Polarization model for water and its ionic dissociation products

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In order to achieve a simple description of aggregates of deformable water molecules, a new model has been constructed which treats H^+ and O^{2-} particles as the basic dynamical and structural elements. The H^+ units are bare protons, while the O^{2-} units possess a form of nonlocal polarizability consistent with their electronic structure. The model yields water molecules which have the correct geometry and dipole moment, and which engage in hydrogen bonding to one another. Minimum-energy structures have been determined for the water dimer and trimer and for small hydrate clusters of H^+ and OH^-; comparison with relevant experiments and quantum–mechanical calculations is satisfactory.

I. INTRODUCTION

As theoretical attention has turned more and more to the task of understanding water and its solutions, an increasing number of model intermolecular potentials has been devised to describe this substance. For many properties of interest it has been sufficient to treat the individual water molecules as rigid bodies. An early example of a rigid molecule pair potential was the one advocated by Rowlinson,[1] which was later used in a Monte Carlo simulation of liquid water.[2] Subsequent studies have revealed the advisability of incorporating many-body effects in an "effective pair potential" for water,[3,4] and this philosophy underlay the construction of the rigid-molecule BNS potential[5] and its successor the ST2 potential.[6] In addition, analytical fits to the Hartree–Fock pair potential for rigid molecules have recently become available.[7]

But in spite of the importance of rigid-molecule models, many phenomena in water demand consideration of molecular distortion. Vibrational motion and its observation in spectroscopy (infrared and Raman) is an obvious case in point. Furthermore, strong electric fields experienced by water molecules in the primary hydration sheaths of ions produce substantial distortions. The extreme limit of molecular distortion is dissociation, which itself deserves to be examined theoretically in condensed phases.

In response to the need for models permitting distortion, a class of central-force models for water has been introduced recently.[8–10] These models permit molecular vibration and dissociation, while stable molecules and their aggregates can result from a balance between the various additive atom-pair potentials that are present. However the mathematical requirement that *only* spherically symmetric pair interactions be present may limit the ultimate precision of these central force models to an undesirable extent.

Consequently we have begun to examine a natural extension of the central force models. On the one hand this extension retains the capacity to describe molecular vibrations and dissociation. On the other hand it

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is able to dispense with the fractional charges that the central forces models had to assign to hydrogen ions to assure that intact molecules possessed proper dipole moments. Furthermore, this "polarization model" includes electronic polarization at optical frequencies, which the central force models did not include.

The polarization model developed herein utilizes a special type of nonadditive interaction. Some readers may regard this as disadvantage. However, we regard its incorporation in the model as a physical and chemical necessity at the level of detail and precision now of interest.

The following Sec. II presents the basic conceptual elements of our polarization model. It is specifically shown how the underlying structure of this model was patterned after classical electrostatics for point particles with charge and polarizability. However certain key modifications were incorporated to account semiempirically for the quantum–mechanical behavior of valence electrons.

The specific choice of functions and parameters necessary to model water is displayed and discussed in Sec. III.

The simplest ion hydrates that may be formed by dissociation of water are the monohydrates of H^+ and OH^-. Their structures and energies, as predicted by the polarization model, are discussed in Sec. IV. Section V provides analogous information for the water molecule dimer and trimer. Higher hydrates of H^+ and OH^- have also been studied, with results collected in Sec. VI.

In an ideal world, accurate quantum–mechanical calculations could be carried out to give the interaction potential for any cluster of water molecules and ionic fragments of interest. Statistical mechanical studies (for example, computer simulation) would of course require that this be done over and over for a representative ensemble of configurations for the cluster. In the real world this is obviously impractical or even impossible. Consequently we are obliged to devise straightforward algorithms to organize available potential-energy information, and to permit rapid estimation of the requisite potential hypersurface over the cluster's full configuration space. It is these organiza-

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tion and estimation tasks for which we have constructed the polarization model.

II. FORMAL PROCEDURE

The polarization model concerns itself with an arbitrary collection of hydrogen and oxygen particles which, by means of postulated forces, can aggregate into intact water molecules. The normal path of water molecule dissociation in condensed phases produces ionic fragments,

$$H_2O \rightleftharpoons OH^- + H^+ , \tag{2.1}$$

which thereupon solvate. Consequently we suppose that the hydrogen particles in the model are fully charged bare protons, and that the oxygens bear two units of negative charge.

The interaction potential Φ for the present model consists of two parts:

$$\Phi = \Phi_I + \Phi_{II} . \tag{2.2}$$

The first of these is composed of a sum of potentials for each pair of particles in the system:

$$\Phi_I = \sum_{i<j=1}^{N_H} \Phi_{HH}(r_{ij}) + \sum_{i=1}^{N_H} \sum_{j=1}^{N_Q} \phi_{OH}(r_{ij})$$
$$+ \sum_{i<j=1}^{N_Q} \phi_{OO}(r_{ij}) . \tag{2.3}$$

The second part Φ_{II} is a nonadditive potential, whose form will be suggested by classical electrostatics for polarizable particles.

Since the hydrogenic particles are merely bare protons, we obviously must choose

$$\phi_{HH}(r) = e^2/r , \tag{2.4}$$

where e stands for the full protonic charge. Analogously, we require that ϕ_{OH} and ϕ_{OO} satisfy the asymptotic limits (as $r \to \infty$):

$$\phi_{OH}(r) \sim -2e^2/r ,$$
$$\phi_{OO}(r) \sim 4e^2/r , \tag{2.5}$$

consistent with the stated charges. But unlike the hydrogens, oxygen particles bear a spatially extended shell of electrons, so that ϕ_{OH} and ϕ_{OO} will deviate from purely Coulombic form at small r. In particular ϕ_{OH} will exhibit behavior characteristic of covalent bond formation, and ϕ_{OO} will manifest electron cloud overlap repulsion.

Each oxygen particle will have a scalar polarizability α. Since application of the present model will predominately involve undissociated water molecules, a value will be assigned to α which agrees with vapor-phase measurements on the water molecule[11]:

$$\alpha = 1.444 \ \text{Å}^3 . \tag{2.6}$$

In classical electrostatics, the dipole moment μ_i induced in particle i is determined by its polarizability and the electric field E_i at that particle due to external sources

$$\mu_i = \alpha E_i . \tag{2.7}$$

The external sources can be both charges q_j and induced moments μ_i:

$$E_i = - \sum_{j \neq i} (r_{ij} q_j)/r_{ji}^3 - \sum_{l \neq i} (T_{il} \cdot \mu_l)/r_{il}^3 , \tag{2.8}$$

where

$$r_{ji} = r_i - r_j ,$$
$$T_{il} = 1 - 3 r_{il} r_{il}/r_{il}^2 . \tag{2.9}$$

For a given set of particle positions, Eqs. (2.7) and (2.8) provide linear relations which determine the fields E_i and moments μ_i uniquely.

The polarization energy corresponding to this classical electrostatic formalism is simply

$$\Phi_p = \frac{1}{2} \sum_{\substack{i,l \\ (i \neq l)}} (\mu_l \cdot r_{li}) q_i / r_{li}^3 . \tag{2.10}$$

On account of the spatial extension of the electron cloud surrounding each oxygen nucleus, Eqs. (2.7), (2.8), and (2.10) are not appropriate for the problem in hand, without modification. We will retain the attractive feature of linear polarization response, but spatial delocalization has to be inserted into the model. This is accomplished first by replacing electric fields E_i by modified vector fields G_i:

$$G_i = - \sum_{j \neq i} (r_{ij} q_j)[1 - K(r_{ji})]/r_{ji}^3$$
$$- \sum_{l \neq i} (T_{il} \cdot \mu_l)[1 - K(r_{il})]/r_{il}^3 . \tag{2.11}$$

The scalar modification function $K(r)$ will differ substantially from zero only at distances comparable to the oxygen electron cloud radius. Dipole moments will then be determined by the exact analog of Eq. (2.7):

$$\mu_i = \alpha G_i . \tag{2.12}$$

The second modification involves the polarization energy, for which the analog of electrostatic result (2.10) is now taken to be

$$\Phi_{II} = \frac{1}{2} \sum_{\substack{i,l \\ (i \neq l)}} (\mu_l \cdot r_{li}) q_i [1 - L(r_{li})]/r_{li}^3 . \tag{2.13}$$

Just as with K, the function L will differ from zero only at small distances. In the case of widely separated particles, the proposed modification thus reduces to conventional electrostatics.

