

Molecular multipole moments of water molecules in ice I_h

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(Received 9 April 1998; accepted 15 June 1998)

We have used an induction model including dipole, dipole–quadrupole, quadrupole–quadrupole polarizability and first hyperpolarizability as well as fixed octopole and hexadecapole moments to study the electric field in ice. The self-consistent induction calculations gave an average total dipole moment of 3.09 D, a 67% increase over the dipole moment of an isolated water molecule. A previous, more approximate induction model study by Coulson and Eisenberg [Proc. R. Soc. Lond. A **291**, 445 (1966)] suggested a significantly smaller average value of 2.6 D. This value has been used extensively in recent years as a reference point in the development of various polarizable interaction potentials for water as well as for assessment of the convergence of water cluster properties to those of bulk. The reason for this difference is not due to approximations made in the computational scheme of Coulson and Eisenberg but rather due to the use of less accurate values for the molecular multipoles in these earlier calculations. © 1998 American Institute of Physics. [S0021-9606(98)52335-5]

I. INTRODUCTION

An understanding of the properties of water and ice requires a quantitative description of the electric field created collectively by the water molecules and the influence the field can have on the atomic scale structure and dynamics. It is, for example, expected that the dipole moment of a water molecule in liquid water is significantly larger than the dipole moment of an isolated water molecule, which has been experimentally measured to be 1.855 D.¹ The dipole moment of a water molecule in a condensed phase environment cannot be measured directly, but estimates based on the measured dielectric constant of water and assuming the molecules can be represented by dipole moments only indicate an increase of the molecular dipole moment by 0.6–1.2 D.^{2,3} The change in molecular electric properties due to the local environment is, in particular, important for the development of accurate intermolecular potential functions describing water–water and water–solute interactions. While most of the attention has been focused on the dipole moment, it is clear that the quadrupole moment is also important for accurately describing the molecular interactions⁴ and the macroscopic dielectric constant.⁵

Ice is a natural starting point for systematically studying these issues since, apart from the proton disorder in ice I_h, the molecular structure is known. Liquid water has the additional complexity of irregular and poorly known ordering of the molecules. Over thirty years ago, Coulson and

Eisenberg⁶ carried out an ingenious calculation of the dipole moment in ice I_h using an induction model. Their calculation gave a net molecular dipole moment of 2.6 D. Unfortunately, their numerical result has frequently been misrepresented. Several authors have incorrectly quoted the paper by Coulson and Eisenberg as giving the molecular dipole moment in liquid water or, as giving the results of a measurement of the dipole moment in ice, or even as giving an experimental measurement of the molecular dipole moment in liquid water. These misquotations seem to perpetuate in the water modeling literature of recent years.

We describe here more accurate and detailed calculations that lead to a significantly larger molecular dipole moment in ice than the one obtained by Coulson and Eisenberg. Our calculations include several higher order terms in the multipolar expansion, and do not make some of the approximations invoked in the induction calculations of Coulson and Eisenberg. The self-consistent multipole iterative scheme that we employed as well as the input parameters for the molecular multipoles are described in Sec. II. Our results are presented in Sec. III. We address the differences between our calculations and those of Coulson and Eisenberg in Sec. IV. In view of the widespread confusion in the literature about their work, we describe their calculations in considerable detail. Our conclusions are presented in Sec. V.

II. MULTIPOLE ITERATIVE METHOD

The starting point of our calculations is the construction of a hexagonal lattice of water molecules representing ice I_h. For the oxygen–oxygen separation we used 2.76 Å, a value

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consistent with the measured density at 273 K.⁷ It is well established that while the oxygen atoms are ordered on a lattice, the protons are to a certain extent disordered, but still follow the “ice rules,”^{8,9} namely that (1) there is one and only one hydrogen atom between each pair of adjacent oxygen atoms, and (2) each oxygen atom has two hydrogens at a close distance (~ 1.0 Å, covalently bonded) and two hydrogens at a larger distance (~ 1.75 Å, hydrogen bonded).

