

Liquid-Vapor Interface Potential for Water

F. H. STILLINGER, JR., AND A. BEN-NAIM

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

(Received 19 July 1967)

The water molecule has been idealized as a point dipole plus point quadrupole, encased in a spherical exclusion envelope. Classical electrostatics has been applied to the determination of the potential field surrounding such a molecule in the wide interfacial region between the liquid and vapor phases, just below the critical temperature. From this result, the mean torque on the molecule in this inhomogeneous region follows, and produces a spontaneous interfacial polarization. The consequent potential difference across the interface has thus been evaluated at several temperatures, and demonstrates the tendency for surface water molecules to orient their protons away from the vapor and into the liquid. A related optical experiment is suggested, involving electric-field dependence of reflected-light ellipsometry.

I. INTRODUCTION

In view of the significance of water as a solvent for electrochemical processes, it is obviously important to understand the nature and magnitude of the potential drop across the water liquid-vapor interface. Although several experiments have been interpreted in such a way as to yield predictions for the surface potential, the results do not even agree in sign.¹ The purpose of this paper is a calculation of this surface potential, using a precise electrostatic model, and a few elementary principles in classical statistical mechanics.

Frenkel² was the first, to the best of our knowledge, to suggest that the permanent quadrupole moment of the water molecule plays a central role in the orientation preference of water molecules in the interfacial zone. The basic concept involved is that molecules in the surface will tend to orient so as to place their electric fields as much as possible in the high-dielectric-constant liquid, rather than the low-dielectric-constant vapor, thereby minimizing the field free energy. If the water molecules possessed only a centrally placed permanent dipole moment, the resulting dipolar field symmetry would render any orientation energetically equivalent to its opposite orientation, so no surface dipole layer would form. The permanent quadrupole moment, however, tends to displace field lines either toward the front or back of the polar molecule, depending on its sign, and the consequent symmetry breaking leads to a surface dipole layer with an associated potential.

In implementation of a quantitative analysis of the water surface potential, we have restricted attention primarily to temperatures just below the critical (374°C) on account of the several simplifications that result. First, it is known that the interfacial zone becomes very wide as the critical point is approached,^{3,4}

¹ R. Parsons, in *Modern Aspects of Electrochemistry*, J. O'M. Bockris and B. E. Conway, Eds. (Academic Press Inc., New York, 1954), Vol. 1, pp. 123-124.

² J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, Inc., New York, 1955), p. 356. We are indebted to Dr. R. A. Lovett for pointing out this reference to us.

³ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), pp. 372-373.

⁴ R. A. Lovett, "Statistical Mechanical Theories of Fluid Interfaces," Dissertation submitted to the University of Rochester, 1965 (unpublished).

so that any molecule resides in a region of slowly varying dielectric constant. The corresponding mean torque on the surface molecules likewise is small, and the statistical mechanical expression for the mean orientational probability may conveniently be linearized to produce explicit results in elementary form.

The next section exhibits the electrostatic problem generated by a dipole-plus-quadrupole source encapsulated in a spherical exclusion volume, located within a region of slowly varying dielectric inhomogeneity. The subsequent section (III) then in turn converts the result to a mean torque potential, an interfacial spontaneous polarization density, and finally to the surface potential. Numerical values for the potential are then calculated from available bulk liquid and vapor properties, as well as molecular parameters. Several comments on the method of calculation are arrayed in a discussion, Sec. IV, where an optical experiment is suggested to confirm our identification of the preferred orientation.

II. ELECTROSTATIC PROBLEM

We adhere to the molecular multipole moment definition contained in the recent review by Krishnaji and Prakash.⁵ Thus, through quadrupolar terms, the electrostatic potential surrounding an isolated molecule in free space has the form ($i, j = 1, 2, 3$)

$$\psi(\mathbf{r}) = r^{-1}q + r^{-3}\mu_i x_i + r^{-5}(x_i x_j - \frac{1}{3}\delta_{ij}r^2)\theta_{ij}, \quad (1)$$

where it is understood that the summation convention applies to repeated subscripts. In terms of the molecular charge density $\rho(\mathbf{r})$, the multipole moments are defined as follows:

$$q = \int \rho(\mathbf{r}) d\mathbf{r},$$

$$\mu_i = \int x_i \rho(\mathbf{r}) d\mathbf{r},$$

$$\theta_{ij} = \frac{1}{2} \int (3x_i x_j - \delta_{ij}r^2) \rho(\mathbf{r}) d\mathbf{r}. \quad (2)$$

⁵ Krishnaji and V. Prakash, *Rev. Mod. Phys.* **38**, 690 (1966).

