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# Proton Chemical Shift of Water in the Liquid State: Computer Simulation Results

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**Abstract:** Molecular dynamics simulations have been employed to determine the relative proton magnetic resonance ($^{1}$H NMR) chemical shifts of water in liquid state. The proton chemical shifts were obtained as a sum of the average electrostatic and van der Waals contributions. In order to compute these contributions, the Buckingham–Marshall–Pople treatment of the electrical field effect on proton magnetic shielding was used. The SPC/E model for water was studied at temperatures of −10, 25, and 100 °C, and the $^{1}$H NMR chemical shifts were found to be in good agreement with experimental data. The dependence in the values of the chemical shifts upon the number of molecules involved in their evaluation was examined in detail. In general, the nearest neighbors of a molecule gave rise to particularly large deshielding effects, whereas more distant molecules were found to increase shielding. The method employed can be utilized in the calculation of proton-shielding changes in any liquid for which the appropriate intermolecular potentials are available.

## 1. Introduction

The proton magnetic resonance ($^{1}$H NMR) chemical shift of water is certainly one of the most important effects which helps to characterize the molecular interactions associated with hydrogen bonding in aqueous systems. Unlike other experimental methods which are commonly used in studies of hydrogen-bonded systems (such as UV, Raman, IR, and dielectric spectroscopy, X-ray, or neutron scattering),[1-3] the $^{1}$H NMR technique (chemical shift measurements) directly probes the electron density at the protons involved in hydrogen bonding, thus providing unique information on specific molecular interactions in liquid water,[1,4,5] electrolyte solutions,[1,3,6,7] solutions of simple nonelectrolytes,[1,3,8-10] and biomolecular systems.[11] It is worthwhile mentioning that among spectroscopic characteristics, only the magnetic resonance shift of water protons has an extremum in its concentration dependence in the water-rich region (90–100 mol % of water) of aqueous nonelectrolyte solutions.[1,8-10] This extreme behavior (also observed for some partial molar thermodynamic properties[1,12]) shows the exceptional sensitivity of proton chemical shifts to structural transformations in liquids and is often considered as spectroscopic evidence for hydrophobic hydration of alcohols, ketones, ethers, and amines, etc. An empirical correlation which exists between the size of the nonpolar group in these systems and the downfield shift of the water protons provides a convenient method of estimating, from NMR data, the "strength" of the hydrophobic hydration in the solvation of polyfunctional molecules.[9]

While extensive experimental data on proton chemical shifts in aqueous systems are now available, many questions still remain concerning their detailed structural interpretations. Such interpretations are largely based upon specific models for the structure in liquid water, and both the generalized "broken-bonds" model[4] and the continuous random-network model[5] can fit experimental results. Apparently this makes any spectroscopic evidence for specific structures inconclusive. An unambiguous statistical–mechanical treatment of the shielding phenomena in liquid water is clearly needed. However, to our knowledge, no one has yet attempted such an investigation. The purpose of this article is to provide a simple and reasonably accurate statistical method with which to calculate the relative position of the resonance in a $^{1}$H NMR spectrum of water from a computer simulation. We then exploited this methodology to compute average chemical shifts for water within molecular dynamics (MD) calculations. We utilized the familiar Buckingham–Marshall–Pople treatment[13,14] of the electrical field effect on the magnetic shielding in order to evaluate the dominant contributions (i.e., electrostatic and van der Waals) to the observed proton shifts. In this study, we have not attempted to estimate the repulsion–overlap effect on the chemical shift which is believed to be very small.[4,16,28] Although we report results from water simulations only, the method employed can be easily extended to the calculation of proton chemical shifts in any liquid for which suitable intermolecular potentials are available.

The remainder of this paper is organized as follows. In section 2, we outline the theoretical background utilized in our simulations, and in section 3, we summarize the computational procedure. The results of the calculations of the $^{1}$H NMR chemical shifts (SPC/E water at −10, 25, and 100 °C) are then presented in section 4. Finally, our conclusions are given in section 5.