The calculations were carried out as follows. A configuration of 2,592 water molecules was generated following the ice rules, filling a $40.6 \times 46.9 \times 44.2$ Å³ simulation box. Periodic boundary conditions were imposed in all three directions to simulate a bulk ice environment. We generated an ice lattice with 96 molecule unit cell with proton disorder, zero total dipole moment, and periodic boundary conditions satisfied in all three directions. We followed the same procedure as Kroes.¹⁰ This cell was periodically repeated three times in each direction to generate the simulation box. The degree of randomness of the ice lattices generated by this method and by other methods was studied by Hayward and Reimers.¹¹ In the notation of Hayward and Reimers we generated a “ $3 \times 2 \times 2$ ” lattice with constraints of the “C2” type. The randomness is characterized by the dipole–dipole autocorrelation coefficients ϕ_n for the n th coordination shell that has radius r_n , defined as

$$\phi_n = \frac{\sum_{i=1}^N \sum_{j=i}^i \mathcal{P}^{(i)} \cdot \mathcal{P}^{(j)} \delta(R_{ij} - r_n)}{\sum_{i=1}^N \sum_{j=i}^i \delta(R_{ij} - r_n)}, \quad (1)$$

where R_{ij} is the distance between dipoles and \mathcal{P} is the dipole moment vector. In our simulation cell $\phi_1 = 0.227$, $\phi_2 = -0.03$, $\phi_3 = -0.179$, and $\phi_4 = -0.015$.

The electric field at a molecule is the sum of the fields produced by its neighbors. In order to systematically study the effect of distant neighbors, only those closer than a given cutoff distance r_{cut} were included in the calculation of the electric potential. The full calculation was then repeated with different values of r_{cut} , up to 20 Å. It turns out (see Sec. III) that it is sufficient to use $r_{\text{cut}} = 7$ Å.

When calculating the electric field, each molecule was represented with a point dipole, quadrupole, octopole, and a hexadecapole moment tensor at the center of mass. The electric field at a molecule due to its neighbors then induces both a dipole moment and a quadrupole moment in the molecule. The i th component of the induced dipole moment is given by¹²

$$\Delta \mathcal{P}_i = \alpha_{ij} E_j + \frac{1}{3} A_{i,jk} \frac{\partial E_j}{\partial r_k} + \frac{1}{2} \beta_{ijk} E_j E_k, \quad (2)$$

where \mathbf{E} is the total electric field (cf. Appendix), α_{ij} is the molecular dipole polarizability, $A_{i,jk}$ the dipole–quadrupole polarizability, and β_{ijk} the first hyperpolarizability. The repeated indices are to be summed over.

The induced quadrupole moment of the molecule is¹²

$$\Delta \mathcal{Q}_{ij} = A_{k,ij} E_k + C_{ij,kl} \frac{\partial E_k}{\partial r_l}, \quad (3)$$

where $C_{ij,kl}$ is the quadrupole–quadrupole polarizability.

Equations (2) and (3) are implicit equations of \mathcal{P}_i and \mathcal{Q}_{ij} . A given molecule polarizes its neighbors and these neighbors in turn induce extra dipole and quadrupole. Since the effect is nonlinear, an iterative procedure is used to solve the equations.

A first order correction to the dipole moment of each molecule is induced by the total electric field (see Appendix) of the neighboring unpolarized molecules

$$\Delta \mathcal{P}_i^{(1)} = \alpha_{ij} E_j^{(0)} + \frac{1}{3} A_{i,jk} \frac{\partial E_j^{(0)}}{\partial r_k} + \frac{1}{2} \beta_{ijk} E_j^{(0)} E_k^{(0)}, \quad (4)$$

and also a first-order correction to the quadrupole moment is induced

$$\Delta \mathcal{Q}_{ij}^{(1)} = A_{k,ij} E_k^{(0)} + C_{ij,kl} \frac{\partial E_k^{(0)}}{\partial r_l}. \quad (5)$$

The first-order induced dipole moments create an additional electric field $\mathbf{E}_d^{(1)}$ and the induced quadrupole moments generate, $\mathbf{E}_q^{(1)}$. The total first order correction field, $\mathbf{E}^{(1)} = \mathbf{E}_d^{(1)} + \mathbf{E}_q^{(1)}$ induces a second-order correction to the dipole moments of

$$\Delta \mathcal{P}_i^{(2)} = \alpha_{ij} (E_j^{(1)}) + \frac{1}{3} A_{i,jk} \frac{\partial E_j^{(1)}}{\partial r_k} + \frac{1}{2} \beta_{ijk} E_j^{(1)} E_k^{(1)}, \quad (6)$$

and a second-order correction to the quadrupole moments of

$$\Delta \mathcal{Q}_{ij}^{(2)} = A_{k,ij} E_k^{(1)} + C_{ij,kl} \frac{\partial E_k^{(1)}}{\partial r_l}. \quad (7)$$

