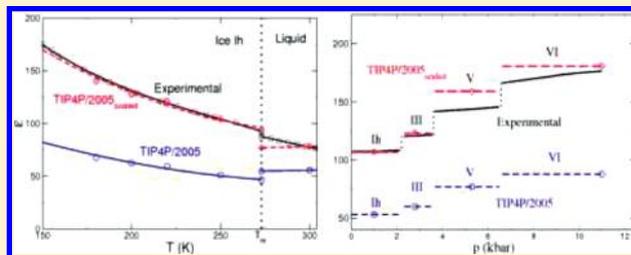


# Dielectric Constant of Ices and Water: A Lesson about Water Interactions

J. L. Aragoes, L. G. MacDowell, and C. Vega\*

Departamento de Química Física, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, 28040, Spain

**ABSTRACT:** In this paper, the dielectric constant has been evaluated for ices Ih, III, V, VI, and VII for several water models using two different methodologies. Using Monte Carlo simulations, with special moves to sample proton-disordered configurations, the dielectric constant has been rigorously evaluated. We also used an approximate route in which proton-disordered configurations satisfying the Bernal–Fowler rules were generated following the algorithm proposed by Buch et al. (Buch, V.; Sandler, P.; Sadlej, J. *J. Phys. Chem. B* **1998**, *102*, 8641), and the dielectric constant was estimated assuming that all configurations have the same statistical weight (as Pauling did when estimating the residual entropy of ice). The predictions of the Pauling model for the dielectric constant differ in general from those obtained rigorously by computer simulations because proton-disordered configurations satisfying the Bernal–Fowler rules can differ in their energies by as much as 0.10–0.30 NkT (at 243 K). These differences in energy significantly affect properties that vary from one configuration to another such as polarization, leading to different values of the dielectric constant. The Pauling predictions differ from the simulation results, especially for SPC/E and TIP5P, but yield reasonable results for TIP4P-like models. We suggest that for three charge models the polarization factor ( $G$ ) in condensed phases depends on the ratio of the dipole to the quadrupole moment. The SPC/E, TIP5P, TIP4P, TIP4P/2005, TIP4P/ice models of water are unable to describe simultaneously both the experimental dielectric constants of water and ice Ih. Nonpolarizable models cannot describe the dielectric constants of the different condensed phases of water because their dipole moments (about 2.3 D) are much smaller than those estimated from first principles (of the order of 3 D). However, the predictions of TIP4P models provide an overall qualitatively correct description of the dielectric constant of the condensed phases of water, when the dipole moment of the model is scaled to the estimated value obtained from first principle calculations. Such scaling fails completely for SPC/E, TIP3P, and TIP5P as these models predict a completely different dielectric constant for ice Ih and water at the melting point, in complete disagreement with experiment. The dielectric constant of ices, as the phase diagram predictions, seems to contain interesting information about the orientational dependence of water interactions.



## INTRODUCTION

Finding simple water models reproducing as many properties as possible constitutes an important subject of research.<sup>1–3</sup> Within the Born–Oppenheimer approximation one could obtain condensed matter properties of water exactly by combining path integral simulations (to incorporate quantum effects on the nuclei distribution) with electronic calculations that would provide the energy of a certain configuration of the atoms of the system. Due to computer limitations, it is not possible right now to solve accurately the electronic Schrodinger equation for a system containing about 300 molecules (a typical number required to obtain condensed matter properties), for about 32 slices of imaginary time<sup>4</sup> (a typical number required to describe properly nuclear quantum effects in water), for about 100 000 time steps (a typical number required to obtain good accuracy in water simulations). Approximations are needed to obtain results within a reasonable time. Approximations can be done either in the description of the nuclear motion (classical vs quantum description) or in the description of the electronic energy (described by an empirical potential or from an approximate treatment of the Schrodinger equation). Thus, four approaches

to water simulations are possible. The first one is using path integral simulations combined with electronic structure calculations. The second one is combining Newton equations for the motion the nuclei with electronic structure calculations. The third possibility is to use an analytical expression for the water interactions combined with path integral simulations. The fourth possibility is to use an analytical water potential along with classical simulations. The analytical water potentials are typically obtained by proposing an empirical expression and determining its parameters to reproduce either experimental properties (empirical potentials) or ab initio results (theoretical based potentials).

In the past few years it has become clear that the potential parameters of empirical water potentials should be chosen to reproduce the complete room pressure isobar of water (from 250 to 450 K).<sup>5</sup> In fact, we have recently proposed a water model

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TIP4P/2005<sup>6</sup> that accurately reproduces the room pressure isobar (and the same is true for the TIP4P-Ew<sup>7</sup> potential). Notice that TIP5P<sup>8</sup> reproduces the location of the maximum in density of water, but it fails in reproducing the complete room pressure isobar. The same is true when an empirical potential is used in path integral simulations (TIP4PQ/2005<sup>9</sup> and the model q-TIP4P/F of Habershon et al.<sup>10</sup> both reproduce the room pressure isobar). The TIP4P/2005 is a simple rigid nonpolarizable model consisting of a Lennard–Jones (LJ) center and three charges. It is somewhat surprising to see how many properties of water can be described correctly by such a simple model.<sup>5,11,12</sup> In particular, the model describes quite well the room pressure isobar (by design), the critical temperature and density,<sup>11</sup> the diffusion coefficient,<sup>6,12</sup> the isothermal compressibility,<sup>12</sup> the coefficient of thermal expansion, the surface tension,<sup>13</sup> the viscosity,<sup>14</sup> the density of ices,<sup>6</sup> the structure of water and ice Ih,<sup>6,15</sup> the relative stability between ices,<sup>16–18</sup> and the equation of state up to pressures of about 30 000 bar.<sup>6</sup> The model also provides a qualitative description of the phase diagram of water<sup>6,19,20</sup> and predicts the melting point of water with an error of about 23 K.<sup>6</sup>

The TIP4P/2005 is a simplification of the true interaction between water molecules and consequently must fail to describe some properties. This is certainly the case, and the model fails in describing vapor properties (second virial coefficient, vapor pressure, and critical pressure). This failure can be understood by considering that the dipole moment of the molecule in the vapor phase is of 1.85 D, whereas the model has a dipole moment of about 2.3 D. The higher dipole moment of the model with respect to that of the isolated molecule is an effective way of accounting for the higher dipole moment of water in the liquid phase with respect to the vapor phase. The lack of polarizability prevents the model for describing vapor and liquid properties simultaneously. Also we have recently shown that to describe the heat capacity of water and ice nuclear quantum effect should be included.<sup>15,21</sup>

Overall, TIP4P/2005 describes quite well the properties of water, and when it fails (vapor properties, heat capacities) there is a clear reason (lack of polarizability, classical treatment of nuclei motion) for that. TIP4P/2005 represents an improvement over other more traditional water models such as TIP3P,<sup>22</sup> TIP5P,<sup>8</sup> or SPC/E<sup>23</sup> in the description of practically all water properties. There is, however, one important exception: the dielectric constant in the liquid phase at room temperature and pressure. For this property the value predicted by TIP4P/2005 was 60 (thus improving the prediction of the original TIP4P with a value of 54) but clearly inferior to the predictions of the models TIP3P, TIP5P, and SPC/E which are 85, 82, and 65, respectively<sup>5</sup> (the experimental value at room temperature and pressure is 78). Motivated by this failure of the model, we have decided to investigate in more detail the predictions of the dielectric constant of the model for the solid phases of water (ices). We want to know if the model also fails for other phases besides water, and if the models that are successful in predicting the dielectric constant of water (TIP3P, TIP5P, SPC/E) are also successful or not in the solid phases.

Ices can be divided into two families. Those in which the protons are ordered (ices II, XI, IX, VIII, XIII, XIV) and those in which protons are disordered (Ih, Ic, III, V, VI, VII, IV, XII). From a microscopic point of view the dielectric constant is related to the fluctuations of the total polarization of the system,  $M$ . It can be obtained easily (although using long runs<sup>24</sup>) for liquid water and for ices in which the protons are ordered. For

ices with ordered protons, the molecules only undergo small vibrations around the equilibrium configuration and for this reason the fluctuations of the total dipole moment are small yielding small dielectric constants (typically less than 5). Thus, the behavior of the dielectric constant of proton-ordered ices is not particularly exciting. However, the situation is completely different for ices with proton disorder. For proton-disordered ices, many configurations exist that have similar energies, separated by large energy barriers (of the order of two hydrogen bonds). These configurations may present quite different values of the total polarization ( $M$ ), so the dielectric constants for these ices are usually large (between 90 and 170). Transitions between different disordered configurations are rare events. Chan et al.<sup>25</sup> have estimated the relaxation time of ice Ih at 250 K to be of about 168  $\mu$ s, and Johari and Whalley<sup>26</sup> suggested that it is of the order of several years at 100 K. For this reason special moves should be introduced in the simulation of proton-disordered ices to obtain dielectric constants. In a series of important papers, Rick and co-workers have shown that SPC/E, TIP4P, and TIP5P underestimate the dielectric constant of ice Ih by a factor of 2 or 3.<sup>27–29</sup> These results were confirmed by Wang et al.<sup>30</sup> Recently two of us have found that TIP4P/2005 and TIP4P/Ice also underestimate the dielectric constant of ice Ih.<sup>31</sup> Is there any reason for this failure of all water models studied?

This paper has three goals. The first is to show that the technique proposed by Rick and Haymet<sup>29</sup> can be applied to determine the dielectric constant of other ices (besides ice Ih and V<sup>31</sup>). We shall evaluate the dielectric constant for ices III, V, VI, and VII for the TIP4P/2005 and TIP4P/Ice models. Second we will compare the dielectric constants obtained for these ices to the experimental results obtained by Whalley<sup>26,32–36</sup> to test if the failure in describing the dielectric constant of ice Ih also extends to the other ices. The third goal is to analyze if the Pauling model can be used to estimate the dielectric constant of ices. The Pauling model of ice contains two key ideas.<sup>37</sup> The first one is that the configurations that contribute most to ice properties are those satisfying the Bernal–Fowler rules.<sup>38</sup> The second is to assume that all configurations that satisfy the Bernal–Fowler rules have the same statistical weight. In the Bernal–Fowler rules, one assumes that ices are formed by water molecules (i.e., two H form a covalent bond to each O) and that each water molecule is forming four hydrogen bonds with the nearest water molecules of the solid, in two of them acting as donor and in the other two acting as acceptor. The model was successful in estimating the residual entropy of ice<sup>39,40</sup> found experimentally, and it is natural to ask if the model can be used to describe the dielectric constant of proton-disordered ices (Ih, III, V, VI, VII).