We stress that K and L are attributes of the *oxygen* particles. In a generalization of the present work in which other atoms heavier than hydrogen were present, separate K and L functions would have to be introduced for each species. Since hydrogen is assumed devoid of electrons and thus nonpolarizable we may take its K and L to be identically zero. In any case, the present study only requires evaluation of G fields at oxygens, so Eqs. (2.11)–(2.13) can be used without species subscripts on K and L.

Experimental data will eventually be used to select appropriate functions K and L. However we can immediately note that at very small distance these functions behave thus:

$$K(r) = 1 - K_3 r^3 + O(r^4) \,,$$
$$(2.14)$$
$$L(r) = 1 - L_3 r^3 + O(r^4) \,,$$

where K_3 and L_3 are positive constants. The first of these requirements follows from the necessary vanishing of the moment induced in an oxygen by a proton that is forced into the oxygen nucleus. The second of these requirements ensures that in the same united atom limit the proton has vanishing interaction with a dipolar extended polarization density.

Just as in the case of conventional electrostatics, the fields G_i and moments μ_i need to be determined from the linear coupled equations (2.11) and (2.12). It is this feature which prevents Φ_{II} from being resolvable into pairwise additive components, in the manner of Φ_I in Eq. (2.3).

III. SELECTION OF FUNCTIONS

In order to complete the specification of the polarization model, definite forms must be chosen for the four functions ϕ_{OH}, ϕ_{OO}, K, and L. We make the choice to conform to conditions (2.5) and (2.14), and to agree in the best manner possible with selected experimental and theoretical data. The data which we have deemed relevant is the following:

(1) geometry, dipole moment, force constants, and dipole derivatives for the isolated water molecule;

(2) energy required in vacuum to break a water into ionic fragments H^+ and OH^-;

(3) geometry and binding energy of the water dimer;

(4) geometry and dehydration energy of $H_3O_2^-$, the singly hydrated hydroxide anion.

In demonstrating how this data guides the function selection process, we first consider the isolated water molecule. Its covalent OH bond lengths are:

$$r_e = 0.9584 \text{ Å} \qquad (3.1)$$

and the bond angle is[12]

$$\theta_e = 104.45° \,. \qquad (3.2)$$

Furthermore, the molecular dipole moment is[13]:

$$\mu = 1.855 \times 10^{-18} \text{ esu cm} \,. \qquad (3.3)$$

Within the polarization model, the dipole moment of the water molecule comprises both a part due to point charges $+e$ and $-2e$ on hydrogen and oxygen, and a part due to polarization of the oxygen by the field of the hydrogens. In terms of the formalism introduced in the preceding Sec. II, the net dipole moment is easily shown to be:

$$\mu = 2er_e \cos(\tfrac{1}{2}\theta_e)\{1 - \alpha r_e^{-3}[1 - K(r_e)]\} \,. \qquad (3.4)$$

With α set equal to the value shown in Eqs. (2.6), it is necessary to have

$$1 - K(r_e) = 0.40910 \qquad (3.5)$$

in order to yield the experimental moment (3.3).

The potential energy for a single water molecule has the following form:

$$\Phi(r_1, r_2, \theta) = e^2/r_{12} + \phi_{OH}(r_1) + \phi_{OH}(r_2)$$
$$- \tfrac{1}{2}e^2\alpha\left\{\frac{[1 - K(r_1)][1 - L(r_1)]}{r_1^4} + \frac{[1 - K(r_2)][1 - L(r_2)]}{r_2^4}\right.$$
$$\left. + \frac{[1 - K(r_1)][1 - L(r_2)] + [1 - K(r_2)][1 - L(r_1)]}{r_1^2 r_2^2}\cos\theta\right\} \,,$$
$$(3.6)$$

where r_1 and r_2 are the OH bond lengths, r_{12} is the HH distance, and θ is the HOH bond angle. The requirement that bond length r_e and angle θ_e produce an extremum in Φ leads to two conditions:

$$0 = \phi'_{OH}(r_e) + \frac{e^2(\cos\theta_e - 1)r_e}{r_{12}^3} + \tfrac{1}{2}\alpha e^2(\cos\theta_e + 1)$$
$$\times\left[\frac{(1-L)K' + (1-K)L'}{r_e^4} + \frac{4(1-K)(1-L)}{r_e^5}\right]; \qquad (3.7)$$

$$(1 - K)(1 - L) = r_e^6/(\alpha r_{12}^3); \qquad (3.8)$$

here it must be understood that r_e is the argument of K, L, K', and L'. In connection with the prior result (3.5), the second of these conditions leads to:

$$1 - L(r_e) = 0.37719 \,. \qquad (3.9)$$

Evidently K and L are required to make important intramolecular corrections to the conventional electrostatic polarization energy.

Within the polarization model, the stability of the nonlinear form of the water molecule arises from a competition. On the one hand the two protons repel each other due to their charges, and this alone would place them on opposite sides of the oxygen (ϕ_{OH} will keep them from receding to infinity). However this antipodal arrangement produces no G field at the oxygen and thus produces no induced moment. Displacing the protons to one side of the oxygen breaks the symmetry, yields a nonvanishing G field, and creates an induced moment. The resulting Φ_{II} polarization interaction is negative, and if it is large enough it can stabilize the displacement. Equation (3.8) ensures that the proper angular displacement occurs as a permanent and stable feature.

It is interesting to note that the energy required to "straighten out" a water molecule at fixed bond lengths r_e is

$$\Delta\Phi(104.45° \to 180°)$$
$$= \frac{e^2}{2r_e} - \frac{e^2}{r_{12}} + \alpha e^2(1 - \cos\theta_e)\frac{(1 - K)(1 - L)}{r_e^4}$$
$$= 19.890 \text{ kcal/mole} \,. \qquad (3.10)$$

This agrees moderately well with a Hartree–Fock calculation (using a double-zeta Gaussian basis) that yielded 23.9 kcal/mole for $\Delta\Phi$.[14]

Next we consider dipole derivatives of the water molecule. One readily finds that the rate of change of μ with bond angle θ, evaluated at the stable molecular geometry, has the form:

$$\left(\frac{\partial\mu}{\partial\theta}\right)_{r_1, r_2} = -er_e\sin(\tfrac{1}{2}\theta_e)\left[1 - \frac{\alpha(1 - K)}{r_e^3}\right]$$
$$= -1.1968 \times 10^{-18} \text{ esu cm/rad} \,. \qquad (3.11)$$

Clough[15] has utilized spectral band data measured for water in the vapor phase to infer the following experimental values of the first-order dipole derivatives:

$$\left(\frac{\partial\mu}{\partial\theta}\right)_{r_1, r_2} = -0.6830\times10^{-18}\ \text{esu cm/rad},$$

$$\left(\frac{\partial\mu(\|)}{\partial r_1}\right)_{\theta, r_2} = 0.1568\times10^{-10}\ \text{esu},$$

$$\left(\frac{\partial\mu(\perp)}{\partial r_1}\right)_{\theta, r_2} = 0.7021\times10^{-10}\ \text{esu}. \tag{3.12}$$

The latter two quantities are components respectively resolved along the molecular symmetry axis, and perpendicular to that axis. Evidently our model value (3.11) is large, nearly by a factor of 2, in comparison with the first of (3.12). However, this discrepancy cannot be removed without seriously altering the fundamental basis of the polarization model.