## 2. Theory

The quantity of primary interest in this study is the proton chemical shift $\delta$ of liquid water relative to its gas value. This chemical shift (hereafter in ppm) has been measured both in the normal temperature range[4,17] and in the supercooled region,[4] and the empirical equation

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$$\delta(T\,°\mathrm{C}) = -4.656 + (11.884 \times 10^{-3})T - (2.006 \times 10^{-5})T^2 \qquad (1)$$

has been found to fit the experimental data (after correction for bulk-magnetic-susceptibility) from −15 to 100 °C to within 0.1% error.

In our statistical–mechanical analysis of the proton-screening phenomena in liquid water, we start from a general relationship[1,4]

$$\langle\delta\rangle = \langle\delta_{\mathrm{el}}\rangle + \langle\delta_{\mathrm{w}}\rangle + \langle\delta_{\mathrm{rep}}\rangle \qquad (2)$$

where $\langle\delta\rangle$ is the average total observed chemical shift (as given by eq 1), $\langle\delta_{\mathrm{el}}\rangle$ represents the effect of electrostatic polarization of the OH bonding electrons by the external electrical field arising from the permanent (i.e., after averaging over the electronic degrees of freedom) charge distribution in the surrounding water molecules, $\langle\delta_{\mathrm{w}}\rangle$ includes the effect of van der Waals forces, and $\langle\delta_{\mathrm{rep}}\rangle$ represents the effect of repulsive overlap on shielding. The angle brackets in eq 2 denote the usual ensemble average.

We first turn our attention to the determination of the electrostatic contribution $\langle\delta_{\mathrm{el}}\rangle$ to the observed chemical shift. It is convenient to express $\langle\delta_{\mathrm{el}}\rangle$ as an average over all protons in the system under consideration. The corresponding relationship is given by

$$\langle\delta_{\mathrm{el}}\rangle = \frac{\sum_i \langle\delta_{\mathrm{el},i}\rangle}{2N} \qquad (3a)$$

where $\langle\delta_{\mathrm{el},i}\rangle$ is the average electrostatic shift for a given proton $i$ and $N$ is the total number of water molecules. In this study, we have chosen to base our evaluation of the electrostatic chemical shifts on the Buckingham–Marshall–Pople formalism,[13,14] which was originally used to predict the $^1$H NMR chemical shifts induced by polar groups within organic molecules. This formalism has been further extended to the calculations of the chemical shifts due to intermolecular hydrogen bonds.[4,5] Recently, similar treatment has also been used to study electrical field effects on the $^{13}$C and $^{19}$F shielding in HF and $CH_3F$.[15] In our adaptation of the Buckingham–Marshall–Pople treatment of the proton-shielding phenomena, we use

$$\delta_{\mathrm{el},i} = -\Phi_{\mathrm{a}}\mathbf{I}_{\mathrm{OH,int}}E_{\mathrm{OH},i} - \Phi_{\mathrm{b}}\mathbf{E}_i^{\,2} \qquad (3b)$$

to compute instantaneous values for the electrostatic chemical shifts of individual protons of water molecules in the liquid state. This calculation can then be easily incorporated into a MD simulation in order to evaluate the ensemble average in eq 3a. In eq 3b, $\Phi_{\mathrm{a}}$ and $\Phi_{\mathrm{b}}$ are the classical screening coefficients (with numerical values of $1.48 \times 10^{-18}$ cm$^3$/erg and $0.74 \times 10^{-18}$ cm$^3$/erg, respectively[14]), $\mathbf{I}_{\mathrm{OH,int}}$ is the internal (molecular) electrostatic field acting on the proton $i$ along the OH bond, $\mathbf{E}_i$ is the total external electrostatic field on the proton, and $E_{\mathrm{OH},i}$ is the component of this external field along the OH bond. The external field $\mathbf{E}_i$ that appears in eq 3b is defined in the usual manner as a sum of the field due to the molecules immediately surrounding the molecule containing proton $i$ and the reaction field which accounts for the bulk material beyond a fixed cutoff. We write that

$$\mathbf{E}_i = \mathbf{F}_i + \mathbf{R} \qquad (4)$$

where $\mathbf{F}_i$ is the average field on the proton $i$ generated by the neighboring molecules and $\mathbf{R}$ is the reaction field.