In short, the main conclusions of this paper are that the Pauling model can not be used to estimate the dielectric constant of ices (although it yields reasonable predictions for TIP4P models), and that the methodology proposed by Rick and Haymet can be used successfully to determine the dielectric constant of water models in the solid phases (ices). Finally, no rigid nonpolarizable model of water is able to describe the dielectric constant of ices. However, the results obtained with the TIP4P/2005 provide a simple explanation for this failure. It is simply due to the fact that the model has a dipole moment of about 2.3 D, whereas in condensed phase the dipole moment is closer to 3 D.<sup>41–45</sup> By rescaling the dipole moment it will be shown that the results are in reasonable agreement for all the condensed phases of water.

## THEORY AND SIMULATION DETAILS

For solids the dielectric constant is a tensor. For a rigid non-polarizable model the elements  $\varepsilon_{\alpha\beta}$  of this tensor can be calculated in computer simulations (when using Ewald sums and conducting periodical boundary conditions) from the expression:<sup>31,46–51</sup>

$$\varepsilon_{\alpha,\beta} = \delta_{\alpha,\beta} + \frac{4\pi}{kTV} [\langle M_{\alpha}M_{\beta} \rangle - \langle M_{\alpha} \rangle \langle M_{\beta} \rangle] \quad (1)$$

where  $\alpha, \beta = x, y, z$  (i.e., a set or orthogonal laboratory frame axes),  $\delta_{\alpha,\beta}$  is a Kronecker delta,  $V$  is the volume of the simulation box, and  $M_{\alpha}$  is the value of the component  $\alpha$  of the total dipole moment of the sample (in the absence of an electric field since the previous formula holds within the linear response framework) and the bracket holds for ensemble average. It should be pointed out that for a polarizable model (or in the case of the experimental results) the first term on the right-hand side (i.e., that with the Kronecker delta) should be multiplied by the infinite frequency value of the tensor component (i.e.,  $\varepsilon_{\infty,\alpha\beta}$ ). This is typically a small number (i.e., for liquid water its value is 1.8, being only slightly larger for ice Ih). For non-ferroelectric materials (i.e., water and all the ices considered in this paper) the average value of the component  $\alpha$  of the polarization of the sample is zero (i.e.,  $\langle M_{\alpha} \rangle = 0$ ) so that the elements of the dielectric tensor can be written simply as:

$$\varepsilon_{\alpha,\beta} = \delta_{\alpha,\beta} + \frac{4\pi}{kTV} \langle M_{\alpha}M_{\beta} \rangle \quad (2)$$

Like any other tensor, the values of the components  $\alpha$  and  $\beta$  depend on the choice of the laboratory reference frame (i.e., the location of the  $X, Y,$  and  $Z$  axes with respect to the unit cell vectors of the solid). In general, components with  $\alpha$  different from  $\beta$  will not be zero. However, there is a choice for the laboratory frame (with respect to the unit cell vectors) that converts the tensor into diagonal form.<sup>52</sup> The three values along the diagonal will be then the three principal dielectric constants, and they could be compared to the experimental values. For crystals of cubic (Ic, VII), tetragonal (III, VI), and orthorhombic symmetry the dielectric tensor becomes diagonal when the laboratory frame axes  $X, Y, Z$  are located along the  $\mathbf{a}, \mathbf{b}, \mathbf{c}$  axis of the unit cell. For crystals of hexagonal symmetry (Ih) the dielectric tensor will be diagonal when  $X, Z$  are chosen along the  $\mathbf{a}$  and  $\mathbf{c}$  unit cell vectors respectively, and  $Y$  is chosen in the direction perpendicular to  $\mathbf{a}$ .<sup>52</sup> For cubic crystals and fluid phases, the three principal dielectric constants will be identical, and for tetragonal and hexagonal crystals the first two principal dielectric constants will be identical but different from the third one. In the case of ice V (monoclinic), it is more convenient to choose the  $X, Y$  axes along the  $\mathbf{a}$  and  $\mathbf{b}$  unit cell vectors respectively, and  $Z$  in the direction perpendicular to the  $\mathbf{a}, \mathbf{b}$  plane. With this choice the dielectric tensor is not diagonal but could be compared easily to experimental results. In fact, with this choice the  $xy(yx)yz(zy)$  are zero but the  $xz(zx)$  component is nonzero. Thus, when reporting dielectric constants of solids one should report the three principal dielectric constants. In the case of a monoclinic crystal (ice V) it is more convenient to report four components ( $xx, yy, zz,$  and  $xz$  for the laboratory frame described above). In many cases experimental values of the three principal dielectric constants are not available. Quite often the properties of a powder formed by many small crystals with random orientation with respect to the electric field are measured. In this case the

experimental reported dielectric constant, denoted as  $\varepsilon$ , is simply the average of the three principal dielectric constants, which is related to the trace of the dielectric tensor:

$$\varepsilon = \frac{1}{3} (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}) \quad (3)$$

The dielectric tensor changes when changing the laboratory frame as  $X^{-1}\varepsilon_{\alpha,\beta}X$ , and this transformation leaves the trace invariant. For this reason, the value of  $\varepsilon$  as given by the trace of the dielectric tensor is invariant to the choice of the laboratory frame. Therefore, for the models used in this work one simply obtains:

$$\varepsilon = 1 + \frac{4\pi}{3kTV} \langle M_x^2 + M_y^2 + M_z^2 \rangle \quad (4)$$

and this is true regardless of the choice for the laboratory frame. For a polarizable model or in the case of the experiment the first term on the right-hand side should be replaced by the infinite frequency dielectric constant  $\varepsilon_{\infty}$ , which does not differ much from one. The previous equation can be rewritten (after dividing and multiplying by  $N$ , the number of molecules) as:

$$\varepsilon = 1 + \frac{4\pi\rho}{3kT} \left[ \frac{\langle \mathbf{M}^2 \rangle}{N} \right] \quad (5)$$

where  $\rho$  is the number density. Experimental measurements of the dielectric constant at a certain  $T$  and density allow to determine the experimental value of  $[\langle \mathbf{M}^2 \rangle / N]$ . Let us now assume that one can identify a characteristic value of the dipole moment of each molecule in the condensed phase. For a nonpolarizable model that would just be the dipole moment of the molecule. Then the previous equation can be rewritten as:

$$\varepsilon = 1 + \frac{4\pi\rho}{3kT} \mu^2 \left[ \frac{\langle \mathbf{M}^2 \rangle}{N\mu^2} \right] \quad (6)$$

Let us define the polarization factor  $G$  as the term in brackets in the previous equation so that:

$$G = \left[ \frac{\langle \mathbf{M}^2 \rangle}{N\mu^2} \right] \quad (7)$$

Then the dielectric constant is given by:

$$\varepsilon = 1 + \frac{4\pi\rho}{3kT} \mu^2 G \quad (8)$$

Thus, for a nonpolarizable model (in which all molecules have the same dipole moment) the value of  $G$  is well-defined. Besides, the expression for  $G$  can be further simplified by noting that:

$$\mathbf{M} = \sum_{i=1}^{i=N} \boldsymbol{\mu}_i \quad (9)$$

and then  $G$  is simply given by:

$$G = \left\langle \left( \sum_{i=1}^{i=N} \mathbf{u}_i \right)^2 \right\rangle / N \quad (10)$$

where  $\mathbf{u}_i$  is a unit vector along the direction of the dipole moment of the molecule.

If simulations are performed using electronic structure calculations then the value of  $[\langle \mathbf{M}^2 \rangle / N]$  is uniquely defined but this is

not the case for  $G$ . One could still use eq 7 to define  $G$  by using the average of the squared dipole moment in the denominator of the expression. However, there are several “arbitrary” criteria to distribute the electronic charge density between the molecules that will lead to different values of the average dipole moment  $\mu$  and consequently to slightly different values of  $G$ .

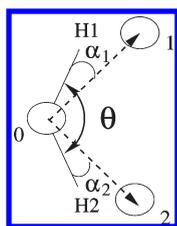
In this work we shall perform computer simulations to determine the dielectric constants (or more generally the dielectric tensor) for several water models and for several ices. In particular we shall consider the proton-disordered ices Ih (at 1 bar), Ic (at 1 bar), III (at 2800 bar), V (at 5300 bar), VI (at 11000 bar), and VII (at 70000 bar), and the clathrate structures sI and sII (at 1000 bar). In most of the cases we shall use the TIP4P/2005 model, although in a few cases we have determined the dielectric constant for the models SPC/E, TIP4P/Ice, and TIP5P. To sample over proton-disordered configurations we shall use the efficient algorithm proposed by Rick and Haymet,<sup>29</sup> which can be regarded as the extension to nonlattice ice models of the algorithm proposed by Rahman and Stillinger.<sup>53</sup> We refer the reader to the original papers, and to our previous work,<sup>31</sup> for a more comprehensive description of the algorithm and here we shall provide only the main details.

Monte Carlo simulations were carried out in the  $NpT$  ensemble.<sup>51</sup> Box deformations were considered using the Parrinello–Rahman method.<sup>54</sup> Coulombic interactions were calculated using the Ewald summation technique.<sup>55</sup> Conducting boundary conditions were employed in all simulations. For fluid phases one can use either Ewald sums or the reaction field technique<sup>49,50,56,57</sup> to obtain the dielectric constant, but for solid phases Ewald sums seem to be the natural choice. Both dispersive and screened-Coulombic interactions up to the cutoff distance were calculated by means of an efficient link cell list.<sup>58</sup> The LJ part of the potential and the real space contribution of the Coulombic interactions was truncated at 8.5 Å for all models (except for ices Ic and V with cutoff 6.5 Å).<sup>51</sup> Usual long-range corrections to the LJ part of the potential were added.

