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Hydrogen bonding definitions and dynamics in liquid water

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X-ray and neutron diffractions, vibrational spectroscopy, and x-ray Raman scattering and absorption experiments on water are often interpreted in terms of hydrogen bonding. To this end a number of geometric definitions of hydrogen bonding in water have been developed. While all definitions of hydrogen bonding are to some extent arbitrary, those involving one distance and one angle for a given water dimer are unnecessarily so. In this paper the authors develop a systematic procedure based on two-dimensional potentials of mean force for defining cutoffs for a given pair of distance and angular coordinates. They also develop an electronic structure-based definition of hydrogen bonding in liquid water, related to the electronic occupancy of the antibonding OH orbitals. This definition turns out to be reasonably compatible with one of the distance-angle geometric definitions. These two definitions lead to an estimate of the number of hydrogen bonds per molecule in liquid simple point charge/extended (SPC/E) water of between 3.2 and 3.4. They also used these and other hydrogen-bond definitions to examine the dynamics of local hydrogen-bond number fluctuations, finding an approximate long-time decay constant for SPC/E water of between 0.8 and 0.9 ps, which corresponds to the time scale for local structural relaxation. © 2007 American Institute of Physics. [DOI: [10.1063/1.2742385](https://doi.org/10.1063/1.2742385)]

I. INTRODUCTION

Water is ubiquitous in nature, playing key roles in a range of fields as varied as biochemistry, earth sciences, and atmospheric chemistry.¹ In addition, water is one of the most common polar solvents used in synthetic chemistry. The power of liquid water as a solvent stems in part from its unusual properties, often attributed to its strong hydrogen-bond (H-bond) network.^{2–4} It is therefore not surprising that so much attention has been devoted to understanding H bonding in water. In particular, this discussion focuses on the number of H bonds per molecule (following common practice we will quote the average number of H bonds that each water molecule participates in, which, technically, is twice the average number of H bonds per molecule), the local order in water (and particularly its symmetry), and the dynamics of the fluctuating H-bond network.

A number of different experimental techniques have been developed to address these issues. X-ray diffraction is sensitive to electron density, which for water of course is highest around the oxygen atoms, and so this technique is particularly useful in obtaining the O–O radial distribution function.^{5,6} Neutron diffraction is sensitive to the positions of the nuclei. Studies with H₂O, D₂O, and mixtures of the two lead to H–H and H–O as well as O–O radial distribution functions.^{7,8} These experimental results, coupled with theoretical analysis, lead to the picture that the local structure of water, while certainly disordered, is more or less tetrahedral, with approximately 3.5 H bonds per molecule. This means that the typical water molecule makes two H bonds through its hydrogen atoms (it is a double donor), and makes two H bonds through its oxygen atom (it is also a double acceptor).

Vibrational spectroscopy, both infrared and Raman, is

also an excellent probe of the local structure in water. This is because a local mode's vibrational frequency is exquisitely sensitive to the local mode's H-bonding environment. Actually, the cleanest information about the local structure in water comes from the vibrational spectroscopy not of neat water, but rather of dilute HOD in either H₂O or D₂O, since in these cases, respectively, the OD or OH local-mode stretch is almost completely decoupled from the other stretches in the liquid, thus functioning well as a local chromophore. Infrared and Raman spectra on these systems have been measured by many.^{9–20} In earlier days some of these experimental results were interpreted to provide evidence for mixture models of water. However, more recent theoretical studies show^{20–31} that these experimental line shapes are, in fact, compatible with modern simulation models, which themselves are compatible with (and, in fact, often parametrized from) the diffraction results, and of course produce a continuum of intermolecular configurations.

More recently x-ray absorption spectroscopy (XAS), x-ray Raman spectroscopy (XRS), and x-ray emission spectroscopy (XES) have been shown to provide information about local structure in liquid water.^{32–39} XAS involves the excitation of a core electron (an O 1s electron in the case of water) to the lowest unoccupied molecular orbital (LUMO). In liquid water this LUMO is extended over at least several molecules, and hence is influenced by the local chemical environment and H-bonded network. The interpretation of the experiments has been quite controversial.^{40–48} One interpretation is that H bonds in liquid water are very asymmetrical, and that on average each molecule is involved in only two strong H bonds (rather than 3.5), and that the typical molecule then is a single donor.^{36,39}

Information about local *dynamics* in liquid water is more

limited; traditionally NMR experiments have been the most revealing. Proton relaxation experiments are complicated by the competition between intramolecular and intermolecular spin-spin coupling, but in principle these contributions to the NMR relaxation time can be separated, thus yielding a clean measurement of the second-rank reorientation correlation time of the H–H intramolecular vector.^{49,50} Quadrupolar relaxation experiments on deuterium (in deuterium-enriched water) and ¹⁷O are in principle more definitive, providing reorientation times of the bond vector and out-of-plane vector, respectively.^{51–53} Although the connection between molecular rotation and H-bond network dynamics has certainly been discussed,^{24,54–57} these NMR experiments do not provide particularly direct information about the dynamics of the H-bond network. More direct information comes from ultrafast vibrational spectroscopy experiments. As described above, a local mode's vibrational frequency is very sensitive to the local H-bond environment, which of course is continually changing in time due to molecular dynamics. The resulting dynamic frequency fluctuations, producing what is known as spectral diffusion, can be measured by transient vibrational holeburning and three-pulse echoes.^{18,19,56–68} Inasmuch as spectral diffusion at longer times is thought to result from rearrangements of the H-bond network,^{23–25,27,28,69–76} these experiments provide valuable information about H-bond dynamics.^{55,77–85}

The interpretations of the experiments discussed above and the theoretical discussion of the static and dynamical aspects of H bonding both rely on a definition of the hydrogen bond in liquid water. Such a definition in turn depends to some extent on our understanding of the physical origin of the hydrogen bond. Some time ago the H bond was viewed as essentially electrostatic in origin.^{86–88} In 1970s Morokuma and co-workers performed *ab initio* calculations on the water dimer with the OH of one water molecule and the O atom of the other all collinear.^{89–91} They calculated the intermolecular binding energy as a function of the intermolecular H–O distance, and concluded that electrostatic interactions between the two water molecules were at the root of the H bond. However, they did observe that at distances below 2.3 Å charge transfer from one water molecule to the other increased dramatically. (Note that the typical OH distance for neighboring molecules in the liquid is about 1.75 Å.) Others consider this charge transfer to be the essence of the H bond.^{92–97} Weinhold and co-workers described H bonding from a donor-acceptor point of view, wherein electrons in the lone-pair orbitals on the O atom of one water molecule are donated to the σ_{OH}^* antibonding orbital situated on the other water.^{93–96} (Note that this use of the words donor and acceptor is exactly opposite to the nuclear definition discussed earlier!) Interesting discussions of the semantics and other issues associated with the electrostatic/charge-transfer conundrum are in the literature.^{41,98–101}

Turning next to a discussion of H-bond definitions, it is important to understand that for a water dimer, all possible diagnostics of H bonding (binding energy, charge transfer, geometric criteria, etc.) are continuous, and so any sharp cutoff separating H-bonded from non-H-bonded configurations is essentially arbitrary. And indeed, for a dimer there is

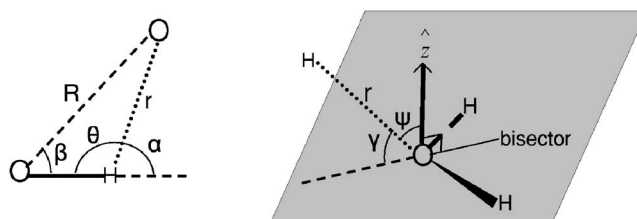


FIG. 1. Pictorial representation of the distances (R and r) and angles (β , θ , α , γ , ψ) discussed in the text. The \hat{z} axis is perpendicular to the molecular plane.

probably no need to invoke any such cutoff. The interest in developing H-bond definitions comes from trying to characterize the liquid state.