In order to exploit these relationships for the chemical shift in our calculations, explicit expressions for the electrical fields must be specified. For point-site models for water (which is the usual case in computer simulations), the external field due to the nearby molecules can be written as

$$\mathbf{F}_i = \sum_j \left(\frac{Q_j}{r_{ij}^2}\right)\frac{\mathbf{r}_{ij}}{r_{ij}} \qquad (5a)$$

the internal molecular field correspondingly becomes

$$\mathbf{I}_{\mathrm{int}} = \sum_k \left(\frac{Q_k}{r_{k\mathrm{H}}^2}\right)\frac{\mathbf{r}_{k\mathrm{H}}}{r_{k\mathrm{H}}} \qquad (5b)$$

and the reaction field is given by

$$\mathbf{R} = \frac{8\pi(\epsilon - 1)}{3V(2\epsilon + 1)}\mathbf{M} \qquad (5c)$$

where $Q_j$ is the partial charge on site $j$, $V$ and $\mathbf{M} = \sum Q_k\mathbf{r}_k$ are, respectively, the volume and the dipole moment of a spherical sample of the system centered on the proton $i$, $\epsilon$ is an estimate of the static dielectric constant of the bulk liquid, and $\mathbf{r}_{ij}$ is the separation vector. We note that in eq 5b, the summation on $k$ is carried over the charges within the molecule excluding the proton under consideration, while in eq 5a the sum is over all charges in the surrounding molecules. (With regard to eq 5a it is worthwhile mentioning that at large separations, explicit point-charge fields can be accurately modeled with the corresponding dipolar fields.) In the present study, we have taken our spherical sample to be the inscribed sphere within the simulation cell.

It follows from the above equations and previous estimates[4,5,14] that the electrostatic proton shifts $\delta_{\mathrm{el},i}$ are largely dominated by the contribution proportional to $E_{\mathrm{OH},i}$ (arising from the action of the external electrostatic field along the OH bond); this contribution is very sensitive to the relative orientations of interacting water molecules and details of the model. Moreover, the permanent electrostatic field $\mathbf{E}_i$ generating the shift $\delta_{\mathrm{el},i}$ has long-range, orientationally-dependent contributions; therefore, it is essential to include more remote molecules in the field calculation, and, indeed, this can be done accurately in computer simulation.

The next step in our statistical consideration is to determine the van der Waals contribution $\langle\delta_{\mathrm{w}}\rangle$ to the observed chemical shift, and in accord with our previous definition of eq 3a, we shall write it as

$$\langle\delta_{\mathrm{w}}\rangle = \frac{\sum_i \langle\delta_{\mathrm{w},i}\rangle}{2N} \qquad (6a)$$

In eq 6a, $\langle\delta_{\mathrm{w},i}\rangle$ is the average van der Waals chemical shift of the proton $i$ which in the present study will be calculated through the well-known expression[4,13–14,16,28]

$$\delta_{\mathrm{w},i} = -\Phi_{\mathrm{b}}\langle E_{0,i}^{\,2}\rangle \qquad (6b)$$

where $\langle E_{0,i}^2\rangle$ is the mean-square value of the fluctuating electrical field on the proton $i$. This field is generated by the rapid zero-point charge fluctuations in the neighboring water molecules; it has a zero mean value while its nonvanishing mean-square $\langle E_{0,i}^2\rangle$ leads to the dispersion effects.

The use of eq 6b in chemical shift calculations depends upon our ability to determine the field fluctuations on the protons of the system. We do this by adopting a recent theory of polyatomic dispersion forces[16,18] which relates $\langle E_{0,i}^2\rangle$ to the mean-square electrical moments $\langle m^2\rangle$ of bonded atoms in molecules. We recall that numerous methods of calculating mean-square values of the fluctuating electrical field exist;[28] our choice has been dictated