Theoretical expressions for the latter two quantities shown in (3.12) can also easily be obtained from the polarization model.

$$\left(\frac{\partial\mu(\|)}{\partial r_1}\right)_{\theta, r_2} = e\cos(\tfrac{1}{2}\theta_e)\left\{1 + \alpha\left[\frac{K'}{r_e^2} + \frac{2(1-K)}{r_e^3}\right]\right\},$$

$$\left(\frac{\partial\mu(\perp)}{\partial r_1}\right)_{\theta, r_2} = e\sin(\tfrac{1}{2}\theta_e)\left\{1 + \alpha\left[\frac{K'}{r_e^2} + \frac{2(1-K)}{r_e^3}\right]\right\}. \tag{3.13}$$

Although we cannot choose $K'(r_e)$ to cause both of these to agree simultaneously with the values (3.12), rough mutual agreement can be produced. By setting

$$K'(r_e) = -1.4100, \tag{3.14}$$

the expressions shown in Eq. (3.13) yield:

$$\left(\frac{\partial\mu(\|)}{\partial r_1}\right)_{\theta, r_2} = 0.36916\times10^{-10}\ \text{esu},$$

$$\left(\frac{\partial\mu(\perp)}{\partial r_1}\right)_{\theta, r_2} = 0.47635\times10^{-10}\ \text{esu}. \tag{3.15}$$

It is important that we have been able to make these charges small in comparison with the full protonic charge (4.8×10^{-10} esu), in qualitative agreement with the small values shown in (3.12). The initiation of the molecular dissociation process involves bond stretch, and if the dipole derivatives for stretch were too large, the potential energy barrier for dissociation in condensed phases might be lowered to an undesirable extent by solvation interactions.

The water molecule possesses four independent harmonic force constants. Their experimentally determined values are the following[16]:

$$\frac{\partial^2\Phi}{\partial\theta^2} = 103.362\ \text{kcal/mole rad}^2,$$

$$\frac{\partial^2\Phi}{\partial r_1^2} = 1218.050\ \text{kcal/mole Å}^2,$$

$$\frac{\partial^2\Phi}{\partial r_1\partial r_2} = -13.651\ \text{kcal/mole Å}^2,$$

$$\frac{\partial^2\Phi}{\partial r_1\partial\theta} = 54.028\ \text{kcal/mole Å rad}. \tag{3.16}$$

Using the mechanical equilibrium condition (3.8), we

find that the polarization model gives the first of these a very simple form:

$$\frac{\partial^2\Phi}{\partial\theta^2} = 3e^2 r_e^4\sin^2\theta_e/r_{12}^5$$

$$= 98.750\ \text{kcal/mole rad}^2. \tag{3.17}$$

The agreement is moderately good, but again not subject to improvement without drastic alteration of the model.

The last two force constants shown in Eq. (3.16) are relatively small in magnitude, perhaps due to the fact that they represent "cross terms" in Φ. When explicit polarization model expressions are derived for these two force constants, those expressions contain K, L, ϕ_{OH}, and their first derivatives, all evaluated at r_e. The values of K, L, and K' have already been chosen, and the remaining three quantities L', ϕ_{OH}, and ϕ'_{OH} have to be constrained to obey the mechanical equilibrium condition (3.7). We have elected to set

$$L'(r_e) = 0.3000, \tag{3.18}$$

which in Eq. (3.7) thereupon requires

$$\phi'_{OH}(r_e) = 64.260\ \text{kcal/mole Å}; \tag{3.19}$$

furthermore this L' choice produces the following "compromise" values for the mixed force constants in the polarization model:

$$\frac{\partial^2\Phi}{\partial r_1\partial r_2} = 69.381\ \text{kcal/mole Å}^2,$$

$$\frac{\partial^2\Phi}{\partial r_1\partial\theta} = -20.350\ \text{kcal/mole Å rad}. \tag{3.20}$$

Although these have the desired small magnitudes, it is not possible to eliminate the unfortunate sign inversion compared to the measured values in Eq. (3.16). Varying L' from the choice (3.18) tends to cause even greater discrepancies between (3.16) and (3.20).

The remaining force constant $\partial^2\Phi/\partial r_1^2$ involves $K''(r_e)$, $L''(r_e)$, and $\phi''_{OH}(r_e)$ when written out for the polarization model. To simplify the process of selecting suitable functions, we have required

$$K''(r_e) = L''(r_e) = 0. \tag{3.21}$$

By choosing

$$\phi''_{OH}(r_e) = 1097.039\ \text{kcal/mole Å}^2 \tag{3.22}$$

the polarization model agrees exactly with the experimental value (3.16) for the bond stretch force constant $\partial^2\Phi/\partial r_1^2$.

The potential energy that must be overcome in order to break a water molecule in vacuum into infinitely separated H$^+$ and OH$^-$ fragments is 395.9 kcal/mole.[17] The expression (3.6) may be utilized to translate this datum into a condition on ϕ_{OH} (assuming r_e is approximately the anion bond length), namely:

$$\phi_{OH}(r_e) = -593.165\ \text{kcal/mole}. \tag{3.23}$$

A combination of experimental and theoretical data, concerning structure and energy of the simplest clus-

ters containing two oxygens, was employed to select a suitable function $\phi_{OO}(r)$. These two clusters were the water molecule dimer $(H_2O)_2$ and the hydroxide anion monohydrate $OH^-(H_2O)$. The detailed selection procedure was quite complex, involving multidimensional search for global potential energy minima for the clusters. Final structures and their relation to the applicable data are discussed in the following Secs. IV and V. In effect we were obliged to find a smooth and mono-

tonic function $\phi_{OO}(r)$ subject to fixed values for that function and its first derivative at $r \cong 2.45$ Å (anion monohydrate) and at $r \cong 2.95$ Å (water dimer).

Subject to all of the conditions thus far mentioned, we have constructed a specific set of functions K, L, ϕ_{OH}, and ϕ_{OO}. Using kcal/mole and Å as energy and length units, respectively, this set has the following explicit form:

$$1 - K(r) = \frac{r^3}{r^3 + 1.855785223(r - r_e)^2 \exp[-8(r - r_e)^2] + 16.95145727 \exp(-2.702563425r)}; \qquad (3.24)$$

$$1 - L(r) = 1 - \exp(-3.169888166r)\{1 + 3.169888166r$$
$$+ 5.024095492r^2 - 17.99599078r^3$$
$$+ 23.92285000r^4\}; \qquad (3.25)$$

$$\phi_{OH}(r) = \frac{332.1669}{r}[10\exp(-3.699392820r) - 2]$$
$$+ [-184.6966743(r - r_e) + 123.9762188(r - r_e)^2]$$
$$\exp[-8(r - r_e)^2]; \qquad (3.26)$$

$$\phi_{OO}(r) = \frac{1328.6676}{r} + \frac{24}{1 + \exp[2.5(r - 2.90)]}$$
$$+ \frac{90}{1 + \exp[8(r - 2.45)]} + \exp[-6(r - 2.70)]. \qquad (3.27)$$

These functions are displayed graphically in Figs. 1-4. This completes the specification of the present version of the polarization model.

The potential energy for an undeformed water molecule has the following value:

$$\Phi[H_2O] \equiv \Phi(r_e, r_e, \theta_e) = -1032.928 \text{ kcal/mole}, \quad (3.28)$$

using the function set (3.24)-(3.27). Of course the zero of energy refers here to completely separated ionic particles $H^+ + H^+ + O^{2-}$.

