X-ray Absorption Spectral Signature of Quantum Nuclei in Liquid Water

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Based on electron-hole excitation theory, we investigate the X-ray absorption spectral signature of nuclear quantum effect in liquid water, whose molecular structure is simulated by path-integral molecular dynamics using the MB-pol model. Compared to spectra generated from classically modeled water structure, quantum nuclei has important effect on spectra in terms of both the spectral energies and their line shapes. At the short-range ordering of H-bond network, the delocalized protons increase the fluctuations on the intramolecular covalency and broaden the pre-edge of the spectra. For intermediate-range and long-range orderings, the observed red and blue shifts of the main-edge and post-edge are attributed to the so-called competing quantum effects, under which both the weak and well-formed H-bonds are promoted. The theoretical spectra are in nearly quantitative agreement with the available experimental data.

The nature of H-bond in network water continues to be at the center of scientific interests [1–12]. Recently, high-resolution X-ray absorption spectroscopy (XAS), has emerged to be a powerful experimental technique to probe the water structure at molecular scale [13–19]. Allowed by Franck-Condon principle [20], the electrons leaving the oxygen core can be described as excited electronic states from an instantaneously frozen snapshot of water at equilibrium. Therefore, XAS spectrum inherits a unique local signature of its molecular environment, complimentary to the scattering experiments [21, 22].

Ab initio theory is desired for an unambiguous interpretation of the underlying molecular structure. However, theoretical prediction has posed a major challenge by itself. The computed XAS spectrum is sensitive to the accuracy of methods in both the adopted electronic and molecular theories. Rigorously, the electron-hole excitation theories, such as the Bethe-Salpeter equation (BSE) [13, 23–25], should be applied beyond the unoccupied electronic structure from density functional theory [26–29]. However, the BSE is computational formidable and has not yet widely applied in water. The above computational burden has been greatly alleviated by the recently introduced approximate BSE solution utilizing localized basis [30]. On the other hand, the modeling of water at molecular level is no less difficult. The difficulty lies at the complex nature of the H-bond structure balanced by many physical interactions. The directional H-bond, as the building block of the near-tetrahedral structure in water, is much weaker than the ordinary (covalent or ionic) chemical bond. Furthermore, the H-bond network is largely modified by the van der Waals interaction, whose energy is even weaker than H-bond by one order of magnitude [31–35]. Worse still, nuclear quantum effects (NQEs) should be properly considered due to the low mass of proton [36, 38]. Under the influence of NQEs, the more delocalized protons are found to introduce an unexpected competing effects in the H-bond network in addition to the softening of liquid structure [37, 39–40]. The quantum nuclei has been shown to have important effects on XAS spectrum [11, 13].

Notwithstanding the significant advances, challenges remain. The precise picture of NQEs on the XAS spectrum at the molecular level remains elusive. Obvious discrepancy is still present between theory and experiment even when NQEs are considered in modeling water [42]. The predicted XAS spectrum presented an overestimated spectral intensity in the main-edge and underestimated spectral energies in the post-edge compared to experiments [13]. The disagreement reflects the delicate nature of NQEs. The delocalized protons by NQEs can either strengthen or weaken the H-bond structure, crucially dependent on the anharmonicity of the potential energy surface [37]. The potential energy should accurately model not only the directional H-bond but also the dispersion forces from many-body effect [44]. Moreover, compared to the bound exciton described by pre-edge, main-edge and post-edge of XAS spectrum are resonant excited states, which are sensitive to the intermediate-range and long-range orderings of H-bond network. A much larger supercell is required to properly describe those delocalized excited states [45].

In this letter, we address the above issues. We take the quantum nuclei into account basing on path integral molecular dynamics (PIMD) simulations [46] with the MB-pol many-body potential energy function [47–49]. The MB-pol enables the accurate modeling of the H-bond and other properties of water across different phases [50, 51], from the water dimer [47] to small clusters [52], and liquid water [49] by including van der Waals interaction. We use the self-consistent enhanced static Coulomb-hole and screened exchange (COHSEX) approximation [53] with maximally localized Wannier functions, which greatly enhances the computational ef-
efficiency of XAS calculations without compromising the accuracy of the results [54, 55]. The theoretical spectrum obtained from PIMD simulation is found to be in excellent agreement with the corresponding experimental data and demonstrates the importance of NQEs for an accurate modeling of XAS spectrum. The broadened pre-edge reflects the significantly increased fluctuations in the covalency of water molecule due to the delocalized protons. More interestingly, the spectral energies of the main-edge and post-edge undergo red and blue shifts under different H-bonded environments. Our analysis shows that the above broadening and shifting can be attributed to the competing quantum effects, in which both weak and well-formed H-bonds are promoted under the influence of quantum nuclei. Our XAS spectra at different temperatures suggest a slightly larger NQEs on the spectrum at lower temperature, which is consistent with our temperature dependent ring-topology analysis of the H-bond network.