The new induced multipoles in turn, create an additional electric field $\mathbf{E}^{(2)}$. This procedure was continued until the magnitude of the n th induced dipole

$$\Delta \mathcal{P}_i^{(n)} = \alpha_{ij} E_j^{(n-1)} + \frac{1}{3} A_{i,jk} \frac{\partial E_j^{(n-1)}}{\partial r_k} + \frac{1}{2} \beta_{ijk} E_j^{(n-1)} E_k^{(n-1)}, \quad (8)$$

and quadrupole moments

$$\Delta \mathcal{Q}_{ij}^{(n)} = A_{k,ij} E_k^{(n-1)} + C_{ij,kl} \frac{\partial E_k^{(n-1)}}{\partial r_l}, \quad (9)$$

became smaller than a given tolerance, 10^{-6} D and 10^{-6} D Å, respectively. Thus, self consistency was obtained up to this level of accuracy. An ensemble average was obtained by averaging the induced dipole on each of the 2,592 water molecules in the simulation cell. Due to the proton disorder, both the magnitude and the direction of the local electric field at a molecule varies, as discussed below.

Ab initio calculated multipole moments for a water molecule up to hexadecapole as well as experimental values for the dipole¹ and quadrupole moments¹³ are given in Table I. The second column corresponds to second-order Moller–Plesset (MP2) level calculations with the aug-cc-pVQZ basis set¹⁴ at the minimum energy configuration (O–H distance 0.9590 Å and H–O–H angle 104.28 degrees).

The column labeled GC in Table I correspond to the values of Glaeser and Coulson¹⁵ which were used in the induction model calculation of Coulson and Eisenberg.⁶ The

TABLE I. Multipole moments of a water molecule used in the self-consistent induction calculations and comparison with values used in previous calculations. The moments are computed using the definitions given in the Appendix. The origin of the coordinate system is located at the center of mass of the molecule. The experimental values for the quadrupole moment are from Ref. 13. GC denote the multipole moments of Glaeser and Coulson (Ref. 15) (which were used by Coulson and Eisenberg in their calculations).

		Exp	MP2	GC	
Dipole	\mathcal{P}_3	-1.855	-1.86	-1.76	$\times 10^{-18}$ e.s.u. cm
Quadrupole	Q_{33}	-0.13	-0.1328	0.142	$\times 10^{-26}$ e.s.u. cm ²
	Q_{11}	2.63	2.6135	0.961	
	Q_{22}	-2.50	-2.4807	-1.103	
Octopole	O_{333}		1.3565	0.470	$\times 10^{-34}$ e.s.u. cm ³
	O_{113}		-2.3288	-0.851	
	O_{223}		0.9723	0.381	
hexadecapole	\mathcal{H}_{3333}		-1.3637		$\times 10^{-42}$ e.s.u. cm ⁴
	\mathcal{H}_{1133}		1.6324		
	\mathcal{H}_{2233}		-0.2687		
	\mathcal{H}_{1111}		-0.3575		
	\mathcal{H}_{1122}		-1.2749		
	\mathcal{H}_{2222}		1.5436		

GC multipoles were originally reported with respect to the oxygen atom, but in order to make the comparison with the other multipole values easier, we have translated them to a coordinate system with origin at the center of mass (see the Appendix). The GC multipole moments were taken from a calculation by McWeeny and Ohno¹⁶ using a very limited basis set, consisting of just seven atomic orbitals: An oxygen core orbital, two lone pair orbitals, two hydrogen orbitals, and two bond orbitals. At the time Coulson and Eisenberg did their calculations, experimentally measured values were not available.

It is evident from Table I that the results of these early *ab initio* calculations are in poor agreement with the experimentally measured values especially for the quadrupole moment. The numerical values of the multipoles used as input in the induction model calculations are, of course, very important in determining the resulting induced dipole moments, as discussed in Sec. IV.