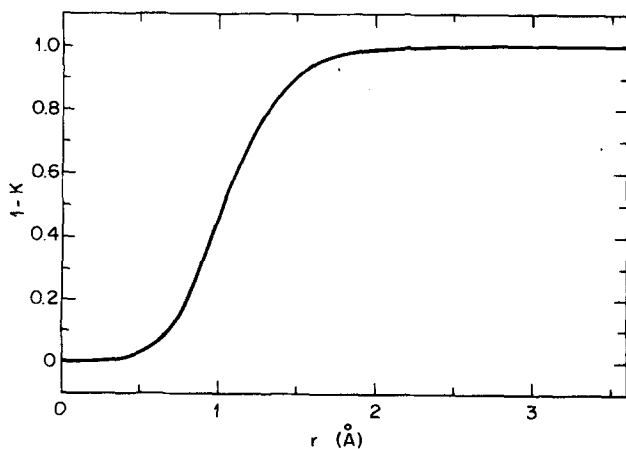The interaction potential for the hydroxide anion may immediately be extracted from Eq. (3.6) by allowing r_2, say, to go to infinity. The resulting function of the single remaining bond length r_1,

$$\phi_{OH}(r_1) - \tfrac{1}{2}\alpha e^2[1 - K(r_1)][1 - L(r_1)]/r_1^4, \qquad (3.29)$$

differs rather little from $\phi_{OH}(r)$ itself (at least when examined graphically). However the polarization term displaces the minimum inward from $r_e = 0.9584$ to 0.8680 Å, possibly a bit shorter than the true bond length for an isolated hydroxide anion.[18] At the distance giving our minimum, we have

$$\Phi[OH^-] = -643.127 \text{ kcal/mole},$$
$$\Phi''[OH^-] = 1626.0 \text{ kcal/mole Å}^2. \qquad (3.30)$$

IV. ION MONOHYDRATES

In evaluating the potential energy Φ by the polarization model prescription, it is necessary to construct a self-consistent set of dipoles according to Eqs. (2.11) and (2.12). We have found that simple iteration of those equations (rather than matrix inversion) provides the most effective means of obtaining these dipoles to high accuracy. Although it is in principle possible that iteration could diverge as a result of a dielectric polarization catastrophe, it has been our experience that no
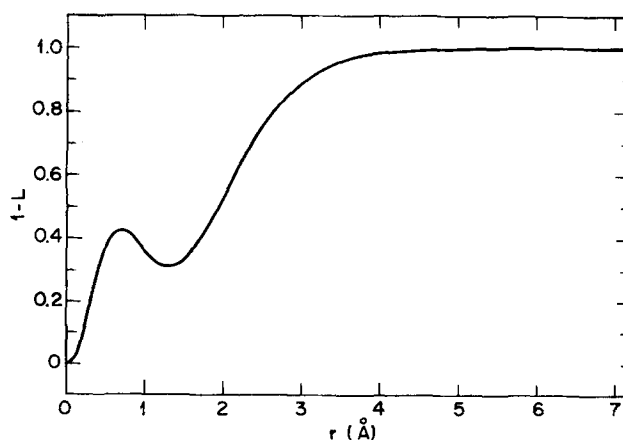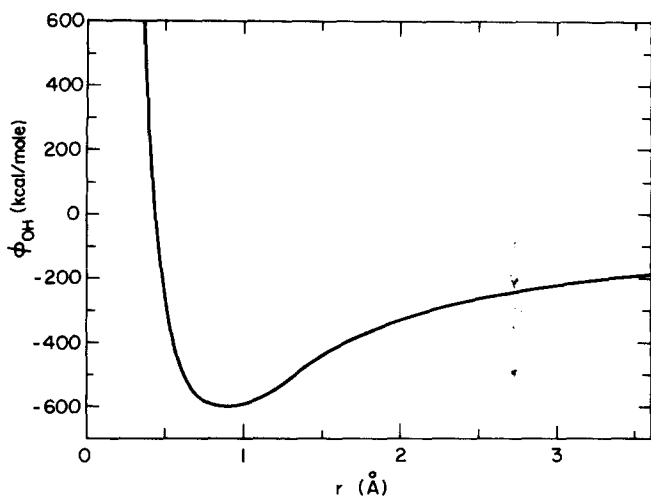

FIG. 1. Polarization response function $1-K$.

FIG. 2. Polarization interaction function $1-L$.

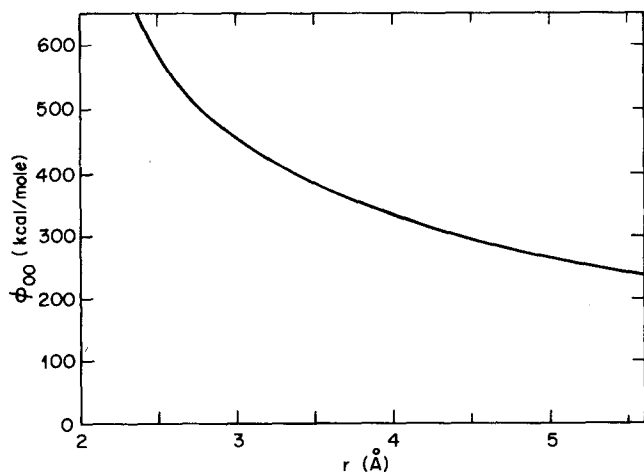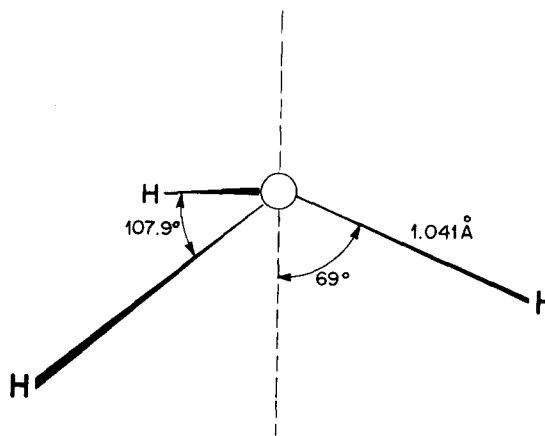FIG. 3. Oxygen—hydrogen bond function ϕ_{OH}.

FIG. 5. Stable structure of the oxonium (hydronium) cation H_3O^+ predicted by the polarization model. This species has symmtery C_{3v}.

such behavior of Eqs. (2.11) and (2.12) will occur in cluster configurations of normal chemical interest.

We have employed a straightforward computer search to locate global (absolute) Φ minima for the clusters considered. For larger clusters (up to sixteen nuclei) the search is quite arduous, and often involves comparison of Φ for distinct local minima in the multidimensional configuration space. We have used several alternative starting structures in the search for some of the clusters. In addition it has been useful for speeding up convergence occasionally to rely on constrained intermediate searches of lower dimensionality.

The reader should be warned that no complete assurance can ever exist that global minima have actually been discovered in any instance. Nevertheless we believe it is unlikely that undiscovered structures of substantially lower potential energy exist for the cases examined.

The oxonium (or hydronium) ion, H_3O^+, is the proton monohydrate. We find that its most stable form is pyramidal, with C_{3v} symmetry. This structure is shown in Fig. 5. Its potential energy is

$$\Phi[H_3O^+] = - 1203.551 \text{ kcal/mole}. \qquad (4.1)$$

Combining this result with the corresponding result (3.28) for the water molecule, we obtain the energy of binding a proton to water:

$$\Phi[H_2O] - \Phi[H_3O^+] = 170.623 \text{ kcal/mole}. \qquad (4.2)$$

Under the C_{3v} symmetry constraint, we have examined the barrier to inversion in H_3O^+. The result is illustrated in Fig. 6. In the planar D_{3h} configuration at the top of the barrier, the OH bonds have increased in length to 1.052 Å, from 1.041 Å at the minima. The inversion barrier has height 3.967 kcal/mole.

Diercksen, Kraemer, and Roos[19] have carried out a quantum—mechanical study of H_3O^+, including configuration interaction corrections to the Hartree—Fock approximation. This is probably the most accurate quantum—mechanical calculation performed for this species to date. These authors also conclude that the stable structure is pyramidal, with C_{3v} symmetry.
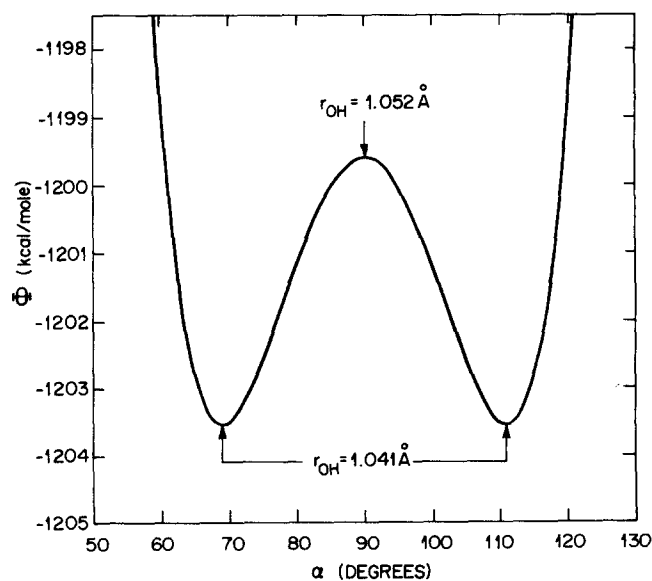

FIG. 4. Oxygen–oxygen pair interaction function ϕ_{OO}.