All calculations were performed in a supercell containing 128 water molecules under periodic boundary conditions. Molecular configurations of liquid water were extracted from classical molecular dynamics (MD) and PIMD simulations carried out with MB-pol at 270, 298, and 360 K, and were then used in calculations of the associated XAS cross sections using the enhanced static COHSEX approximation [53]. All XAS spectra were calculated by enforcing the same area from 533 to 546 eV as in the experimental lineshape and aligning the pre-edge features to the experimental value of 535 eV [28, 42, 44]. Additional details about the spectral simulations are given in the Supporting Information (SI).

The XAS spectra of liquid water calculated using configurations from MD and PIMD simulations at 298 K are shown in Fig. 1(a), along with the corresponding experimental spectrum [16]. In the spectrum from MD simulation, the energy of the post-edge is underestimated and both intensities of the main-edge and post-edge are overestimated compared to experiment. In addition, two sub-peaks appear within the main-edge, which are separated from the pre-edge feature by a rather deep minimum that is absent in the experimental spectrum. These drawbacks are corrected in the spectrum from PIMD simulation, which is in nearly quantitative agreement with the corresponding experimental spectrum.

It is known that the pre-edge feature in the XAS spectrum of liquid water is associated with short-range ordering of the H-bond network [29]. To provide further molecular-level insights into the relationship between the pre-edge feature and the structure of liquid water predicted by both MD and PIMD simulations, the correlation between the fluctuations of the covalent OH bonds and the pre-edge excitation energies is shown in Fig. 1(b), with the corresponding distributions of excitation energies shown in Fig. 1(c). While both covalent OH bond distributions centered around 0.97 Å and 535 eV, the fluctuations are significantly larger in the PIMD simulation due to the zero point energy effects. From this comparison, it is possible to attribute the differences in the pre-edge feature of the MD and PIMD spectra to intra-molecular structural changes associated with NQEs which, resulting in proton delocalization, affect the covalent character of the OH bond within each water molecule.

As shown in Fig. 1(d), the pre-edge feature in the spectrum from MD simulation is entirely contributed by a bound exciton with 4a1 character, which is well separated from the main-edge resonant excited states with 2b2 character. In the spectrum from PIMD simulation, the pre-edge excitation energies are statistically linearly correlated with the broadening of the covalent OH bond distribution in Fig. 1(c), which reflects the existence of the competing quantum effects in liquid water. NQEs allow protons to move more easily along the direction of H-bonds, which thus facilitates the forming (breaking) of H-bonds and the consequent decrease (increase) of the co-
valent character of the associated OH bonds. Within this scenario, the excitation energies are reduced (increased) due to the increase (decrease) of Coulomb interactions between the protons and the electron lone pairs of the oxygens on the neighboring water molecules, as demonstrated by the negative correlation obtained in Fig. 1(c). NQEs are thus responsible for the broadening of spectrum between 533 and 535.7 eV, which leads to nearly quantitative agreement with the experimentally observed pre-edge feature. Due to proton delocalization, the energies of the low-lying resonant excited states with $b_2$ character are also lowered by NQEs. As shown in Fig. 1(e), the pre-edge feature in the spectrum from PIMD simulation cannot be exclusively associated with excitations with $4a_1$ character, but also contains contributions from excitations with $2b_2$ character, which results in a smoother separation at $\sim$535.7 eV between the pre-edge and main-edge features in Fig. 1(a).