Our induction model calculations made use of the experimentally measured dipole and quadrupole moments. For the octopole and hexadecapole moments we used the values computed at the MP2/aug-cc-pVQZ level of theory, listed in Table I. The agreement of the dipole and quadrupole moments at the MP2/aug-cc-pVQZ level of theory with the experimental ones justifies the use of the higher moments (octopole and hexadecapole) computed at this level of theory. In addition to these, the induction calculations made use of the experimentally measured molecular dipole polarizability, α_{ij} .¹⁷ Results of previous *ab initio* calculations were used for the values of the dipole-quadrupole polarizability, $A_{i,jk}$,¹⁸ the quadrupole-quadrupole polarizability, $C_{ij,kl}$,¹⁸ and the first hyperpolarizability, β_{ijk} .¹⁹ The values that we used for the polarizabilities are given in Table II.

III. RESULTS

The average molecular dipole moment obtained in the self-consistent induction calculation is shown in Fig. 1 as a

TABLE II. Values of the polarizabilities used in the self-consistent induction calculations. All quantities are in atomic units ($[\alpha_{ij}] = a_0^3$, $[\beta_{ijk}] = a_0^6/e a_0$ and $[A_{i,jk}] = a_0^4$ and $[C_{ij,kl}] = a_0^5$). The coordinate reference frame of the molecule was defined as: \hat{e}_1 along the bisector of the molecule, axis \hat{e}_2 perpendicular to \hat{e}_1 and on the plane of the molecule, and axis $\hat{e}_3 = \hat{e}_1 \times \hat{e}_2$.

α_{11}	10.311 ± 0.088
α_{22}	9.549 ± 0.088
α_{33}	9.907 ± 0.02
$\alpha_{\text{isotropic}}$	9.922
β_{111}	5.4715
β_{122}	0.5445
β_{133}	10.029
$A_{1,11}$	-1.694
$A_{1,22}$	5.943
$A_{1,33}$	-4.249
$A_{2,12}$	-10.323
$A_{3,13}$	3.096
$C_{11,11}$	11.930
$C_{11,22}$	-6.829
$C_{11,33}$	-5.101
$C_{12,12}$	7.862
$C_{13,13}$	13.142
$C_{22,22}$	11.685
$C_{22,33}$	-4.856
$C_{23,23}$	7.045
$C_{33,33}$	9.957

function of the cutoff radius, r_{cut} . Clearly, the calculation has converged at $r_{\text{cut}} = 7 \text{ \AA}$. The converged value of the dipole moment is 3.09 D. The error bars shown in Fig. 1 correspond to the variation among the molecules in the sample. Due to the proton disorder, no two molecules are in exactly the same environment. For a 20 Å cutoff, the standard deviation in the dipole moment is 0.03 D.

Figure 2 shows the magnitude and direction of the various components of the electric field at a typical molecule. The length of an arrow represents the magnitude of the elec-

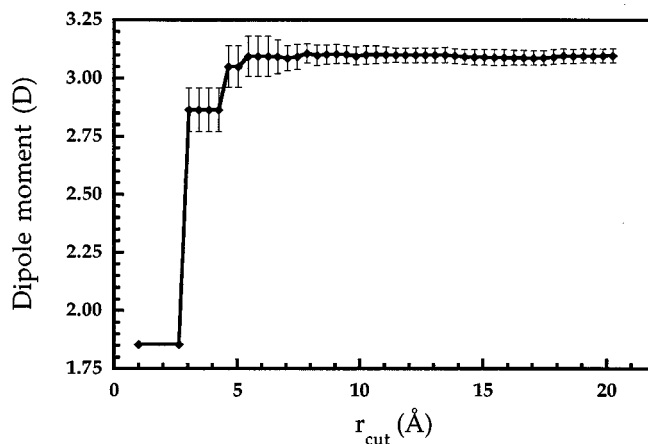


FIG. 1. Convergence of the calculated molecular dipole moment as a function of the cutoff distance used in summing up the electric potential due to the neighbors. The error bars correspond to the fluctuations due to the different environments seen by the various molecules in the proton disordered ice I_h . The results show that it is sufficient to include only neighbors that are closer than 7 Å when evaluating the electric field at a given molecule.