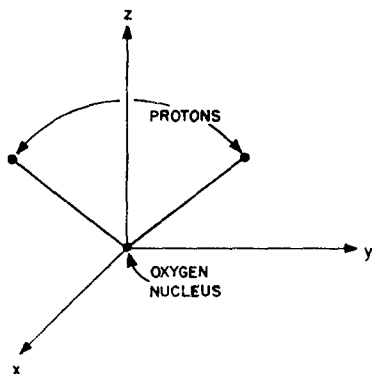


FIG. 1. Cartesian coordinate system located in the water molecule, which diagonalizes the quadrupole tensor θ . The origin is at the oxygen nucleus, the z axis is the symmetry axis, and the y axis lies in the molecular plane.

Figure 1 displays the most convenient choice of Cartesian coordinate systems for description of the water molecule. The origin is placed at the oxygen nucleus, the x axis is perpendicular to the plane of the molecule (the y - z plane), and the z axis is the two-fold symmetry axis oriented in the same direction as the permanent dipole moment. On account of the molecular symmetry, the quadrupole tensor is diagonal in this coordinate system.

Before entering into consideration of the inhomogeneous interfacial zone, we first specify the molecular electrostatic problem within the bulk of either the liquid or vapor phase. In this simple case, the dielectric constant ϵ would be position independent in the absence of any constraints on the system. We wish, however, to consider the case of a water molecule held fixed at the origin, possessing in fact the orientation shown in Fig. 1. The remainder set of molecules, which respond dielectrically to the field set up by the fixed molecule, are not uniformly distributed throughout the region, but are excluded from the neighborhood of the origin by the fixed central molecule. For this reason we associate with this dielectric medium a spherical exclusion cavity of radius a , concentric with the oxygen nucleus at the origin. Outside this sphere the macroscopic dielectric constant ϵ will be presumed everywhere to apply, but inside, the dielectric constant will be taken as unity. The situation is exhibited in Fig. 2.

Under the given circumstances it is natural to describe the electrostatic potential ψ in terms of spherical coordinates r, θ, φ . For $r > 0$, ψ will satisfy Laplace's equation

$$\nabla^2 \psi(r, \theta, \varphi) = 0, \quad (3)$$

plus the standard boundary conditions, and at $r=0$ will possess singularities characteristic of the dipolar and quadrupolar sources imputed to the fixed water molecule. Let

$$Y_{lm}(\theta, \varphi) = P_l^{|m|}(\cos\theta) \exp(im\varphi) \quad (4)$$

stand for the unnormalized spherical harmonics which

satisfy the equation

$$\nabla^2 Y_{lm}(\theta, \varphi) + l(l+1) Y_{lm}(\theta, \varphi) = 0. \quad (5)$$

The electrostatic potential ψ adopts two distinct forms inside (in) and outside (out) the spherical dielectric cavity, each of which may be expanded in spherical harmonics,

$$\psi_{in}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} [A_{lm} r^l + B_{lm} r^{-l-1}] Y_{lm}(\theta, \varphi),$$

$$\psi_{out}(r, \theta, \varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} C_{lm} r^{-l-1} Y_{lm}(\theta, \varphi). \quad (6)$$

Continuity of ψ at $r=a$ requires

$$a^{2l+1} A_{lm} + B_{lm} = C_{lm}, \quad (7)$$

while continuity of the radial component of the displacement vector at $r=a$ yields the relation

$$a^{2l+1} l A_{lm} - (l+1) B_{lm} = -(l+1) \epsilon C_{lm}. \quad (8)$$

Therefore, we must have

$$A_{lm} = \{ (l+1)(1-\epsilon) / a^{2l+1} [l + (l+1)\epsilon] \} B_{lm},$$

$$C_{lm} = \{ (2l+1) / [l + (l+1)\epsilon] \} B_{lm}. \quad (9)$$

The coefficients B_{lm} multiplying the singular parts of ψ_{in} , are determined by the central water molecule's multipole moments. With

$$\begin{aligned} z &= r \cos\theta, \\ y &= r \sin\theta \cos\varphi, \\ x &= r \sin\theta \sin\varphi, \end{aligned} \quad (10)$$

the transformation between the Cartesian coordinates of Fig. 1 and the spherical polar coordinates, it is easy to obtain the B_{lm} from Eq. (1) and the explicit Y_{lm} expressions.⁶ One finds that

$$\begin{aligned} B_{1,0} &= \mu_z \equiv \mu, \\ B_{2,0} &= \theta_{zz}, \\ B_{2,2} = B_{2,-2} &= \frac{1}{12} (\theta_{yy} - \theta_{xx}), \end{aligned} \quad (11)$$

and all other B_{lm} are vanishing. This completes specification of the potential field surrounding a fixed water molecule in the homogeneous interior of either bulk phase.

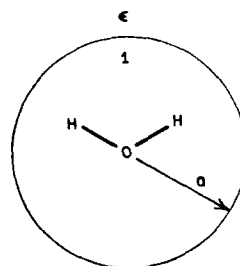


FIG. 2. Spherical dielectric cavity of radius a surrounding a fixed water molecule.