For example, within a given simulation model one can calculate the distribution of binding energies for all pairs of molecules in the liquid. This distribution has two peaks: the peak at lower binding energy corresponds mostly to near neighbors, and the peak at higher binding energy corresponds for the most part to pairs of molecules that are spatially distant, and hence have weak interaction energies.^{4,102–104} These two peaks are separated by a minimum, and the position of the minimum provides a natural cutoff between H-bonded pairs (those with energies within the lower peak), and non-H-bonded pairs (those with energies within the higher peak).^{103,104} It is understood that this double-peaked structure is a consequence of statistical-mechanical averaging and packing effects in the liquid. Moreover, the energy cutoff is a function of density and temperature, and thus cannot be considered a fundamental H-bond definition. Nonetheless, such an energy cutoff does provide a definite and useful criterion for H bonding in the liquid.^{77,80,81,103,104}

The other major thread regarding H-bond definitions for the liquid involves geometric rather than energetic criteria. For example, the O–O radial distribution function has a peak at short distances corresponding to the first solvation shell, a minimum at slightly larger distances, and then further structure at larger distances. Thus it is natural to use the position of the minimum as a distance cutoff, considering any pair of molecules with an O–O distance R less than the cutoff to be H bonded.^{105,106} As in the case of the energetic criterion, this cutoff is necessarily temperature and density dependent. In addition, this O–O definition is quite generous, considering some pairs of molecules to be H bonded that intuitively would seem not to be. More to the point, then, is a similar distance cutoff but involving the H–O radial distribution function,^{107,108} since at least in this case for a pair to be H bonded the H atom on one molecule and the O on another must be relatively close. This H–O criterion, involving the H–O distance r , is more restrictive than the O–O one, and so it necessarily leads to a smaller number of H bonds per molecule. Others have expanded upon these “distance-only” criteria by including one or more angles corresponding to the dimer geometry.^{109–111} For the most part the angles considered are θ and β (see Fig. 1). This leads to four possible pairs of one distance and one angle, and of course criteria involving all four: R and β ,^{36,55,78,79,81,84,112} R and θ ,^{85,113–115} r and β ,^{23,24,83,112,116} and r and θ (Refs. 112 and 117) have been

developed! Although the angular cutoffs may correspond intuitively to our notions of a H bond, the actual values for the cutoffs are quite arbitrary, and so in this sense these definitions are on even less firm ground than the energetic or distance-only cutoffs. Calculations with different simulation models and techniques, using various of these H-bonding definitions, have yielded numbers of H bonds per molecule that are typically between 3 and 4.

Given the arbitrary nature of the angular cutoffs in the various distance-angle definitions discussed above, there is a need to develop methods to determine in a systematic manner sensible cutoffs for any reasonable distance-angle pair. The radial distribution functions [and hence their corresponding potentials of mean force (PMFs)] provide clear cutoffs for distance-based definitions. In this paper we extend this idea to distance-angle definitions. Thus, for one particular water model (the SPC/E model¹¹⁸), we calculate two-dimensional (2D) PMFs for various choices of distance-angle pairs (we note that a related 2D probability distribution for the R - β pair has been calculated previously by Gallagher and Sharp¹¹⁹). In each case there is a low-energy basin at short distances separated from another region at longer distances by a saddle. A natural boundary separating these two regions would be the lines of steepest ascent from the saddle point. Alternatively, here we consider the equipotential contour that goes through the saddle point, and use the branch that encloses the short-distance basin as a 2D H-bonding cutoff. The difference between these two (steepest ascent and equipotential) definitions is minimal, since the only configurations for which they differ have relatively high free energy, and therefore are not particularly likely. For each of a number of distance-angle definitions we then calculate the number of H bonds per molecule, and of course for each of these definitions we obtain a different value (however, again, always finding numbers between 3 and 4).

Armed at least with a systematic way of defining cutoffs for each distance-angle choice, but faced with a plethora of different choices that lead to different numbers of H bonds per molecule, one wonders: Is one of the choices preferable to the others? Here one seems to have very little to go on, and therefore it is likely that there is no clear answer to this question. Nonetheless, motivated by a renewed appreciation for the charge-transfer nature of the H bond, and by the recent XAS, XRS, and XES experiments whose interpretation relies to a great extent on the electronic structure of liquid water, in this paper we consider an electronic structure-based definition of the H bond. Such an idea very recently appeared in a paper by Fernández-Serra and Artacho.¹²⁰ They performed an *ab initio* molecular dynamics simulation of liquid water, characterizing H bonding by the electronic bond order between intermolecular pairs of H and O atoms. The distribution of such bond orders is double peaked, and as above the minimum allows for a natural H-bonding cutoff.

Our approach is related but different, in that we want to see if an electronic structure-based definition can be used within the context of *classical* simulation models. To this end we perform a classical simulation of SPC/E water, extract a large number of close-by dimers, perform *ab initio* calcula-

tions on each of these dimers, and characterize H bonding by the electronic occupancy of the σ_{OH}^* orbital, as suggested by Weinhold and co-workers. We next determine which of the many possible pairs of distance and angle variables can provide the best map between occupancy and geometry. For this particular pair (which turns out to be r and ψ —see Fig. 1), this map is used in a subsequent simulation to calculate the distribution of occupancies for all dimers. As above, this distribution is double peaked, yielding a natural occupancy cutoff between H-bonded and non-H-bonded pairs of molecules. This occupancy cutoff corresponds (through the map) to a two-dimensional contour in distance-angle space, which turns out not to be very different from the PMF contour we obtained in the same space. The occupancy cutoff yields 3.4 H bonds per molecule.

Finally, within the classical SPC/E simulation, we use each of the H-bonding definitions discussed above to calculate the time-correlation function (TCF) of the H-bond number fluctuations. The TCFs for most definitions are similar, with a rapid initial drop on the time scale of 70–80 fs, followed by a slower decay with a time constant of about 0.8–0.9 ps. This latter value is the characteristic time for making and breaking H bonds in liquid water (for the SPC/E model), and as discussed elsewhere⁷⁶ is somewhat shorter than the value obtained from ultrafast vibrational spectroscopy experiments. In this context we have also calculated the occupancy fluctuation TCF, which shows features very similar to the frequency fluctuation TCF,⁷⁶ including an oscillation at about 135 fs corresponding to the intermolecular H-bond stretch. This similarity is, in fact, quite natural, since the occupancy and frequency are thought to be highly correlated.⁹⁷

The outline of the paper is as follows. In Sec. II we discuss various statistical-mechanical definitions of the H bond based on classical molecular dynamics simulations. In Sec. II A we describe the simulation procedure we have employed. We discuss the energetic definition in Sec. II B. The various geometric definitions, from the simple distance-only definitions to the more complicated distance-angle definitions, are discussed in Secs. II C and II D, respectively. In Sec. III we discuss our electronic structure-based H-bond definition. We discuss the dynamics of the H-bond network in terms of various TCFs in Sec. IV. We present our conclusions in Sec. V.