Since the main-edge and post-edge features are associated with resonant exciton states, they effectively probe the intermediate-range and long-range orderings within the H-bond network [45]. NQEs on the XAS spectrum in this energy range are thus attributed to intermolecular structural changes induced by the presence of delocalized protons. The underlying molecular configurations giving rise to the main-edge and post-edge features can thus be captured by the proton-transfer coordinate $v$, which is sensitive to inter-molecular proton displacement [40]. The proton-transfer coordinate is defined as $v = d(O-H) - d(O'-H)$, which involves a hydrogen atom H, an oxygen atom O covalently bonded to the H, and a second acceptor oxygen atom O', with $d$(A-B) representing the distance between atom A and B. From the analysis of $v$ as a measure of the H-bond strength, the local H-bonded environment can be conveniently divided into two classes as weak/broken and well-formed H-bond structures (see Fig. 2(a) and SI). Consequently, the XAS spectrum can then be decomposed corresponding to these two classes (Figs. 2(b) and 2(c), respectively). The weak/broken region in Fig. 2(a) describes the partial collapse of the H-bond network, resulting in a more disordered H-bonded environment that facilitates stronger localization of excited states with $b_2$ character. This, in turn, shifts the oscillation strength of the main edge excitations in the spectrum from PIMD simulation to relatively lower energy ($\sim$537 eV). At the same time, the intensity of the post-edge feature decreases accordingly to satisfy the optical sum rule as shown in Fig. 2(b). On the other hand, the well-formed region in Fig. 2(a) represents strongly H-bonded environments that promote hybridization of the electronic excitations over neighboring water molecules. Therefore, the main-edge oscillation strength in the spectrum from PIMD simulation shifts to relatively higher energy ($\sim$538 eV), which is accompanied by an increase in the post-edge intensity as shown in Fig. 2(c).

As shown in Fig. 2(a), NQEs induce nontrivial structural changes to the H-bond network of water. In particular, weak/broken H-bonded configurations are slightly enhanced by NQEs, resulting in more disordered local H-bonded environments, which are responsible for the small red shifts in the main-edge and post-edge features of the decomposed spectrum from PIMD simulation in Fig. 2(b). Relatively larger differences exist between MD and PIMD configurations within well-formed H-bonded environments. Configurations with $v > -0.7$ Å, corresponding to highly delocalized protons, are promoted by NQEs. This shifts the associated oscillation strength to higher energies and lead to the relatively large blue shift as seen from the decomposed spectrum from PIMD simulation in Fig. 2(c). It should be noted that additional broadening is also due to proton delocalization along the direction normal to the proton-transfer coordinate, which makes the spectral lineshape from PIMD simulation less structured. This analysis thus shows that the explicit treatment of NQEs in computer simulations of liquid water is necessary to correctly reproduce the experimental spectral lineshape at 298 K, in terms of both broadening
and shifting of excitation energies. In particular, the opposite trend of the shifting of oscillation strength in the weak/broken and well-formed H-bonded environment in Fig. 2(b) and (c) can be attributed as an evidence of the competing quantum effect.

To provide further insights into the role NQEs play in determining the local structure of liquid water, XAS spectra were also calculated at 270 and 360 K as shown in Fig. 3. Similar to the XAS spectra obtained at 298 K, NQEs broaden the pre-edge and smooth the main-edge for all temperatures. Additionally, spectral difference between quantum and classical simulations at 270 K is slightly larger than 360 K. Due to the different extent of thermal fluctuations and magnitude of associated De Broglie wavelengths, the local structure of the H-bond network in liquid water changes significantly as a function of temperature, which is reflected in different spectral lineshapes. Here we analyze the topology of the underlying H-bond network in terms of ring structures [56], whose ring size distributions at 270, 298 and 360 K are shown in Fig. 4. As a reference, crystalline ice I\text{h} whose ring size distributions at 270, 298 and 360 K are only comprised of six-member rings. In liquid water, due to the fluctuating nature of the H-bond network, there is a distribution of ring sizes, and the number of large-sized rings increases with increased temperature. Consistently, the oscillation strength in the XAS spectra gradually shifts from the post-edge feature to the main-edge feature with increased temperature, which, at the same time, indicates a progressive softening of the liquid structure. At all temperatures examined in this study, NQEs are found to soften the structure of liquid water, as indicated by slightly broader ring size distributions with more large-sized rings obtained from the PIMD simulations. As expected based on the dependence of De Broglie’s wavelength on temperature, the differences between MD and PIMD ring size distributions are more pronounced at lower temperature, which is consistent with previous X-ray scattering measurements [57][58]. Such topological H-bond network differences between MD and PIMD at lower and higher temperatures are also consistent with the spectral change in Fig. 3.

In conclusion, we have reported a systematic analysis of the XAS spectra of liquid water calculated at different temperatures from state-of-the-art simulations carried out at both classical and quantum levels using the MB-pol potential energy function. Our results demonstrate that specific features of the XAS spectra directly report the role NQEs play at both intra- and inter-molecular levels. While proton delocalization, on one hand, enhances the fluctuations of the water covalent OH bonds, on the other hand, it leads to an overall softening of the H-bond network. The competing quantum effect on the H-bond network results in distinct changes to the main-edge and the post-edge features of XAS spectra compared to predictions derived from a classical representation of liquid water. These findings reinforce the notion that both an accurate representation of the underlying Born-Oppenheimer potential energy surface and a rigorous account of NQEs are necessary for a correct description of liquid water.

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