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by the necessity to use a scheme which is practical in a computer simulation and transferable in calculations with different molecules. On the basis of London's treatment of dispersion interactions, it has been shown in ref 18 that

$$\langle E_{0,i}{}^2\rangle = 2\sum_j \frac{\langle m_j^2\rangle}{r_{ij}^6} \qquad (7)$$

in which the summation is carrying over all the atoms $j$ in the surrounding molecules. Homer and Mohammadi[18] suggest that the values of the mean-square electrical moments of bonded atoms required in eq 7 may be further approximated by the values of $\langle m^2\rangle$ for the inert gases that are closest to the atoms of interest in the periodic table. Their approach has been tested with a large number of simple molecules,[16,18] and the results seem to indicate that both the heats of vaporization and the shielding constants are successfully reproduced. Thus, we assume

$$\langle m_j^2\rangle = \langle m_{\text{inert}}^2\rangle \qquad (8a)$$

in which

$$\langle m_{\text{inert}}^2\rangle = \frac{3 I_{\text{inert}}\alpha_{\text{inert}}}{2} \qquad (8b)$$

where $I_{\text{inert}}$ and $\alpha_{\text{inert}}$ are, respectively, the first ionization potential and the polarizability of the corresponding inert gas atoms. Applying this scheme to water molecules, we have

$$\langle m_{\text{H}}^2\rangle = \langle m_{\text{He}}^2\rangle \qquad (9a)$$

and

$$\langle m_{\text{O}}^2\rangle = \langle m_{\text{Ne}}^2\rangle \qquad (9b)$$

(Numerical values for $\langle m_{\text{He}}^2\rangle$ and $\langle m_{\text{Ne}}^2\rangle$, deduced from eq 8b using first ionization potentials and polarizabilities of He and Ne atoms, are equal to $12.111 \times 10^{-36}$ and $20.45 \times 10^{-36}$ erg cm$^3$, respectively.[18]) We can then express eq 7 in the form

$$\langle E_{0,i}{}^2\rangle = 2\left(\sum_{j\in\{\text{H}\}} \frac{\langle m_{\text{He}}^2\rangle}{r_{ij}^6} + \sum_{j\in\{\text{O}\}} \frac{\langle m_{\text{Ne}}^2\rangle}{r_{ij}^6}\right) \qquad (10)$$

which provides us with a convenient route to calculate $\delta_{\text{w},i}$ (and consequently $\langle\delta_{\text{w}}\rangle$) in a computer simulation. It is necessary to point out that, in comparison with the electrostatic proton shifts which are proportional to $r^{-3}$ (in dipole representation), the van der Waals shifts are proportional to $r^{-6}$.

Finally, we shall briefly consider the repulsion–overlap contribution[28] to the chemical shift of water. This contribution, unfortunately, can not be described with a simple statistical-mechanical model. There is currently no satisfactory theory which correlates $\delta_{\text{rep}}$ with molecular parameters suitable for a computer simulation. Meanwhile, several semiempirical approximations have been suggested[4,28] which, in principle, estimate the relative "weight" of repulsion–overlap in screening effects, and one of these approaches correlates $\delta_{\text{rep}}$ with the values of the overlap integrals.[4] It has been found[4] that for water molecules at distances of 2.8–3.0 Å (typical nearest neighbor separations), the repulsion–overlap gives rise to a very small shift ($\delta_{\text{rep}} \leq 0.02$ ppm, or less then 1% of the experimental values). In view of all these factors, we have not included the repulsion–overlap contribution in our analysis.

## 3. Computational Details

Table I. Thermodynamic Properties of the SPC/E Model for Water

| T (°C) | $\langle U_Q\rangle$ (kJ/mol), ±0.1% | $\langle U\rangle$ (kJ/mol), ±0.1% |
|---|---|---|
| −10 | −53.29 | −43.60 |
| 25 | −50.30 | −41.48 |
| 100 | −44.41 | −37.11 |

In this article, we report results of the $^1$H NMR chemical shift ($\langle\delta_{\text{el}}\rangle + \langle\delta_{\text{w}}\rangle$) of water from MD simulations performed with the SPC/E potential.[19] This effective pair potential can be written as

$$u = u_Q + u_{\text{LJ}} \qquad (11a)$$

where

$$u_Q = \sum_k^{\text{on } j}\sum_l^{\text{on } j} \frac{Q_k Q_l}{r_{kl}} \qquad (11b)$$

is the Coulombic term in which the summation runs over the site charges ($k$ and $l$) of the molecules ($i$ and $j$) and

$$u_{\text{LJ}} = 4\epsilon_{\text{LJ}}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] \qquad (11c)$$

is the Lennard–Jones term which is evaluated only between oxygen sites. In the SPC/E model, each water molecule contains three charged sites, a charge of −0.8476 e on the oxygen position and two charges of 0.4278 e on the hydrogen positions placed tetrahedrally at distances of 1.0 Å from the oxygen site. The Lennard–Jones parameters of the SPC/E potential are $\epsilon_{\text{LJ}} = 0.6517$ kJ/mol and $\sigma = 3.166$ Å.