II. STATISTICAL-MECHANICAL HYDROGEN-BOND DEFINITIONS

The main goal of this section is to use classical molecular dynamics simulations to obtain 2D PMFs for different distance-angle pairs, and from each of these PMFs to develop a H-bond definition. For completeness we also consider the usual energetic and distance-only definitions.

A. Simulation procedure

Classical molecular dynamics (MD) simulations were performed in the *NVE* ensemble using the SPC/E empirical pair potential.¹¹⁸ Our simulation box contained 128 molecules and the size of the box was chosen to give the number

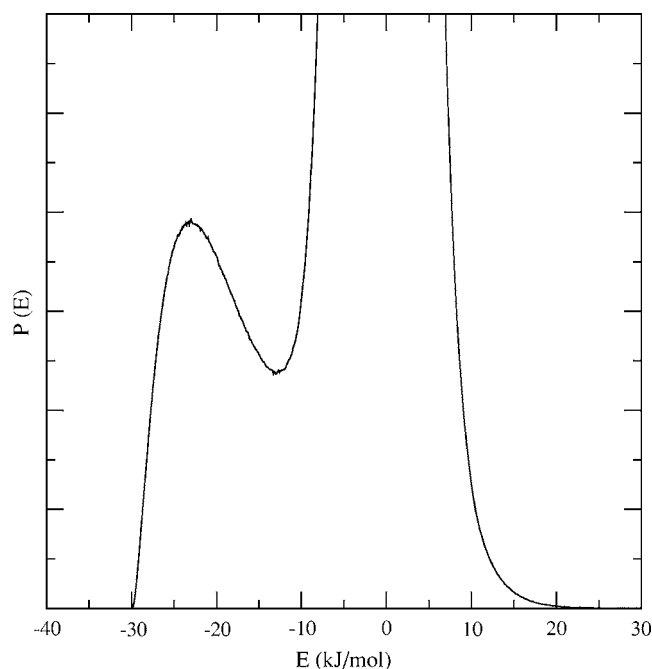


FIG. 2. The distribution of pair energies at 300 K.

density of water at 300 K ($3.32 \times 10^{28} \text{ m}^{-3}$).² We used periodic boundary conditions, and approximations to the Ewald sum were employed to take into account the long-range contributions to the electrostatic interactions.¹²¹ Rotations were treated using quaternions,¹²² and the equations of motion were integrated using the leap-frog algorithm¹²³ with a time step of 1 fs. The system was equilibrated to 300 K by rescaling the velocities of the particles.

B. Energetic definition

We first examine the energetic definition,^{77,80,81,103,104} by calculating (with the SPC/E model) the potential energy of every pair of water molecules in our simulation. The distribution of these pair energies (Fig. 2) shows a minimum at -12.9 kJ/mol , which is lower than the value of about -10 kJ/mol determined earlier for the ST2, TIP4P, and SPC water models.^{4,102–104} However, we have used a different water model, namely, the SPC/E model, and moreover we have included the Ewald sum in our simulation (though not in the evaluation of the pair energies), and therefore it is not surprising that our minimum has shifted. We define two water molecules to be H bonded if their interaction energy is less than this cutoff value of -12.9 kJ/mol . Using this definition, for each molecule we can specify the number, n , of H bonds it participates in. The average number of H bonds, $\langle n \rangle$, and the variance of the number of H bonds, $\langle \delta n^2 \rangle$, are 3.2 and 0.72, respectively, as shown in Table I.

C. Distance-only definitions

1. R definition

The simplest H-bond definition involves only the O–O distance, R .^{105,106} The O–O radial distribution function is shown in Fig. 3, and the minimum at 3.30 \AA was taken to be the H-bond cutoff. With this definition $\langle n \rangle = 4.3$, which is of

TABLE I. Summary of H-bond statistics for various definitions. For each definition are listed the relevant cutoff, the average number of H bonds per molecule, $\langle n \rangle$, the variance of these H-bond number fluctuations, $\langle \delta n^2 \rangle$, the fraction of molecules that are double donors, f_{DD} , and the rms deviation between the actual and fitted occupancy.

Definition	Cutoff	$\langle n \rangle$	$\langle \delta n^2 \rangle$	f_{DD}	$\text{rms} \times 10^3$
E	$E = -12.9 \text{ kJ/mol}$	3.2	0.72
R	$R = 3.30 \text{ \AA}$	4.3	0.84	...	5.9
r	$r = 2.41 \text{ \AA}$	3.7	0.56	0.83	3.2
$R-\beta$	$W = 1.23kT$	3.6	0.60	0.77	3.3
$r-\alpha$	$W = 0.58kT$	3.6	0.59	0.80	3.1
$r-\gamma$	$W = 1.20kT$	3.6	0.56	0.78	2.2
$r-\psi$	$W = 0.82kT$	3.2	0.78	0.63	1.5
$r-\psi$	$N = 0.0085$	3.4	0.67	0.70	...

course simply the coordination number of the first solvation shell. As discussed earlier, this definition is not very restrictive, and, in fact, counts some pairs of molecules to be H bonded that at least intuitively should not be. It is interesting to decompose $g_{OO}(R)$ in terms of the contributions from the nearest oxygen, the second-nearest oxygen, etc., as is shown in the figure. The difference in the positions of these sub-peaks highlights the significant amount of disorder in liquid water.

2. r definition

As discussed earlier a more reasonable distance-only definition involves the H–O intermolecular distance r . $g_{OH}(r)$ is shown in Fig. 4. Taking the position of the first minimum at $r = 2.41 \text{ \AA}$ to be the cutoff, every intermolecular H–O pair in the liquid is either H bonded (if r is less than the cutoff) or not H bonded (if r is greater than the cutoff). Thus we find that $\langle n \rangle = 3.7$, as shown in Table I. As above it is interesting to decompose the first peak into the contributions from the

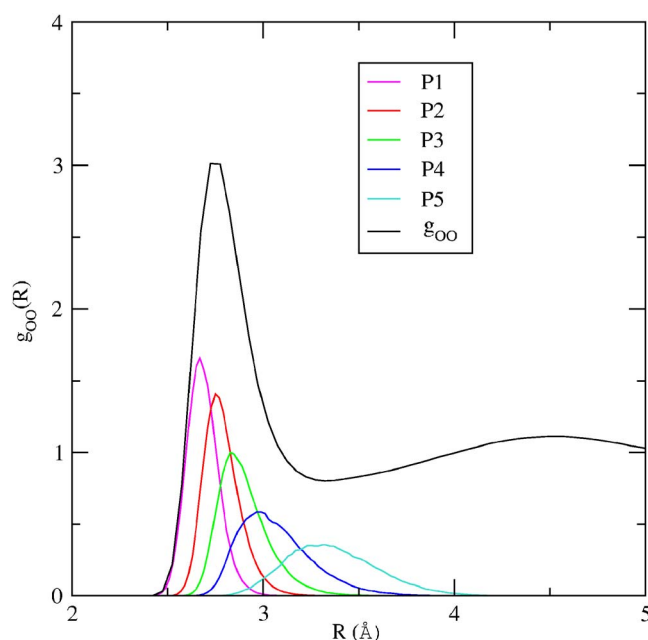


FIG. 3. The O–O radial distribution function, $g_{OO}(R)$. Also shown are the distributions of the first five nearest neighbors (P1 refers to the nearest neighbor, P2 to the second, and so on).