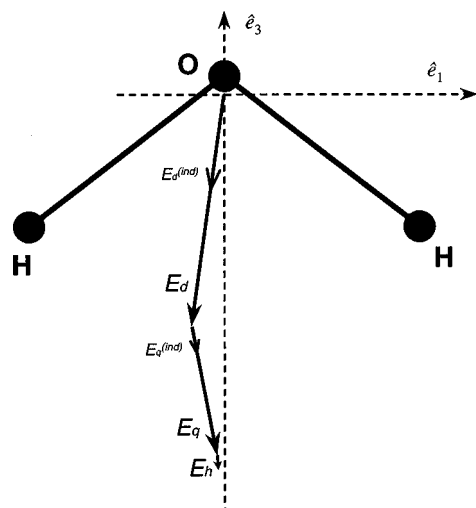


FIG. 2. Various components of the local electric field at a typical molecule showing the magnitude and direction of the field with respect to the bisector of the molecule. The length of each arrow represents the magnitude of the electric field components averaged over all molecules in the ice sample. The dipole field vector is labeled E_d , the quadrupole field E_q , and the field due to higher multipoles E_h (octopolar plus hexadecapolar field). The angle between the arrows and the bisector of the molecule is the average of the polar angle of the electric field component when choosing the bisector as polar axis. The smaller superimposed arrows $E_d^{(ind)}$ and $E_q^{(ind)}$ are the electric fields due to the induced parts of the dipoles and quadrupoles. Even though the direction of the individual electric field components deviates somewhat from the direction of the bisector, the total field (and, therefore, the induced dipole moment) are to a good approximation pointing along the bisector.

tric field component averaged over the molecules in the sample: The induced quadrupole moment produces 20% of the quadrupole field while the induced dipole moment accounts for 40% of the total field generated by the dipoles. The effect of the self-consistency in the calculation is significant: The dipole after the first iteration is only 2.70 D and it increases by 14% in subsequent iterations. The dipolar and quadrupolar fields increase by 15% and 6%, respectively, in the second and subsequent iterations.

A large value for the induced quadrupole moment was obtained. The principal axes of the total quadrupole moment are almost the same as those of the free molecule. The angle between the original axes and the new principal axes is always less than 0.5° , with an average value of 0.15° . The average eigenvalues of the quadrupole moment are $(Q_{11}, Q_{22}, Q_{33}) = (3.29, -3.14, -0.15) \times 10^{-26}$ e.s.u. cm^2 , an increase of 25%, 26%, and 14% over the value for an isolated molecule.

In order to quantify the effect of the dipole-quadrupole polarizability $A_{i,jk}$, the quadrupole-quadrupole polarizability

TABLE III. Calculated values for the molecular dipole moment of water in ice I_h at the various levels of the multipolar expansion and increasing levels of response to multipolar fields within the self-consistent induction scheme. All the dipole moments are expressed in Debye.

Expansion	α	α, A	α, A, C	α, A, C, β
\mathcal{P}, \mathcal{Q}	2.94	2.89	2.98	2.97
$\mathcal{P}, \mathcal{Q}, \mathcal{O}$	3.00	2.94	3.04	3.04
$\mathcal{P}, \mathcal{Q}, \mathcal{O}, \mathcal{H}$	3.05	2.99	3.10	3.09

ity $C_{ij,kl}$, the first hyperpolarizability β_{ijk} , and the hexadecapole field, we calculated the induced dipole moment ignoring these contributions one at a time. We find that the dipole-quadrupole and the quadrupole-quadrupole polarizabilities have a significant and opposite effect. If $A_{i,jk}$ and $C_{ij,kl}$ are not taken into account, i.e., when there are no induced quadrupole moments, the total dipole moment is predicted to be 3.05 D, which is 0.04 D smaller than the result of the full calculation. After including $A_{i,jk}$ the total dipole is 2.99 D and after including the quadrupole-quadrupole polarizability, $C_{ij,kl}$, the result is 3.09 D. Ignoring the nonlinear effects introduced by β_{ijk} we obtain a dipole moment of 3.10 D, showing that the effect of this correction is very small. Suppressing the hexadecapole moments had a small but significant effect. The total dipole moment predicted with a multipole expansion up to octopole is 3.04 D.

The above results are summarized in Table III for the various levels of molecular multipolar expansions ($\mathcal{P}, \mathcal{Q}, \mathcal{O}, \mathcal{H}$) and increasing levels of response to multipolar fields.

The anisotropy of the dipole polarizability was tested by using only the isotropic component of the polarizability. Averaging the induced dipole moment over all possible directions of the electric field gives the average of the three eigenvalues of the anisotropic tensor. The anisotropy of the polarizability is quite important. The dipole moment induced with the isotropic part is 3.16 D, larger by 0.07 D than the dipole induced with the full anisotropic polarizability.