Our MD simulations have been carried out with samples of 108 molecules at temperatures of −10, 25, and 100 °C. Some test calculations were conducted with 256 particles at 25 °C, and no system-size dependence in the chemical shift values was detected. Isothermal conditions were maintained throughout with a Gaussian thermostat. We have also chosen to work at constant volume using experimental densities. In our calculations, we have utilized a truncated octahedral geometry for the simulation cell[22] and periodic boundary conditions.[20,21] The Ewald summation technique was used to evaluate the long-range Coulombic forces. In our implementation of the Ewald summation technique, the real space sum was carried over all nearest images, the Fourier space sum was truncated after the first 395 independent lattice vectors (corresponding to $n^2 \leq 53$), and the value of the convergence parameter $\kappa$ was 6.4. The reaction field contribution due to the surrounding dielectric continuum was calculated from the corresponding relationship given elsewhere,[20,21] the dielectric constant of the continuum boundary $\epsilon'$ was taken to be that of real water at the temperature of interest. The Lennard–Jones interactions were truncated spherically at a cutoff of $(3^{1/2}/4)L$, where $L$ is the length of the cube containing the truncated octahedron. The isokinetic equations of motion were integrating using a fourth-order Gear algorithm[23] and a time step of 1.25 fs. At each temperature, the system was equilibrated for 0.1 ns and averages were accumulated over the subsequent 0.5 ns. The orientational coordinates of the water particles were expressed in terms of quaternion parameters[20] which enabled us to carry out the calculation of the electrical fields (and their appropriate projections) on protons in an efficient manner.

## 3. Results and Discussion

Results for the thermodynamic properties of SPC/E water, including the average Coulombic energy $\langle U_Q\rangle$ and the average configurational energy $\langle U\rangle$, at temperatures of −10, 25, and 100 °C are given in Table I. We point out that these values of $\langle U_Q\rangle$ and $\langle U\rangle$ contain a positive self-energy correction of 5.22 kJ/mol, as suggested in ref 19. As we might expect, the thermodynamic properties obtained in this study are in very good agreement with previous calculations.[19]

Our major simulation results, the estimates for the $^1$H NMR chemical shifts of water, are presented in Figure 1, where the electrostatic and van der Waals contributions are shown along with the total computed chemical shifts. Also included in Figure 1 for comparison is the experimental temperature dependence (from eq 1) of the proton chemical shifts in $H_2O$. We estimate the statistical uncertainty in our values to be approximately 0.5% for the van der Waals term and 1% for the electrostatic term. We also remark that the reaction field contribution to the electrostatic chemical shifts as defined by eqs 3 and 4 is rather small (not more than 5% of $\langle\delta_{\text{el}}\rangle$), even for 108 particles, and might easily be ignored for larger samples. It can be seen in Figure 1 that the

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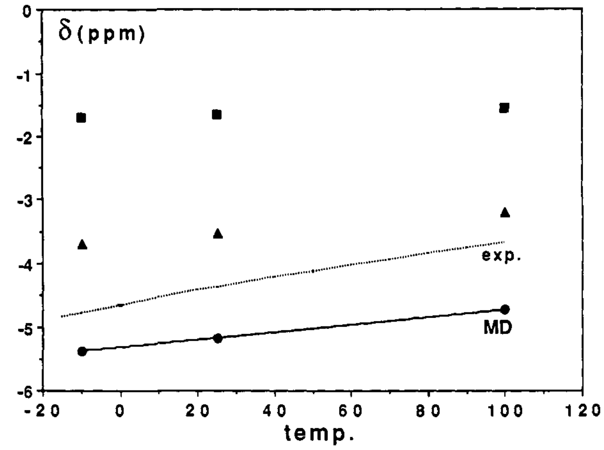

**Figure 1.** $^1$H NMR chemical shift of water in the liquid state. The triangles, the squares, and the circles, respectively, are the electrostatic, the van der Waals, and the total computed chemical shifts. The dotted line is the experimental temperature dependence (eq 1).

overall agreement between the simulation results and experimental data is very good at all temperatures; the magnitude of the total proton deshielding in liquid water and the character of the temperature dependence of the deshielding are both successfully reproduced. As we might also expect, the electrostatic term for this highly polar liquid is dominant in the total proton-shielding changes.

