

# Study of the water octamer using the polarization model of molecular interactions

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A geometry search was carried out to locate the global energy minimum for  $(\text{H}_2\text{O})_8$ , in its full 66 dimensional space of relative configurations. The "polarization model" was used to represent interactions. The optimal structure uncovered has nine nearly linear hydrogen bonds, and amounts to an aqueous analog of the saturated hydrocarbon bicyclo[2.2.2] octane. This structure is recognizable as a fragment of the hexagonal ice crystal, and thus may be important as a prenucleation cluster for that phase. The zwitterionic form of the octamer was found to have no region of local stability.

## I. INTRODUCTION

As a result of both experimental<sup>1</sup> and theoretical<sup>2-7</sup> studies, the nature of water molecule interactions has become reasonably well understood. While these basic investigations have been limited of necessity to the smallest gas phase clusters of water molecules (primarily dimers and trimers), the general importance of hydrogen bonding in clusters has clearly emerged. Relevance to condensed-phase phenomena was also obvious since the peculiar properties of solid and liquid water owe their explanations to the energetic and geometric characteristics of hydrogen bonds.

It has been profitable to fit the available information on water molecule interactions to relatively simple empirical potential functions.<sup>7-11</sup> On the one hand, this serves as a conceptual aid for visualizing the forces that stabilize various cluster and crystal structures. On the other hand, it is a way to encode and interpolate complicated potential energy data in a form that can be used to good advantage in statistical mechanical theory<sup>12</sup> and computer simulation.<sup>13-17</sup>

The present paper is devoted to study of the water octamer  $(\text{H}_2\text{O})_8$  in what we believe is its most stable configuration. This cluster is too large for direct quantum-mechanical study, and to the best of our knowledge has not clearly been identified in experiments designed to form and detect small water clusters. Consequently, for this investigation we have utilized one of the newest semiempirical models for water molecule interactions, the "polarization model."<sup>18</sup> In this approach it is possible and feasible to adjust the coordinates of all 24 nuclei independently in seeking a global minimum energy structure.

The specific case of the water octamer commands attention on at least two counts. First, the preferred structure turns out to be recognizable as a part of the hexagonal ice (but *not* cubic ice) network, and may thus be important in nucleation kinetics of ice in the supercooled vapor. Second, this preferred structure permits formation of an  $\text{OH}^-(\text{H}_2\text{O})_6\text{H}_3\text{O}^+$  ion pair by simple proton

displacement, which makes it an interesting candidate for study of the dissociation process.

The following Sec. II provides a brief recapitulation of the polarization model. Section III contains its application to study of the minimum-energy octamer. Section IV describes the process of zwitterion formation by concerted dissociation, and the study of the stability of that zwitterion against spontaneous neutralization. Finally, several points raised by the present calculation are discussed in Sec. V.

## II. POLARIZATION MODEL

The polarization model was originally devised for water with such a form that it could naturally incorporate molecular polarizability, distortion, and dissociation.<sup>18</sup> Its primary objective is to assign a potential energy  $\Phi$  to any configuration of hydrogen and oxygen particles, not merely those constituting intact water molecules. Furthermore, the component functions of the model were intended to be transferable to a wide variety of aqueous and nonaqueous systems.<sup>19</sup>

Each atomic particle is assigned a fixed oxidation state (electrostatic charge) and a scalar polarizability. In the case of water the hydrogens are regarded as bare protons  $\text{H}^+$  having zero polarizability, while the oxygens are regarded as doubly charged anions  $\text{O}^{2-}$  with polarizability  $1.444 \text{ \AA}^3$ .