⁶ I. M. Ryshik and I. S. Gradshteyn, *Tables of Series, Products, and Integrals* (Veb Deutscher Verlag der Wissenschaften, Berlin, 1963), pp. 360, 364.

Now we consider the more complicated case of a water molecule in the inhomogeneous interfacial zone. By virtue of the assumption that the temperature T is only slightly less than the critical temperature T_c , the dielectric constant $\epsilon(\mathbf{r})$ should vary sufficiently slowly with position \mathbf{r} (relative to the fixed molecule) such that over the region in which the molecule's electrostatic potential ψ is significant, a linear estimate of $\epsilon(\mathbf{r})$ should suffice (i.e., a two-term Taylor expansion). Figure 3 shows the general spatial relations between the Cartesian coordinate system fixed as before in the given water molecule, and the local dielectric-constant gradient direction which, of course, is normal to the planar interface. The linear dielectric-constant expression therefore may be written

$$\epsilon(\mathbf{r}) \cong \epsilon(0) + |\nabla\epsilon(0)| r \cos\gamma, \quad (12)$$

in terms of the angle γ between $\nabla\epsilon$ and the polar direction of interest.⁷ We note for later use that the general addition theorem for Legendre polynomials⁸ permits elimination of $\cos\gamma$ in favor of functions of the angles α, β, θ , and φ (see Fig. 3),

$$\cos\gamma = \cos\alpha \cos\theta + \sin\alpha \sin\theta \cos(\beta - \varphi). \quad (13)$$

The electrostatic potentials inside and outside the spherical dielectric discontinuity surface may still be taken in the form of the general expansions shown in Eq. (6), with the previous B_{lm} assignments in Eq. (11) still applicable. Also, the conditions shown in Eq. (7) arising from continuity of ψ are valid in this more general circumstance. However, the radial ψ derivative condition corresponding to the rather simple previous Eq. (8) becomes far more elaborate; it is

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} [la^{l-1}A_{lm} - (l+1)a^{-l-2}B_{lm}] Y_{lm}(\theta, \varphi) = - \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} [\epsilon(0) + |\nabla\epsilon(0)| a \cos\gamma] [a^{l-1}A_{lm} + a^{-l-2}B_{lm}] \times (l+1) Y_{lm}(\theta, \varphi), \quad (14)$$

where Eq. (7) has been utilized in elimination of the coefficients C_{lm} . Due to the θ, φ dependence of $\cos\gamma$ as shown in Eq. (13), the coefficients of the explicitly shown spherical harmonics Y_{lm} in Eq. (14) may not be individually equated.

When $\Delta T = T_c - T$ is small, so $|\nabla\epsilon|$ is everywhere small in the interface, it is appropriate to seek a solution to our interfacial electrostatic problem linear in the local value of the gradient. Therefore, set

$$A_{lm} \cong A_{lm}^{(0)} + |\nabla\epsilon| a A_{lm}^{(1)}. \quad (15)$$

The $A_{lm}^{(0)}$ have precisely the form shown in the first Eq. (9), with the dielectric constant taken to be $\epsilon(0)$, since neglect of the local gradient reduces the electrostatic problem to the preceding case of homogeneity.

The quantities $A_{lm}^{(1)}$ may next be determined after substitution of Expression (15) into Eq. (14), followed by linearization with respect to $|\nabla\epsilon|$,

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} [l + (l+1)\epsilon(0)] a^{l-1} A_{lm}^{(1)} Y_{lm}(\theta, \varphi) = - \sum_{l=0}^{\infty} \frac{(l+1)(2l+1)a^{-l-2}}{l + (l+1)\epsilon(0)} B_{lm} \cos\gamma Y_{lm}(\theta, \varphi). \quad (16)$$

On account of the fact that $\cos\gamma$, Eq. (13), consists of two parts respectively proportional to $\cos\alpha$ and $\sin\alpha$ we conclude from the linearity of Eq. (16) that the same will be true for the $A_{lm}^{(1)}$,

$$A_{lm}^{(1)} = \cos\alpha A_{lm}^{(c)} + \sin\alpha A_{lm}^{(s)}. \quad (17)$$

We see in the following section that only the $\cos\alpha$ part of $A_{lm}^{(1)}$ contributes to the interfacial polarization and potential, so only the $A_{lm}^{(c)}$ need to be determined. Therefore, use Eqs. (13) and (17) to convert Eq. (16) to

$$\sum_{l=0}^{\infty} \sum_{m=-l}^{+l} [l + (l+1)\epsilon(0)] a^{l-1} A_{lm}^{(c)} Y_{lm}(\theta, \varphi) = - \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} \frac{(l+1)(2l+1)a^{-l-2}}{l + (l+1)\epsilon(0)} B_{lm} \cos\theta Y_{lm}(\theta, \varphi). \quad (18)$$

