Dipole moment of water from Stark measurements of H2O, HDO, and D2O

Shepard A. Clough

Air Force Cambridge Research Laboratories (AFSC) Bedford, Massachusetts 01730

Yardley Brees and Gerald P. Klein

National Bureau of Standards, Boulder, Colorado 80302

Laurence S. Rothman

Air Force Cambridge Research Laboratories (AFSC) Bedford, Massachusetts 01730

(Received 7 May 1973)

INTRODUCTION

The dipole moment of the water molecule has been determined by several authors using methods including Stark effect and bulk dielectric measurements. This paper describes the determination of the equilibrium dipole moment for the water molecule using Stark effect measurements on two H2O transitions, six HDO transitions, and one D2O transition. In a subsequent article the determination of the dipole moment will be described by Dyke and Muenter using a molecular beam method on three H2O and three D2O 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 
\[ H = -\mu \cdot \delta = -M \delta, \]
where \( \mu \) is the dipole moment operator, \( \delta \) is the electric field, and \( M \) is the projection of the dipole moment on the space-fixed (field) axis. \( M \) is expanded through the second order as follows:

\[ ^0M = \sum_a \langle \mu_a \rangle \Phi_a, \]
\[ ^1M = \sum_a \sum_i \frac{1}{\hbar} \langle \mu_a \rangle \partial_q \Phi_a, \]
\[ ^2M = \sum_a \sum_{ij} \frac{1}{\hbar^2} \langle \mu_a \rangle \partial_q \partial_q \Phi_a, \]

where the superscript on \( M \) denotes the order of magnitude in an appropriate expansion parameter \( \lambda \), \( \Phi_a \) 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 \( \langle \mu_0 \rangle \), 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 \( \langle \mu_0 \rangle \) 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

\[ ^0M^\dagger_{ij} = \langle \mu_{ij} \rangle, \]
\[ ^1M^\dagger_{ij} = \langle \mu_{ij} \rangle, \]
\[ ^2M^\dagger_{ij} = \sum_k \langle \mu_{ij} \rangle \langle \mu_{kj} \rangle \epsilon_{jk} + \sum_k \langle \mu_{ij} \rangle \langle \mu_{kj} \rangle \epsilon_{kj} + \sum_k \langle \mu_{ij} \rangle \langle \mu_{kj} \rangle \epsilon_{kj}, \]

where we follow the notation of Rothman and...
DIPOLE MOMENT OF WATER

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

<table>
<thead>
<tr>
<th></th>
<th>HOH</th>
<th>DOH*</th>
<th>DOD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>(b)</td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td>(\frac{\partial \mu}{\partial \eta_1})</td>
<td>-0.0216</td>
<td>0.0050</td>
<td>-0.0224</td>
</tr>
<tr>
<td>(\frac{\partial \mu}{\partial \eta_2})</td>
<td>0.161</td>
<td>0.120</td>
<td>0.107</td>
</tr>
<tr>
<td>(\frac{\partial \mu}{\partial \eta_3})</td>
<td>0</td>
<td>0.0950</td>
<td>-0.0401</td>
</tr>
</tbody>
</table>

*Constants for DOH and DOD are calculated from observed values for HOH. See Ref. 10.

Clough\(^8\) in which \([\ , \ ]_R\) and \([\ , \ ]_L\) indicate rotational anticommutators and commutators, respectively. \(\mathcal{H}_{ij}\) is the matrix element of the vibration-rotation Hamiltonian in the principal axis, harmonic oscillator representation and \(\epsilon_{ij} = 1/\left(\epsilon_{ii} - \epsilon_{jj}\right)\) (for \(i \neq j\), \(\epsilon_{ij} = 0\)). For the numerical constants needed in the calculations, force constants were derived from the work of Benedict \(\textit{et al.}\)\(^9\). Unfortunately, unambiguous values for \(\frac{\partial \mu}{\partial \eta_1}\) which contribute directly to the coefficient of \(\phi_a\) in \(\phi_M\),

\[
\langle 000 | \frac{\partial \mu_a}{\partial \eta_1} | q_a^2 \rangle \langle 000 \rangle = \frac{1}{2} \frac{\partial \mu_a}{\partial \eta_1} \phi_M^2,
\]