Comparing the present results with those obtained in earlier model calculations of liquid water chemical shifts, we find noticeable difference in the values of the van der Waals terms. The previously reported estimate for the van der Waals shift in liquid water, which had been obtained on the basis of eq 6b by considering the properties of $H_2O$ molecules in free rotational states, was approximately −0.9 ppm.[1,4] Our simulation results based on the direct application of eq 6b to interacting waterlike particles give values for the van der Waals shifts that are ~70% larger in magnitude. At the same time, we observe that the van der Waals term is less sensitive to temperature variations than the electrostatic term, apparently due to the short-range character of the van der Waals forces. In general, detailed information on different contributions to the observed chemical shifts could be very helpful in theoretical explanations of shielding phenomena in liquids, and in future work, we hope to carry out a complete analysis of the electrostatic and dispersion effects in various solvents.

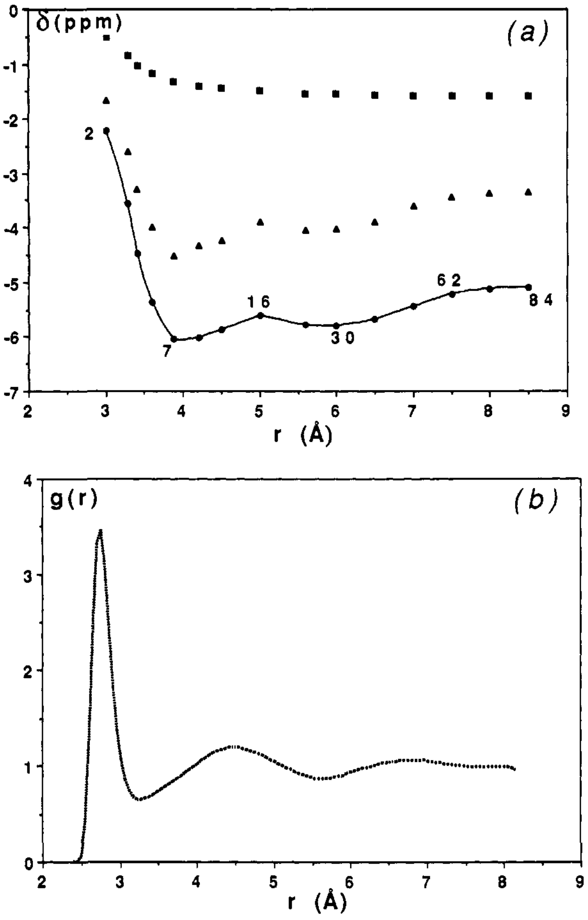

**Figure 2.** (a) Distance dependence in the value of the proton chemical shift. The symbols are defined as in Figure 1. The numbers indicate the number of molecules included in the shift calculation. (b) Radial distribution function for the SPC/E model for water. All results are for −10 °C.