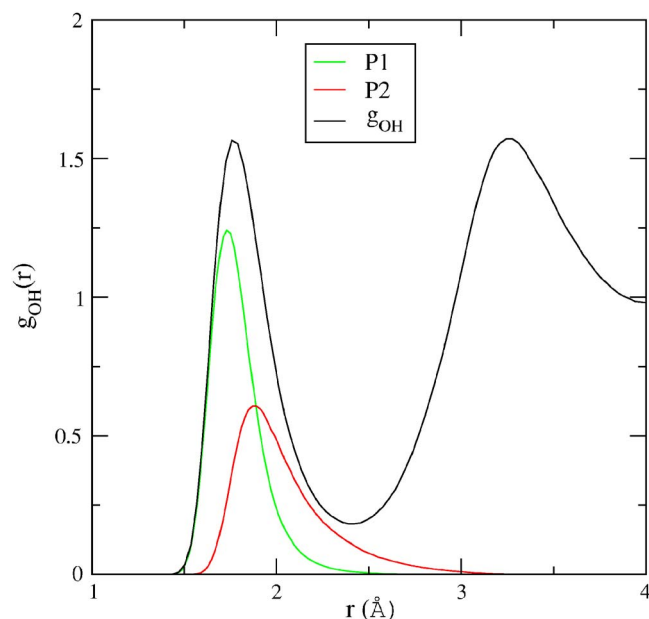


FIG. 4. The O-H radial distribution function, $g_{\text{OH}}(r)$. Also shown are the distributions of the nearest and second-nearest neighbors, P1 and P2, respectively.

nearest H (on a different molecule) to a given O, and the second-nearest H, as shown in the figure. Again this shows the significant disorder in the liquid. It is important to emphasize the point that even though the underlying water model has a symmetric charge distribution on each of its molecules, because of the statistical disorder in the liquid the H bonds themselves are asymmetric, in the sense that one of the two donor (or acceptor) H bonds is invariably significantly longer than the other. Thus simple water models with symmetrical fixed-charged molecules, while certainly an oversimplification of real water, are compatible with the existence of asymmetrical H bonds, as seemingly implied by the recent x-ray experiments.^{36,43,45}

With this H-bond definition we can classify molecules as double donors (both H atoms are involved in one or more H bonds), single donors (one H atom is involved in one or more H bonds), or nondonors. Of particular interest is the fraction of the molecules that are double donors, f_{DD} ; for this definition $f_{\text{DD}}=0.83$, as shown in Table I.

D. Distance-angle definitions

As described in the Introduction, each of the above distance-only definitions has been extended by focusing on one of the two angles θ or β in Fig. 1. Of the four possible distance-angle pairs, only two are convenient for our 2D PMF analysis, because only two (R and β , and r and θ) describe polar coordinate systems. Therefore we focus only on these two (for the latter we consider α , the complement of the angle θ , instead of θ itself—see Fig. 1). These two definitions focus on the relative orientation of the OH of the donor and the O of the acceptor. Alternatively, from an electronic structure or chemical point of view, one might also consider the relative orientation of the donor H with respect to the electron distribution of the acceptor O.^{109–111} Two relevant such angles, γ and ψ , are also shown in Fig. 1. γ is the

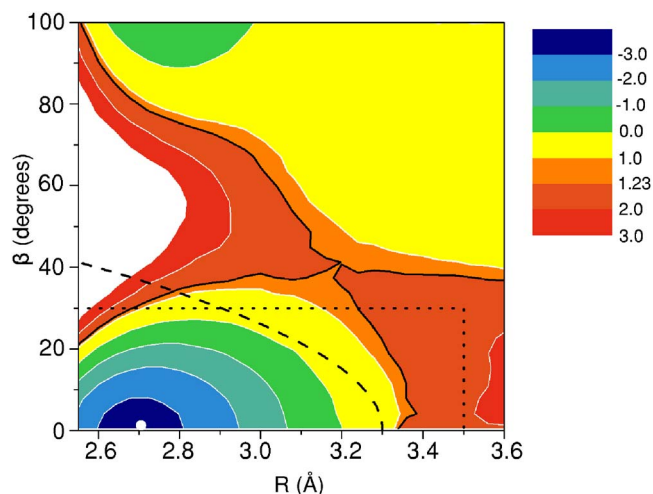


FIG. 5. Contour plot of $W(R, \beta)$ (at 300 K). The contours in the legend have units of kT . The global minimum is shown by the white dot. The contour at $1.23kT$ (black line) passes through the saddle point. Also shown is the rectangular H-bonding cutoff (dotted line) of Luzar and Chandler (Refs. 78 and 79) and the parabolic H-bonding cutoff (dashed line) of Wernet *et al.* (Ref. 36).

angle that the intermolecular O-H ray makes with the extension of the bisector of the acceptor molecule, and ψ is the angle this ray makes with the out-of-plane ray \hat{z} of the acceptor molecule. Note that this out-of-plane ray corresponds to the orientation of the out-of-plane p_z orbital on the acceptor molecule. In this section we also consider r - γ and r - ψ pairs, both of which describe polar coordinate systems.

1. R-beta definition

First we consider the R - β pair. Recall that the radial distribution function $g_{\text{OO}}(R)$ can be defined by the ratio of the average number of O atoms in a shell between R and $R+dR$ from a given O atom, to the same number if the molecules were noninteracting.¹²³ The latter number is of course $\rho 4\pi R^2 dR$, where ρ is the molecular density. To define the angle β we choose one of the O-H rays from the O atom at the origin to be the z axis for the polar coordinate system. By analogy, then, we define $g(R, \beta)$ to be the ratio of the average number of O atoms in a shell between R and $R+dR$ from a given O atom if the relevant angle is between β and $\beta+d\beta$, to the same number if the molecules were noninteracting. In this case the latter number is $\rho 2\pi \sin \beta d\beta R^2 dR$.

We then define the PMF

$$W(R, \beta) = -kT \ln g(R, \beta), \quad (1)$$

contours for which (from the MD simulation) are shown in Fig. 5. The plot shows a minimum at about $R=2.7$ Å and $\beta=0^\circ$, and a saddle point of about $1.23kT$ at about $R=3.2$ Å and $\beta=40^\circ$. As discussed in the Introduction the lines of steepest ascent from the saddle point would provide a convenient dividing surface between the minimum (H-bonded states) and non-H-bonded states. Alternatively we can consider the dividing surface to be the branch of the equipotential that passes through this saddle point and encircles the minimum, which is shown as the black line in the figure. The difference between these two definitions involves

