for  ${}^0\mu^2$  can be obtained from calculated values of  ${}_0\gamma_a$ ,  ${}_2\gamma_a$ , and  $\sin\phi_0$ . This approach gives the best fit to the observed data and provides a measure of the experimental precision of the data since the rms error depends only on the assumed functional dependence. On the other hand, since there may be high correlation between  ${}_0\Gamma$  and  ${}_2\Gamma$ , this method does not provide reliable values for  ${}^0\mu$ . The transition frequencies (listed to the nearest megahertz) and the results of Method I including values of  ${}_0\Gamma$  and  ${}_2\Gamma$  are tabulated in Table II. The values given here vary slightly from those previously reported by Beers and Klein. These differences, most of which are within expected error limits, are due to a revision of some of the modulation errors and to adjustments in the weighting of some of the observations.

For Method II the data from each transition are utilized to obtain a value for  ${}^0\mu^2$  (also  ${}^0\mu^2 \sin^2\phi_0$ , if desired) using an expression for the shifts obtained from Eq. (12). In a third approach, Method III, the data for each isotopic species are analyzed using Eq. (12) to obtain a value of  ${}^0\mu^2$  for the three isotopes. The final method, Method IV, combines all the data together to obtain a single value for  ${}^0\mu^2$  (and again, if desired,  ${}^0\mu^2 \sin^2\phi_0$ ). When the data are combined, weights have been assigned to the measurements for each rotational transition which are inversely proportional to the rms error obtained for that transition from Method II. The results from Methods II, III, and IV are given in Table III.

The methods described for analyzing the DOH data allow for the determination of the angle through which the equilibrium coordinate system must be rotated to obtain principal axes. The change in the angle  $\phi_0$  as determined from the data is of the order of magnitude of the error and the improvement in the fit is not significant. Consequently, for the calculations on DOH the angle derived from the analysis of the structure has been assumed,  $\phi_0 = 21.05735^\circ$ .

The dipole moment constants given in Table III are for the equilibrium dipole moment. The effective dipole moment for the ground vibrational states of the three isotopes may be obtained by adding the second order coefficients of  $\Phi_\alpha$  from

TABLE II. Analysis of the Stark shift using Method I for which  $\nu_{\text{Stark}} = ({}_0\Gamma + {}_2\Gamma M^2)\mathcal{E}^2$ . The errors in the constants correspond to  $3\sigma$ .

Molecule	Transition	Frequency (MHz)	${}_0\Gamma$ (MHz (kV/cm) <sup>-2</sup> )	$\delta({}_0\Gamma)$ (MHz (kV/cm) <sup>-2</sup> )	${}_2\Gamma$ (MHz (kV/cm) <sup>-2</sup> )	$\delta({}_2\Gamma)$ (MHz (kV/cm) <sup>-2</sup> )	rms error (MHz)
HOH	3(1, 3) ← 2(2, 0)	183 310	0.077514	0.00011	-0.042180	0.00017	0.0027
	6(1, 6) ← 5(2, 3)	22 235	0.198564	0.0011	-0.009598	0.00015	0.007
DOH	2(1, 1) ← 2(1, 2)	241 562	-0.039080	0.0020	0.136290	0.00033	0.019
	2(2, 0) ← 3(1, 3)	266 161	0.071483	0.020	1.195894	0.020	0.044
	4(2, 2) ← 4(2, 3)	143 727	-0.114946	0.0014	0.026165	0.00009	0.013
	5(1, 5) ← 4(2, 2)	120 778	0.220745	0.00042	-0.027153	0.000024	0.006
	7(3, 5) ← 6(4, 2)	87 963	0.274479	0.0027	-0.404038	0.0027	0.022
	7(3, 4) ← 7(3, 5)	151 616	-0.096857	0.0013	0.006326	0.000027	0.012
DOD	4(1, 4) ← 3(2, 1)	151 710	0.129867	0.0008	-0.042510	0.00010	0.014

Eqs. (7)–(9) to the appropriate results for  ${}^0\mu_\alpha$  from Table III, Method III. We obtain for

HOH,  $\mu_b = \mu_x = -1.8546 \pm 0.0006$  D;

DOH,  $\mu_b = -1.7318 \pm 0.0009$  D,

$\mu_a = -0.6567 \pm 0.0004$  D,

$\mu_x = -[\mu_a^2 + \mu_b^2]^{1/2} = -1.8521 \pm 0.0012$  D,

DOD,  $\mu_b = \mu_x = -1.8558 \pm 0.0021$  D.

These values for DOH are applicable in the representation in which the rotational Hamiltonian is of the form

$$H_R = A\mathbf{P}_a^2 + B\mathbf{P}_b^2 + C\mathbf{P}_c^2$$

+ (terms of higher power in angular momentum).