It is well-known that a standard Metropolis algorithm incorporating only displacement and rotation attempts cannot properly sample ice proton disorder. These movements will only sample small lattice vibrations, but are unable to modify the assumed hydrogen bond arrangements. An algorithm for exploring hydrogen bond arrangements was proposed by Rahman and Stillinger for a simple tetrahedral lattice model.<sup>53</sup> This algorithm was also exploited later on to study the order/disorder transition of ice on a lattice<sup>59,60</sup> and was extended recently for off-lattice water models.<sup>29</sup> The method requires first to search for a closed loop of hydrogen bonds. Molecules belonging to the loop have one proton that is bond donor inside the loop (inner bond) and another that is not (outer bond). The attempted move consists in rotating each of the molecules successively about the outer bond by 120° until a full hydrogen bond arrangement with opposite sense has been established along the loop. The attempted move is accepted or rejected according to the usual Monte Carlo criteria. Whereas this algorithm works well for tetrahedral lattices, the acceptance may become too low in off lattice systems. Rick and Haymet have argued that a greater acceptance is achieved by rotating the molecule such that the new bond lies on the plane formed by the outer hydrogen, the oxygen atom of the rotating molecule and the next oxygen on the loop (see Figure 2 of our previous paper<sup>31</sup>). The topology of loops in a crystal was studied by Rahman and Stillinger.<sup>53</sup> They found that rings could be classified into three classes: (i) true closed loops with six

molecules, (ii) true closed loops with more than six molecules, and (iii) percolating loops, which span one full linear dimension of the simulation box and are closed by virtue of the toroidal boundary conditions. By performing a Markov chain<sup>51</sup> over these three type of loops rotations, all the hydrogen bond arrangements may be sampled in principle. Closed loops moves of types i and ii change very little the total dipole moment of the simulation box (in fact, for a perfect Ih or Ic lattice the change is exactly zero<sup>59</sup>). These moves provoke only small fluctuations in the total dipole moment within the Markov chain. However, percolating loops of type iii provide dramatic changes in the total dipole moment of the simulation box. For this reason percolating loops are absolutely required to properly sample the fluctuations of the total dipole moment of the sample and to obtain reliable values of the dielectric constant. The probability acceptance of loop rotations (of type ii or iii) decreases as the size of the loop increases. The size of the system should be chosen so that there is a small but reasonable probability of accepting moves of type iii that really contribute to the evaluation of the dipole moment fluctuations. For this reason the algorithm of Rick and Haymet is more efficient for systems of moderate size. In this work, the number of molecules chosen for the simulations was Ih (360), Ic (216), III (324), V (224), VI (360), VII (432), sI (368), and sII (136). For each system 8–12 independent simulations of one million cycles each was done (after an initial equilibration run of about 40 000 cycles). A cycle is defined as  $N$  trial moves ( $N$  being the number of molecules of the system). MC translation, rotation, and loop moves were performed in the ratio 45:45:10. The error was estimated from the standard deviation between the results of the eight independent runs.

Finally, we shall use the Pauling model to estimate the dielectric constant of proton-disordered ices. In the Pauling model one assumes that the statistical significantly configurations satisfy the Bernal–Fowler rules and all have the same probability. Therefore, to evaluate the dielectric constant of ices using the Pauling model all that is needed is an algorithm that generates configurations satisfying Bernal–Fowler without any energetic bias.<sup>61,62</sup> We used the algorithm proposed by Buch et al.<sup>61</sup> to generate these configurations. The algorithm of Buch et al. has been used by many authors in the last years to generate proton-disordered configurations in the study of ices. The algorithm of Buch et al.<sup>61</sup> is of topological type (i.e., no energy or temperature enters in the algorithm). We typically generated 50 000 independent configurations satisfying the Bernal–Fowler rules. Let us just explain briefly some technical aspect of the calculations. Crystallographic positions (as determined from experimental data) were used to determine the position of the oxygens within the unit cell (the shape of the simulation box was obtained from an  $NpT$  run of the ice at the considered  $T$  and  $p$ ). First, it should be noted that the  $O_1-O-O_2$  angle between a central oxygen O and two of its nearest neighbors  $O_1$  and  $O_2$  is tetrahedral for ices Ih, Ic, and VII, but it can adopt values significantly different from the tetrahedral value for ices III, V, and VI. An excellent compilation of the  $O-O-O$  angles present in ices III, V, and VI can be found on the web page of Chaplin.<sup>63</sup> Besides the bond angle of the rigid model (i.e., 105.4 for TIP4P and TIP5P models, and 109.5 for SPC/E) will in general be different to the  $O-O-O$  angle. Therefore, a criterion to determine the precise orientation of the water molecule within the ice should be provided. In this work the orientation of the water molecule was selected in such a way that the H–O–H bisector was coincident with the  $O_1-O-O_2$  bisector and that the H–O–H is on the same plane



**Figure 1.** Figure 1 Sketch to illustrate the criterion used to determine the orientation of the water molecule within the ice for the Pauling model. The three oxygen atoms and the two hydrogens are on the same plane. The  $O_1-O_0-O_2$  bisector and the  $H_1-O-H_2$  bisector are coincident. According to that,  $\alpha_1 = \alpha_2$ . Notice that the direction of the bisector is the same regardless of the bond angle of the water model  $\theta$ .

**Table 1. Values of  $G$  for Several Solid Phases of Water Obtained from 50000 Proton Disordered Configurations Satisfying the Bernal–Fowler Ice Rules (Pauling Model)<sup>a</sup>**

phase	Pauling model	TIP4P/2005	SPC/E	TIP5P
Ih	3.02 (4)	2.54 (5)	1.74 (10)	1.40 (8)
Ic	3.01 (4)	2.54 (5)		
III	2.49 (3)	2.28 (37)	1.24 (41)	
V	2.50 (4)	2.70 (43)		
VI	2.89 (3)	2.85 (26)	2.17 (88)	
VII	3.01 (5)	2.94 (10)		

<sup>a</sup>The values of  $G$  at 243 K obtained from computer simulations of TIP4P/2005 (this work) are also presented. For SPC/E and TIP5P, the values of  $G$  for ice Ih were taken from the simulation results of Rick et al.<sup>28</sup> For SPC/E, the values of  $G$  for ices III and VI as obtained in the computer simulations of this work at 243 K are also presented.

as the  $O_1-O-O_2$  (as illustrated in Figure 1). Although there is no a unique criterion to locate the water molecule when forming hydrogen bonds to two nearest neighbors, the criterion chosen here appears to be a reasonable one. An additional advantage of this criterion is that the direction of the dipole moment of each water molecule is the same regardless of the water model considered. Therefore, the value of  $G$  obtained with this criterion does not depend on the selected water model (of course the dielectric constant will be different since the water models differ in their dipole moment). Notice that the Pauling algorithm can be used to determine anisotropies of the dielectric constant. One can define the tensor:

$$G_{\alpha,\beta} = \langle M_{\alpha}M_{\beta} \rangle / (N\mu^2) \quad (11)$$

so that the value of  $G$  is just the average of the trace of the  $G_{\alpha,\beta}$  tensor. The dielectric tensor can be obtained easily from the  $G$  tensor using the expression:

$$\varepsilon_{\alpha,\beta} = \delta_{\alpha,\beta} + \frac{4\pi\rho}{kT} \mu^2 G_{\alpha,\beta} \quad (12)$$

## RESULTS

**The Pauling Model.** The values of the  $G$  factor as obtained in this work are presented in Table 1. Obviously for the Pauling model the values of  $G$  do not depend on temperature (all configurations have the same probability regardless of the temperature), although the dielectric constant still depends on temperature, as can be concluded from the inspection of eq 8.  $G$  does not depend on the water model, and the reason was

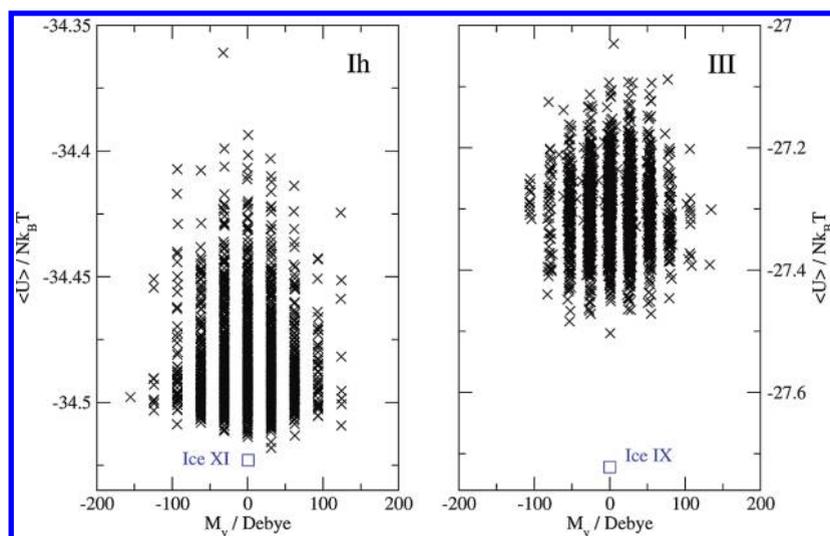
described in the previous section (there is a very small dependence on the model through the dependence of the unit cell parameters with the potential model). Ices for which the 4 nearest neighbor oxygens of each oxygen atom form a perfect tetrahedral arrangement (Ih, Ic, VII) present a  $G$  factor of 3 (within the statistical uncertainty). This is in agreement with all previous estimates for ices Ih and Ic.<sup>64–68</sup> When the nearest neighbors form a distorted tetrahedron then the  $G$  factor is smaller than 3, being 2.5 for ice III, 2.5 for ice V, and of 2.9 for ice VI. The values of  $G$  reported here are in relative good agreement with those estimated by Johari,<sup>69–73</sup> which were obtained approximately for the Pauling model counting all possible configurations between a central molecule and the second or third nearest neighbors.