The potential energy  $\Phi$  is postulated to consist of two parts

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

The first of these  $\Phi_I$ , is a sum of atom-pair potentials

$$\Phi_I = \sum \phi_{ij}(r_{ij}) ,$$

where for any given pair  $i, j$  the function  $\phi_{ij}$  includes charge-charge interaction, covalency effects, and overlap repulsion. The second part of  $\Phi$ , i.e.,  $\Phi_{II}$ , is a generalization of the charge-induced dipole energy familiar from classical electrostatics and as such is a manifestly many-body potential. Details necessary for

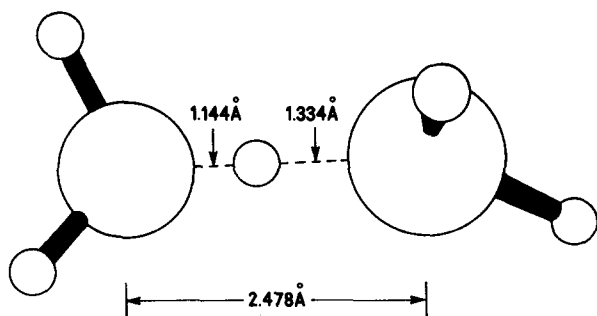


FIG. 1. Structure of the doubly hydrated proton.

full specification of  $\Phi_I$  and  $\Phi_{II}$  are contained in an Appendix.

Once the form of  $\Phi$  has been fixed it is a straightforward matter to implement a computer search for minimum energy structures. In the case of two hydrogens and one oxygen the minimum energy structure corresponds (by construction) to the known water molecule geometry,<sup>20</sup> with bond angle  $104.45^\circ$  and OH bond lengths  $0.9584 \text{ \AA}$ . Furthermore, the dipole moment of this intact molecule (again by construction) agrees with the experimental value of  $1.855 \text{ D}$ .<sup>21</sup> The value of the potential energy at this stable minimum is found to be

$$\Phi[\text{H}_2\text{O}] = -1032.928 \text{ kcal/mole} .$$

The convention adopted by the polarization model is that the configuration of infinitely separated ionic particles corresponds to  $\Phi = 0$ .

The hydronium cation  $\text{H}_3\text{O}^+$  is correctly predicted by the polarization model to have  $C_{3v}$  symmetry. Its stable pyramidal distortion owes its existence to the dipole induced by the hydrogens in the oxygen, and is analogous to the nonlinear stable distortion similarly produced in  $\text{H}_2\text{O}$ . The OH bond lengths in  $\text{H}_3\text{O}^+$  are  $1.029 \text{ \AA}$ , while the angle between any OH bond and the threefold axis is  $68.4^\circ$ . The potential energy is

$$\Phi[\text{H}_3\text{O}^+] = -1201.842 \text{ kcal/mole} ,$$

which in connection with the water molecule value above gives  $168.914 \text{ kcal/mole}$  for the proton attachment energy to a single water molecule. (It should be noted that these last two energies differ very slightly from corresponding numbers given in Ref. 18, on account of changes in the basic polarization model functions as stated in the Appendix.)

We also note the structure of the doubly hydrated proton for which

$$\Phi[\text{H}_5\text{O}_2^+] = -2268.285 \text{ kcal/mole} .$$

Details are specified by Fig. 1. The excess proton sits asymmetrically between the two solvating water molecules, forming a short ( $2.478 \text{ \AA}$ ) hydrogen bond. In spite of this asymmetry it may be misleading to view the given structure as merely a singly hydrated hydronium cation. The OH bond at the left side in Fig. 1 is severely stretched, placing the bridging hydrogen less than  $0.10 \text{ \AA}$  from the midpoint of the oxygens. No doubt a very small reduction in O-O separation would induce the bridging hydrogen to take up residence at that midpoint.

At any rate we find that the analogous anion  $\text{H}_3\text{O}_2^-$ , which has the slightly shorter O-O separation of  $2.45 \text{ \AA}$ , is indeed held together by a symmetrical hydrogen bond.

### III. STABLE OCTAMER

Our technique for seeking the most stable octamer structure was straightforward. Starting from some initial configuration, a digital computer moves each of the 16 hydrogens and eight oxygens in turn by small increments. If the total polarization model energy  $\Phi$  decreases as a result of a given coordinate increment, that displacement is retained. If  $\Phi$  increases, it is rejected. The computer continues this test and move procedure, decreasing increment sizes when necessary from the initial choice  $0.1 \text{ \AA}$ , until a local  $\Phi$  minimum is located in the 66 dimensional space of relative coordinates.