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:**

\[
\phi_M = \phi_0 \phi_1,
\]

\[
\phi_0 = 0,
\]

\[
\phi_1 = -0.0067 \phi_0 + 1.06 \times 10^{-4} \{\phi_0, P_a^2\} - 3.34 \times 10^{-6} \{\phi_0, P_b^2\} - 4.05 \times 10^{-4} \{\phi_0, P_c^2\} - 3.34 \times 10^{-5} \{\phi_0, (P_a P_a + P_b P_b)\} + 6.69 \times 10^{-5} \{\phi_0, (P_a P_b + P_b P_a)\}.
\]

**DOH:**

\[
\phi_M = \phi_0 \cos \phi_0 \phi_1 + \phi_0 \sin \phi_0 \phi_1,
\]

\[
\phi_0 = 0,
\]

\[
\phi_1 = -0.0088 \phi_0 + 1.78 \times 10^{-3} \{\phi_0, P_a^2\} - 9.13 \times 10^{-5} \{\phi_0, P_b^2\} - 9.53 \times 10^{-5} \{\phi_0, P_c^2\} - 1.44 \times 10^{-4} \{\phi_0, (P_a P_a + P_b P_b)\} + 3.66 \times 10^{-4} \{\phi_0, (P_a P_b + P_b P_a)\} + 0.0067 \phi_0 + 6.70 \times 10^{-5} \{\phi_0, P_a^2\} + 2.34 \times 10^{-4} \{\phi_0, P_b^2\} - 5.21 \times 10^{-4} \{\phi_0, P_c^2\} + 1.18 \times 10^{-4} \{\phi_0, (P_a P_a + P_b P_b)\};
\]

**DOD:**

\[
\phi_M = \phi_0 \phi_1,
\]

\[
\phi_0 = 0,
\]

\[
\phi_1 = -0.0052 \phi_0 + 5.33 \times 10^{-4} \{\phi_0, P_a^2\} + 8.40 \times 10^{-7} \{\phi_0, P_b^2\} - 2.55 \times 10^{-4} \{\phi_0, P_b^2\} - 2.21 \times 10^{-5} \{\phi_0, (P_a P_a + P_b P_b)\} + 4.07 \times 10^{-5} \{\phi_0, (P_a P_b + P_b P_a)\}.
\]

Using these expressions and the rotational constants in a principal axis representation for HOH, DOH, and DOD\(^11\) 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 \(M^2\), \(\delta^2\), and \(\mu_0^2\) where \(M\) is the projection of the total angular momentum along the space-fixed axis. Using the usual second order perturbation treatment,\(^12\) we obtain

\[
2^{\delta^2} E = \sum_a \mu_a^2 \left(\delta_{\alpha a} + \delta_{\beta a} \frac{\partial \mu_a}{\partial \eta_1}\right)^2,
\]

where \(\alpha, \beta\) is the coefficient of \(M^0\) 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 \(2^{\delta^2} E\) 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
or in a more useful form as

\[ E = \sum_i E_i = \sum_i \Delta E_i = \sum_{\text{perturbations}} |\delta E_i|, \]

where \( \delta E_i \) is the result obtained from second order perturbation treatment, and the \( \Delta E_i \) are the matrix elements in the energy representation for the perturbation \( \Delta \).

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

\[ \delta E = \frac{1}{2} \sum_{\text{perturbations}} \left| \sum_{\text{perturbations}} \epsilon_{im} \right|^2, \]

and may be evaluated from the expression

\[ \delta E = \frac{1}{2} \sum_{\text{perturbations}} \left| \sum_{\text{perturbations}} \epsilon_{im} \right|^2. \]

Diagonal elements of the polarizability tensor have been calculated for HOH by Liebmann and Moskowitz and we have adopted the following polarizability constants: \( \rho_{zz} = 1.651 \), \( \rho_{xy} = 1.452 \), and \( \rho_{xx} = 1.226 \) cm\(^3\). With these values the maximum correction to the observed frequency shifts is 0.4 kHz for the HOH transitions, 0.4 kHz for the DOD transition, and ignoring the off-diagonal element of the polarizability \( (\rho_{ab}) \). These corrections are not significant.

