Electrons and Hydrogen-Bond Connectivity in Liquid Water

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The network connectivity in liquid water is revised in terms of electronic signatures of hydrogen bonds (HBs) instead of geometric criteria, in view of recent x-ray absorption studies. The analysis is based on *ab initio* molecular-dynamics simulations at ambient conditions. Even if instantaneous threadlike structures are observed in the electronic network, they continuously reshape in oscillations reminiscent of the *r* and *t* modes in ice ($\tau \sim 170$ fs). However, two water molecules initially joined by a HB remain effectively bound over many periods regardless of its electronic signature.

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Water is an extremely intriguing liquid that continues to excite the interest of scientists in many disciplines. Many of its anomalous properties [1,2] originate in the hydrogen bonds (HBs) among water molecules [3,4]. The concept of a network liquid emerges naturally from this HB connectivity, an intuitive image that has provided interesting insights into the properties of water [1,5]. Direct structural information to characterize such network structure is hard to obtain experimentally. Diffraction techniques [6,7] offer radial distribution functions (RDFs) very naturally, but rely on reverse Monte Carlo techniques using force-field models to obtain further structural information [8]. Spectroscopic probes provide a rich source of complementary information. X-ray emission [9,10] and x-ray absorption [11–13] (XAS) spectroscopies explore the electronic states of the liquid right below and above the Fermi level, respectively. In particular, the work by Wernet *et al.* [13] has recently introduced an extremely interesting new component into the study of liquid water, by relating a pre-edge feature in the XAS spectra with broken HBs. The authors propose to determine connectivity by looking at an electronic-structure signature of the HBs. Their conclusion is daring: the average coordination in liquid water would be ~2 instead of the previously accepted value slightly under 4, displaying a filamentous picture, instead of the distorted, partly broken and fluctuating tetrahedral network described in so many papers before [6,7,14,15].

Is it right? This would be the wrong question to ask. The kind of network depends on the definition of the hydrogen bond, and furthermore, on deciding whether two given molecules in a given configuration are bonded or not. There is no direct physical HB observable and there is arbitrariness in the choice of what is actually measured. Instead, we address the question of how relevant the newly proposed network image is for the description of the liquid in the sense of the insights it offers. The conventional criterion [5] for HB is based on geometric considerations: an oxygen-oxygen distance within the first peak of the O-O RDF, and an upper critical bend angle α (see Fig. 1). This "geometric" definition is based on total energy considerations in contrast to the newly proposed "electronic" one. In this Letter we explore the adequacy of the newly proposed probe, including its time scale, virtually instantaneous as compared with atomic motions.

Electronic-structure calculations have been performed based on density-functional theory (DFT), within the generalized-gradient approximation [Becke-Lee-Yang-Parr (BLYP)] [16,17]. The SIESTA method is used [18,19] with a basis set of atomic orbitals at the double-ζ polarized level [20]. For liquid water at ambient conditions, *ab initio* molecular-dynamics (AIMD) simulations have been performed in the microcanonical ensemble, based on the DFT forces and the Born-Oppenheimer approximation. Further details are found in Ref. [15]. Approximate XAS spectra have been obtained for selected configurations (see below).

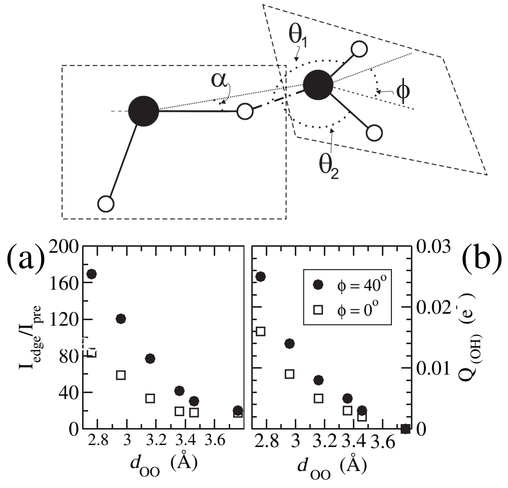

FIG. 1. XAS peak intensity ratio $I_{\mathrm{edge}}/I_{\mathrm{pre}}$ (a), and bond order Q_{OH} (b) versus intermolecular distance for two values of the flap, $\phi = 40°$ and $0°$, for the HB between an acceptor molecule and a clean (001) ice surface.

The pseudoatomic orbitals in the basis set have been transformed following the projector-augmented wave method [21] into all-electron atomic orbitals for calculating matrix elements. For our basis set, neglecting the very small intermolecular matrix elements was found to give an adequate approximation for the purposes of this Letter. The strong excitonic effect introduced by the attraction between the core hole and the excited electron is estimated in the $Z + 1$ approximation [22].