In the calculations of Coulson and Eisenberg, discussed below, the simplifying approximation is made that the dipolar component of the total electric field at each molecule points in the direction of the bisector of the molecule. We tested this assumption in our calculations and the results are shown in Fig. 2. For each molecule in the sample, we defined the polar axis as the bisector of the molecule and evaluated the polar angle of the various electric field vectors. The average values of the polar angles are indicated by the arrows in Fig. 2. The electric field due to the dipoles alone is as much as 16° off the bisector axis (with an average polar angle of 7°). However, the total electric field at a molecule lies very nearly along the direction of the bisector, with a maximum polar angle of 1.7° and a mean value of 0.7° . Even though the direction of the individual components deviates from the direction of the bisector of the molecule, the total field, and the induced dipole moment are to a good approximation pointing along the bisector.

IV. THE METHOD OF COULSON AND EISENBERG

We now review the induction calculation carried out by Coulson and Eisenberg. As noted earlier, the results of their calculation are still very widely referred to but are frequently misrepresented.

Coulson and Eisenberg included a molecular dipole moment, quadrupole moment, and octopole moment as well as an isotropic dipole polarizability in their model. The total electric field at a molecule was divided into two parts: The field produced by the dipoles, \mathbf{E}_d , and the field produced by the higher order multipoles (quadrupoles and octopoles), \mathbf{E}_h . The total field at a given molecule due to neighbors within a 9.6 Å radius induced a dipole moment given by

$$\Delta \mathcal{P}^{(1)} = \alpha \mathbf{E} = \alpha (\mathbf{E}_d + \mathbf{E}_h), \quad (10)$$

where α is the isotropic molecular polarizability. A value of $\alpha = 1.59 \text{ \AA}^3$ was used in their calculations (induced quadrupoles or hyperpolarizabilities were not taken into account). An interesting simplifying assumption was made by Coulson and Eisenberg that enabled them to analytically sum up the iterative induction calculation to infinite order. The total dipole field \mathbf{E}_d at a molecule was assumed to be parallel to the unpolarized dipole moment ($\mathcal{P}^{(0)}$) of the molecule

$$\mathbf{E}_d = c \mathcal{P}^{(0)}, \quad (11)$$

c being a constant of proportionality. The first-order correction to the dipole then becomes

$$\Delta \mathcal{P}^{(1)} = \alpha (c \mathcal{P}^{(0)} + \mathbf{E}_h) = \alpha c \left(\mathcal{P}^{(0)} + \frac{\mathbf{E}_h}{c} \right). \quad (12)$$

Assuming that all the molecules in the bulk are equivalent, the same dipole moment is induced in all the molecules. The induced dipole moment in all the surrounding molecules then generates an extra dipole field $\mathbf{E}_d^{(1)}$ proportional to the first-order correction of the dipole moment

$$\mathbf{E}_d^{(1)} = c \Delta \mathcal{P}^{(1)}, \quad (13)$$

that induces a second-order correction to the dipole moment

$$\Delta \mathcal{P}^{(2)} = \alpha \mathbf{E}_d^{(1)} = (\alpha c)^2 \left(\mathcal{P}^{(0)} + \frac{\mathbf{E}_h}{c} \right). \quad (14)$$

The n th order correction to the dipole moment is

$$\Delta \mathcal{P}^{(n)} = \alpha \mathbf{E}_d^{(n-1)} = \alpha c \Delta \mathcal{P}^{(n-1)} = (\alpha c)^n \left(\mathcal{P}^{(0)} + \frac{\mathbf{E}_h}{c} \right), \quad (15)$$

and the total induced dipole moment is

$$\Delta \mathcal{P} = \sum_{n=1}^{\infty} \Delta \mathcal{P}^{(n)} = \left(\mathcal{P}^{(0)} + \frac{\mathbf{E}_h}{c} \right) \sum_{n=1}^{\infty} (\alpha c)^n, \quad (16)$$

$$\Delta \mathcal{P} = \frac{\alpha c}{1 - \alpha c} \left(\mathcal{P}^{(0)} + \frac{\mathbf{E}_h}{c} \right) = \frac{\alpha}{1 - \alpha c} (\mathbf{E}_d + \mathbf{E}_h), \quad (17)$$

$$\Delta \mathcal{P} = \frac{|\mathcal{P}^{(0)}| \alpha \mathbf{E}}{|\mathcal{P}^{(0)}| - \alpha |\mathbf{E}_d|}. \quad (18)$$

Therefore, by making a simplifying assumption about the direction of the induced dipole, Coulson and Eisenberg were able to calculate analytically the total induced dipole moment in a bulk molecule in terms of the multipoles of the isolated molecule and the dipole polarizability.