Line strengths calculated from Eqs. (7)–(9) and corroborated by the Stark measurements enable improved atmospheric transmission calculations in the infrared. A tabulation of HOH energy levels, transition frequencies, and transition intensities using the dipole moment function reported here, will be published shortly.<sup>18</sup>

Aside from errors in the Stark data, the principal source of error in our analysis is in the higher order coefficients in the dipole moment expansion. More accurate experimental values of the first derivative constants, particularly for DOH and DOD, would be highly desirable. An estimate of the magnitude of the contribution to  ${}^2M$  from neglected terms of the type  ${}^2(\partial^2\mu_\alpha/\partial q_i^2)$  can be made from the observed intensities of the  $2\nu_1$ ,  $2\nu_2$ , and  $2\nu_3$  infrared bands of HOH. The strongest of these is  $2\nu_2$  and if it is assumed that all the intensity of that band is attributable to the dipole moment expansion, we obtain  $|{}^2(\partial^2\mu_\alpha/\partial q_i^2)| \approx 0.0066$  D. A calculation of the second order contribution to the  $2\nu_2$  band intensity from mechanical anharmonicity is of the order of 0.008 D. Consequently it is expected that the correction to the dipole moment from this source is of the order of

$$\langle 000 | (\partial^2\mu_b/\partial q_i^2) q_i^2 | 000 \rangle \approx \pm 0.0033 \text{ D.}$$

A more accurate determination of the dipole moment projection operator depends on the availability of these higher order constants from experiment or from *ab initio* calculations.

In conclusion we should like to discuss a number of points about which there appears to be confusion in the literature. The projection of the molecular dipole moment on a space-fixed axis  $Z$  for an asymmetric rotor in a given vibration–rotation state designated by  $[(v), J, K_a, K_c, M]$  is independent of field (neglecting polarizability) and is characterized by the good quantum number  $M$ , since

TABLE III. The dipole moment for the water molecule. Errors correspond to  $3\sigma$ . For DOH, the rotation angle to principal axes has been taken as  $\phi_0 = 21.05735^\circ$ . Negative values of  ${}^0\mu_x$  correspond to the dipole moment pointing in the negative  $x$  direction in Fig. 1.

Molecule	Transition	Method I <sup>a</sup>		Method II		Method III		Method IV	
		rms error (MHz)	${}^0\mu_x$ (D)	$\delta({}^0\mu_x)$ (D)	rms (MHz)	${}^0\mu_x$ (D)	$\delta({}^0\mu_x)$ (D)	${}^0\mu_x$ (D)	rms (MHz)
Water									
HOH									
	$3(1, 3) \leftarrow 2(2, 0)$	0.0027	-1.8480	0.0005	0.003	-1.8479	0.0006	-1.8473	0.005
	$6(1, 6) \leftarrow 5(2, 3)^b$	0.007	-1.8477	0.0015	0.007				0.008
DOH									
	$2(1, 1) \leftarrow 2(1, 2)$	0.019	-1.8489	0.0024	0.022	-1.8463	0.0012		0.019
	$2(2, 0) \leftarrow 3(1, 3)$	0.044	-1.8412	0.012	0.044				0.029
	$4(2, 2) \leftarrow 4(2, 3)$	0.013	-1.8463	0.0024	0.014				0.044
	$5(1, 5) \leftarrow 4(2, 2)$	0.006	-1.8453	0.0009	0.007				0.014
	$7(3, 5) \leftarrow 6(4, 2)$	0.022	-1.8506	0.006	0.022				0.010
	$7(3, 4) \leftarrow 7(3, 5)$	0.012	-1.8428	0.0033	0.013				0.026
DOD									0.016
	$4(1, 4) \leftarrow 3(2, 1)$	0.014	-1.8506	0.0021	0.014	-1.8506	0.0021		0.014
									0.023

<sup>a</sup>See Table II. <sup>b</sup>Stark shifts measured by W. Kirchhoff.

$P_z$  commutes with the Hamiltonian. For microwave Stark measurements, it is not the dipole moment of the transition that is observed as is sometimes implied, but rather the energy difference between two eigenstates, each state being characterized by its own expectation value of the dipole moment projection operator. From results published up to this point it is not possible to establish a difference between the effective dipole moment for the three isotopes, this difference being certainly less than 0.003 D. Finally we have observed no anomalous behavior of the dipole moment for DOH and the dipole moment projection function is evidently given adequately by Eq. (8).

*Note added in proof:* The representation for which Eq.'s (7), (8), and (9) are applicable, is that designated as the  $\Phi$  form, Reduction (a), [i.e., for  $I'$ ,  $\tilde{T}_6(bbcc) = \tilde{\Phi}_4(bbccc) = \tilde{\Phi}_5(ccbbb) = \tilde{\Phi}_6(bbcca) = 0$ ] by K. K. Yallabandi and P. M. Parker, J. Chem. Phys. **49**, 410 (1968). These equations in other representations, including that currently referred to as the Watson form in which  $\tilde{D}_6^* = \tilde{H}_6 = \tilde{H}_9 = \tilde{H}_{10} = 0$ , are available from SAC. The operator  $S'$  used to obtain these equations includes the effect of first order distortion, Coriolis, and anharmonic (cubic) terms in the Hamiltonian.

#### ACKNOWLEDGMENTS

We are pleased to acknowledge the many constructive discussions we have had with F. X. Kneizys in the course of this work. Also we are grateful to W. Kirchhoff for allowing us to use his results on the 22 GHz  $H_2O$  transition and to W. S. Benedict who has collaborated with us on the interpretation of the molecular data on water.

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