The spherical harmonics Y_{lm} satisfy the following recurrence relation⁹:

$$\cos\theta Y_{lm}(\theta, \varphi) = [(l+|m|)/(2l+1)] Y_{l-1,m}(\theta, \varphi) + [(l-|m|+1)/(2l+1)] Y_{l+1,m}(\theta, \varphi), \quad (19)$$

⁷ The symbols $\epsilon(0)$ and $\nabla\epsilon(0)$ of course refer to the dielectric properties of the interface at the position where the fixed water molecule is to be placed, but evaluated *before* this molecule is put in position. With the fixed molecule in place, the dielectric constant again becomes unity within the a sphere, and is equal to the previous value only outside that sphere.

⁸ J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Co., New York, 1941), p. 408, Eq. (46).

⁹ Reference 6, p.351, Eq. 6.733(2).

where on the right side one must take $Y_{lm}=0$ if $|m|>l$. After utilizing this identity in Eq. (18) for those terms corresponding to nonvanishing B_{lm} , the right-hand side of this equation (18) simplifies to

$$-\left\{ \frac{2a^{-3}}{1+2\epsilon(0)} B_{1,0} Y_{0,0}(\theta, \varphi) + \frac{6a^{-4}}{2+3\epsilon(0)} B_{2,0} Y_{1,0}(\theta, \varphi) + \frac{4a^{-3}}{1+2\epsilon(0)} B_{1,0} Y_{2,0}(\theta, \varphi) + \frac{9a^{-4}}{2+3\epsilon(0)} B_{2,0} Y_{3,0}(\theta, \varphi) \right. \\ \left. + \frac{3a^{-4}}{2+3\epsilon(0)} B_{2,2} [Y_{3,2}(\theta, \varphi) + Y_{3,-2}(\theta, \varphi)] \right\}. \quad (20)$$

Finally, the $A_{lm}^{(c)}$ are obtained by matching up spherical harmonic coefficients on both sides of Eq. (18). The nonzero results are

$$A_{0,0}^{(c)} = -2B_{1,0}/a^2\epsilon(0)[1+2\epsilon(0)], \\ A_{1,0}^{(c)} = -6B_{2,0}/a^4[1+2\epsilon(0)][2+3\epsilon(0)], \\ A_{2,0}^{(c)} = -4B_{1,0}/a^4[1+2\epsilon(0)][2+3\epsilon(0)], \\ A_{3,0}^{(c)} = -9B_{2,0}/a^6[2+3\epsilon(0)][3+4\epsilon(0)], \\ A_{3,2}^{(c)} = A_{3,-2}^{(c)} = -3B_{2,2}/a^6[2+3\epsilon(0)][3+4\epsilon(0)]. \quad (21)$$

III. SURFACE POTENTIAL

We have attributed to the water molecule both a point dipole and a point quadrupole. The corresponding charge densities may be taken as¹⁰

$$\rho_d(\mathbf{r}) = -\mathbf{u} \cdot \nabla \delta(\mathbf{r}), \\ \rho_q(\mathbf{r}) = -\frac{1}{3}\boldsymbol{\theta} : \nabla \nabla \delta(\mathbf{r}), \quad (22)$$

where \mathbf{u} is the dipole vector and $\boldsymbol{\theta}$ the quadrupole tensor. Within the interior of either the liquid or vapor phases, isotropy assures the vanishing of any mean torque on the distribution $\rho_d + \rho_q$. But within the interfacial zone the anisotropic part of the inner-region potential,

$$\psi_{in}^{(1)}(\mathbf{r}) = |\nabla \epsilon| a \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} A_{lm}^{(1)} r^l Y_{lm}(\theta, \varphi), \quad (23)$$

produced by the local dielectric constant gradient will give rise to a torque. The torque potential V may be

obtained by combining the last two equations:

$$V(\alpha, h) = \frac{1}{2} \int [\rho_d(\mathbf{r}) + \rho_q(\mathbf{r})] \psi_{in}^{(1)}(\mathbf{r}) d\mathbf{r}; \quad (24)$$

of course it depends on orientation angle α , as well as position within the interface (denoted by "height" h).