After averaging over the possible orientations of each molecule in a configuration of molecules satisfying the ice rules, Coulson and Eisenberg predicted a total dipole moment of 2.6 D for the water molecule in ice I_h . This number represents an average over different arrangements of protons, with some orientations resulting in molecular dipole moments as low as 1.9 D and others as high as 3.1 D. This result is significantly smaller than the value 2.96 D that we obtain using a more elaborate scheme and the question naturally arises what the important difference is.

We repeated our numerical induction calculation using the same input parameters as Coulson and Eisenberg (multi-

poles and molecular polarizability) and neglecting dipole-quadrupole polarizability, hyperpolarizability, and the hexadecapole moment of the molecule. Using a system size similar to theirs that includes 121 molecules and averaging over 50 configurations, we obtained a net dipole moment of 2.65 ± 0.08 D in good agreement with the result of Coulson and Eisenberg. This shows that the simplifying assumption made in their calculation, namely that the total dipole field is parallel to the permanent dipole moment of the molecule, Eq. (11), is in fact good enough. This is also evident from the analysis of our results, presented in Sec. III, which show that although the field does not lie exactly along the bisector of the molecule, the deviations are effectively small.

We then repeated the calculation, now including the experimentally determined dipole and quadrupole moments and dipole polarizability, and the MP2 calculated octopole and hexadecapole moments as given in Tables I and II. The resulting net dipole moment was 3.04 ± 0.04 D. This shows that the reason for the low value obtained by Coulson and Eisenberg is a result of the numerical values of the multipole moments they used as input in their model.

V. CONCLUSIONS

We have used a self-consistent induction model to study the electric field in ice and found that the best estimate for the dipole moment of a water molecule in ice I_h is 3.09 D. This value represents a 67% increase over the dipole moment of an isolated water molecule. Our estimate is significantly higher than the one reported earlier by Coulson and Eisenberg who also used a similar but more approximate induction model. The main reason for the difference between our results and the earlier estimates lies in the numerical values for the quadrupole moment of the isolated molecule. Coulson and Eisenberg relied on the best estimates of multipole moments from first principle calculations at the time which included a very small basis set. We have used the experimental values for the dipole and quadrupole moments (the latter obtained after Coulson and Eisenberg carried out their calculation) and the results of accurate *ab initio* calculations for the higher octopole and hexadecapole moments. When the same set of multipoles are used as input, the method of Coulson and Eisenberg gave very similar results as our more detailed model, indicating that the approximations used by Coulson and Eisenberg to simplify the induction calculations are quite valid.

The multipolar expansion for the electric field in the ice crystal was carried out to what seems to be reasonably good convergence. As an indicator of the effect of various terms in the expansion, we have focused on the net dipole and quadrupole moment per molecule obtained in the self-consistent calculation. The inclusion of dipole-quadrupole and quadrupole-quadrupole polarizability has small but significant effect on the dipoles; it increases the dipole moment of the water molecules by 0.04 D. The polarizability has a more dramatic effect on the quadrupoles increasing the magnitude by 14% to 25% depending on the component. It is important to go beyond the quadrupole and include also the (fixed) octopole moment of the molecules. This increases the net

dipole moment by 0.07 D. The hexadecapole moment, however, has a small effect on the dipole moment (increasing it by 0.05 D).

A remarkable feature in the self-consistent calculations is how little effect distant neighbors have on the field at a given molecule. It is sufficient to include the electric field from neighbors within a 7 Å radius in order to get the converged, large system value of the induced dipole moment to 99% (see Fig. 1) as was already made by Coulson and Eisenberg. This is, of course, not true when the molecules are modeled by point charges, as is most frequently done in simulation studies of water and water solutions.

