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Ultrafast Core-Hole-Induced Dynamics in Water Probed by X-Ray Emission Spectroscopy

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The isotope effect and excitation-energy dependence have been measured in the oxygen *K*-edge x-ray emission spectrum (XES). The use of XES to monitor core decay processes provides information about molecular dynamics (MD) on an ultrafast time scale through the O1*s* lifetime of a few femtoseconds. Different nuclear masses give rise to differences in the dynamics and the observed isotope effect in XES is direct evidence of the importance of such processes. MD simulations show that even the excitation-energy dependence in the XES is mainly related to differences in core-excited-state dynamics.

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X-ray emission spectroscopy is an excellent tool to relate experiment to electronic structure calculations, since it provides an atom-specific projection of the local density of states [1]. Recently, the x-ray emission spectrum (XES) of liquid water and its excitation-energy dependence have been measured and interpreted in terms of different hydrogen bond configurations [2,3]. At low excitation energies, singly H-bond donating species (SD) are predominantly excited while tetrahedral, doubly H-bond donating (DD), configurations were assumed both to dominate in the liquid and to be probed at high excitation energies [2,3].

In contrast, the x-ray absorption spectrum (XAS) of liquid water with a characteristic preedge peak (at 535 eV) and a pronounced main edge (at 537–538 eV) has been interpreted in terms of most molecules in the liquid having only two strong H-bonds [4,5]. If the interpretation of the XAS data is correct and contrary to the above assumption, we would primarily probe the same species (SD molecules) over the whole XAS spectrum of the liquid and, according to the above interpretation of x-ray emission in terms of different species, XES would be independent of excitation energy. How can we reconcile the interpretations of the XES and XAS of liquid water?

We have recently shown that the core-ionized state of water molecules in ice undergoes ultrafast molecular dissociation, and that the H_2O/D_2O isotope effect in the XES of ice can be quantitatively reproduced by taking into account the finite lifetime of the core hole [6]. In ice, there is no energy dependence in the XES for excitation energies covering the whole XAS spectrum [6], but it is an open question what happens to water molecules with unsaturated H-bonds after core excitation.

XES of normal and deuterated liquid water at ambient pressure were recorded using custom-designed copper liquid cells with a liquid volume of 3 μl. Prior to each experiment, the liquid was carefully purified by suitable degassing steps. High-brightness radiation from a third-generation undulator source [BL8.0, Advanced Light Source (ALS)] was used to excite the liquid through a 100 nm thick Si_3N_4 membrane and the subsequent x-ray emission was recorded in the Soft X-ray Fluorescence (SXF) end station with a high-resolution Rowland-circle spectrograph. The temperature of the copper liquid cell was kept slightly above the freezing point of water to minimize temperature-induced effects. Detection through the Si_3N_4 membrane enables the study of liquid water, but the consequent intensity loss, in combination with the small fluorescence cross section, makes the experiments delicate to perform (count rate ~33 counts/s). Nevertheless, by adding 15 single spectra (total counting time about 150 min) a relatively high signal-to-noise ratio has been obtained (see Fig. 1).

For excitations above the preedge feature in the liquid water XAS, the XES is indeed independent of excitation energy, and these are thus denoted "postedge XES". For excitation energies below the preedge the XES exhibits a more complex energy dependence which we will not address in the present study. The XES for preedge ($h\nu_{\mathrm{exc}} =$ 534.5 eV) and postedge excitations are presented in Fig. 1. We find both an isotope effect and significant differences between the preedge and postedge XES, which points to an excitation-energy dependence in the excited-state dynamics. The isotope effect in the postedge XES for liquid water is more pronounced than that for ice [6], and in the preedge XES for normal water the bonding $1b_1$ and $3a_1$ states together form a featureless plateau. How can we interpret this observed excitation-energy dependence in the XES?

First, the core-excited-state dynamics will depend on the excitation energy. Since the core-excitation-induced nuclear motion occurs on the same time scale as the decay