The potential $V(\alpha, h)$ by itself would tend to produce a polarization density within the interfacial zone, but it would not be correct to assume that this polarization $\mathbf{P}(h)$ is produced only by the direct orienting effect of V on the molecules. Associated with \mathbf{P} is a mean interfacial electric field¹¹

$$\mathbf{E}(h) = -4\pi\mathbf{P}(h). \quad (25)$$

For small ΔT , this field will be sufficiently homogeneous in the neighborhood of any given molecule in the interface to produce a cavity field,

$$\mathbf{E}_{cav}(h) = \{3\epsilon(h)/[1+2\epsilon(h)]\}\mathbf{E}(h), \quad (26)$$

at the center of that molecule's a sphere. This cavity field then interacts with the molecule's dipole moment to produce an additional torque potential ($E=|\mathbf{E}|$),

$$V_{cav}(\alpha, h) = -\{3\epsilon(h)\mu E(h)/[1+2\epsilon(h)]\} \cos\alpha \\ = -GE(h) \cos\alpha. \quad (27)$$

The total torque potential $V+V_{cav}$ may next be used to find the polarization density \mathbf{P} by direct evaluation of the relevant orientational average:

$$\mathbf{P}(h) = \rho(h)\mu\mathbf{u} \left[\int_{-1}^{+1} d(\cos\alpha) \cos\alpha \exp\left(-\frac{V(\alpha, h) + V_{cav}(\alpha, h)}{kT}\right) \right] / \int_{-1}^{+1} d(\cos\alpha) \exp\left(-\frac{V(\alpha, h) + V_{cav}(\alpha, h)}{kT}\right) \\ \cong -\frac{\rho(h)\mu\mathbf{u}}{2kT} \int_{-1}^{+1} d(\cos\alpha) \cos\alpha [V(\alpha, h) + V_{cav}(\alpha, h)]. \quad (28)$$

Here $\rho(h)$ stands for the molecular density at position h , \mathbf{u} is the unit vector in the $\nabla\epsilon$ direction (pointing from vapor to liquid), and we have used the fact that the torques go to zero as $\Delta T \rightarrow 0$ to linearize the integrands.

It was remarked in the previous section that $\psi_{in}^{(1)}$ contains contributions varying with molecular orientation as both $\sin\alpha$ and $\cos\alpha$, and it is evident from Eq. (24) that the same is true of $V(\alpha, h)$. However, only the $\cos\alpha$ part of $V(\alpha, h)$ can contribute to the linearized polarization expression (28), so we are required only to consider the $\cos\alpha$ part of $\psi_{in}^{(1)}$. By inserting the results (21) into Eq. (24), we find for the $\cos\alpha$ part of $V(\alpha, h)$,

$$V^{(c)}(\alpha, h) = -\{5|\nabla\epsilon(h)|\mu\theta_{zz}/a^3[1+2\epsilon(h)][2+3\epsilon(h)]\} \cos\alpha \\ = -F \cos\alpha. \quad (29)$$

¹⁰ These expressions may easily be verified by partial integration in the integral potential expression, so as to reproduce Eq. (1).

¹¹ The negative sign obtains because the polarization is spontaneous, not induced by \mathbf{E} .

Next compute $\mathbf{E}(h)$ from Eq. (25), using Integral (28) for \mathbf{P} with $V^{(c)}$ in place of V :

$$\begin{aligned} -\mathbf{E}(h) &= \frac{2\pi\rho(h)\mu\mathbf{u}}{kT} \int_{-1}^{+1} d(\cos\alpha) \cos^2\alpha [F + GE(h)] \\ &= \frac{4\pi\rho(h)\mu}{3kT} [F + GE(h)]\mathbf{u}. \end{aligned} \quad (30)$$

We may now solve for $\mathbf{E}(h)$; after the explicit forms for F and G are inserted, the interfacial field becomes expressed in the following form ($\beta = 1/kT$):

$$-\mathbf{E}(h) = \frac{20\pi\mu^2\beta\theta_{zz}\rho(h)\nabla\epsilon(h)}{3a^3[2+3\epsilon(h)][1+2\epsilon(h)+4\pi\beta\mu^2\rho(h)\epsilon(h)]}. \quad (31)$$

The potential difference between the deep interiors of the vapor ($h = -\infty$) and liquid ($h = +\infty$) phases now follows by integration:

$$\begin{aligned} \bar{\psi}_l - \bar{\psi}_v &= \frac{20\pi\beta\mu^2\theta_{zz}}{3a^3} \\ &\times \int_{-\infty}^{+\infty} \frac{\rho(h)\epsilon'(h)dh}{[2+3\epsilon(h)][1+2\epsilon(h)+4\pi\beta\mu^2\rho(h)\epsilon(h)]}. \end{aligned} \quad (32)$$

In the strict sense, our potential formula (32) should be restricted to small ΔT in view of the approximations upon which it depends. So far as the limiting behavior near T_c is concerned, the factor $\epsilon'(h)$ in the integrand possesses the only important h variation, so $\rho(h)$ and $\epsilon(h)$ in the remaining factors may simply be replaced by their values at the critical point, ρ_c and ϵ_c . The integral then becomes trivial, so we find that the critical region interfacial potential drop has an elementary