The collection of 24 particles required to form eight water molecules is sufficiently large that many local minima evidently exist, even after discounting the possibility of permutation of identical particles. Our search routine discovered several of these. However, large displacements were then imposed to permit jumps to the neighborhood of other local minima. We do not claim to have investigated the entire collection of minima, and indeed there will probably always remain some uncertainty about whether the absolute  $\Phi$  minimum has been discovered.

Nevertheless, we believe that we have generated either the structure with absolute minimum energy, or one lying close to it in energy. Figure 2 shows the corresponding arrangement. Nine nearly linear hydrogen bonds are arranged in three chains of three, to hold the water molecules in an aqueous analog of the saturated hydrocarbon bicyclo[2.2.2]octane. Note that one of the hydrogen bond chains is polarized in a direction opposite to that of the other two chains. The pendant hydrogens

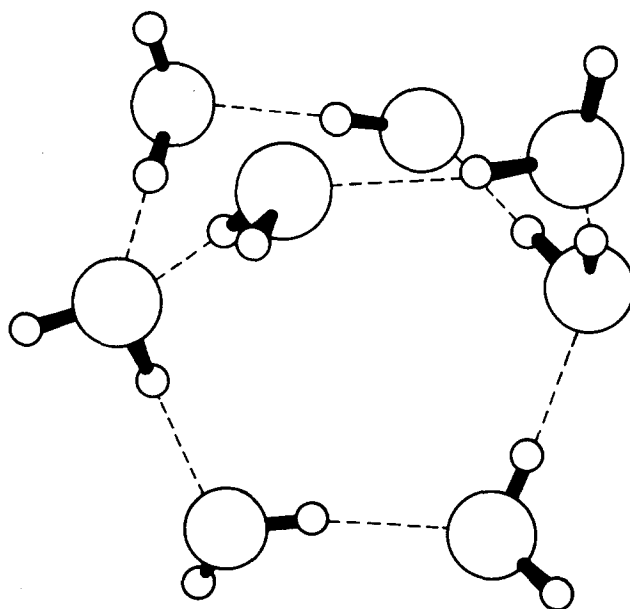


FIG. 2. Structure of the water octamer at what is thought to be the global energy minimum. Dashed lines indicate hydrogen bonds.

TABLE I. Nuclear coordinates for neutral (*N*) and zwitterionic (*Z*) octamers.<sup>a</sup>

Nucleus	<i>N</i>			<i>Z</i>		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
H1	-0.011	0.040	-0.748	1.615	0.357	0.973
H2	0.893	0.223	0.580	2.607	0.031	3.210
H3	2.509	0.097	2.322	0.923	-0.117	4.906
H4	2.988	1.190	1.343	-0.112	0.222	-0.707
H5	-2.773	1.845	1.018	2.866	1.151	0.809
H6	-1.255	1.534	0.927	-2.792	1.895	1.080
H7	-1.089	-1.366	0.978	-1.282	1.509	0.922
H8	-1.282	-2.890	0.803	-1.163	-2.887	0.822
H9	1.611	-0.105	4.495	-1.053	-1.329	0.889
H10	3.078	-0.665	4.670	3.259	-0.952	4.135
H11	-1.346	3.126	4.476	-1.224	3.108	4.406
H12	-1.725	2.212	3.285	-1.643	2.162	3.227
H13	-1.488	-2.311	3.243	-2.589	-2.173	4.414
H14	-2.425	-2.520	4.463	-1.595	-2.219	3.181
H15	-0.532	0.739	4.954	-0.421	0.766	4.874
H16	-0.570	-0.857	4.947	-0.508	-0.898	4.886
O1	-0.080	0.131	0.219	-0.127	0.194	0.216
O2	2.488	0.354	1.322	2.486	0.439	1.352
O3	-1.923	2.152	1.364	-1.929	2.179	1.383
O4	-1.603	-2.155	1.347	-1.528	-2.148	1.322
O5	2.548	-0.129	4.053	2.667	-0.174	4.139
O6	-1.585	2.219	4.287	-1.465	2.178	4.244
O7	-1.499	-2.333	4.255	-1.640	-2.212	4.213
O8	0.009	-0.071	5.230	0.051	-0.088	5.289