FIG. 6. Inversion barrier in H_3O^+. The complex is constrained to C_{3v} symmetry, and OH bond lengths have been adjusted to minimize energy at each value of the axial angle α.

They find OH bond lengths equal to 0.972 Å, and HOH angles equal to 111.6°. The proton–water binding energy in their work is 172.8 kcal/mole, and the inversion barrier is 2.05 kcal/mole. Overall the polarization model agrees rather well with their conclusions.

In order to compare calculated proton–water binding energies to experimental proton affinities of water, it is necessary to account for zero-point energy in the water and in H_3O^+, respectively. Diercksen, Kraemer, and Roos estimate that this destabilizes the complex ion by 5.28 kcal/mole compared to unbound H^+ and H_2O, thus leading them to conclude that the proton affinity of water is 167.5 kcal/mole.[19] If we adopt the same estimate of zero-point destabilization, then the polarization model leads to a proton affinity for water of 165.34 kcal/mole.

Unfortunately the experimental values for the proton affinity of water scatter rather widely. van Raalte and Harrison[20] reported 151 ± 3 kcal/mole, while Beauchamp and Butrill[21] claim to find 164 ± 4 kcal/mole. For D^+ $+D_2O$ DePas, Leventhal, and Friedman[22] obtained 184 ± 7 kcal/mole. At present the best that can be claimed is that rough consistency exists between these scattered results, and those obtained by quantum mechanics and by our polarization model.

Although the structure of H_3O^+ in the gas phase has not been determined, neutron diffraction studies of this complex ion in crystals support the suggested pyramidal shape. Fournier and Allavena[23] have surveyed the available evidence which yields OH bonds averaging 1.01 Å in length, and HOH angles in the range 108°–111°.

Our minimum-energy structure for $H_3O_2^-$, the monohydrate of OH^-, is presented in Fig. 7. It is planar, with symmetry C_2. The central hydrogen is involved in a short symmetrical hydrogen bond (2.530 Å between the oxygens). In this arrangement there is no way to distinguish which end is water, and which is hydroxide. The potential energy of this stable cluster is

$$\Phi[H_3O_2^-] = -1714.752 \text{ kcal/mole}. \quad (4.3)$$

Hence we predict that the binding energy of the hydroxide anion to a water molecule is:

$$\Phi[H_2O] + \Phi[OH^-] - \Phi[H_3O_2^-] = 38.697 \text{ kcal/mole}. \quad (4.4)$$

The central hydrogen in Fig. 7 resides in a potential well with a single minimum as it moves along the oxy-
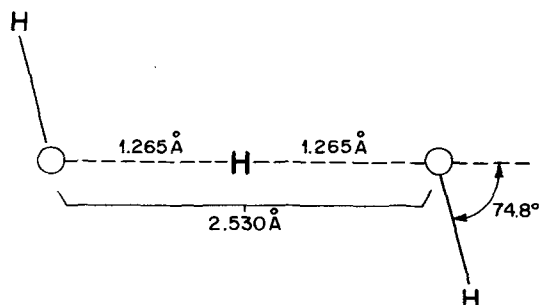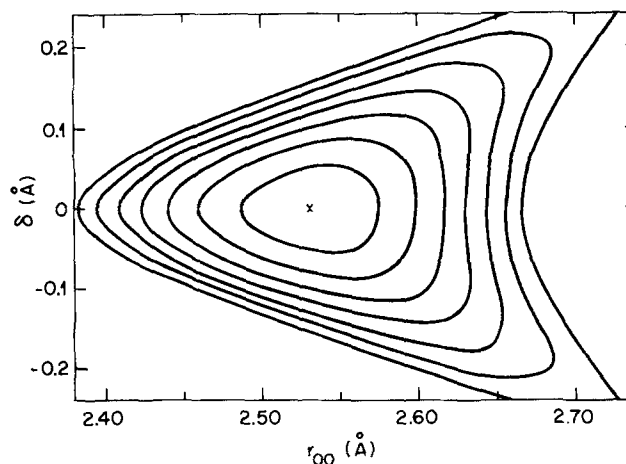

FIG. 8. Partial contour of $OH^-(H_2O)$ hydrogen bond potential. r_{OO} is the distance between oxygens, and δ is the displacement of the hydrogen from the midpoint (see Fig. 7). Successive contours represent 1 kcal/mole increments. Pendant OH bonds have the same lengths and off-axis angles shown in Fig. 7.

gen–oxygen axis. However that single-minimum feature smoothly transforms to double-minimum behavior as the distance between the oxygens increases. Figure 8 shows a contour diagram of cluster potential energy in the two-dimensional space generated by the central hydrogen displacement and the oxygen pair distance. These geometric variations leave pendant OH groups invariant with respect to angle and bond length. The critical oxygen–oxygen distance separating single from double minimum behavior in $H_3O_2^-$ is found to be 2.62 Å.

Unfortunately no gas-phase measurements of energies or structures are available for the hydrates of OH^-. However Newton and Ehrenson[24] have carried out an extensive quantum-mechanical study of the hydrates both of OH^- and of H^+, which we have found to be useful both as a source of input data, and for comparison. These authors find that $H_3O_2^-$ is planar, with a short hydrogen bond which places the two oxygens 2.45 Å apart. The pendant OH groups are off-axis as in our own result. However they find that the bridging hydrogen sits asymmetrically in either of two positions that are 0.23 Å apart, with an intervening low energy barrier. The water binding energy to OH^- computed by Newton and Ehrenson is 40.73 kcal/mole.

We must again stress that aspects of the Newton–Ehrenson result for $H_3O_2^-$, with suitable interpretation, were used to aid us in selection of an appropriate function $\phi_{OO}(r)$. Specifically, those aspects were the OO bond length and the water affinity of OH^-. In view of the tendency for Hartree–Fock calculations with small functional bases to predict excessively strong and short hydrogen bonds,[25] we consciously elected to have our bond length slightly longer and our water affinity slightly less than those of Newton and Ehrenson.

At least superficially it appears that the Newton–Ehrenson calculations (Hartree–Fock approximation with a limited set of basis functions) predict a smaller OO distance than we do at which double-minimum be-

FIG. 7. Minimum energy structure for $OH^-(H_2O)$.
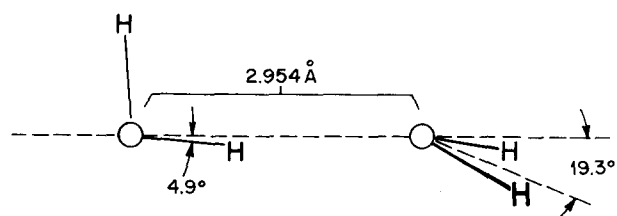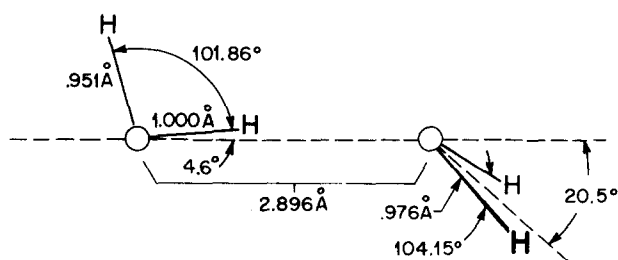
(a) FROZEN MONOMERS

(b) RELAXED MONOMERS

FIG. 9. Minimum-energy structures for water dimers. In (a) the monomers are "frozen" in the isolated molecule shape (0.9584 Å bond lengths, 104.45° bond angle); in (b) the monomers are free to relax to perturbed shapes.

havior for the bridging hydrogen becomes single-minimum behavior. However the greater difficulty of their calculations relative to our own prevented Newton and Ehrenson from carrying out a full multidimensional geometry search for $H_3O_2^-$ as we were able to do. Consequently the status of their apparent double minimum result is uncertain. Clearly it is desirable to have a more extensive quantum-mechanical study of $H_3O_2^-$ to illuminate this aspect of the problem.