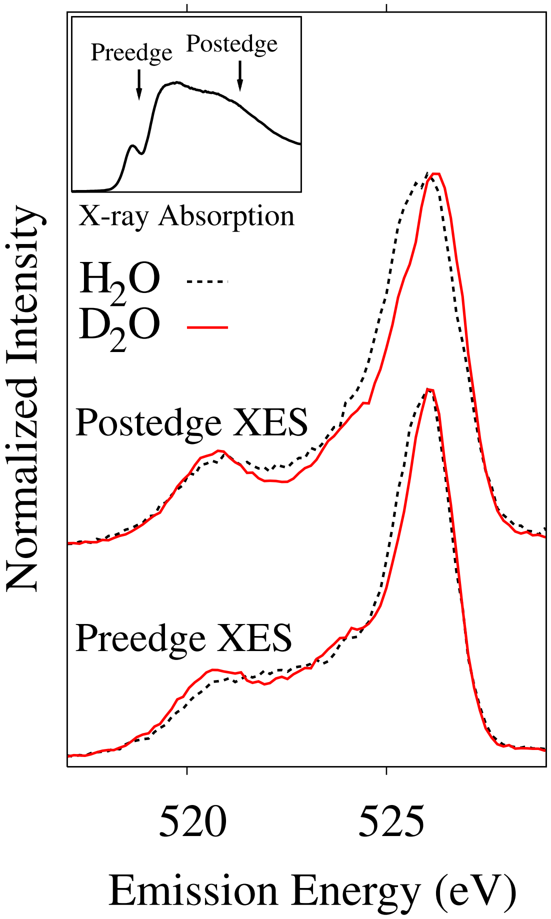

FIG. 1 (color online). The isotope effect in the preedge ($h\nu_{\rm exc} = 534.5$ eV) and postedge ($h\nu_{\rm exc} = 541.1$ eV) x-ray emission spectra of liquid water. In the inset, the excitations are indicated on the XAS taken from Ref. [5].

of the core hole, the resulting XES will not be representative for the ground state geometry. In the XAS postedge region, the excited states are highly delocalized, and the excitation can be treated as nonselective, i.e., a core ionization. For selective preedge excitations, the localized core exciton can influence the excited-state dynamics. Second, due to the transition matrix elements involving the intermediate core-excited state, there might be an anisotropy in the emitted x-rays resulting in intensity variations in the XES [2]. Finally, according to the interpretation of the XAS, the XES from the XAS preedge should arise solely from SD molecules, whereas the postedge XES is due to a distribution of different H-bond arrangements [5].

The XES for both the liquid and the isolated molecule are modeled by spectrum calculations for configurations along core-excited-state *ab initio* (AI) molecular dynamics (MD) simulations to investigate the effects of the finite lifetime of the core hole. The trajectories for the condensed phase are generated in periodic MD simulations [7], and the initial conditions for the excited-state Born-Oppenheimer dynamics are sampled over the ground state Car-Parrinello MD simulation [8]. In view of the conclusions in Ref. [5], indicating strong disagreement between the distributions of H-bond conformations from MD simulations and XAS experiments, we do not perform averaging over the MD trajectories. Instead we will consider contributions from specific characteristic H-bond situations, as, e.g., when the excited oxygen resides in a water molecule in a SD or DD H-bond configuration [5]. The distribution of H-bond conformations is determined by the balance of several weak interactions including both cooperativity and anticooperativity effects; as such it represents a challenge to simulations as well as present exchange-correlation functionals [9,10]. In contrast, the core hole effectively introduces a H_2F^+ species and thus generates a very strong force in the molecule, which dominates and makes the simulations mainly sensitive to the H-bond configuration. It also allows us to neglect tunneling contributions, and classical dynamics should thus be a reasonable approximation.

The spectrum calculations (using ground state wave functions [1]) and gas phase MD simulations (starting from a geometry optimized water molecule) are performed in an all-electron framework [11], whereas the condensed phase MD simulations employ pseudopotentials [6,7,12]; the spectra are rather insensitive to the choice of functional. The liquid water model consisted of 32 molecules in periodic boundary conditions at room temperature and normal density. The dynamics after the nonselective excitations is described simply by removing an oxygen $1s$ electron in the all-electron case or replacing the $1s^2$ pseudopotential for one oxygen with a pseudopotential for a $1s^1$ core-hole state; disregarding the excited electron is motivated by the extremely fast (< 0.5 fs) charge transfer rate for similar excitations of tetrahedrally H-bond coordinated water molecules in bulk ice [13]. A selective excitation is modeled by instead inserting that electron in the formerly unoccupied $4a_1$ band, this allows the state to localize as indicated by the slow transfer rate (> 20 fs) for excitations at the preedge [13]. For the isolated molecule, the next-lowest core-excited state ($2b_1$) could be obtained by first optimizing the lowest core excitation and then removing the singly occupied valence orbital from the orbital space to be used in the optimization of the next-lowest core-excited state [14]. The final comparison to the experimental data involves an exponential averaging of the XES along the excited-state trajectory using a lifetime of 3.6 fs for the core hole [15]. The effect in the XES due to the anisotropy in the emitted x-rays was modeled according to Eq. (1) in Ref. [2].