Notwithstanding the importance of the XAS experimental data for this and other purposes, the probe provides a rather indirect measure of the electronics of the hydrogen bond, not least because of the mentioned excitonic effect. This and other difficulties [23,24] (broadening, alignments) make it very difficult to obtain quantitative comparisons for the liquid phase. We find it more useful for our purposes to use a ground-state probe that we validate against XAS data in cleaner systems. This validation is two-sided. On one hand we test our chosen probe, on the other, we test the extent to which the XAS probe reflects the properties of the electronic ground state.

A very natural choice for describing electronic bonding within our method is bond order. In its simplest definition [25], the bond order between two atoms, 1 and 2, is $Q_{1,2} = \sum_{\mu}^{1} \sum_{\nu}^{2} \rho^{\mu\nu} S_{\nu\mu}$, where μ (ν) sums over the basis functions associated to atom 1 (2), and ρ and S are the density and overlap matrices, respectively. Bond orders depend on the choice of basis, and their arbitrariness has been described at length (see Ref. [26] and references therein). It is relative changes in that value that we use in this work, and these are shown below to be meaningful enough to support its conclusions. Mulliken's bond orders are compared with Mayer's [27], from which the same conclusions are drawn. We believe that any other electronic-structure signature of the bonding [26] would reflect the same physics.

There has been a controversy [28–31] on the covalence of the HB and on its bonding or antibonding character, which would seem to affect our choice of electronic probe. The electronic characteristics of the HB were nicely illustrated with maximally localized Wannier functions [30]. They can also be described in terms of an intramolecular polarization (rehybridization within the molecules) and intermolecular polarization or charge transfer (admixture of orbitals of different molecules), if using the language of single-molecule orbitals [32], or of atomic orbitals, in either mono- or multideterminantal wave functions [29]. The physics of the interactions behind the HB is, however, quite clear if one avoids the semantic problems that have been partly behind that controversy. In a typical HB there is an important electrostatic attraction that dominates the energetics [30]. In addition, there is a deformation of the electronic cloud around O's accepting a lone pair towards the donating H, in response to the field generated by the latter. There are other effects (e.g., quantum fluctuations of the protons) that are energetically less significant in principle, but could still be important for liquid water. They are beyond the scope of this Letter. The mentioned polarization of the lone pair happens at the expense of a slight contraction of the electron cloud involved in the O-H bond within the donor molecule, due to Pauli exclusion [30]. This last deformation is the one behind the antibonding character of the HB discussed in the literature [29]. However, the original deformation of the O's lone-pair towards the proton remains clearly bonding. In this study we thus concentrate on Q_{OH}, between the donor H and the acceptor O.

In order to compare XAS and Q_{OH} we have calculated XAS spectra for a four-layer (001) ice slab, with the surface molecules exposing nondonated protons (dangling HBs). Repeated slabs are separated by 15 Å of vacuum. An extra water molecule has been placed on top of one of the surface molecules, and its position has been varied. Figure 1 shows the XAS calculated for the donor surface molecule and Q_{OH} for that HB as a function of HB O-H distance for two different values of the flap angle, ϕ (see Fig. 1). $\phi \approx 40°$ corresponds to an ideal tetrahedral arrangement as in ice. A zero flap angle gives a rather unfavorable situation, since the proton faces midway between both lone pairs of O (in the nodal plane of the acceptor's HOMO orbital, of C_{2v}'s B_1 character), which partly inhibits the electronic deformation.

We focus on two distinctive features of the XAS spectrum directly related to the pre-edge observed in the experiments: (i) the relative intensity of the first and second peaks, related to edge and pre-edge features, and (ii) the energy difference between both peaks ΔE. The spectral intensity is taken from the Z approximation (initial state), while ΔE is obtained from the $Z + 1$ approximation, given its sensitivity to final-state effects; see discussion by Cavalleri *et al.* [22]. Figure 1 shows that $\phi = 0°$ produces an intensity ratio twice as large as $\phi = 40°$ for the same d_{OO}. This remarkable effect is closely reproduced by Q_{OH}, as well as the distance dependence. ΔE increases with distance in a similar manner (not shown), also well replicated by the bond order (the effect of the flap angle is less noticeable in this case). A detailed study of the dependence of Q_{OH} on intermolecular geometry in a water pair can be found in Ref. [33]. It is important to note that both magnitudes (XAS and Q_{OH}) agree in not displaying any obvious feature (discontinuity, zero, minimum) that would define a natural threshold for HB breaking. We will thus refrain from establishing an arbitrary criterion for the moment and explore what can be learned independent of it.