V. WATER POLYMERS

In order to ensure that the polarization model will be useful for the study of pure liquid water, it is necessary to show that proper hydrogen bonding occurs in uncharged aggregates of undissociated molecules. For that reason we have examined dimers and trimers of water molecules.

The dimer has been studied in two versions. The first involves monomers "frozen" intramolecularly into the stable isolated molecule shape (0.9584 Å, 104.45°). The second version permits arbitrary intramolecular relaxation. Comparison of potential energy minima for the two cases establishes the level of significance of intramolecular relaxation in hydrogen bonding.

The geometric structures of both the "frozen" and the unconstrained dimers are shown respectively in Figs. 9(a) and 9(b). Both versions exhibit a nearly linear hydrogen bond, and both possess a plane of sym-

metry containing the three nuclei of the proton donor molecule and the oxygen of the proton acceptor molecule. These are qualitative attributes also shared by all of the recent quantum-mechanical studies of the minimum-energy dimer.[26]

The binding energy of the "frozen" dimer in Fig. 9(a) is 5.402 kcal/mole, relative to widely separated monomers. The fully relaxed dimer in Fig. 9(b) has binding energy 6.95 kcal/mole, so that the intramolecular relaxation produces an extra 1.55 kcal/mole of binding. One can see that this stronger bonding entails a shrinkage of the distance between oxygens from 2.954 to 2.896 Å.

Hartree–Fock calculations for the water dimer with extensive basis function sets have been performed by several research groups. The most accurate results for "frozen" monomers indicate hydrogen bond length (between the oxygens) of about 3.0 Å, and a binding energy of about 5 kcal/mole.[26] Restoration of the electron correlation effects that are absent in the Hartree–Fock approximation ought to shrink the hydrogen bond length slightly, and increase its strength by roughly 1 kcal/mole,[26] thereby yielding good agreement with the polarization model.

Dyke, Mack, and Muenter[27] have studied the water dimer experimentally using molecular beam electric resonance spectroscopy. They concur with the theoretical conclusion of the various quantum-mechanical studies (and the present work) that the stable dimer is a "translinear" complex. Furthermore they conclude that the distance between oxygens is 2.98 ± 0.01 Å.

Once again we stress that the bond length and binding energy of the water dimer were used as criteria to select $\phi_{00}(r)$. However this selection has no direct effect on positions of hydrogens, which we see nevertheless occur in qualitative agreement with quantum-mechanical and experimental studies.

The structure of the optimal water trimer is shown in Fig. 10. The component monomers in this trimer were permitted to distort from their own geometry. The trimer energy was found to be

$$\Phi[(H_2O)_3] = -3114.457 \text{ kcal/mole}. \qquad (5.1)$$

Subtracting three times the monomer energy (3.28), we find that the intermolecular binding in this trimer is 15.672 kcal/mole.
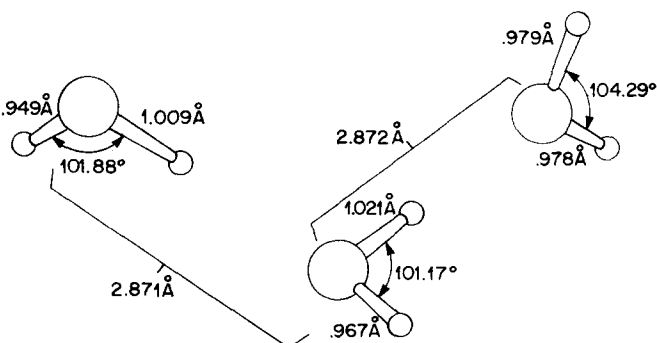

FIG. 10. Minimum-energy structure for the water trimer.

The bonding in the trimer shown in Fig. 10 can best be described as a sequential pair of hydrogen bonds. The molecule on the left acts as proton donor to the central molecule, which in turn donates a proton to the molecule at the right. The end molecules interact relatively weakly on account of their greater distance from one another. Notice that the OH covalent bonds involved in the two hydrogen bonds are stretched by amounts slightly greater than that shown in Fig. 9(b) for the dimer.

In addition to the global trimer minimum for Φ indicated in Fig. 10, there are other local minima of higher Φ in the multidimensional configuration space. The set of these other minima include "double donor" and "double acceptor", trimers, both of which also involve two hydrogen bonds, and which are conventionally named according to the role of the central water molecule that participates in both bonds.[25] Although they differ in some minor geometric details from those considered here, the sequential, double donor, and double acceptor trimers of nearest neighbors exist in ice in 4:1:1 ratio.

The available quantum mechanical calculations for water molecule trimers agree that the sequential trimer is the most stable form.[28] These calculations also reveal that the three-molecule interaction energy contains a substantial nonadditive component, i.e., a specific three-molecule potential. Because the polarization model includes the manifestly nonaddive potential Φ_{11} [Eq. (2.2)], it becomes interesting to see if the model can mimic the quantum-mechanical nonadditivity results.

Consequently we have carried out a set of calculations for each of the sequential, double donor, and double acceptor trimers. For simplicity, and for di-
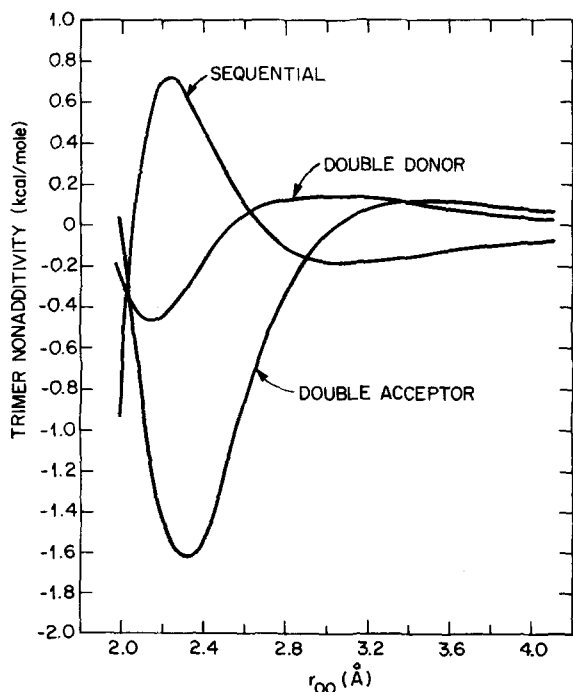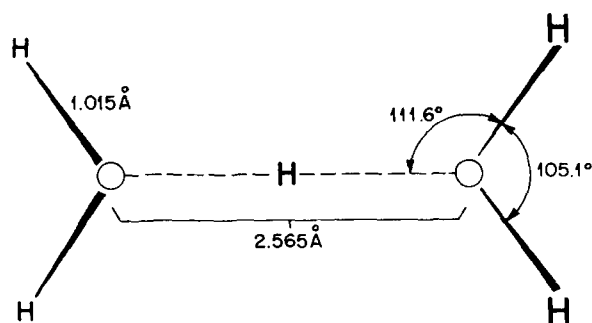

FIG. 12. Structure predicted for $H^+(H_2O)_2$ by the polarization model. The symmetry is C_{2h}.

rectness of comparison with the quantum-mechanical calculations, our calculations were restricted to "frozen" monomers, to strictly linear hydrogen bonds both of which had equal length, and to the tetrahedral bond directions that occur in ice. Thus our trimers conform geometrically to those examined in Ref. 25 by Hankins, Moskowitz, and Stillinger.

Figure 11 shows the three-molecule nonadditivity thus generated by the polarization model, plotted against the common length of the two hydrogen bonds involved. When the bond length exceeds 3.0 Å, the nonadditive contribution stabilizes the sequential trimer, but destabilizes the other two. This pattern agrees qualitatively with that which emerges from quantum mechanics, though the results shown in Fig. 11 tend to be considerably smaller in magnitude. With bond lengths smaller than 3.0 Å the quantum results continue to be ordered as they are at larger lengths, whereas the double donor and double acceptor trimers tend to become stabilized by nonadditive interactions in the polarization model.