**ANALYSIS AND RESULTS**

The experimental details of the measurements have been discussed at length by Beers and Klein for the data taken by them. The Stark shifts for the 22 GHz HOH line \((61,6-52,3)\) were kindly provided by Kirchhoff. The values for the electric fields for the latter data were readjusted using the constants obtained by Muenter 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 \( \delta^2 \) and \( M^2 \delta^2 \) to obtain quanti-
ties $\delta$ and $\gamma$ in the expression for the Stark shift,

$$\nu = \nu_0 + \delta \Gamma \Delta^2 + \gamma \Delta M^2 \Delta^2,$$

where

$$\delta \Gamma = \mu_\alpha^2 (\gamma_\alpha + \sin^2 \phi_\alpha (\gamma_\beta - \gamma_\alpha))$$

and

$$\gamma \Gamma = \mu_\alpha^2 (\gamma_\beta + \sin^2 \phi_\alpha (\gamma_\alpha - \gamma_\beta)).$$

Values for $\mu^2$ can be obtained from calculated values of $\gamma_\alpha$, $\gamma_\beta$, and $\sin \phi_\alpha$. 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 $\delta \Gamma$ and $\gamma \Gamma$, this method does not provide reliable values for $\mu^2$. The transition frequencies (listed to the nearest megahertz) and the results of Method I including values of $\mu^2$ and $\Delta M$ 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 $\mu^2$ (also $\mu^2 \sin^2 \phi$ 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 $\mu^2$ for the three isotopes. The final method, Method IV, combines all the data together to obtain a single value for $\mu^2$ (and again, if desired, $\mu^2 \sin^2 \phi$). 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
Eqs. (7)–(9) to the appropriate results for $\mu_{a}$ from Table III, Method III. We obtain for HOH, $\mu_{b} = \mu_{c} = -1.8546 \pm 0.0006$ D,

$$\mu_{a} = -0.6567 \pm 0.0004 \text{ D},$$

$$\mu_{a} = -\left(\mu_{a}^2 + \mu_{b}^2\right)^{1/2} = -1.8521 \pm 0.0012 \text{ D},$$

DOD, $\mu_{b} = \mu_{c} = -1.8558 \pm 0.0021$ D.

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

$$H_R = AP_{a}^{2} + BP_{b}^{2} + CP_{c}^{2}$$

+ (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.\(^{18}\)

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 $^{3}M$ from neglected terms of the type $^{3}(\partial\mu_{a}/\partial q_{b}^{2})$ 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 $2\nu_3$ and if it is assumed that all the intensity of that band is attributable to the dipole moment expansion, we obtain $\left|^{3}(\partial\mu_{a}/\partial q_{b}^{2})\right| = 0.0066$ D. A calculation of the second order contribution to the $2\nu_3$ 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

$$\langle 000 | (\partial^2 \mu_{a}/\partial q_{b}^{2}) | 000 \rangle = \pm 0.0033 \text{ D}.$$  

A more accurate determination of the dipole moment projection operator depends on the availability of these higher order constants from experiments or from \textit{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 $(\nu, J, K_a, K_c, M)$ is independent of field (neglecting polarizability) and is characterized by the good quantum number $M$, since
**Dipole Moment of Water**

\( \mathbf{P} \) 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 \( \text{D}_2\text{O} \) 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 \( \mathbf{\Phi} \) form. Reduction (a), \( \{ \text{i.e., for } \mathbf{I}' \mathbf{I} \} \), \( \mathbf{\Phi}_G (\text{bbcc}) = \mathbf{\Phi}_G (\text{bbccccc}) = \mathbf{\Phi}_G (\text{ccbbbb}) = \mathbf{\Phi}_G (\text{bbccaa}) = 0 \) by K. K. Yallabandi and P. M. Parker, J. Chem. Phys. 48, 410 (1968). These equations in other representations, including that currently referred to as the Watson form \( \mathbf{\Phi} = \mathbf{I} \), \( \mathbf{S} = \mathbf{H} \), \( \mathbf{P} = \mathbf{I} \mathbf{S} \mathbf{H} \), 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 \( \text{H}_2\text{O} \) transition and to W. S. Benedict who has collaborated with us on the interpretation of the molecular data on water.