The Q_{OH}'s are then calculated in an AIMD simulation of liquid water for all water pairs within a first coordination shell, as defined by the first peak in the O-O RDF. The first point that becomes apparent is that every water molecule is mainly donating one strong HB, while the second bond order is 2.2 times weaker in average, partly supporting the one-dimensional network picture proposed in Ref. [13].

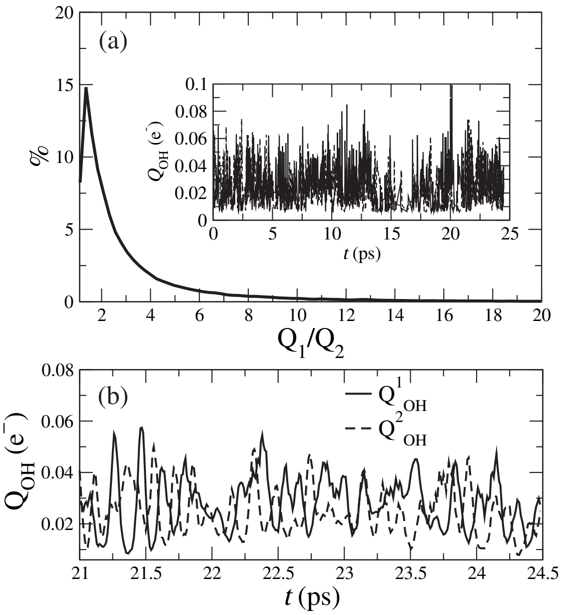

FIG. 2. (a) Distribution of strong to weak bond-order ratio in the liquid during a 25 ps AIMD run. (b) Evolution of the donating $Q_{\rm OH}$'s for a given molecule (zoom of the inset).

The asymmetry is, however, not extreme, as can be seen in the distribution of strong to weak bond-order ratio in Fig. 2.

Figure 2(b) shows a fragment of the time evolution of the $Q_{\rm OH}$ on the two donated HBs for a representative molecule (the complete trajectory is shown in the inset). The figure shows a clear oscillation with a period of $\sim$170 fs. It would correspond to the intermolecular *r* and *t* vibrations in ice (hindered rotation and translation) [34]. An intermolecular O-H under-damped oscillation with a period of $\sim$170 fs has been indeed directly observed in liquid water [35] using ultrafast infrared spectroscopy. The figure shows that the oscillation in $Q_{\rm OH}$ is more pronounced than what is expected from Fig. 2(a), with lower values 5 times smaller than the higher ones. It shows that an antiphase vibration of both donating HBs only accounts for part of the oscillation, the remaining part coming from the in-phase vibration that would weaken (strengthen) both donated HBs simultaneously. The figure also shows that a single HB survives many such extreme cycles before breaking (the average lifetime for a HB is a few ps) [5,33].

HBs with low enough values of instantaneous $Q_{\rm OH}$ are certainly contributing to the measured XAS pre-edge. The XAS probe is thus reflecting a very pronounced electronic effect, a swinging of the electron cloud of the lone pair following the "flapping" and stretching of HBs, which appears to XAS as if many HBs were broken. Considering the antiphase component, that behavior would give rise to a pulsating 1D filamentlike network image, relevant for *electron* dynamics. It is, however, irrelevant to the liquid dynamics, since it is apparent in Fig. 2 that the molecules in a HB are still effectively bound even when the electron deformation is very small. The inclusion of quantum fluctuations to the nuclear dynamics could even exaggerate the beating effect, since quantum and thermal fluctuations are comparable in scale (the zero point motion of a 170 fs oscillation is 12 meV).

Figure 3 shows the distribution of $Q_{\rm OH}$ for all the water pairs in the liquid with $r_{\rm OO} < 3.5$ Å, for two different definitions of bond order. In both cases there is a clear minimum at small values of the bond order, with $\sim$25% HBs below that threshold. It offers a natural criterion (albeit still arbitrary) for determining the presence of a HB, namely, $Q_{\rm OH} > Q_{\rm OH}^{\rm min}$ [36]. Interestingly, the width of the distribution for the HBs ($2\Delta Q_{\rm OH} = 0.030$, $\bar{Q}_{\rm OH} = 0.023$) is comparable to that for a single oscillating HB through its lifetime (the one in Fig. 2: $2\Delta Q_{\rm OH} = 0.026$, $\bar{Q}_{\rm OH} = 0.020$). This means that the very different HB strengths are not so much due to different configurations as the liquid flows (on the time scale of several ps, the HB lifetime) but remarkably related to these 170 fs vibrations.