We have also determined the value of the dielectric constant from NpT simulations including loop moves as described in the previous section. The value of  $G$  can then be obtained using the expression:

$$G = \frac{(\varepsilon - 1)3kT}{(4\pi\rho\mu^2)} \quad (13)$$

We found that  $G$  depends on  $T$  (increasing slightly as  $T$  increases) but the changes in the temperature range 200–273K are rather small.<sup>31,74</sup> Therefore, we shall report the value of  $G$  at 243 K. The values of  $G$  obtained from NpT simulations for the TIP4P/2005 at the temperature of 243 K are presented in Table 1. Let us start by discussing the results for ice Ih. For ice Ih the Pauling model yields a value of 3, whereas the simulations results are  $G = 2.54$  for TIP4P/2005, 1.74 for SPC/E, and 1.40 for TIP5P. The first conclusion to be drawn is that for ice Ih, the Pauling model is unable to predict the value of  $G$  obtained in the simulations. Furthermore the value of  $G$  found in the simulations changes dramatically from one water potential to another. This is puzzling since all these water models present a dipole moment close to 2.3 D. Thus,  $G$  is quite sensitive to the charge distribution used to describe Coulombic interactions in the water model. However, in a previous work<sup>31</sup> we found that the value of  $G$  for ice Ih obtained with the TIP4P, TIP4P/2005, and TIP4P/Ice models was practically the same. A possible explanation is that the value of  $G$  depends not on the value of the dipole moment, but rather on the value of the ratio of the dipole to quadrupole moment ( $\mu/Q_T$ ). The suggestion that the quadrupole moment should be used to describe the dielectric constant of water models was first proposed by Rick.<sup>27</sup> For the three TIP4P like models the ratio of the dipole to the quadrupole moment is almost identical and very close to  $1.0 \text{ \AA}^{-1}$ . For the SPC/E, the ratio of the dipole to quadrupole moment is of about  $1.155 \text{ \AA}^{-1}$ , and for the TIP5P this ratio is of about  $1.46 \text{ \AA}^{-1}$ .<sup>75</sup> This suggestion is consistent with the work of Steinhäuser et al.,<sup>24</sup> where it was clearly shown that the value of  $G$  for liquid water was practically identical for SPC and SPC/E (two models with different dipole moment but with the same value for the ratio  $\mu/Q$ ) and quite different for SPC and TIP3P (which present almost the same dipole moment but a different value of the ratio of the dipole to quadrupole moment).

In previous work we have found that the phase diagram of water is quite sensitive to the ratio of the dipole to the quadrupole moment.<sup>75–77</sup> When this ratio is high (as in SPC/E, TIP3P, and TIP5P) one obtains phase diagrams that are not qualitatively correct (with ice II being the stable phase at room pressure and with ices III and V disappearing from the phase diagram).



**Figure 2.** Average configuration internal energy (as obtained from MD runs) vs component  $y$  of the total dipole moment ( $M_y$ ) for ice Ih (left) and ice III (right). The results of 2000 different proton-disordered configurations satisfying the Bernal–Fowler rules are presented. No loop moves were used so that the plotted energies are the average energy of a certain proton-disordered configuration. Results for ice Ih were obtained at 200 K, 1 bar. Results for ice III were obtained at 243 K, 2800 bar. The results were obtained using the TIP4P/2005 model. Open squares represents the average configurational energies of the proton-ordered phases of the ices Ih and III, ices XI and IX, respectively. The proton-ordered phase XI corresponds to the antiferroelectric one,<sup>102</sup> which is the ground state of this model.

Models with the negative charge located at the H–O–H bisector (as TIP4P or TIP4P/2005) have a dipole/quadrupole ratio of about one and yield qualitatively correct phase diagram predictions. Thus, we conclude that both phase diagram predictions, and the values of  $G$ , are quite sensitive to the ratio of dipolar to quadrupolar forces. It seems that the different orientational dependence of the potential interactions at long distances between different water models dramatically affects these two properties. In fact the value of  $G$  can be rewritten as:

$$G = \left\langle \sum_{i=1}^{i=N} \sum_{j=1}^{j=N} (\mathbf{u}_i \cdot \mathbf{u}_j) \right\rangle / N = 1 + \left\langle \sum_{j=2}^{j=N} \mathbf{u}_1 \cdot \mathbf{u}_j \right\rangle \quad (14)$$

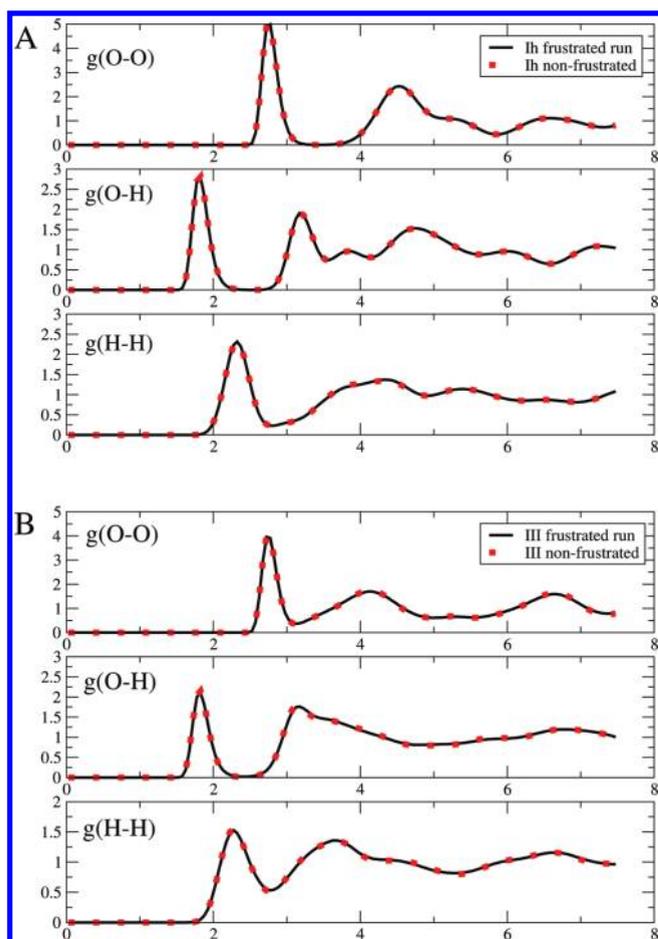
and thus it is now more clear why  $G$  contains information about the orientational dependence of the water interactions.

Let us now focus on the prediction of the Pauling model for the rest of the ices. It is clear that in the particular case of the TIP4P/2005 the Pauling model predictions for ices III, V, VI, and VII agree reasonably well with those obtained from the simulations of the model. The largest difference between the Pauling model and the results of TIP4P/2005 are for ice Ih, and the difference is about 15%. In summary, in general the Pauling model can not be used to estimate the value of  $G$  for water rigid nonpolarizable models. However, it can predict the value of  $G$  for TIP4P models with an error below 15%. Interestingly the Pauling model seems to work better for TIP4P geometries than for SPC/E or TIPSP charge distributions.

What is the experimental value of  $G$ ?  $G$  can not be obtained from experiments since the experimental value of the dipole moment in condensed phases can not be measured. By using DFT and classical molecular dynamics Car et al.<sup>45</sup> determined that the average value of the modulus of the dipole moment was 3.09 D for water and 3.32 D for ice Ih when using the MLWF criterion to distribute the electronic charge.<sup>78</sup> These values are in line with some other estimates.<sup>41–44</sup> Using the experimental

value of the dielectric constant of ice at 273 K, i.e., 95, one obtains  $G = 2.55$ , in rather good agreement with the value obtained here for the TIP4P models.

With the Pauling model one assumes that all configurations satisfying the Bernal–Fowler rules have the same statical weight. However, the idea that this assumption is not strictly true has been in the air since 1952.<sup>79–81</sup> To gain further understanding about the typical differences in energy between different proton-disordered configurations, we performed MD simulations for about 0.2 ns of 2000 different proton-disordered configurations obtained with the algorithm of by Buch et al.<sup>61</sup> The simulations were performed using Gromacs,<sup>82</sup> and Ewald sums (using PME to accelerate the calculations<sup>83</sup>), with a cutoff of 8.5 Å for both the LJ part of the potential and for the real part of the Ewald sum. We did not introduce Rick and Haymet Monte Carlo moves during the MD runs, so that in the MD simulations the molecules just vibrate around the equilibrium position without changing the proton configuration. The average potential energies obtained in the MD runs are presented in Figure 2 for ices Ih and III. The energies are shown as a function of the component  $y$  of the total dipole moment ( $M_y$ ). As it can be seen the energies of different proton-disordered configurations are quite similar but certainly not identical. The distribution of energies seems to be broader for ice III when compared to ices Ih. Differences in internal energies between different proton-disordered configurations are of about  $0.10nkT$  for ice Ih and of about  $0.30nkT$  for ice III. Obviously these differences in energy are important for those properties that change significantly from one proton-disordered configuration to another as for instance the polarization of the system thus being relevant to understand the value of the dielectric constant of the system. However these differences in energy are not so relevant for those properties that are rather similar in the different proton-disordered configurations (as for instance the radial distribution function). In fact in Figure 3 the radial distributions (O–O, H–H, and O–H) obtained from a  $NpT$  run of a single proton-disordered configuration is compared to that obtained



**Figure 3.** (A) Radial distribution functions (O–O, H–H, O–H) of ice Ih at 1 bar and 243 K as obtained from MC runs including loop moves (red symbols) and from simulations of a single proton-disordered configuration (black solid line). (B) Radial distribution functions (O–O, H–H, O–H) of ice III at 2800 bar and 243 K as obtained from MC runs including loop moves (red symbols) and from simulations of a single proton-disordered configuration (black solid line).  $x$  axis is the distance in Å.

from an  $NpT$  simulation including loop moves (thus sampling the proton disorder). As it can be seen, they are quite similar proving that radial distribution functions of ices can be estimated reasonably well from just a proton-disordered configuration.