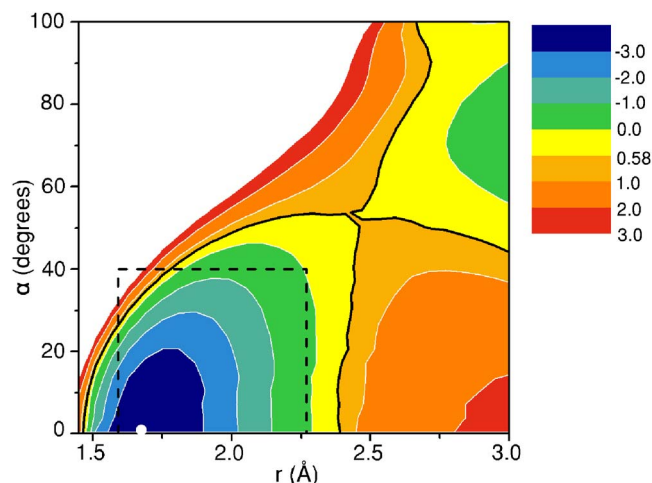


FIG. 6. Contour plot of $W(r, \alpha)$. The contours in the legend have units of kT . The global minimum is shown by the white dot. The contour at $0.58kT$ (black line) passes through the saddle point. Also shown is the rectangular H-bonding cutoff (dashed line) of Kuo and Mundy (Ref. 117).

configurations with free energies at least $4kT$ above the minimum, which therefore are not very probable, implying that these differences are not very important. This equipotential dividing surface was then used in a subsequent simulation to determine the average and variance of the number of H bonds per molecule, with the results of 3.6 and 0.60, respectively. The former is quite a bit smaller than that for the R definition of 4.3, as discussed earlier. The fraction of double donors for this definition is $f_{DD}=0.77$.

Others have also considered dividing surfaces for this pair of distance and angle variables. For example, Luzar and Chandler^{78,79} considered a rectangular dividing surface, with $R=3.5$ Å and $\beta=30^\circ$. This rectangle is also shown in Fig. 5, and gives a number of H bonds per molecule of 3.6. In concert with their XAS and XRS studies, Wernet *et al.*³⁶ proposed a different dividing surface, given by

$$R = (3.3 - 0.00044\beta^2)\text{Å}, \quad (2)$$

where β is in degrees. This parabola is also shown in Fig. 5, and yields 3.3 H bonds per molecule.

2. r - α definition

In a completely analogous manner we also consider the r - α pair (see Fig. 1), the 2D PMF for which is given in Fig. 6. For this pair the equipotential that passes through the saddle point is at about $0.58kT$. Using this equipotential as a cutoff we obtain 3.6 H bonds per molecule, and $f_{DD}=0.80$. For the same pair of coordinates Kuo and Mundy defined a rectangular H-bonding region, with 1.59 Å $< r < 2.27$ Å and $\alpha < 40^\circ$, which is also shown in Fig. 6. This definition gives $\langle n \rangle = 3.2$ H bonds per molecule.

3. r - γ definition

The angle γ , shown in Fig. 1, is the angle between the extension of the HOH molecular bisector of the acceptor molecule, and the intermolecular O–H ray. Similar to before, $g(r, \gamma)$ is defined to be the ratio of the average number of H atoms in a shell between r and $r+dr$ from a given O atom if

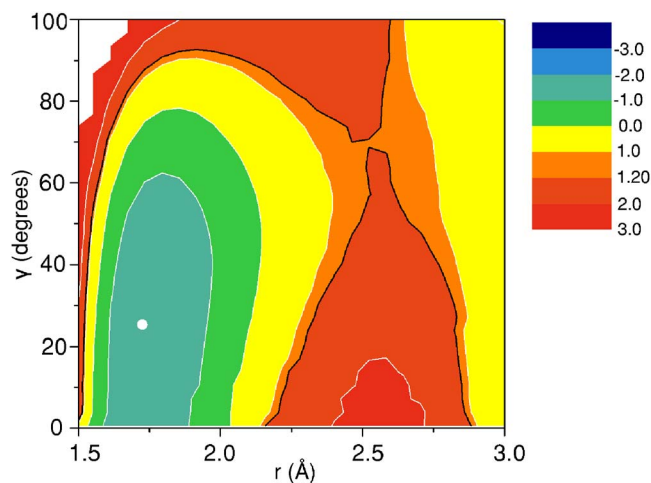


FIG. 7. Contour plot of $W(r, \gamma)$. The contours in the legend have units of kT . The global minimum is shown by the white dot. The contour at $1.20kT$ (black line) passes through the saddle point.

the relevant angle is between γ and $\gamma+d\gamma$, to the same number if the molecules were noninteracting. In this case the latter is $\rho 2\pi \sin \gamma d\gamma r^2 dr \times 2$ (the factor of 2 comes about since there are two H atoms per molecule). The PMF for this definition is shown in Fig. 7; the equipotential passing through the saddle point is at about $1.20kT$. The equipotential cutoff definition gives 3.6 H bonds per molecule, and $f_{DD}=0.78$.

4. r - ψ definition

The last angle that we studied is ψ , the angle between the intermolecular O–H vector and the out-of-plane vector on the acceptor molecule, as shown in Fig. 1. Note that $0^\circ \leq \psi \leq 180^\circ$, but since the resulting PMF is symmetric about 90° , we only show the contours for $0^\circ \leq \psi \leq 90^\circ$. The 2D PMF for this pair is shown in Fig. 8. The equipotential passing through the saddle has a value of about $0.82kT$. The number of H bonds per molecule with this definition is 3.2,

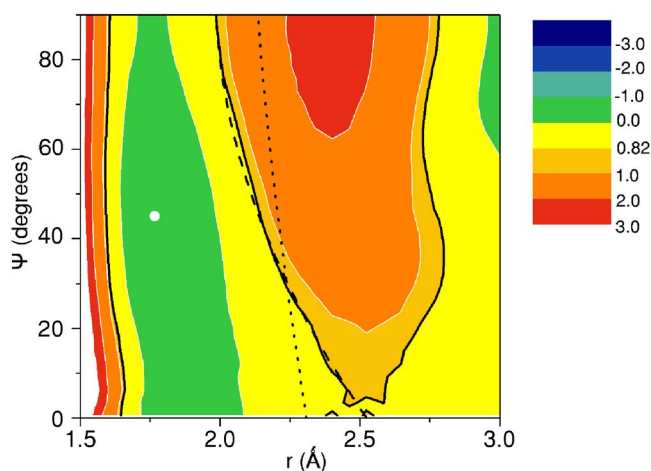


FIG. 8. Contour plot of $W(r, \psi)$. The contours in the legend have units of kT . The global minimum is shown by the white dot. The contour at $0.82kT$ (black line) passes through the saddle point. Also shown is a quadratic approximation (dashed line) to this equipotential (as discussed in the text), and the curve (dotted line) representing the cutoff for an occupancy of 0.0085.

and $f_{DD}=0.63$. For later use we note that the equation for the equipotential contour cutoff is given approximately, for $0^\circ \leq \psi \leq 90^\circ$, by

$$r = (2.52 - 0.011\psi + 0.000\,057\psi^2)\text{\AA}, \quad (3)$$

where ψ is in degrees. For $90^\circ \leq \psi \leq 180^\circ$ in the above ψ should be replaced by its complement.

E. General remarks

Of the definitions discussed the r - ψ and pair energy are the most restrictive in that the average number of H bonds (3.2) is smallest in these two cases. The geometric definitions in r and various angles are more restrictive than the r -only definition. In general the differences in the number of H bonds among these definitions are not large, and all definitions give the average number of H bonds to be between 3 and 4 per molecule. The variances for these definitions are between 0.56 and 0.84, consistent with the fact (from simulation) that there are molecules in the liquid with anywhere from one to five H bonds. The fraction of double donors ranges from 0.63 to 0.83; thus a majority of the molecules are double donors.