We suspect that three-molecule nonadditivity (particularly at small distances) may be very sensitive to basis set size in quantum mechanical calculations. Furthermore, its dependence on electron correlation effects has not been adequately studied yet. Consequently we are not yet in a position to draw definitive conclusions about the validity of polarization model nonadditivity. However the present indications are that it may be deficient in its description of small distance trimers.

VI. HIGHER HYDRATES OF H^+ AND OH^-

In addition to the ion monohydrates discussed in Sec. IV, we have also examined some higher hydrates of H^+ and OH^-. Table I collects minimum energies and corresponding hydrogen bond lengths for clusters containing up to five oxygen atoms. Included as well are the energies required to remove one water molecule from the cluster, to an undistorted state at infinity.

When the oxonium cation H_3O^+ adds a water molecule to form $H^+(H_2O)_2$, the resulting complex has the minimum-energy structure shown in Fig. 12. This structure displays a short symmetrical hydrogen bond, and in that respect it is analogous to $OH^-(H_2O)$ shown earlier

FIG. 11. Three-molecule potential nonadditivity.

TABLE I. Properties of hydrated ions in the polarization model.[a]

Species	Potential energy[b]	Single H_2O removal energy[b]	Lengths of hydrogen bonds[c]
H_2O	−1032.928		
H^+	0		
$H^+(H_2O)$	−1203.551	170.623	
$H^+(H_2O)_2$	−2272.599	36.120	2.565
$H^+(H_2O)_3$	−3326.05	20.52	2.572, 2.761
$H^+(H_2O)_4$	−4379.05	20.07	2.566, 2.792, 2.808
$H^+(H_2O)_5$	−5427.25	15.27	{ 2.570, 2.812, 2.837, 2.841
OH^-	−643.127		
$OH^-(H_2O)$	−1714.752	38.697	2.530
$OH^-(H_2O)_2$	−2771.88	24.20	2.544, 2.712
$OH^-(H_2O)_3$	−3825.88	21.07	2.543, 2.766, 2.780
$OH^-(H_2O)_4$	−4872.87	14.06	{ 2.550, 2.821, 2.830, 2.854

[a]Results refer to minimum energy structures thus far discovered.
[b]Energies in kcal/mole.
[c]Bond lengths in Å.

in Fig. 7. The structure shown does not permit H_3O^+ and H_2O portions uniquely to be distinguished. Instead the two oxygens are equivalent, and possess a pyramidal arrangement of three hydrogens. The cluster may be viewed as a vertex-sharing pair of oxonium units.

On the basis of their quantum mechanical calculations, Newton and Ehrenson[24] likewise find that $H^+(H_2O)_2$ contains a short (2.36 Å) symmetrical hydrogen bond. However their structure has symmetry D_{2d}, in contrast with symmetry C_{2h} in our own result. The fact that "H_3O" groupings at each end of their cluster are planar, not pyramidal, may result from an inadequate basis set size; indeed their oxonium ion itself was planar, not pyramidal as apparently it should be. Newton and Ehrenson find that 43.7 kcal/mole is the energy to remove one water from $H^+(H_2O)_2$, while we calculate this energy to be 36.120 kcal/mole.

It is worth noting that the $H^+(H_2O)_2$ unit occurs in some acid hydrate crystals. A good example is perchloric acid dihydrate, whose crystal structure has been reported by Olovsson.[29] The $H^+(H_2O)_2$ unit in this solid is rather similar to the one we have found, with a short (probably symmetrical) hydrogen bond 2.424 Å long, a center of symmetry, and pyramidal arrangement of hydrogens around each oxygen. Of course one can always question the role of crystal forces in maintaining a given observed structure, which might thereby differ from the gas-phase structure. In particular we might guess that compressive stresses tend to reduce the hydrogen bond length [as they do for $(H_2O)_2$ by 0.23 Å upon formation of ice Ih]. Nevertheless we regard this crystallographic observation as partial verification of our result.

When another water molecule is added to form the proton trihydrate, $H^+(H_2O)_3$, the resulting minimum-energy structure in our model has no symmetry. As Table I shows, its two hydrogen bonds are inequivalent, having lengths 2.572 and 2.761 Å. The cluster may best be described as a strongly hydrogen-bonded $H^+(H_2O)_2$ unit, one of whose pendant hydrogens weakly bonds to the oxygen of the third water molecule.

The lowest-energy structure obtained by Newton and Ehrenson for $H^+(H_2O)_3$ has symmetry C_{2v}, due perhaps to their incomplete geometry search.[24] They predict that the binding energy of the third molecule to $H^+(H_2O)_2$ is 31.0 kcal/mole, to compare with our value 20.52 kcal/mole.

Addition of yet another water molecule in our model to form $H^+(H_2O)_4$ apparently leads to attainment of an absolute energy minimum with an open (noncyclic) hydrogen-bond structure. This structure also fails to exhibit any symmetry, though it is close to having a center of inversion; it is possible that further refinement of our calculations might restore that symmetry. As it stands, the cluster possesses a central $H^+(H_2O)_2$ "core" similar to that shown in Fig. 12, while the two additional water molecules are bound at either end by hydrogen bonds.

We note in passing that another locally stable structure was also found for $H^+(H_2O)_4$, but about 4.7 kcal/mole higher in energy. This less stable alternative superficially could be regarded as an H_3O^+ unit, with a water of hydration along each of its OH "arms." However we have noticed that there is a spontaneous tendency for one of three hydrogens bonds to shorten essentially to a symmetrical hydrogen bridge, while the other two remain long. Evidently at this level of hydration, the polarization model seems not to favor retention of

recognizable H_3O^+ units in either locally or globally stable clusters.

Newton and Ehrenson[24] predict that $H^+(H_2O)_4$ has symmetry D_{3h}, and consists of a recognizable planar H_3O^+, to which the remaining three water molecules are bonded. They find that 21.4 kcal/mole is required to remove one water molecule from their cluster, while we find that 20.07 kcal/mole is required for ours.

Our tentative structure of minimum energy for $H^+(H_2O)_5$ once again has no symmetry. Nevertheless it clearly exhibits a short-bond $H_5O_2^+$ unit on to which are attached (by longer hydrogen bonds) the remaining three water molecules. Referring to Fig. 12 for $H_5O_2^+$, these three additional water molecules act as proton acceptors for the pendant protons shown there, with two arranged at one end of the $H_5O_2^+$ unit and one at the other end. It seems likely that the remaining pendant proton would accommodate yet another water molecule in the next solvation stage.

Newton and Ehrenson[24] carried out a very limited study for $H^+(H_2O)_5$, concluding that the water detachment energy was 17.7 kcal/mole. We have obtained 15.27 kcal/mole for this quantity.

The series of hydrates of H^+ is roughly paralleled by that of OH^-. The parallelism is most obvious in comparing $H^+(H_2O)_{n+1}$ with $OH^-(H_2O)_n$, i.e., clusters with an equal number of oxygens. Table I shows that these "complementary" clusters have equal numbers of hydrogen bonds, and roughly comparable water removal energies. Detailed geometric examination also reveals structural similarities. The first of these similarities was already pointed out, namely the existence of short symmetrical hydrogen bridges both in $H^+(H_2O)_2$ and in $OH^-(H_2O)$ (Figs. 12 and 7, respectively).

In analogy with $H^+(H_2O)_3$, the geometric structure of $OH^-(H_2O)_2$ may be described as a short, essentially symmetric hydrogen bond in an $H_3O_2^-$ unit (Fig. 7), with a more weakly bound terminal water molecule. The pattern of oxygen atoms is approximately the same in the two complementary clusters. Similarly, the pattern of oxygen atoms is approximately the same in $H^+(H_2O)_4$ and in $OH^-(H_2O)_3$; a central short-bond unit has water molecules bonded relatively weakly at either end. In the case of $OH^-(H_2O)_4$, the oxygen pattern once again is similar to that of the complementary $H^+(H_2O)_5$, with each incorporating a single short hydrogen bridge in a noncyclic structure; in both, furthermore, two pendant water molecules are attached at one end of the central short-bond unit, and one is attached at the other end.