**The Dielectric Constant of Ice: Experiment versus Water Models.** In Table 2 the dielectric constant for ice Ih obtained in this work and the value of  $G$  are compared to that obtained by other authors. There are very few calculations of the dielectric constant of ices for common water models. For ice Ih there are only the results of Rick and Haymet<sup>27–29</sup> and those of Wang et al.<sup>30</sup> For other ices, the only available results are those of Rick for argon and hydrogen sII clathrate hydrates,<sup>84</sup> and those of MacDowell and Vega for ice V.<sup>31</sup> The results of this work are in agreement with those of other authors (i.e. they agree within their respective error bars), and that gives us confidence about the methodology used in this work.

In Figure 4 the probability distribution of  $p(M_y)$  is shown. The peaks appears for multiples of the total dipole moment of a percolating loop (see the discussion of Rick where it is seen that jumps in  $M$  occurs in multiples of the percolating loop<sup>27</sup>). As can be seen, configurations with zero dipole moment have the highest probability.

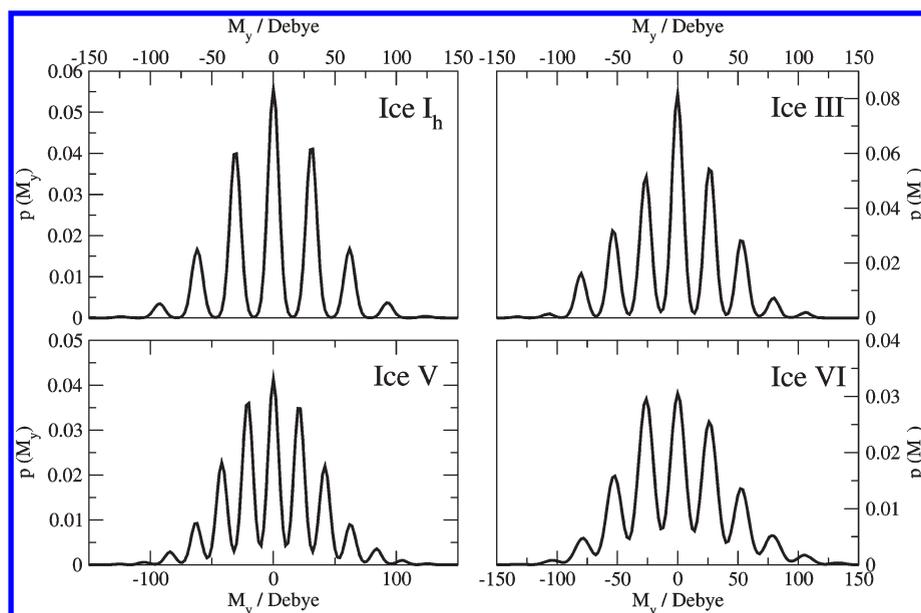
**Table 2.** Dielectric Constants at Room Pressure of Ice Ih As Obtained in This Work and in Previous Work<sup>a</sup>

model	author	$T$ (K)	$\rho$ (g cm <sup>-3</sup> )	$\epsilon$	$G$
TIP4P	Rick, Haymet (2003)	240	0.920	48 (1)	2.54 (5)
TIP4P	MacDowell, Vega (2010)	240	0.940	47 (1)	2.44
TIP4P	Wang (2008)	240	0.920	51 (1)	2.7
TIP4P/2005	MacDowell, Vega (2010)	240	0.922	53	2.5
TIP4P/2005	This work	243	0.922	53 (2)	2.54 (5)
TIP4P/Ice	MacDowell, Vega (2010)	240	0.910	57	2.6
TIP5P	Rick (2005)	240	0.976	30 (3)	1.34
TIP5P	This work	243	0.979	31	1.40
Experiment	Whalley (1981)	240		107	
SPC/E	MacDowell, Vega (2010)	200	0.950	49	1.80
SPC/E	Rick, Haymet (2003)	200	0.920	50	1.90
experiment	Whalley (1981)	200		130	

<sup>a</sup> Notice that for TIP4P and SPC/E Wang and Rick used the experimental value of the density of ice at room temperature and pressure (0.92 g cm<sup>-3</sup>) to obtain  $G$ , whereas we used the density of the model at room pressure and at the considered  $T$ .

In Table 3 the dielectric constants of ice Ih for TIP4P/2005, SPC/E and TIP5P at 243 K and for liquid water at 298 K are presented, along with the experimental results. It is obvious that all models fail in describing the dielectric constant of ice Ih, with the deviation from experiment increasing in the order TIP4P/2005, SPC/E, TIP5P. For water the situation is quite different. The model TIP5P overestimates the dielectric constant by about 10%. The model SPC/E underestimates the dielectric constant by 10%. The model TIP4P/2005 underestimates the dielectric constant by about 25%. In the fluid phase the values of  $G$  are larger than those of ice Ih. Large values of  $G$  for the fluid phase are not so unusual for water models. For instance Steinhauser et al.<sup>24</sup> reported a value of  $G$  at room  $T$  and  $p$  higher than five for the TIP3P model.

In Figure 5 the experimental dielectric constants of ice Ih and water are presented. Interestingly the experimental curve of the dielectric constants of ice Ih seems to be a continuation of that obtained for liquid water. This suggests the existence of strong tetrahedral ordering in liquid water at the melting point. In fact, these models predict highly tetrahedral ordering of liquid water near the melting point.<sup>85</sup> However, for TIP5P the dielectric constant drops by a factor of 3 when going from the liquid to the solid phase, in clear disagreement with the experimental results. The results for the SPC/E model are presented in Figure 6. Again, for the SPC/E the dielectric constant drops by a factor of 2 when going from the liquid phase to ice Ih. In Figure 5 and Figure 6 the results obtained using the TIP4P/2005 model have been included. For this model the dielectric constants of ice Ih and water at the melting point are quite similar (although in this case the value found for the solid phase is somewhat smaller). Obviously all water models (SPC/E, TIP5P, TIP4P/2005) are only approximations to the true interaction between water molecules. What is the origin of the enormous difference between the trends in the experimental values of the dielectric constant and those found for the models? In Table 3, we have included in the last column the value of the dipole moment that will bring the predictions of the model in agreement with the experimental values. We are implicitly assuming that the value of  $G$  is not affected by the increase of charge required to increase the magnitude of the dipole while keeping the charge distribution.



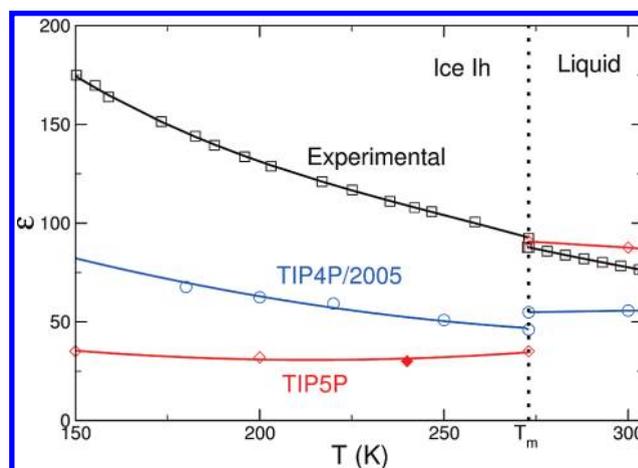
**Figure 4.** Probability distribution of the component  $y$  of the total dipole moment ( $M_y$ ) for ices Ih, III, V, and VI obtained from MC runs of the TIP4P/2005 at 243 K including loop moves. For each ice, the considered pressure is that reported in Table 4.

**Table 3. Dielectric Constants at Room Pressure for Water<sup>5,6,12</sup> at 298 K and for Ice Ih at 243 K for Several Water Models<sup>a</sup>**

model	phase	$T$ (K)	$\rho$ (g cm <sup>-3</sup> )	$\epsilon$	$G$	$\mu_{\text{effective}}$ (D)
TIP4P/2005	water	298	0.998	59	3.27	2.66
TIP4P/2005	lh	243	0.922	53	2.54	3.32
TIP5P	water	298	0.983	91	5.13	2.12
TIP5P	lh	243	0.979	31	1.40	4.31
SPC/E	water	298	0.998	70	3.68	2.49
SPC/E	lh	243	0.946	39	1.74	3.93
experiment	water	298	0.998	78.2		
experiment	lh	243	0.917	107		

<sup>a</sup>The effective dipole moments ( $\mu_{\text{effective}}$ ) needed to reproduce the experimental values (assuming that the value of  $G$  is constant) of the dielectric constant (78.4 for water at 298 K and 107.2 for ice Ih at 243 K) are also reported.