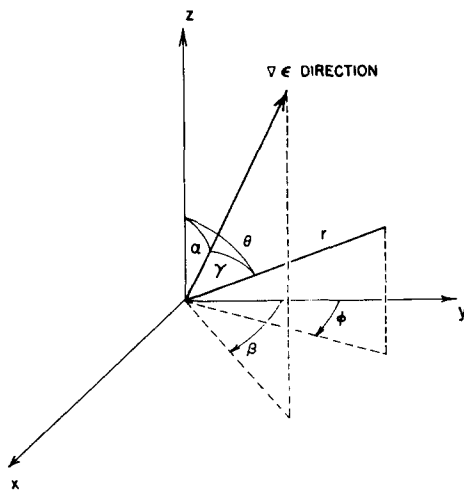


FIG. 3. Angles defined by the direction of the dielectric constant gradient ($\nabla\epsilon$) in the interface, relative to the Cartesian (xyz) coordinate system attached to the water molecule as in Fig. 1.

TABLE I. Values (in volts) of the surface potential $\bar{\psi}_l - \bar{\psi}_v$ calculated from Eq. (33). Liquid-phase dielectric constants have been taken from Ref. 15, and ϵ_v for the vapor obtained from Eq. (34). For water, $t_c = 374^\circ\text{C}$.

$t(^{\circ}\text{C})$	ϵ_l	ϵ_v	$\bar{\psi}_l - \bar{\psi}_v$ (V)
370	9.74	6.55	1.003×10^{-8}
360	11.22	5.98	1.65×10^{-8}
350	12.61	5.65	2.20×10^{-8}
340	14.10	5.35	2.78×10^{-8}
330	15.51	5.24	3.28×10^{-8}
320	16.88	5.07	3.79×10^{-8}

form:

$$\bar{\psi}_l - \bar{\psi}_v \sim \frac{20\pi\beta\mu^2\theta_{zz}\rho_c(\epsilon_l - \epsilon_v)}{3a^3(2+3\epsilon_c)(1+2\epsilon_c+4\pi\beta\mu^2\rho_c\epsilon_c)}. \quad (33)$$

ϵ_l and ϵ_v are the bulk-phase dielectric constants at the temperature of interest, and we see that their difference primarily controls the rate at which $\bar{\psi}_l - \bar{\psi}_v$ vanishes with ΔT .

Equation (33) may indeed be applicable to polar fluids other than water, if the spherical dielectric cavity approximation is appropriate. Since all factors in the right-hand member of Eq. (33) are positive, with the possible exception of θ_{zz} , we see that for this class of polar fluids the sign of the axial quadrupole moment is decisive in determining the direction of preferential surface orientation, and therefore the sign of the surface potential.

We have used Eq. (33) to calculate $\bar{\psi}_l - \bar{\psi}_v$ for water at several temperatures just below T_c . The results are displayed in Table I. The following data were used:

Critical temperature^{12a}:

$$T_c = 674.15^\circ\text{K};$$

Critical density^{12a}:

$$\begin{aligned} \rho_c &= 0.329 \text{ g/cm}^3 \\ &= 1.096 \times 10^{22} \text{ molecules/cm}^3; \end{aligned}$$

Critical dielectric constant^{12b}:

$$\epsilon_c = 7.8;$$

Molecular dipole moment^{12c}:

$$\mu = 1.87 \times 10^{-18} \text{ esu} \cdot \text{cm}.$$

In addition, a was chosen to be the oxygen-oxygen distance of closest approach, as observed in the ice lattice,¹³ equal to 2.76×10^{-8} cm. Subcritical liquid

¹² (a) N. E. Dorsey, *Properties of Ordinary Water-Substance* (Reinhold Publ. Corp., New York, 1940), p. 558. (b) From supercritical steam dielectric constants of J. K. Fogo, S. W. Benson, and C. S. Copeland [J. Chem. Phys. **22**, 209 (1954)], we have obtained the cited value for ϵ_c by extrapolation to T_c . (c) R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths Scientific Publication, Ltd., London, 1959), p. 1.

¹³ J. L. Kavanau, *Water and Water-Solute Interactions* (Holden-Day, Inc., San Francisco, Calif., 1964), p. 1.

dielectric constants ϵ_l are available from measurements by Hasted¹⁴ and by Akerlof and Oshry,¹⁵ and from them the unmeasured critical-region vapor values were estimated from a "law of rectilinear diameters," patterned after that known to be obeyed by the coexisting densities¹⁶

$$1/\epsilon_c = \frac{1}{2}[1/\epsilon_l(T) + 1/\epsilon_v(T)]. \quad (34)$$

Finally, we took $\theta_{zz} = 0.364 \times 10^{-26}$ esu·cm², which is the average of the theoretical values reported in Sec. VIII of Ref. 5.¹⁷

Table I shows that the mean electrostatic potential in the interior of the liquid $\bar{\psi}_l$, is larger than that for the vapor. Consequently, we must conclude that interfacial water molecules prefer to orient themselves with their protons pointing toward the liquid phase.