At this point we might reiterate that any one- or two-variable definition of H bonding necessarily provides an incomplete geometric (and hence energetic) description, since six variables are required to specify completely the relative positions of two rigid water molecules. As such, these incomplete descriptions can admit configurations as being H bonded that do not make physical sense. For example, the R definition might consider two molecules to be H bonded even if no H atom is in the region between the two oxygens. Or the R - β definition can admit configurations as being H bonded when *two* H atoms are in the region between the two oxygens. For the most part one is spared from these problems since for reasonable simulation models these unphysical configurations are quite unlikely to occur. In any case, any residual problems are a necessary consequence of a reduced but simpler description.

Each of the global minima in Figs. 5–8 is shown as a white dot. One sees in all cases that the values of the angle at the minimum and at the saddle point differ considerably. While it would most likely be an oversimplification to assume that pairs of molecules break H bonds by moving from the minimum to the saddle point in any one of the fixed PMFs in Figs. 5–8, nonetheless, the above feature of the PMFs does suggest that H-bond breaking and molecular rotation are intimately connected.⁵⁵ In this context it would be interesting to plot trajectories of pairs of H-bonded molecules in one or more of these 2D spaces to see to what extent these trajectories cross our cutoff contours near the saddle points.

The PMFs for R - β and r - α are qualitatively different from those for r - γ and r - ψ . For the former the PMFs have deep minima, saddle points about $4kT$ above the minima, and if the intermolecular geometry is significantly bent ($\beta > 40^\circ$ or $\alpha > 50^\circ$) one does not form an H bond, independent of distance. On the other hand, for the PMFs based on acceptor angles γ and ψ , the minima are much shallower and broader,

such that H bonds can exist for $\gamma < 90^\circ$ and for *any* value of ψ , and saddle points are less than $2kT$ above the minima.

III. ELECTRONIC STRUCTURE HYDROGEN-BOND DEFINITION

In the previous section we have shown how for a given pair of intermolecular distance and angle coordinates, from the 2D PMF one can arrive at an unambiguous H-bond definition. We have considered a number of different pairs, and for each pair we obtain a different number of H bonds per molecule. One then wonders: Is there any particular reason to favor one pair over another? More generally, different experiments may be sensitive to different aspects of H bonding, and hence different definitions might be appropriate for different experiments. In particular, neutron (and to a lesser extent x-ray) diffraction measures nuclear positions, and so for these experiments a geometric criterion may make the most sense. On the other hand, XAS, XRS, and XES experiments are sensitive to the electronic structure of the liquid, and so for these experiments an electronic structure-based definition may make more sense. This would then lead one to ask: Are electronic structure-based definitions and geometric definitions compatible? In this section we make a first pass at answering these two questions.

Proponents of the charge-transfer nature of the H bond have proposed different electronic structure methods for its description.^{92–96,120} We have chosen to use the natural bond orbital (NBO) donor-acceptor picture of H bonding of Weinhold and co-workers.^{93–96} From a NBO point of view the H bond is formed from the interaction of the lone-pair orbitals on the O atom of one water molecule (the electron donor) with a σ_{OH}^* antibonding orbital situated on the other water molecule (the electron acceptor). In the monomer the lone-pair orbitals are filled, while the σ^* orbitals are empty. For a H-bonded dimer, however, the interaction between these orbitals leads to electron transfer from the donor to the acceptor. Therefore a suitable parameter to quantify the degree of H bonding in this case is the electronic occupancy N of the σ^* orbital.

To explore this idea for liquid water we performed electronic structure calculations on 10 000 dimers selected from our classical MD simulation. To minimize the correlation between these dimers, our selection algorithm was as follows: we chose a water molecule at random after every 50 fs interval; one of the H atoms of the selected water molecule was randomly chosen; and the water molecule with its O atom closest to this H was selected to form the dimer. The NBO analysis was carried out within the GAUSSIAN98 software package¹²⁴ using density functional theory with the B3LYP exchange-correlation functional^{125–127} and the aug-cc-PVDZ basis set, keeping all intramolecular bond lengths and angles at their SPC/E geometries. These dimer calculations led to a distribution of occupancies, spread between 0 and 0.06, with an average occupancy of 0.021. There is indeed a substantial amount of electron transfer for a neutral dimer!

We would like to perform similar calculations for all dimers in the liquid, at each time step in the MD simulation, in much the same way that we calculated binding energies

for each dimer in Sec. II B, but this goal is of course unobtainable. Keeping the intramolecular degrees of freedom fixed for both molecules in a dimer, there are a total of six variables (five angles and one distance) needed to specify the relative geometry. Since the electronic structure depends only on this geometry, these six variables uniquely determine the occupancy N . However, perhaps N is only strongly dependent on some subset of these variables, meaning that one might be able to find an approximate “map” from this subset to N . Suppose further that this subset consists of just one or two variables, examples of choices for which are discussed above. Thus our first objective is to determine which of the one- or two-variable descriptions used above can provide the best map (the one with the smallest rms deviation of the fitted occupancy to the actual occupancy).

For example, plotting N versus SPC/E binding energy E for these 10 000 dimers leads to so much scatter that we did not attempt to find a reasonable fitting function. Thus the binding energy is not highly correlated with the occupancy, and so this description will not provide a good map. Plotting N as a function of R for these 10 000 dimers, an exponential produces a reasonable fit, and the resulting rms deviation is 5.9×10^{-3} . The same is true using r instead of R , and the rms deviation is 3.2×10^{-3} . For each of the two-variable possibilities we assume that N is a product of two functions—one that depends on the distance variable, and one that depends on the angle variable. For the distance function we choose an exponential, and for the angular function a quadratic seems to be adequate. Thus for each pair we perform a global four-parameter fit, and the rms deviations are shown in Table I. Of all the possibilities, one sees that the rms deviation is smallest for the r - ψ pair, which (0.0015) is over a factor of 10 smaller than the average occupancy of 0.021. For that pair the map is

$$N(r, \psi) = \exp(-r/0.343 \text{ \AA})(7.1 - 0.050\psi + 0.00021\psi^2), \quad (4)$$

where ψ is in degrees, and $0^\circ \leq \psi \leq 90^\circ$ (for $90^\circ \leq \psi \leq 180^\circ$ ψ should be replaced by its complement). Thus for a given r the occupancy is highest when $\psi=0^\circ$. Figure 9 shows a scatter plot of $N(r, \psi)$ versus the actual occupancy N for each dimer. The residuals do not appear to be systematic.

It is perhaps surprising that the best map comes from the r - ψ pair, and not, for example, from the R - β or r - α pairs widely used in H-bonding definitions. However, from an electronic donor-acceptor point of view, the orientation of the donor orbitals would be at least as important as that of the σ^* acceptor orbital, since the donor orbitals are more directional and the acceptor orbital is more spherical. Along these same lines one can rationalize why the r - ψ pair is better than, for example, the r - γ pair—electron-donating effectiveness comes from the directional properties of the donating orbitals, which in this case are due to the p_z orbital (from which direction ψ is defined).