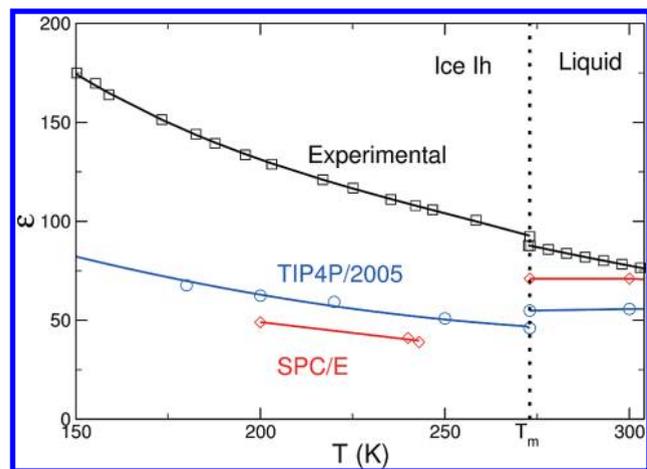
In a previous work Abascal and Vega have shown that for a certain water model the value of the ratio  $\mu/Q^{75,76}$  is not modified when increasing the magnitude of the charges without changing its location. If the hypotheses that  $G$  depends mainly on  $\mu/Q$  is true, then the value of  $G$  of a certain water model would not change significantly when increasing the magnitude of the charges while keeping the charge distribution. In fact the dipole moment increase from TIP4P to TIP4P/2005 to TIP4P/Ice without affecting the value of  $G$  (notice that for these three models the charge distribution is practically identical). We have further tested this assumption by evaluating the value of  $G$  for ice Ih (at 243 K and 1 bar) for a TIP4P like toy model, having the following parameters  $\mu = 3.32D$ ,  $q_H/e = 0.8014$ ,  $\sigma = 3.2123 \text{ \AA}$ ,  $\epsilon/k = 207.73K$  and  $d_{OM} = 0.1546 \text{ \AA}$  (this choice of parameters provides a reasonable prediction for the density of ice Ih).<sup>86</sup> We found that even for this TIP4P toy model (with a very high dipole moment) the value of  $G$  was 2.59, in good agreement with the value found for the TIP4P/Ice (2.53) and TIP4P/2005 (2.54)



**Figure 5.** Dielectric constant of ice Ih and water for TIP4P/2005 (circles and blue solid lines) and TIP5P (diamonds and black solid lines) compared to the experimental values (squares and black solid lines). The asterisk represents the dielectric constant of the TIP5P model at 240K calculated by Rick.<sup>27</sup>

models at the same thermodynamic conditions. Also for liquid water, Steinhauser et al.<sup>24</sup> found that the value of  $G$  for the SPC and SPC/E models<sup>24</sup> (two models differing in the dipole but having the same value for  $\mu/Q$ ) was practically identical. In fact we have also found that for ice Ih, the value of  $G$  was practically identical for SPC and SPC/E. Thus it seems reasonable to assume that the value of  $G$  is affected mostly by the way the charges are distributed but not by their magnitude.

The results of Table 3 are surprising. To bring the results of TIP5P in agreement with experiment, the dipole moment in the liquid phase should be 2.12 D and that of ice Ih should be 4.31 D. It is difficult to accept that the dipole moment multiplies by a factor of 2 when going from water to ice Ih. Also it is difficult to accept that the dipole moment of the molecule in the liquid phase is smaller than that obtained in a cluster of 6 water molecules.<sup>87</sup>



**Figure 6.** Dielectric constant of ice Ih and water for TIP4P/2005 (circles and blue solid lines) and SPC/E (diamonds and red solid lines) compared to the experimental values (squares and black solid lines).

Thus it is likely that the TIPSP model provides incorrect estimates of  $G$ , the reason being that it incorrectly predicts the orientational dependence of the water interactions. In fact Steinhauser nicely illustrated how the function  $G(r)$  (i.e., the value of  $G$  obtained including correlations between molecules up to a distance of  $r$ ) can be related to orientational correlation functions.<sup>24</sup> Atom–atom correlation functions are well described by TIPSP but these functions are just projections of the pair correlation function. The results for SPC/E are more reasonable, but still predicting a dipole moment in ice Ih about 40% higher than in the fluid phase. In the case of TIP4P/2005 it predicts that the dipole moment in the solid phase is about 20% higher than in water. Although there is no unique way of determining the molecular dipole moment from first principle calculations (nor experimentally) it seems reasonable to assume that first principle calculations can provide reasonable hints about the ratio of the dipole moment in ice Ih and in liquid water provided that the same criterium is used in both phases to distribute the electronic charge density among the molecules. Values of the dipole moment reported for ice Ih span the range 3.1–3.3 D. Values of the dipole moment for liquid water span the range 2.6–2.9 D. For instance, the AMOEBA model<sup>88</sup> (which yields a good value of the dielectric constant for liquid water) predicts 2.78 D for the liquid and 3.10 D for ice Ih. Using these numbers the ratio of dipole moment of the water molecule in ice Ih and in water should be of about 1.1–1.3. The TIPSP model would require a ratio of about 2, the SPC/E requires a ratio of about 1.6 and the TIP4P/2005 would require a ratio of about 1.25. These findings suggest that TIP4P/2005 provides reasonable values of  $G$ , and fails in describing the dielectric constant of liquid water because it has a dipole moment of 2.3 D (instead of a value of about 2.9 D that would be more appropriate for liquid water and a value of 3.3 D that would be more appropriate for ice Ih).

To reproduce the energy of water (including nuclear quantum effects effectively through the values of the parameters of the potential), point charge models require a dipole moment of 2.3 D. In fact, for about 30 years all rigid nonpolarizable models designed for water end up with a dipole moment around this value. However, when performing a first principle calculations, the energy of water is still reproduced (when including nuclear quantum effects) and the water molecule presents a much higher

dipole moment. Why is this so? When performing first principle calculations the interaction between water molecules is obtained by solving the Schrodinger equation, whereas it is obtained via an empirical expression when using simple water models. There is no reason to assume that single molecule properties should be identical, when different expressions are used to reproduce the vaporization enthalpy of water, which provides an idea of the strength of the intermolecular forces. Although it is gratifying to see how many properties can be reproduced by using a rigid nonpolarizable model, such simplistic description is not enough to describe either the properties of the gas phase (including small clusters) or the dielectric constants in condensed phases.

In summary, it is unlikely that a nonpolarizable model can describe the dielectric constant of the condensed phases of water (one can be successful for one phase, but one will fail dramatically for the other phases). However, at least the results of TIP4P/2005 allow a simple explanation and allow to rationalize the obtained results. The structure predictions are good (i.e., good  $G$  values), but the dipole moment used is wrong.

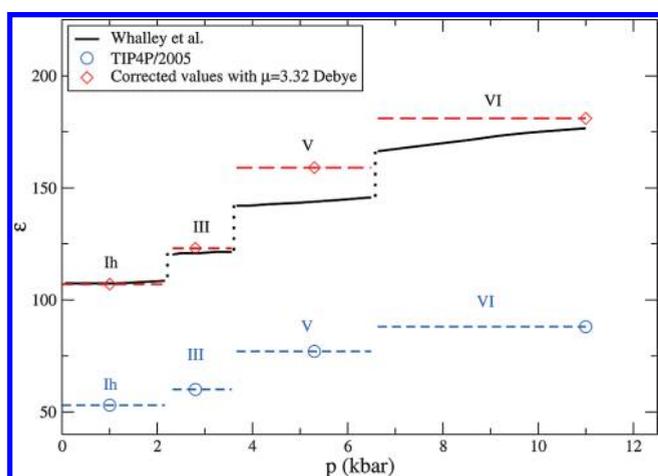
It may seem that we are taking our conclusions based only on the results for ice Ih and water too far. Whalley determined the dielectric constant also for ices III, V, VI, and VII.<sup>26,32–36</sup> Therefore, it is possible to test these ideas to other solid phases. In Table 4 the dielectric constant for ices Ih, III, V, and VI for TIP4P/2005 and TIP4P/Ice, and the sI and sII clathrate structures for TIP4P/Ice are presented. In agreement with our previous discussion, the value of  $G$  obtained for these two TIP4P like models are quite similar. Experimental results of the dielectric constant have also been included. The average value of the total dipole moment  $\langle M \rangle$  (in Debye) along the run should be zero if the run is sufficiently long. In most of the cases the average of the dipole moment is smaller than the dipole moment of one or two water molecules. The acceptance probability  $p$  of the Rick and Haymet moves is also reported. To obtain the number of successful Rick and Haymet moves one should multiply the length of the runs (8 000 000 cycles) by the number of successfully trial attempts to change the proton-disordered configuration ( $N \times (10/100) \times AC$ ) where  $AC$  is the probability of accepting the trial move which is typically of about 0.003. Thus, our runs were able to sample about 600 000 proton-disordered configurations. We found that this was sufficient to obtain reliable dielectric constants. More evidence of that is obtained from the plots of the probability distribution of  $p(M_y)$  presented in Figure 4. They are symmetric with respect to  $M_y = 0$ , which is an indirect indication that we are sampling with the same probability configurations with positive and negative values of the polarization along the  $y$  axis.

A comparison of the dielectric constants obtained from experiment and from the simulations of the TIP4P/2005 model is shown in Figure 7. As it can be seen the TIP4P/2005 does not describe the dielectric constant of ices III, V, and VI (this is not surprising since it already failed for ice Ih). We know from previous work that the density predictions of TIP4P/2005 for ices and hydrates are quite good.<sup>6,89</sup> Let us now assume that the model yields reasonable predictions for  $G$  and that to compare to experiment one should rescale the molecular dipole moment to a more reasonable value, that is, 3.32 D. For the time being we shall assume that the dipole moment of water in ices III, V, and VI is similar to that of ice Ih (although not fully correct this appears at least as a reasonable approximation<sup>90</sup>). By scaling the dielectric constant by this dipole moment, the corrected values of the dielectric constants for ices Ih, III, V, and VI are 107, 123, 159,