IV. DISCUSSION

There are several sources of error in our calculation. The most serious undoubtedly is the spherical-dielectric-cavity assumption. Unfortunately, so little is known about local dielectric properties on the molecular scale at present that a more elaborate assumption for water seems out of the question. In the case of some other more elongated polar molecules (such as OCS or BrCN) an ellipsoidal cavity assumption might be warranted, but the more generalized calculation would still involve application of macroscopic electrostatics to the microscopic regime.

We have based our use of the spherical dielectric cavity centered specifically about the water molecule's oxygen nucleus on the facts that the protons are rather deeply buried in the oxygen's electron cloud (at a distance of 0.96 Å from the oxygen nucleus compared to 1.4 Å for the molecule's van der Waals radius) and that neighbor oxygens have equal distances from a central oxygen in the ice lattice. If it were required instead to place the sphere center at the point 0, 0, l in the coordinate system shown in Fig. 1, then the quadrupole quantity θ_{zz} would transform to the new value $\theta'_{zz} = \theta_{zz} - 4l\mu$. Conceivably, then, a sufficiently large value for the center shift l could reverse the sign of the surface potential upon use of θ'_{zz} in Eq. (33).

The possibility that the water molecule would polarize as a result of the reaction field it induces within

its spherical cavity has not, of course, been considered. As Onsager¹⁸ has remarked, this effectively only enhances the water molecule's dipole moment, and would not in itself change the surface potential sign. Likewise the analogous change in quadrupole moment of the molecule under the influence of the reaction field has been disregarded, since no relevant molecular information whatever is available.

Although higher-order molecular multipoles than the quadrupole were not considered in our analysis one may show that their effect in the critical region for which the dielectric-constant expression (12) is valid is entirely negligible. Similarly the implicit use of local dielectric isotropy (whereby the usual inhomogeneous region dielectric tensor is replaced by a scalar) may be shown to be asymptotically correct as ΔT vanishes.

In spite of the fact that our derivation of surface potential, Eq. (33), has relied heavily on simplifications that obtain near the critical point, it is hard to imagine that the orienting agency operative at high temperatures should be superseded by another basically different one at ordinary temperatures. For this reason it may not be wholly incorrect to estimate the order of magnitude of $\bar{\psi}_l - \bar{\psi}_v$ at 25°C by means of Eq. (33). If we only modify this equation by using the correct β at this lower temperature, as well as $\epsilon_v \cong 1$, $\epsilon_l = 78.30$, the predicted surface potential is 0.029 V. In view of the approximations, this is probably an underestimate.

Finally we raise the possibility that an optical experiment on the water liquid-vapor surface could determine the direction of spontaneous surface polarization, and thereby hopefully verify our result. The relevant argument may be based on the Helmholtz free-energy functional utilized by (among others) Ornstein and Zernike,¹⁹ and by Cahn and Hilliard.²⁰ Upon extension to include the usual electrostatic field free energy, it has the following form:

$$F[\rho, \mathbf{E}] = \int \{ f(\rho) + \frac{1}{2}B(\nabla\rho)^2 + \frac{1}{8}\pi\epsilon\mathbf{E}\cdot\mathbf{E} \} d\mathbf{r}. \quad (35)$$

$f(\rho)$ is the macroscopic free-energy density for homogeneous fluids, and B is a positive constant. The integral in Eq. (35) covers the entire fluid system, and the observed density distribution $\rho(\mathbf{r})$ minimizes the functional subject to fixed total amount of matter.

In the case of nonpolar fluids with external electric fields absent, the interfacial width is established as a balance between $f(\rho)$, tending to produce an infinitely sharp density discontinuity, and the squared-gradient term which becomes infinitely large in this limit. For water the spontaneous interfacial zone polarization

¹⁴ J. B. Hasted, *Progr. Dielectrics* **3**, 101 (1961).

¹⁵ G. C. Akerlof and H. I. Oshry, *J. Am. Chem. Soc.* **72**, 2844 (1950).

¹⁶ Reference 3, pp. 262-263.

¹⁷ Recently the somewhat smaller value $\theta_{zz} = 0.1505 \times 10^{-26}$ esu·cm² has been privately communicated to us by J. Moskowitz, D. Neumann, and P. Liebman on the basis of a seemingly very complete Gaussian-basis Hartree-Fock approximate wavefunction for the water molecule. To the extent that this may represent the best currently available determination for θ_{zz} , the surface potential values reported in Table I would have to be scaled down accordingly. However, the sign would be unchanged.

¹⁸ L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).

¹⁹ L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Addison-Wesley Publ. Co., Reading, Mass., 1958), p. 367.