<sup>a</sup>Coordinates in Å.

along the chains (i. e., those not involved directly in hydrogen bonds) exhibit rotatory twists in opposite directions near the two opposite bridgeheads; this apparently serves to minimize hydrogen repulsions. The structure has no symmetry, so an equivalent mirror image structure also exists.

The energy at the given configuration was found to be

$$\Phi[(\text{H}_2\text{O})_8] = -8336.25 \text{ kcal/mole} .$$

By subtracting eight times the energy given above for a single H<sub>2</sub>O we find that the octamer binding energy is

$$\Phi[(\text{H}_2\text{O})_8] - 8\Phi[\text{H}_2\text{O}] = -72.83 \text{ kcal/mole} .$$

One ninth of this last value is 8.09 kcal/mole which might be construed as the mean hydrogen bond energy in the complex. That this mean energy is greater in magnitude than the dimer binding energy in the polarization model (6.71 kcal/mole) can probably be regarded as a reflection of "hydrogen-bond cooperativity."<sup>5, 22, 23</sup>

The nine hydrogen-bonded oxygen-oxygen distances (in Å) were found to be 2.774, 2.799, 2.804, 2.888, 2.916, 2.942, 2.946, 2.965, and 2.970. The average of these (2.889 Å) is slightly smaller than the oxygen-oxygen distance found for the optimal dimer (2.90 Å), which again suggests the presence of hydrogen-bond cooperativity. The nine covalent OH bond lengths along the hydrogen bonds average 1.021 Å in length, indicating a slight stretch compared to the monomer value 0.9584 Å. Coordinates for each of the 24 atoms in the octamer are listed in Table I (heading *N*).

The dipole moment of the (presumably) optimal octamer was found to be 4.61 D (directed essentially from

right to left in Fig. 2).

A particularly intriguing aspect of the structure shown in Fig. 2 consists in recognition that it is a fragment of hexagonal ice. Figure 3 shows the crystal structure of the latter in highly schematic fashion, with lines indicating hydrogen bonds and vertices indicating the loca-

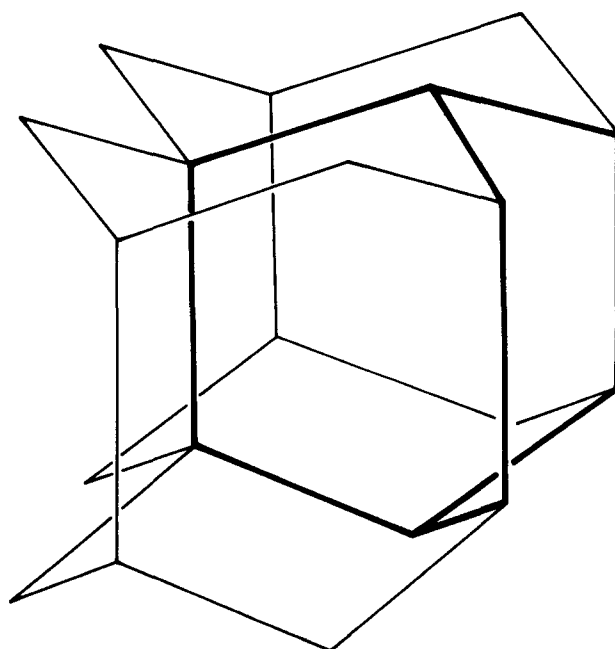


FIG. 3. Fitting of the octamer onto the lattice of hexagonal ice.

tion of oxygen atoms. The fitting of the octamer into this extended periodic network is shown by heavy outlines. It should be kept in mind that in order to fit properly the octamer has to be "untwisted" slightly along the axis through its bridgehead oxygens, and then compressed slightly to the oxygen-oxygen distance in ice (2.74 Å). We believe that no smaller set of water molecules spontaneously exhibits hexagonal ice geometry in nearly as vivid a fashion.