ACKNOWLEDGMENTS

We wish to thank Geert-Jan Kroes for the computer code to generate configurations of ice I_h with proton disorder, and Professor A. J. Stone for helpful suggestions. Part of this work was performed under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC06-76RLO 1830 with Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory. Computer resources were provided by the Division of Chemical Sciences and by the Scientific Computing Staff, Office of Energy Research, at the National Energy Research Supercomputer Center (Berkeley, CA).

APPENDIX: DEFINITIONS OF MULTIPOLE MOMENTS

Several different definitions of the multipole moments of a charge density are in use in the literature. The difference among them are signs, constants of proportionality and some being linear combinations of the others. In this appendix we give the definitions of the multipoles in Cartesian coordinates used in Table I.

The total charge density of the molecule $\rho(\mathbf{r})$ is

$$\rho(\mathbf{r}) = \rho_e(\mathbf{r}) + \sum_i q_i \delta(\mathbf{r} - \mathbf{r}^{(i)}), \tag{A1}$$

where ρ_e is the electronic charge density, q_i is the ionic charge of the i th ion (one proton charge for each of the hydrogen atoms and eight for the oxygen), $\mathbf{r}^{(i)}$ is the position of the i th nucleus, $\delta(\mathbf{r})$ is the Dirac delta function, and the sum is over all the nuclear charges. The molecular multipole moments are obtained by integrating over the charge density of the molecule. The electric dipole moment is defined as

$$\mathcal{P}_i = \int d^3r \rho(\mathbf{r}) r_i. \tag{A2}$$

The quadrupole moment is defined as

$$\mathcal{Q}_{ij} = \frac{1}{2} \int d^3r \rho(\mathbf{r}) (3r_i r_j - r^2 \delta_{ij}), \tag{A3}$$

where δ_{ij} is the Kroenecker delta. We chose to measure \mathbf{r} from the center of mass of the molecule. The octopole moments are defined as

$$\mathcal{O}_{ijk} = \frac{1}{3!} \int d^3r \rho(\mathbf{r}) [15r_i r_j r_k - 3r^2 (r_i \delta_{jk} + r_j \delta_{ki} + r_k \delta_{ij})], \tag{A4}$$

and the components of the hexadecapole as

$$\begin{aligned} \mathcal{H}_{ijkl} = & \frac{1}{4!} \int d^3r \rho(\mathbf{r}) [105r_i r_j r_k r_l - 15r^2 (r_i r_j \delta_{kl} \\ & + r_i r_k \delta_{jl} + r_i r_l \delta_{jk} + r_j r_k \delta_{il} + r_j r_l \delta_{ik} + r_k r_l \delta_{ij}) \\ & + 3r^4 (\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk})]. \end{aligned} \tag{A5}$$

The electric field can be obtained from the gradient of Eq. (24).

$$U = \frac{\mathcal{P}_i r_i}{r^3} + \frac{\mathcal{Q}_{ij} r_i r_j}{r^5} + \frac{\mathcal{O}_{ijk} r_i r_j r_k}{r^7} + \frac{\mathcal{H}_{ijkl} r_i r_j r_k r_l}{r^9}. \tag{A6}$$

With these definitions, the electrostatic potential generated by a molecule is

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_d(\mathbf{r}) + \mathbf{E}_q(\mathbf{r}) + \mathbf{E}_o(\mathbf{r}) + \mathbf{E}_h(\mathbf{r}), \tag{A7}$$

where the dipole field is

$$E_d(\mathbf{r})_n = 3 \frac{\mathcal{P}_i r_i}{r^5} r_n - \frac{\mathcal{P}_n}{r^3}, \tag{A8}$$

the quadrupole field is

$$E_q(\mathbf{r})_n = 5 \frac{\mathcal{Q}_{ij} r_i r_j}{r^7} r_n - 2 \frac{\mathcal{Q}_n r_n}{r^5}, \tag{A9}$$

the octopole field is

$$E_o(\mathbf{r})_n = 7 \frac{\mathcal{O}_{ijk} r_i r_j r_k}{r^9} r_n - 3 \frac{\mathcal{O}_n r_n}{r^7}, \tag{A10}$$

and the hexadecapole field is

$$E_h(\mathbf{r})_n = 9 \frac{\mathcal{H}_{ijkl} r_i r_j r_k r_l}{r^{11}} r_n - 4 \frac{\mathcal{H}_n r_n}{r^9}. \tag{A11}$$

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