Armed with a map that takes us from dimer geometry to orbital occupancy, from snapshots of our MD simulation we can now calculate an approximate distribution of occupancies for all dimers in the liquid, as shown in Fig. 10. As anticipated, this distribution has two peaks. The peak at

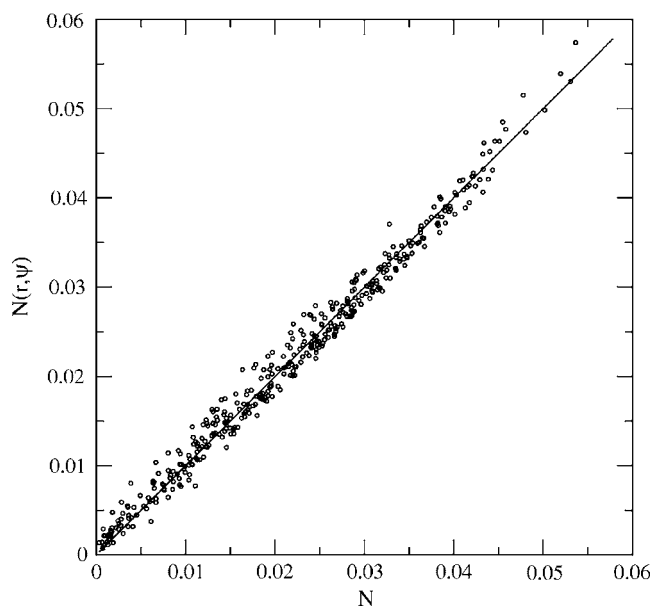


FIG. 9. Fitted occupancy $N(r, \psi)$ vs occupancy N from *ab initio* calculations. If the correlation were perfect all points would lie on the diagonal (solid line).

small N corresponds to the many weakly interacting dimers, while the peak at about 0.02 corresponds to those nearby dimers with significant electron transfer. This distribution has a minimum at $N=0.0085$, and in the same spirit as before we can propose this value as a cutoff between H-bonded and non-H-bonded molecules. Thus for every intermolecular pair of O and H atoms, we use the map to determine the occupancy, and if the value is greater than 0.0085 the atoms are involved in a hydrogen bond. Using this criterion gives 3.4 H bonds per molecule, and $f_{DD}=0.70$.

From the map the cutoff at 0.0085 leads to a 2D cutoff in r - ψ space, which is shown as the dotted line in Fig. 8. This

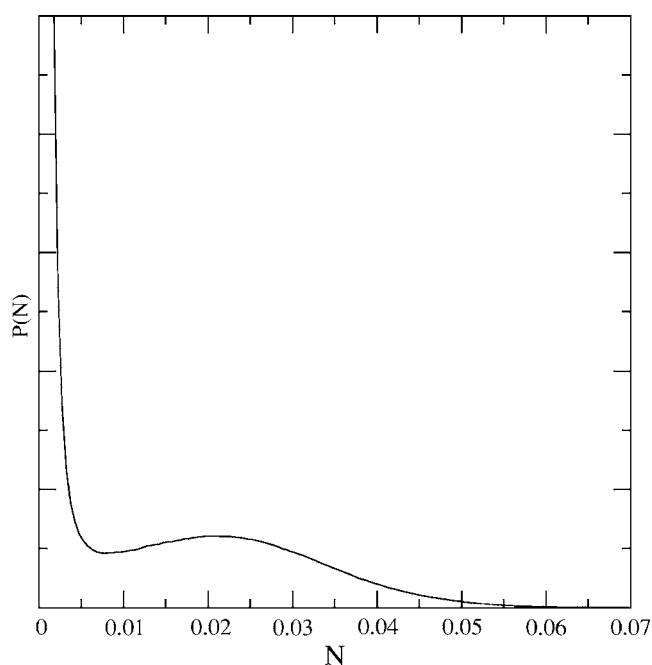


FIG. 10. The distribution of occupancies for the liquid, using Eq. (4) to estimate the occupancy. The minimum is at $N=0.0085$.

contour is qualitatively similar to the equipotential contour from the PMF. In this sense the electronic structure and PMF definitions for the r - ψ pair are reasonably compatible. Note, however, that the numbers of H bonds for these two definitions differ by about 0.2.

IV. HYDROGEN-BOND NUMBER FLUCTUATION DYNAMICS

In the above we have discussed various H-bonding definitions for liquid water, and for each have calculated the average number of H bonds per molecule. Of course as a result of equilibrium molecular dynamics, the number of H bonds a given molecule participates in changes with time. The simplest way to characterize these H-bond number fluctuations is with the following (normalized) time-correlation function (TCF):

$$C(t) = \langle \delta n(t) \delta n(0) \rangle / \langle \delta n^2 \rangle, \quad (5)$$

where $\delta n(t) = n(t) - \langle n \rangle$. From the simulation we have calculated this TCF for each of the many H-bonding definitions discussed above. We find that all of the geometric definitions lead to qualitatively similar results; for simplicity we show only a few representative TCFs (using the r -only definition, the r - ψ definition with the PMF cutoff, and the r - ψ definition with the occupancy cutoff) in Fig. 11. All the TCFs that were calculated show an initial fast decay followed by a slower decay. The initial fast decay for the energetic definition is on a time scale of about 40 fs, while for the other definitions it occurs in between 70 and 80 fs. All definitions produce a long-time approximately exponential relaxation with a time constant of between 0.8 and 0.9 ps. Evidently, then, this is the slowest time for local H-bond rearrangement in liquid water (within the SPC/E model). Note, however, that since free energy barriers separating states with different H-bond numbers are not sufficiently high, H-bond number fluctuations do not describe a Markovian kinetics problem, implying that the long-time decay of the TCF is not strictly exponential. In fact, Luzar and Chandler have discussed the nonexponential decay of a related time-correlation function in terms of an interplay between H-bond dynamics and diffusion.^{78,79}

As discussed in the Introduction, recent ultrafast vibrational spectroscopy experiments have shed considerable light on H-bonding dynamics in liquid water. These experiments do not measure the above TCF directly, rather they measure a complicated nonlinear TCF of fluctuating transition dipoles and vibrational frequencies.¹²⁸ In the ideal world, unfortunately not realized for liquid water,^{74,76} these experiments would, in fact, measure the two-point frequency TCF. We and others have argued that the long-time decay of this frequency TCF is related to the H-bond rearrangement time. Although one cannot obtain this frequency TCF directly from experiment, one can calculate the full nonlinear echo observable for a given simulation model, and compare with experiment.⁷⁶ This comparison shows that the long-time spectroscopic properties are reasonably well described by the SPC/FQ model,¹²⁹ whose long-time decay of the frequency TCF occurs in about 1.5 ps.⁷³ From this we conclude that the