It may be significant that the octamer shown in Fig. 2 does *not* fit into the lattice for cubic ice, the form that can be prepared at very low temperature.<sup>24</sup> The corresponding fragment required by this alternative polymorph is a tricyclic decamer with 12 hydrogen bonds.

#### IV. ZWITTERION FORMATION AND STABILITY

Our optimized water octamer (Fig. 2) can serve as the starting point for study of one aspect of the water molecule dissociation reaction. In particular, we can examine the process which dissociates the bridgehead molecule at its left end, and transfers the proton liberated to the right end bridgehead molecule. The result would be a zwitterion consisting of OH<sup>-</sup> and H<sub>3</sub>O<sup>+</sup> separated by six intact water molecules. Basic questions to be answered are what energy is required to effect the dissociative proton transfer, and whether the zwitterion represents a local  $\Phi$  minimum in the 66 dimensional configuration space of the cluster.

We have noted before that the bottom chain of three hydrogen bonds in Fig. 2 has an orientation that is opposite to that of the other two. In fact, this orientation is well suited for the proton transfer by concerted motion of all three hydrogens along that chain. The end product of such a concerted shift will be the desired zwitterion, and the chain involved will finally have its orientation reversed to conform to the others.

Figure 4 (solid curve) shows how the polarization model  $\Phi$  varies as the concerted shift of three protons is executed. Point *N* is the neutral optimized octamer, while point *Z* is the zwitterion. All eight oxygen nuclei are rigidly held in place while the three protons along the bottom chain move linearly toward the recipient oxygens at precisely the same rate. The other 13 hydrogens were permitted to readjust their positions at each stage of the shift to minimize  $\Phi$  for the constrained structure. At point *Z* in Fig. 4 covalent bonds of approximately the same length as those at *N* have reformed along the bottom chain. Coordinates for the zwitterion are displayed in Table I (heading *Z*).

The zwitterion configuration *Z* lies about 41 kcal/mole higher in energy than *N*. However, at least along the reaction coordinate presented in Fig. 4, these states are separated by a very high barrier, which in fact lies 140 kcal/mole above *N*, 99 kcal/mole above *Z*. The reason for this barrier is clear enough. At the midway point of the displacement the three original covalent OH bonds have essentially broken, while the three new bonds have yet to form.

The existence of the high barrier might lead one to suspect that the zwitterion could exist as a metastable

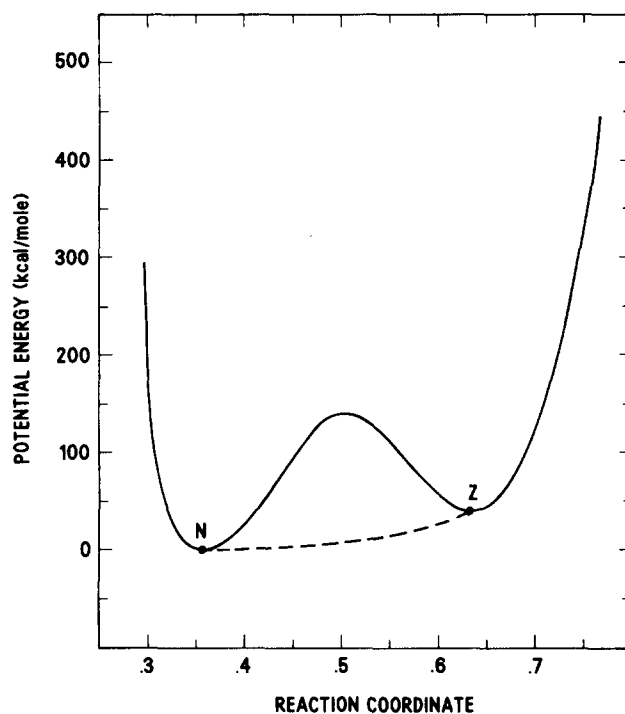


FIG. 4. Energy variation for zwitterion formation. The solid curve shows how  $\Phi$  varies for the three-proton concerted shift, with oxygens clamped and other protons permitted to relax. *N* is the position for the optimized octamer; *Z* is the zwitterion. The dashed curve indicates schematically the barrier-free return path for the totally unconstrained complex.