**Table 4. Dielectric Constants and G Factor for the Different Ice Phases for the TIP4P/2005, TIP4P/Ice, SPC/E, and TIP5P Models<sup>a</sup>**

model	phase	<i>p</i> (bar)	<i>T</i> (K)	$\rho$ (g cm <sup>-3</sup> )	<i>U</i> (kcal mol <sup>-1</sup> )	$\epsilon$	<i>G</i>	AC
TIP4P/2005	liquid	1	298	0.997	-11.43	59	3.27	
TIP4P/2005	Ih	1	243	0.922	-13.41	53 (2)	2.54	0.058
TIP4P/2005	Ic	1	243	0.924	-13.42	53 (2)	2.54	0.050
TIP4P/2005	III	2800	243	1.168	-13.33	60 (8)	2.28	0.013
TIP4P/2005	III	2800	220	1.175	-13.51	70 (6)	2.40	0.011
TIP4P/2005	V	5300	243	1.268	-13.13	77 (12)	2.70	0.005
TIP4P/2005	V	5300	180	1.288	-13.60	105 (15)	2.69	0.002
TIP4P/2005	VI	11000	243	1.374	-12.99	88 (8)	2.85	0.004
TIP4P/2005	VII	70000	243	1.721	-10.90	113 (4)	2.94	0.021
SPC/E	Ih	1	243	0.946	-13.02	39 (3)	1.74	0.018
SPC/E	III	2800	243	1.193	-13.11	35 (11)	1.24	0.002
SPC/E	VI	11000	243	1.396	-12.45	71 (35)	2.17	0.004
TIP4P/Ice	liquid	1	298	0.993	-11.25	65	3.20	
TIP4P/Ice	Ih	1	243	0.910	-14.84	57 (2)	2.53	0.056
TIP4P/Ice	III	2800	243	1.155	-14.78	75 (6)	2.60	0.012
TIP4P/Ice	V	5300	243	1.253	-14.56	76 (11)	2.45	0.004
TIP4P/Ice	VI	11000	243	1.355	-14.41	86 (17)	2.57	0.003
TIP4P/Ice	sI	1000	243	0.809	-14.58	45 (1)	2.46	0.073
TIP4P/Ice	sII	1000	243	0.798	-14.61	43 (1)	2.38	0.064
TIP5P	liquid	1	298	0.983	-9.69	91	5.15	
TIP5P	Ih	1	243	0.979	-12.41	31 (2)	1.40	0.010
TIP5P	Ih	1	200	0.993	-12.79	35 (4)	1.29	0.014
TIP5P (Rick data)	Ih	1	240	0.976		30 (3)	1.34	
experimental	liquid	1	298	0.996		78		
experimental	Ih	0	243	0.917		107		
experimental	III	2300	243	1.155		120		
experimental	V	5000	243	1.258		144		
experimental	VI	11000	243	1.350		176		
experimental	VII	23300	200	1.66		127		

<sup>a</sup> The experimental values are taken from ref 26 (ice Ih), ref 33 (ice III), ref 32 (ice V), ref 35 (ice VI), and ref 36 (ice VII). The column labeled as AC gives the probability of acceptance of a trial loop move.

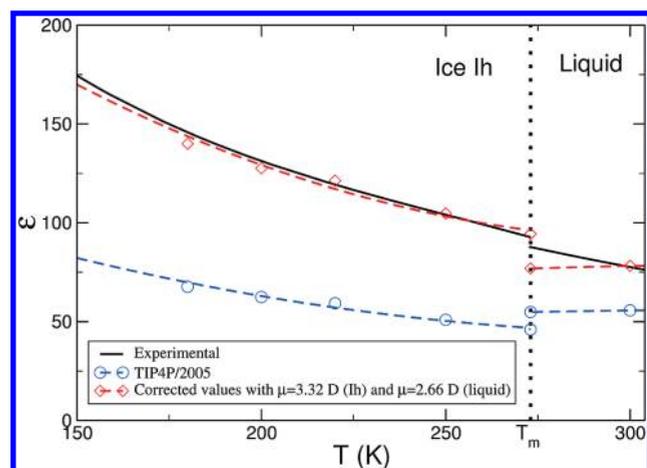


**Figure 7.** Dependence on pressure of the dielectric constant for ices Ih, III, V, and VI at 243 K. Dielectric constant obtained for the TIP4P/2005 model (circles and dashed line) compared to the experimental values (black solid lines). Corrected values of the dielectric constant for the TIP4P/2005 with a dipole moment of 3.32 D (diamonds and red dashed line).

181, to be compared with the experimental values of 107, 120, 144, 176. This scaling is also shown in Figure 7. To show that the scaling also provides a way to rationalize the dielectric constant at room pressure in Figure 8 we plot the values of the dielectric constant of water and ice Ih as a function of temperature at this pressure. The TIP4P/2005 does not match the experimental values of the dielectric constant. However, rescaling the dielectric constants of the TIP4P/2005 using a dipole moment of 3.32 D for ice Ih, and a dipole moment of 2.66 D for water, the predictions are in much better agreement with experiment. In summary, by using the values of *G* predicted by TIP4P/2005, and rescaling the value of the dipole moment to a value closer to the value obtained from first principle calculations it is possible for the first time to yield a qualitatively correct description of the dielectric constant of the condensed phases of water.

**Anisotropy of the Dielectric Constant.** The dielectric constant is a tensor and contains information about the dependence of the response function of the system (polarization, which is just the total dipole moment per volume unit) with respect to the electric field. In fact, one can write:

$$\mathbf{P} = \epsilon_0(\boldsymbol{\epsilon} - \mathbf{I})\mathbf{E} \quad (15)$$



**Figure 8.** Dependence on temperature of the dielectric constant of ice Ih and liquid water. Dielectric constant obtained for the TIP4P/2005 model (circles and dashed line) compared to the experimental values (black solid lines). Corrected values of the dielectric constant for the TIP4P/2005 with a dipole moment of 3.32 D for ice Ih and 2.66 D for the fluid phase (diamonds and red dashed line).

where  $\mathbf{P}$  and  $\mathbf{E}$  are vectors denoting the polarization of the system and the total electric field acting on the solid (formed by the external electric field and the internal electric field due to the polarization of the sample) and  $\boldsymbol{\epsilon}$  and  $\mathbf{I}$  are the dielectric constant tensor and the identity matrix, respectively. In this work we have computed the dielectric tensor for several solid phases. The laboratory frame chosen to compute the dielectric tensor was described in the methodology section. The dielectric tensor was computed along the Monte Carlo runs that included loop moves. We present the results for the TIP4P/2005 model in Table 5. For cubic ices (Ic, VII) the three principal values of the dielectric constant are identical (within the error bar), as it should be for a cubic crystal. For ice Ih, the hexagonal symmetry requires two identical components along the  $X$  and  $Y$  axes and allows a different one along the  $Z$  axis. It can be seen that the anisotropy of the dielectric constant of ice Ih (as given by the difference between the  $Z$  and the  $X$  and  $Y$  components) is, at least for the TIP4P/2005, very small. This is in agreement with the results of Rick for ice Ih using other water models. For the tetragonal crystals (III, VI) the two components  $X$  and  $Y$  should be identical and different from the component along the  $Z$  axis. For ice III this is clearly the case. The components along the  $X$  and  $Y$  are identical to within the error bar, and clearly different from the  $Z$  component. The anisotropy of the dielectric constant in ice III is large, and the dielectric constant along the  $Z$  axis is less than one-third of that along the  $X$  and  $Y$  axes. For ice VI, the anisotropy is similar to ice III. The components  $X$  and  $Y$  are equal (within the large error bar obtained in this case) and seems to be larger than the  $Z$  component. The results seem to indicate that the dielectric constant along the  $Z$  axis is about half of that found along the  $X$  and  $Y$  axis. For ice V (monoclinic) the  $XX$ ,  $YY$ , and  $ZZ$  can be different. Notice also that the choice of laboratory frame chosen in this work for ice V has a nonzero  $XZ$  component. For ice V it is found that the  $X$  and  $Y$  components are rather similar. However the value of the dielectric constant along the  $Z$  component is roughly half of the value along the  $Y$  component. From the results of this work it is suggested that the dielectric constant along the  $Z$  axis is significantly smaller (roughly speaking half) than the value of the dielectric constant along the  $X$  and  $Y$  axes. This has

**Table 5.** Dielectric Tensor of Proton Disorder Phases of Ice at 243 K As Obtained by Computer Simulations (Including Loop Moves to Sample Proton Disorder) and Using the TIP4P/2005 Model<sup>a</sup>

phase	$G$	$\epsilon$	$\epsilon_{xx}$	$\epsilon_{yy}$	$\epsilon_{zz}$	$\epsilon_{xz}$
TIP4P/2005						
Ih	2.54 (5)	53 (2)	53 (2)	53 (2)	53 (2)	0
Ic	2.54 (5)	53 (2)	53 (2)	53 (2)	53 (2)	0
III	2.28 (37)	60 (8)	80 (15)	84 (11)	15 (5)	0
V	2.70 (43)	77 (12)	81 (22)	97 (12)	53 (11)	-5 (7)
VI	2.85 (26)	88 (8)	102 (40)	115 (36)	41 (10)	0
VII	2.94 (10)	113 (4)	111 (7)	111 (9)	117 (5)	0
Pauling Model						
Ih	3.02 (4)	63	64	63	63	0
Ic	3.01 (4)	63	63	62	63	0
III	2.49 (3)	65	71	71	54	0
V	2.50 (4)	71	71	76	61	-7
VI	2.89 (3)	93	100	99	80	0
VII	3.01 (5)	126	124	128	125	0

<sup>a</sup> For each ice the pressure was the same as that presented in Table 4. For ices Ih, Ic, III, VI, and VII, the laboratory frame was chosen so that the dielectric tensor is diagonal, and for this reason the  $xz$  component is zero. For ice V the laboratory frame was chosen so that  $X$  and  $Y$  go along the direction of the vectors  $\mathbf{a}$  and  $\mathbf{b}$  of the unit cell, and  $Z$  was chosen along the direction perpendicular to the  $\mathbf{ab}$  plane. For this reason the dielectric tensor is not diagonal and there is a nonzero  $XZ$  component. We have also included the predictions of the Pauling model for TIP4P/2005. In the Pauling model, the dielectric tensor does not depend on temperature.

important consequences as it suggest that the energy of ices III, V, and VI in the presence of an external electric field would depend significantly on the orientation of the electric field with respect to the crystal (and that probably could affect significantly to the phase transitions<sup>91</sup>). In fact, the energy to polarize a crystal in an electric field  $\mathbf{E}$  is given by the expression:<sup>52</sup>

$$U_{\text{electric}} = \frac{\epsilon_0 V}{2} (\boldsymbol{\epsilon} \mathbf{E}) \cdot \mathbf{E} = \frac{\epsilon_0 V}{2} \sum_i \sum_j \epsilon_{ij} E_j E_i \quad (16)$$

It is clear that the energy of a crystal in an electric field will depend on the direction of the applied electric field with respect to the crystal. It would be quite interesting to determine experimentally the anisotropy of the dielectric constant of ices III, V, and VI. To the best of our knowledge nothing has been done in this area. For ice Ih there are some experimental results on the anisotropy of the dielectric constant. However they are contradictory as certain measurements suggest strong anisotropy, whereas others suggest small anisotropy.<sup>92</sup> Our results clearly support the presence of small anisotropy for ice Ih.