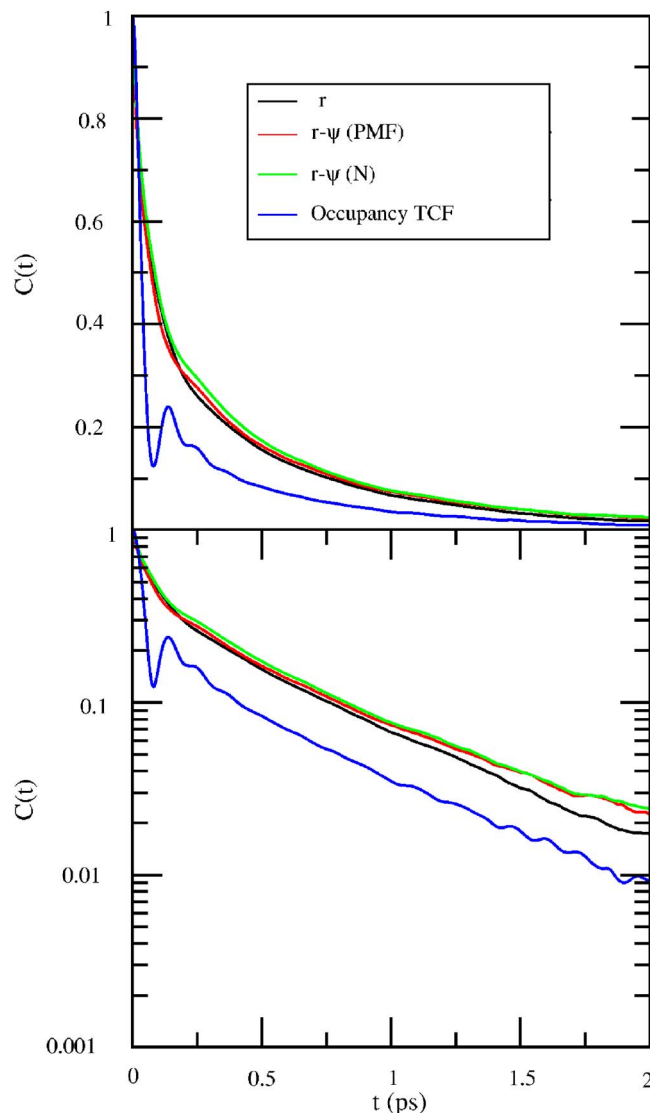


FIG. 11. H-bond number fluctuation TCF for three H-bond definitions: the r -only definition, the r - ψ definition with the PMF cutoff, and the r - ψ definition with the occupancy (N) cutoff. Also shown is the normalized occupancy TCF from the liquid simulation using Eq. (4) to determine the occupancy.

actual time for H-bond rearrangement in liquid water is about 1.5 ps, indicating that such relaxation in the SPC/E model is somewhat too fast.

The ultrafast peak shift experiments^{18,66} also show interesting dynamics at short times. In particular, the peak shift has an underdamped oscillation with a period of about 150–170 fs, which has been attributed to the intermolecular H-bond stretch.^{22,27,66} The H-bond number fluctuation TCFs do not show this oscillation, since the H-bond definitions involve sharp cutoffs. We can also consider a related TCF, the occupancy fluctuation TCF. Inasmuch as occupancy and frequency are expected to be highly correlated,⁹⁷ one might guess that the occupancy TCF, which does not involve any discontinuities, would also show the short-time oscillation observed in the peak shift and in the (theoretical) frequency TCF. Thus we calculated the normalized occupancy TCF for each OH bond in the simulation, and then averaged over all bonds. The results are shown in Fig. 11. One indeed sees a

strong underdamped oscillation with a period of about 135 fs, in qualitative agreement with the experimental period.^{18,66}

V. CONCLUDING REMARKS

Geometric criteria for H bonding in liquid water have been discussed by many. Often these criteria involve one distance and one angle for a given pair of molecules. For each of a number of such distance-angle pairs we have presented a systematic method to determine H-bonding cutoffs. Our approach involves the construction of 2D PMFs for each distance-angle pair. The H-bonding cutoff separating H-bonded from non-H-bonded configurations is given by the equipotential contour that passes through the saddle point. Applying this algorithm for a number of distance-angle pairs gives between 3.2 and 3.6 H bonds per molecule.

We have also made an attempt to understand and define H bonds in liquid water from an electronic structure perspective. We have used the NBO definition of Weinhold and co-workers in which the degree of H bonding between two molecules is given by the occupancy, N , of the relevant antibonding σ_{OH}^* orbital. We showed that, in fact, this occupancy depends strongly on only two (out of a possible six) geometric variables, r and ψ , and a reasonably accurate map between these two variables and N allows us to calculate N (approximately) for all dimers in the liquid. From the distribution of these occupancies we arrive at an occupancy cutoff, and hence at an electronic structure-based definition of H bonding in liquid water, which yields 3.4 H bonds per molecule. The concomitant 2D cutoff in r - ψ space is qualitatively similar to the cutoff obtained from the PMF method. The similarity of these two curves, from two quite different approaches, provides some support for the idea that appropriately chosen geometric and electronic structure-based definitions of H bonds may be compatible. We can then suggest either of these H-bond definitions for the r - ψ pair as an alternative to the many others that have been proposed. To this end we note that simple analytical formulas for the cutoffs appear in Eq. (3) and, together with a cutoff value of $N=0.0085$, Eq. (4).

Our electronic structure-based definition leads to a concept of H bonding in liquid water somewhat different from the conventional one. That is, traditionally one focuses on the donor OH orientation, whereas our definition focuses on the acceptor orientation. In particular, we find that one can form a H bond for *any* value of the angle ψ , although for this to occur the intermolecular O-H distance must be closer when $\psi=90^\circ$ than when $\psi=0^\circ$. The r - ψ definition, like other distance-angle definitions, does not exclude some dimer configurations from being considered H bonded that intuitively should be excluded. However, for reasonable simulation models such configurations are unlikely enough that this is not a problem in practice. We also might emphasize that our r - ψ definition that emanates from the electronic properties of H bonding, like the other geometric definitions, does not necessarily have direct implications for the energetics of H bonding.

Using our various H-bond definitions we have also cal-

culated the equilibrium H-bond number fluctuation TCF. All of the TCFs show roughly bimodal decay, with time scales of 70–80 fs and 0.8–0.9 ps. The latter corresponds to the time scale of local H bonding and hence structural rearrangement in liquid water (within the SPC/E model). Elsewhere⁷⁶ we have discussed the connection of these results to recent ultrafast spectroscopy experiments. The latter, together with theory, suggests that this local H-bonding relaxation time in real water is closer to 1.5 ps.

As discussed in the Introduction, it is important to emphasize that any definition of H bonding in liquid water is essentially arbitrary, and is not any more fundamental for the liquid than it is for gas-phase dimers. We have tried to make these definitions less arbitrary, by providing systematic prescriptions for obtaining them. The fact that different choices for the relevant geometric variables and a quite different electronic structure approach all lead to quite similar results for both the statics and dynamics of H-bond number fluctuations does perhaps suggest that these ways of considering H bonds in the liquid can be insightful.

Our results are consistent with the traditional idea that water is highly disordered, but with more or less tetrahedral local symmetry, with at least three H bonds per molecule, some of which are stronger than others, and a majority of water molecules are double donors. This is not the picture proposed by Wernet *et al.* on the basis of their XAS and XRS experiments.³⁶ Supporters of this latter picture could quite correctly point out that perhaps our electronic structure definition is not the best one for these experiments. They could also quite correctly point out that fixed-charge classical models such as SPC/E do not describe real water, and so the configurations we have used in our analysis are not representative. Regarding the latter, however, at this point it seems clear from Car-Parrinello and other *ab initio* MD studies,^{48,112,130} and from simulation models developed from first principles,¹³¹ that even models as simple as SPC/E make qualitatively correct structural predictions. Ultimately, resolution of issues such as these will probably come not from arguments about the semantics of H bonding, but rather from calculating experimental observables from microscopic configurations statistically generated from liquid-state simulation models, and indeed such calculations of XAS spectra for water have recently appeared.^{40,45,46}

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