species. However, it must be re-emphasized that all eight oxygen nuclei were clamped in place during the displacement. Obviously, the two charged ends of the zwitterion strongly attract one another and would at the least be expected to produce substantial compressive distortion. To establish whether or not the zwitterion really enjoys the status of local stability requires a careful study of  $\Phi$  in the full 66 dimensional configuration space.

In fact, there is no such local stability for the octameric zwitterion. Subsequent calculations reveal that a path exists (denoted schematically by the dashed curve in Fig. 4) in the full configuration space that continuously connects *Z* to *N* without any intervening barrier. We have discovered this path simply by using *Z* as the starting configuration in our search routine with small increments. The computer then steps the system monotonically downward in potential energy until the optimized neutral octamer *N* is recovered. This process at an intermediate stage causes the average O-O bond lengths to decrease to about 2.76 Å, while bonds along the return chain shorten to about 2.5 Å. Evidently, this contraction is sufficient to eliminate the barrier-producing energy cost of bond breaking that in the constrained octamer precedes bond reforming.

#### V. DISCUSSION

Not only can a single octamer be fitted into the hexagonal ice crystal, but an entire crystal can be broken into octameric fragments of the type shown in Fig. 2.

Of course, this requires that the crystal have a special arrangement of hydrogens, which represents only one of the many canonical "Pauling" arrangements.<sup>25</sup> Starting with an alternative canonical arrangement of hydrogens in the hexagonal ice lattice would result in octamers having nonoptimal arrangements of pendant hydrogens.

There is no conceivable experimental circumstance in which hexagonal ice would be formed by direct assembly of intact octamers. However, the octamer may indeed be an important prenucleation cluster for condensation of a cold, supersaturated vapor to form eventually an ice crystallite (at least under circumstances where heterogeneous nucleation is unimportant). However, we are not aware that this species specifically has been considered in published work in the area.<sup>26</sup> The further growth of an octamer presumably would proceed by accretion of monomers or dimers. It would be interesting to apply the known equations of motion for the polarization model<sup>27</sup> to the study of this accretion (and subsequent re-arrangement) kinetics by computer simulation.

Kistenmacher *et al.* have examined the preferred arrangements for small clusters containing eight or fewer water molecules.<sup>28</sup> They utilized only rigid molecules confined to the monomer geometry, and a pairwise additive intermolecular potential chosen to fit a large but discrete set of Hartree-Fock computations. These authors have remarked pointedly on the existence of many local minima for the larger sets of molecules, and have exhibited three locally stable groupings of eight molecules. None of their three octamer structures appears to resemble the bicyclo[2.2.2]octane form shown in Fig. 2, however, and indeed their maximum binding energy (47.3 kcal/mole) is substantially less than that found in the present work (72.83 kcal/mole). We suggest that using their model a more complete search in the neighborhood of the bicyclo[2.2.2]octane structure model would eventually uncover a more stable arrangement.

The inability of the octamer to support a locally stable zwitterion has important implications for the theory of proton transfer reactions in water.<sup>29</sup> Eigen and DeMaeyer<sup>30</sup> have adapted Debye's theory of ionic reactions in solution to neutralization of H<sup>+</sup> and OH<sup>-</sup>, with the conclusion that once these species approach to within 7.5 ± 2 Å of one another (in water) no energy barrier to recombination can exist. Since the oxygen ends of the octamer in Fig. 2 are only 5.016 Å apart, our results are consistent with those of Eigen and DeMayer. We estimate informally that a cluster of at least 14 water molecules (arranged to be a fragment of cubic ice) would be required to support a locally stable zwitterion, since this many molecules appears to be required to achieve the requisite distance in a rigid framework.