²⁰ J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).

has associated with it an electric field as shown in Eq. (25), and the last term in the integrand of Eq. (35) acts then to widen the interface even more than the squared-gradient term alone would do.

If an external electric field is applied normal to the surface so as to reinforce the spontaneous field, the width should increase even more. But if the external field acts so as to cancel out the spontaneous field, the interfacial zone should decrease in width (for at least a limited range of external field magnitudes).

The well-developed technique of optical ellipsometry has, in fact, been applied to estimation of water surface

thickness.²¹ We therefore suggest that similar experiments be performed with variable electric fields to establish which field sign minimizes the width. In view of the calculation presented in this paper, the result of such measurement would constitute an indirect determination of the water molecule's quadrupole moment.²²

²¹ K. Kinoshita and H. Yokota, *J. Phys. Soc. Japan* **20**, 1086 (1965).

²² In principle, the external-electric-field dependence of the surface tension should also reflect the direction of spontaneous surface-zone polarization, but the experimental measurement would probably pose more severe difficulties than the ellipsometric determination.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 47, NUMBER 11 1 DECEMBER 1967

Vibronic Coupling in the Exciton States of the Rigid-Lattice Model of Molecular Crystals*

M. R. PHILPOTT

Institute of Theoretical Science, University of Oregon, Eugene, Oregon

(Received 26 June 1967)

The vibrational structure of the Frenkel exciton states of a molecular crystal is investigated by a variational technique using a rigid-lattice-model Hamiltonian. The spirit of the weak coupling formalism is strictly adhered to by constructing crystal wavefunctions from products of isolated molecule wavefunctions so that the only parameters of the theory are Franck-Condon factors and vibrational frequency shifts. The basis set consists of all vibronic, i.e., single particle, states belonging to the same electronic state transforming according to a given wave vector, plus a set of two-particle states in which vibronic and ground vibrational excitation occupy different sites. Interactions between single-particle states are treated in detail, as are interactions between one- and two-particle states. However, part of the interaction between certain two-particle states is neglected and this makes the treatment progressively less accurate for higher vibrational states and stronger coupling. Electron exchange effects, coupling of excitons to photons, higher electronic states, and ion-pair states are not considered.

It is shown how each element of the conventional weak coupling energy matrix is supplemented by terms which account for the interaction between one- and two-particle states as well as interactions among the two-particle states. For a given wave vector each single-particle state is accompanied by a family of two-particle bands which rapidly increases in size for higher vibrational states. In the weak coupling limit the families are widely separated, while intermediate coupling corresponds to two-particle bandwidths comparable with the vibrational spacing. The onset of strong coupling corresponds to overlapping of adjacent families.

I. INTRODUCTION

Interactions between electronic excitation and vibrational modes in crystals play an important role in determining the structure of the optical spectra as well as controlling the efficiency of energy migration and degradation processes.¹⁻⁵ For crystals of polyatomic molecules the intramolecular binding forces are generally much stronger than the intermolecular

forces even when electronic excitation is present. As a result the vibrational modes separate into low-energy lattice modes (torsional, optical, and acoustic) which replace the translational and rotation degrees of freedom of the gas phase, and modes corresponding closely to the intramolecular vibrations of isolated molecules.^{6,7}

* Research supported by the National Science Foundation Grant GP6002.

¹ J. Frenkel, *Phys. Rev.* **37**, 17, 1276 (1931).

² J. Frenkel, *Physik Z. Sowjetunion* **9**, 158 (1936).

³ R. E. Peierls, *Ann. Physik* **13**, 905 (1932).

⁴ A. S. Davydov, *Theory of Molecular Excitons*, translated by M. Kasha and M. Oppenheimer (McGraw-Hill Book Co., New York, 1962).

⁵ A. S. Davydov, *Zh. Eksperim. i Teor. Fiz.* **18**, 210 (1948); *Soviet Phys.—Usp.* **7**, 145 (1964) [*Usp. Fiz. Nauk* **82**, 392 (1964)].

⁶ H. C. Wolf, *Solid State Phys.* **9**, 1 (1959); R. M. Hochstrasser, *Ann. Rev. Phys. Chem.* **17**, 457 (1966).

⁷ For large planar molecules like the aromatic hydrocarbons recent calculations, e.g., D. B. Scully and D. H. Whiffen, *J. Mol. Spectry.* **1**, 257 (1957), and D. Steele, *ibid.* **15**, 333 (1965), have shown that out-of-plane vibrations may overlap the lattice modes in frequency. However, since these out-of-plane vibrations are not excited or only very poorly excited in electronic transitions from the ground level their consideration is secondary to those vibrational modes which are strongly excited. Some lattice vibrations of benzene crystals have been calculated by I. Harada and T. Shimanouchi, *J. Chem. Phys.* **44**, 2016 (1966).