The Newton-Ehrenson studies of OH^- hydrates[24] also reveal a complementarity with their own corresponding H^+ hydrates (involving equal numbers of oxygens). However we have noted disparities between their structures and ours, which can now be regarded as disparities between *pairs* of their structures and *pairs* of ours. Again we stress that the differences may be due to their incomplete geometry searches. Successive water detachment energies of $OH^-(H_2O)$ through

TABLE II. Heats of reaction for $H^+(H_2O)n \rightarrow H^+(H_2O)n\text{-}1 + H_2O$ at 300 °K and 1 atm.

| n	ΔH^a		
	Present work	Newton–Ehrenson[b]	Experiment[c]
2	36.72	44.3	36
3	21.12	31.6	22.3
4	20.67	22.0	17
5	15.87	18.3	15.3

[a]Enthalpies in kcal/mole.
[b]Reference 24.
[c]Reference 30.

$OH^-(H_2O)_4$ were found by Newton and Ehrenson to be 40.7, 30.1, 23.1, and 20.7 kcal/mole, respectively; our own results are 38.697, 24.20, 21.07, and 14.06 kcal/mole.

Using mass analysis of ions formed in irradiated water vapor, Kebarle *et al.*[30] have determined equilibrium constants for the reactions

$$H^+(H_2O)_n \rightleftarrows H^+(H_2O)_{n-1} + H_2O ,$$
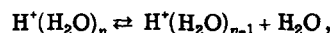
from which enthalpies of reaction at 300° K were calculated. These enthalpies have been entered into Table II, for $n = 2$, 3, 4, and 5. A rough estimate for these reaction heats may be obtained from the polarization model by adding RT to the previously calculated water removal energies. This assumes (for $n > 1$) that vibrational contributions are negligible; in any event insufficient information is available at the moment to do otherwise. The resulting 300° K estimates both for the present polarization model and for the Newton–Ehrenson calculations are entered into Table II. Considering the several uncertainties, the polarization model seems to be performing satisfactorily in representing gas-phase cation clusters.

VII. DISCUSSION

The basic results reported here for the polarization model of water are encouraging. No doubt some refinement of the functions K, L, ϕ_{OH}, and ϕ_{OO} could be achieved to improve those results. But even without such refinements it seems worthwhile to apply the polarization model in its present form to a wide variety of further studies.

Simulations of liquid water with the polarization model, using either the Monte Carlo or molecular dynamics methods,[26] is a desirable goal. Although first indications from small cluster structures reported here suggest that the hydrogen-bonded random network character of the liquid would obtain, this needs to be checked quantitatively. Indeed it is important to establish the extent to which the polarization model can reproduce the well-known thermodynamic and kinetic anomalies exhibited by liquid water.[31]

Because the present model includes both electronic and nuclear polarization effects under the influence of external electric fields, it should yield a realistic de-

scription of dielectric properties. In particular it should be possible to use this model to determine the change in molecular dipole moment that accompanies condensation of water vapor to a liquid or solid phase.

Perhaps the most significant area of application for the polarization model will be in study of proton transfer reactions in water.[17] The simplest of these reactions is the acid–base neutralization that involves recombination of solvated H^+ and OH^- ions. An interesting version of this neutralization can be carried out theoretically by arranging for gas-phase collision of two ion–hydrate clusters such as those studied in this paper; the energy released by the neutralization may be sufficient to fission the combined cluster into diverging fragments of variable size and number.

It seems plausible to suppose that the polarization model could be extended to include other atoms. Specifically, the same type of program that was followed for water herein could be applied to HF, another strongly hydrogen-bonding substance. Subsequent formulation of "mixing rules" for the atom-pair function for oxygen and fluorine then would permit arbitrary mixtures of H_2O and HF to be modeled. Such liquid solutions are acidic, and study of the nature of ion solvation in these solutions would be important. In particular one could assess the validity of Eigen's view of the nature of solvated H^+ in bulk aqueous solutions[32] with the aid of computer simulation.

Further extension of the model to incorporate monatomic ions (such as the other halides and alkali metal cations) also seems feasible. To have in hand a realistic means of modelling the corresponding aqueous solutions would have enormous benefit for electrochemistry.

[1] J. S. Rowlinson, Trans. Faraday Soc. 47, 120 (1951).
[2] J. A. Barker and R. O. Watts, Chem. Phys. Lett. 3, 144 (1969).
[3] F. H. Stillinger, J. Phys. Chem. 74, 3677 (1970).
[4] F. H. Stillinger, J. Chem. Phys. 57, 1780 (1972).
[5] A. Ben–Naim and F. H. Stillinger, "Aspects of the Statistical–Mechanical Theory of Water," in Structure and Transport Processes in Water and Aqueous Solutions, edited by R. A. Horne (Wiley–Interscience, New York, 1972), Chap. 8.

[6] F. H. Stillinger and A. Rahman, J. Chem. Phys. 60, 1545 (1974).
[7] H. Popkie, H. Kistenmacher, and E. Clementi, J. Chem. Phys. 59, 1325 (1973).
[8] H. L. Lemberg and F. H. Stillinger, J. Chem. Phys. 62, 1677 (1975).
[9] A. Rahman, F. H. Stillinger, and H. L. Lemberg, J. Chem. Phys. 63, 5223 (1975).
[10] F. H. Stillinger and A. Rahman, J. Chem. Phys. 68, 666 (1978).
[11] D. Eisenberg and W. Kauzmann, The Structure and Properties of Water (Oxford University, New York, 1969), p. 15.
[12] C. W. Kern and M. Karplus, in Water, A Comprehensive Treatise, Vol. 1, edited by F. Franks (Plenum, New York, 1972), p. 37.
[13] T. R. Dyke and J. S. Muenter, J. Chem. Phys. 59, 3125 (1973).
[14] L. C. Snyder and Z. Wasserman, unpublished results.
[15] S. A. Clough, private communication.
[16] D. F. Smith, Jr. and J. Overend, Spectrochim. Acta Part A 28, 471 (1972).
[17] F. H. Stillinger, in Theoretical Chemistry: Advances and Perspectives, Vol. 3, edited by H. Eyring and D. Henderson (Academic, New York, 1978), pp. 177–234.
[18] R. Janoschek, H. Preuss, and G. Diercksen, Int. J. Quantum Chem. 1, 649 (1967).
[19] G. H. F. Diercksen, W. P. Kraemer, and B. O. Roos, Theor. Chim. Acta (Berlin) 36, 249 (1975).
[20] D. van Raalte and A. G. Harrison, Can. J. Chem. 41, 3118 (1963).
[21] J. L. Beauchamp and S. E. Butrill, Jr., J. Chem. Phys. 48, 1783 (1968).
[22] M. DePas, J. J. Leventhal, and L. Friedman, J. Chem. Phys. 49, 5543 (1968).
[23] M. Fournier and M. Allavena, Theor. Chim. Acta (Berlin) 42, 145 (1976).
[24] M. D. Newton and S. Ehrenson, J. Am. Chem. Soc. 93, 4971 (1971).
[25] D. Hankins, J. W. Moskowitz, and F. H. Stillinger, J. Chem. Phys. 53, 4544 (1970); ibid., Erratum 59, 995 (1973).
[26] F. H. Stillinger, Adv. Chem. Phys. 31, 1 (1975).
[27] T. R. Dyke, K. M. Mack, and J. S. Muenter, J. Chem. Phys. 66, 498 (1977).
[28] B. R. Lentz and H. A. Scheraga, J. Chem. Phys. 58, 5296 (1973).
[29] I. Olovsson, J. Chem. Phys. 49, 1063 (1968).
[30] P. Kebarle, S. K. Searles, A. Zolla, J. Scarborough, and M. Arshadi, J. Am. Chem. Soc. 89, 6393 (1967).
[31] F. H. Stillinger, Phil. Trans. R. Soc. London Ser. B 278, 97 (1977).
[32] M. Eigen and L. DeMaeyer, Proc. R. Soc. London Ser. A 247, 505 (1958).