After monitoring the electronic deformation as a signature for connectivity, we finish this study by assessing the effect of such deformation on the liquid structure itself. Having observed how the electronic cloud deforms in response to stretch and flap, it should be expected that the energetics would be affected by the flap, and so would the configurations visited in AIMD trajectories. In Fig. 4 the distribution of flap angles obtained from AIMD and two classical nonpolarizable models (SPCE and TIP5P) are compared [37]. The angles θ_1 and θ_2 (as defined in Fig. 1) within the first coordination shell are used to characterize both flap and twist. The distributions show clear differences. The main difference between SPCE and TIP5P is the fact that the latter puts negative charges around the center of the electron lone pairs, which induces a more realistic flap response. It is, however, exaggerated, since the polarization is static. AIMD distributions reflect both the preference for the tetrahedral geometry and the flexibility given by the dynamical response of the electron cloud. It has been argued [13,22,38,39] that, in spite of these differences, AIMD lines up with any force field so far to produce qualitatively wrong configurational sampling of liquid water. It is certainly true that there are clear shortcomings in our scheme (BLYP approximations for exchange and correlation, neglect of protonic quantum effects) as well as in others. What we propose here, how-

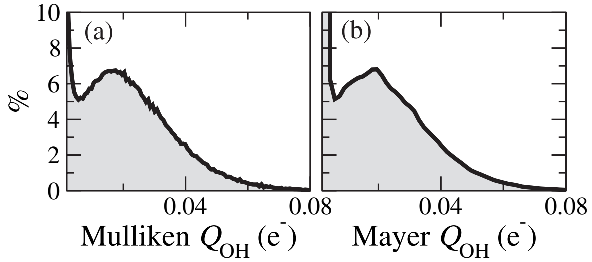

FIG. 3. Distribution of bond orders in a 25 ps AIMD liquid simulation, using Mulliken's [25] (a) and Mayer's [27] (b).

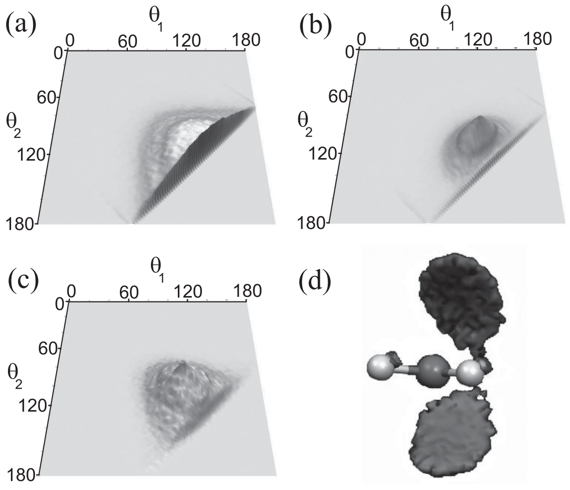

FIG. 4. Distribution of θ_1 and θ_2 angles (as in Fig. 1) in liquid water, for (a) SPCE [40] and (b) TIP5P [4] force fields, and (c) AIMD. Darker regions indicate higher values. The $\theta_1 = \theta_2$ diagonal represents pure flap. Moving normal to that diagonal represents twist. The maximum value along the diagonal is for zero flap (abrupt cut for rigid molecules). (d) Isosurface of the AIMD distribution of donating H's around a molecule.

ever, is a highly plausible explanation of the experimental results that does not imply the paradigm shift proposed by these authors.

In summary, using our electronic probe for HB connectivity we observe what could be described as 1D filamentous structures, but they are pulsating in a 170 fs period, the geometric connectivity surviving intact for many periods and thus many reshapings of the filaments. Even if this image of pulsating filaments is not relevant for the description of the liquid, it is likely that questions addressing its electronic structure could benefit from it.

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[36] If one does use the $Q_{\rm OH}^{\rm min}$ criterion, HBs do not "break" while oscillating. In fact, in $Q_{\rm OH} \sim Q_{\rm OH}^{\rm min}$ cases, the XAS curve in Fig. 1 saturates to the broken HB value, supporting this criterion. For $\phi = 40°$ this happens at $d_{\rm OO} \sim 3.8$ Å (instead of the 3.3 Å of Ref. [13]), which would give less broken HBs (average coordination of 3.5 for our AIMD run) even if the configurations were the same.
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