In our simulations, we have also examined the distance (or cutoff) dependence in the chemical shifts for liquid water by computing contributions due only to those molecules within specific truncation spheres surrounding the molecule under consideration. The results at −10 °C are shown in Figure 2a. It can be seen that while the electrostatic shifts do not have a simple dependence upon the cutoff distance (or the number of nearest neighbors involved in the calculation of the shifts), the van der Waals shifts appear to be quite insensitive to the details of the local order (as exhibited by its simple dependence on $r$). The relationship of these dependencies to the structure in the liquid becomes apparent if we compare them with the OO radial distribution function $g(r)$ plotted in Figure 2b. It is clear from Figure 2 that the first hydrogen-bonded neighbors give rise to particularly large deshielding effects. The influence of more distant and more weakly interacting neighbors (second and third, etc.) is opposite to that we observed for first neighbors, i.e., they increase shielding. This leads to a minimum in $\langle \delta_{el}(r) \rangle$ (or maximal deshielding) for a cutoff of ~3.8 Å. We remark that the average number of molecules within the sphere of a 3.8-Å radius is seven. It can also be seen in Figure 2 that more remote (5 Å $< r <$ 6 Å) second neighbors of the molecule under consideration appear to cause a weak deshielding on its protons, leading to a flat second minimum in $\langle \delta_{el}(r) \rangle$ at 6 Å. This indicates that the second neighbor shell, as defined by $g(r)$, consists of molecules which have significantly different average orientations of their dipole vectors depending on their separation. Clearly the behavior of $\langle \delta_{el}(r) \rangle$ suggests a more complex average structure in the liquid than is perhaps implied by a simple interpretation of the peaks in $g(r)$. The average local structure in liquid water will be explored in much greater detail in a future article.[24] These simulation results essentially confirm the major conclusion of nonempirical quantum mechanical studies of magnetic shielding in small water clusters[25,26] that distant molecules may cause noticeable polarization effects in proton magnetic shielding and that the shielding constants are very sensitive to the relative orientations of these molecules. However, our simulation approach enabled us to study polarization effects under conditions which closely model the real liquid.

As mentioned above, the unambiguous structural interpretation of experimental data for the chemical shifts of water in solutions is still missing despite the fact that an enormous amount of literature[1,3,6,9-11] has now accumulated. Given our success with liquid water chemical shifts simulation, it would be interesting now to carry out similar investigations for aqueous solutions. Several problems are noteworthy. First, it is desirable to clarify the origin of the downfield proton chemical shifts observed in the water-rich region of nonelectrolyte solutions.[8,9] Structural data from computer simulations for this concentration region are available for a number of systems, and an analysis of the chemical shifts on the basis of these molecular distributions seems to be straightforward. Second, an examination of the character of the concentration dependencies of the proton chemical shifts in electrolyte solutions[6] should be carried out. In electrolyte solutions, both positive and negative concentration dependencies have been observed for the salts which are close in nature (KF vs KCl and LiCl vs NaCl, etc.). This computer simulation technique is well equipped to deal with the large number of factors to be considered in determining the origins of such differences. Finally, it is certainly important to implement the current methodology in simulations of biomolecules in solutions, whose NMR spectra are particularly difficult to interpret.

Concluding our structural discussion of liquid water chemical shifts, we would only add that many ab initio studies[15,26-29] have confirmed the validity of simple semiempirical formulas for shielding constants which, in our opinion, provide a valuable, practical guide in statistical-mechanical calculations.

## 5. Conclusions

In this article, we have reported results from computer simulations for proton chemical shifts of water in the liquid state. The chemical shifts of water protons are widely used as an empirical probe of hydrogen bonding in aqueous systems; yet their analysis from the statistical-mechanical point of view has been rather limited. One of the principal aims in this study has been to develop, in a simple, practical manner, a method with which to investigate proton-shielding phenomena in computer simulations.

In this work, we have calculated the $^1$H NMR chemical shifts of the SPC/E model for water as the sum of electrostatic and dispersion contributions. To evaluate these contributions, we have used the classical Buckingham–Marshall–Pople treatment of the electrical field effect on proton shielding. Three temperatures (−10, 25, and 100 °C) have been examined. We find that both the magnitude of the chemical shifts calculated and their temperature dependence agree well with experimental observations.

In our simulations, we have also investigated the distance dependence in the chemical shift (or the dependence in the value of the chemical shift upon the number of molecules involved in the shift evaluation). Both electrostatic and dispersion contributions were examined, and we observed a remarkable sensitivity of the electrostatic shifts to the local (molecular) environment. In general, the first neighbors in water structure were found to cause particularly large deshielding effects, whereas more distant molecules tended to increase shielding.

Given the success of this initial study of proton chemical shifts of water, an extension of this work to other liquids is clearly needed. Work is currently underway to examine the proton chemical shifts of electrolyte solutions. We remark that because of their sensitivity to liquid structure, $^{19}$F chemical shifts[15,30] may also be considered as suitable candidates for computer simulations.

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