Finally we have evaluated the anisotropy of the dielectric constant using the Pauling model. The Pauling model allows one to compute the generalized polarization tensor  $G_{\alpha\beta}$ , which does not depend on temperature. With the choice used in this work to locate the orientation of the molecules within the crystal it does not depend either on the considered water model. The dependence of the dielectric tensor with the water model comes simply from the value of the dipole moment of the model. We have computed the  $G_{\alpha\beta}$  tensor using the Pauling model. The obtained

**Table 6. Fractional Occupancy for the Hydrogen Atoms of Ice III and V for the TIP4P/2005 Model As Obtained from the MC Runs of This Work When Including Loop Moves<sup>a</sup>**

phase	<i>p</i> (bar)	<i>T</i> (K)	$\alpha$ (%)	$\beta$ (%)	$\gamma$ (%)	$\delta$ (%)
III	2800	243	50.8 (3)	25.6 (2)		
III	2800	220	50.9 (3)	23.2 (3)		
III exp.	2500	240	35 (2)	52 (4)		
V	5300	243	53 (1)	46 (1)	55 (1)	55 (1)
V	5300	180	58 (2)	44 (2)	55 (1)	55 (2)
V exp.	5000	237	43.5 (1.5)	29.9 (1.6)	50.2 (1.2)	76.4 (1.9)

<sup>a</sup> For ice III there are only two types of hydrogen positions labeled as  $\alpha$  and  $\beta$  (see ref 97 for details about these two kinds of hydrogen positions). An occupancy of 50% represents full disorder whereas an occupancy of 0 or 100% represents full order. For ice V there are four types of hydrogen positions labeled as  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  (see Ref 97 for details about these four kinds of hydrogen positions). The experimental values are taken from Ref 93.

dielectric tensor predicted by the Pauling model for the TIP4P/2005 model is shown in Table 5. As it can be seen the Pauling model describes reasonably well the average dielectric constants (i.e., the average of the trace) for ices III, V, VI, and VII. As previously discussed, the largest difference is found for ices Ih and Ic (although the predictions are still reasonable). Concerning the predictions for the anisotropy, it is clear that the Pauling model already predicts a lower value of the dielectric constant along the *Z* axis for ices III and VI, and to a lesser extent for ice V. However, the predicted anisotropy is smaller than that found in the simulations. We conclude that the Pauling model provides hints about the trends that can be found in the anisotropy of the dielectric constant, but underestimate the anisotropy of the dielectric tensor.

**Occupation Analysis of the Partial Proton-Ordered Phases.** It is well-known from experimental work that ices III and V present partial proton disorder<sup>93–96</sup> and that affects the value of the estimated configurational entropy of those ices.<sup>97</sup> Proton ordering has also been found on the surface of ice Ih.<sup>98,99</sup> The simulations of this work, which include loop moves, allow us to analyze the possible existence of partial proton ordering for these ices. In fact, one can obtain the populations of the different type of hydrogen positions along the runs. Results for the hydrogen site occupancies for ices III and V obtained from simulations of the TIP4P/2005 model are presented in Table 6. The calculated populations are compared to the experimental ones. For ice V the occupancies predicted by the model are close to 50% (fully disordered). Experimentally for ice V, the populations for hydrogens of type  $\alpha$  and  $\gamma$  are close to 50%, but the populations of type  $\beta$  and  $\delta$  are clearly different. Notice that the experimental occupancies tend to a value of 50% as the temperature increases. It is likely that the transition between a proton-ordered phase (ice XIII<sup>100</sup>) and a proton-disordered phase (ice V) predicted by the TIP4P/2005 occurs at temperatures lower than found experimentally. That was already found for the XI–Ih transition, which occurs at temperatures of about 25 K for the model,<sup>31,101,102</sup> whereas experimentally it occurs at temperature of about 75 K. That would explain why, for a temperature of about 240 K, the model predicts full proton disorder of ice V whereas experimentally there is only partial proton disorder. For ice III, we have found noticeable proton ordering when using the TIP4P/2005 (i.e., the occupancies of the different type of hydrogen positions are not of 50%). In fact,

in Table 6 it can be seen that for TIP4P/2005 the value of  $\alpha$  is close to 50%, whereas the value of  $\beta$  is about 25%, thus indicating partial proton ordering. When comparing the results of the models with those obtained experimentally, it is seen that experimentally the value of  $\beta$  is close to 50%, whereas the value of  $\alpha$  is of about 35%. There are two possible explanations for this disagreement between the results of the model and those found experimentally. Either the model fails in describing the experimental trends, or the labeling of  $\alpha$  and  $\beta$  used in this work is the opposite to that adopted by Lobban et al.<sup>93</sup>

## CONCLUSIONS

In this work we have computed the dielectric constant of several solid phases of water (ices Ih, III, V, VI, and VII) using computer simulations that include moves able to sample the proton disorder. Most of the results were obtained for the TIP4P/2005, although in certain cases results for TIP5P and SPC/E were also obtained. Also, the Pauling model was used to estimate the dielectric constant by generating proton-disordered configurations that satisfy the Bernal–Fowler rules and assuming that they have the same probability. Finally, we compared the simulation predictions for the dielectric constant to experimental results. The main conclusions of this work are:

(1) For ices with a perfect tetrahedral coordination the value of *G* obtained from the Pauling model is 3, whereas for ices that form a distorted tetrahedra the value of *G* decreases slightly to values around 2.6.

(2) The Pauling model can not be used to estimate the value of the dielectric constant of a certain water model. In fact, for ice Ih, it predicts a value of *G* of 3, whereas the simulation results for TIP5P and SPC/E yield that the value of *G* is of 1.4 and 1.9, respectively. However, for TIP4P-like models the predictions of the Pauling model seem to be closer to those obtained in the simulations.

(3) Proton-disordered configurations satisfying the Bernal–Fowler rules present, in general, different energies. Thus, differences in the value of *G* between different water models arise from the differences between the successfully selected configurations.

(4) Certain thermodynamic properties, for instance radial distribution functions, do not differ much between different configurations satisfying the Bernal–Fowler rules. Thus, using just an snapshot appears as a reasonable approximation. However, this is not the case of the dielectric constant, since different configurations differ significantly in their respective polarizations.

(5) For three charge models, it is suggested that the value of the polarization factor *G*, depends only on the ratio of the dipolar to quadrupolar moment. Therefore, we suggest that for three charge models  $G = G(\mu/Q)$ . Increasing the charges for a certain charge geometry modifies the dielectric constant but not the value of *G*. Thus, *G* contains information about the orientational dependence of water interactions, and this is in common with phase diagram predictions that were found to be quite sensitive to this ratio.

(6) Nonpolarizable models fail in describing simultaneously the dielectric constant of ice Ih and water. The only models that predict (in agreement with experiment) a similar dielectric constant for the fluid phase and ice Ih are TIP4P-like models. We argue that these models predict a reasonable value for the ratio of the dipole to quadrupole moment (of about one), whereas other common water models (TIP3P, TIP5P, or SPC/E) predict a large value for this ratio.

(7) When the predictions of the dielectric constants of the TIP4P/2005 are scaled using a dipole moment estimated from first principles, then the model is able to predict qualitatively the dielectric constant of the fluid phase and of the proton-disordered ices Ih, III, V, and VI.

One concludes that if one wants to describe water by a LJ center and three charges, then the TIP4P geometry provides an overall better description of water. This is somewhat surprising, since the first water model ever, the Bernal–Fowler model of water, was indeed a TIP4P-like model.<sup>38</sup> The model is able to predict the existence of many ice polymorphs.<sup>103</sup> Interestingly, most of the water models developed recently from first principle calculations for small clusters use a fitting function in which the negative charge is located at the H–O–H bisector (as in TIP4P), starting with the pioneering work of Clementi,<sup>104</sup> and following with the work of Jordan<sup>105</sup> or Xantheas.<sup>106</sup> Obviously, these models also include polarization, a feature missing in the TIP4P-like models. It is likely that the inclusion of polarizability within a TIP4P-like geometry<sup>84,107</sup> will improve the description of the dielectric constant of water in condensed phases.

In summary, common nonpolarizable models can not describe the dielectric constant of the condensed phases of water (you can be successful for one phase, but will fail dramatically for the other phases). However, at least the results of TIP4P/2005 allow a simple explanation and a route to rationalize the results. The model yields good estimates of  $G$ , but the model uses an incorrect value of the dipole moment. It is gratifying to see that by using reasonable values of the dipole moment of water in the fluid and solid phases, the TIP4P/2005 predictions for the dielectric constants are in reasonable agreement with experiment. The inclusion of nuclear quantum effects was crucial to understand the failure of popular water models in reproducing the heat capacity of water.<sup>21</sup> However for the dielectric constant the inclusion of nuclear quantum effects will improve (but not correct) the disagreement between experiment and theory found for TIP4P/2005. In fact, models optimized for path integral simulations have a slightly larger dipole moment than those optimized for classical simulations.<sup>9,10</sup> For instance q-TIP4P/f has a dipole moment of about 2.35 D, whereas TIP4PQ/2005 has a dipole moment of 2.38 D (both values being slightly larger than the value of the TIP4P/2005, namely 2.3 D). This increase in the dipole moment would increase slightly the dielectric constant (the value of  $G$  is not expected to be modified much by the inclusion of nuclear quantum effects) but will not bring the predictions into agreement to experiment. Thus nuclear quantum effects seems not to be the key to improve the predictions of the dielectric constants obtained by simple non polarizable models. It seems that only including polarization one could describe quantitatively the dielectric constants of water in condensed phases.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: cvega@quim.ucm.es.

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