Finally, it should be stressed that the polarization model may eventually be useful in studying the molecular properties of ice itself. It seems to offer an appropriate tool for examining the distribution of molecular dipole moments in the solid. In addition, it could shed light on the geometry and energy of point defects in ice, specifically the important Bjerrum and ionic defects that control electrical transport behavior.<sup>31</sup>

## APPENDIX

Three distinct atom pair functions are comprised in  $\Phi_{\text{I}}$ . Upon using Å as the distance unit and kcal/mole as the energy unit, the functions have the following forms:

$$\phi_{\text{HH}}(r) = \frac{332.1669}{r},$$

$$\phi_{\text{OH}}(r) = \frac{332.1669}{r} [10 \exp(-3.69939282r) - 2] + [-184.6966743(r - r_e) + 123.9762188(r - r_e)^2] \times \exp[-16(r - r_e)^2],$$

$$\phi_{\text{OO}}(r) = \frac{1328.6676}{r} + 8.255 \exp[-18.665(r - 2.45)] + \frac{84.293}{1 + \exp[2.778(r - 2.56)]} - \frac{12.299}{1 + \exp[4.817(r - 3.10)]}.$$

In the second of these,  $r_e$  stands for the equilibrium bond length in water (0.9584 Å). The reader should be aware that  $\phi_{\text{OH}}$  and  $\phi_{\text{OO}}$  as shown here differ somewhat from the functions used in Ref. 18, as a result of improvements subsequently effected in the polarization model.

The polarization interaction  $\Phi_{\text{II}}$  requires self-consistent calculation of induced dipole moments on each of the oxygen particles. The moment  $\mu_l$  on particle  $l$  is determined by ( $\mathbf{r}_{lj} = \mathbf{r}_j - \mathbf{r}_l$ ):

$$\mu_l = -\alpha \sum_{j(\neq l)} \frac{\mathbf{r}_{lj} q_j}{r_{lj}^3} [1 - K_{\text{O}}(r_{lj})] - \alpha \sum_{m(\neq l)} \frac{\mathbf{T}_{lm} \cdot \mu_m}{r_{lm}^3} [1 - K_{\text{O}}(r_{lm})].$$

Here  $\alpha = 1.444 \text{ \AA}^3$  is the oxygen polarizability. The first sum covers all charges  $q_j$  (excluding that on  $l$ ) while the second sum includes all other dipoles  $\mu_m$ . Also the dyadic tensor  $\mathbf{T}_{lm}$  is defined by

$$\mathbf{T}_{lm} = \mathbf{1} - \frac{3\mathbf{r}_{lm}\mathbf{r}_{lm}}{r_{lm}^2}.$$

The dimensionless factors  $1 - K_{\text{O}}$  account for spatial extension of the polarizable electron cloud about each oxygen. Specifically, we have

$$1 - K_{\text{O}}(r) = r^3 / [r^3 + F(r)],$$

$$F(r) = 1.855785223(r - r_e)^2 \exp[-8(r - r_e)^2] + 16.95145727 \exp[-2.702563425r].$$

In all cases of interest in the present paper, simple iteration of the simultaneous linear equations for the  $\mu_l$  converges rapidly, eliminating the need for matrix inversion.

Once the induced moments have been obtained the polarization energy can be computed as a sum of modified charge-dipole interactions:

$$\Phi_{\text{II}} = \frac{1}{2} \sum_{j(\neq l)} \frac{(\mu_l \cdot \mathbf{r}_{lj}) q_j}{r_{lj}^3} [1 - L_{\text{O}}(r_{lj})],$$

The dimensionless factors  $1 - L_{\text{O}}$  also account for electron cloud extension, with

$$1 - L_O(r) = 1 - \exp(-3.169888166r)[1 + 3.169888166r + 5.024095492r^2 - 17.99599078r^3 + 23.92285r^4].$$

Both  $1 - K_O$  and  $1 - L_O$  are unchanged in the present work from the forms used in the initial studies in Ref. 18.

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