In Fig. 2, the XES for an isolated water molecule is monitored along the core-excited-state dynamics for each excitation as a function of time after core-hole creation. The $1b_2$ peak corresponds to the out-of-plane lone pair, and the $3a_1$ and $1b_1$ states are bonding orbitals. The lifetime averaged XES for selective excitations into the $4a_1$ and $2b_1$ states and the nonselective excitation qualitatively reproduce the energy dependence in the XES [2]. The MD simulation "ansatz" captures the essential differences, such as the intensity profiles in the XES, the blueshift of the $1b_1$ peak in the selectively excited spectra and the redshift of the $1b_1$ peak in the nonselective XES. In particular, the featureless plateau for the XES of the lowest core-excited state, $4a_1$, is very well reproduced. After nonselective excitations only the HOH angle undergoes a significant change. For the two selective excitations the water molecule exhibits a rapid elongation of both OH-bonds, followed in the core-excited $4a_1$ state by dissociation of one of the bonds after more than 10 fs. This may seem at variance with the ultrafast dissociation observed experimentally within the core-hole lifetime [16]. However, in the present simulations we are not monitoring the excitation energy, which varies with the distortions of the molecule. By selecting specifically configurations with an excitation energy according to the narrow-band excitation used in the experiment, we find that only a part of the Franck-Condon profile actually leads to ultrafast dissociation [17].

We select a SD configuration from MD simulations with one donating and one accepting H-bond as a model example for the liquid to examine how the XES data could be compatible with the interpretation of the XAS data [5]. The bond dynamics in the preedge and postedge excited states is presented in Fig. 3; a DD configuration is included for comparison. The large initial asymmetric distortion seen in Fig. 3 for the chosen DD configuration does not significantly influence the core-excited dynamics because of the strong central force due to the core hole. Because of the complexity of the liquid state, many different configurations from the ground state MD simulation were studied to validate the results.

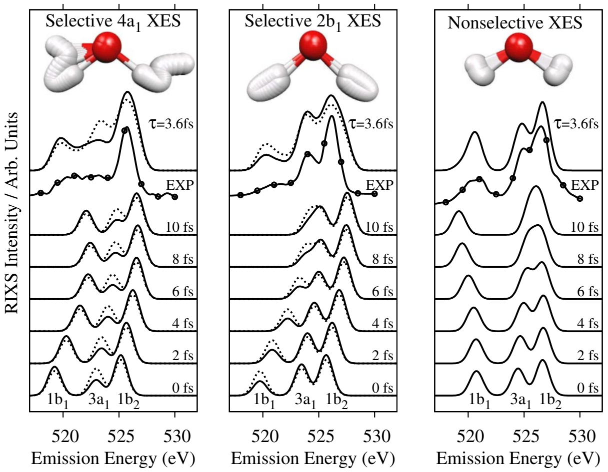

FIG. 2 (color online). Theoretical x-ray emission spectra for an isolated water molecule, calculated for structures along the core-excited-state dynamics. (The MD trajectories during 0–20 fs are presented above the spectra.) At the top of each graph, the lifetime averaged XES are shown with (full lines) and without (dashed lines) taking into account the angular dependence. The former reproduces the experimental (full lines with circles) data [2] well.

The excited-state AIMD simulations for the two isotopomers are started from identical initial conditions, with appropriate scaling of the velocities of the deuterium atoms. The isotope effect is apparent, but even more important is the striking difference in dynamics for the two different excited states. The postedge excitation of a SD species results in dissociation of the H-bonded OH group, whereas for the preedge excitation the uncoordinated OH group dissociates. Because of rehybridization in asymmetric H-bonding situations, the preedge excited core exciton localizes in a strongly antibonding orbital on the uncoordinated OH group. DD configurations are only nonresonantly excited and show similar dynamics as previously observed for bulk ice; i.e., both OH groups begin to dissociate [6].

In Fig. 4, the resulting preedge and postedge excited XES for the SD species differ less dramatically than in the gas phase (see Fig. 2), since dissociation occurs also in the nonselective case in the condensed phase. Nevertheless, for the preedge excitation the rapid drift in the $1b_1$ and $3a_1$ energy levels will result in the featureless plateau seen in the experimental preedge XES (Fig. 1). From the simulations as seen in Fig. 4, we find that the excited molecule must have unsaturated H-bonds to exhibit an excitation-energy dependence in the XES (and in the excited-state dynamics). Because of rehybridization of the unoccupied orbitals, there is no excitation-energy dependence in the angular dependence of the x-ray emission [2], in contrast to the isolated molecule.

The $1b_2$ peak is broader in the postedge XES for liquid water than for ice [6]. This is due to a broader distribution of H-bond lengths and different DD and SD species in the liquid as compared to ice, which will influence the core hole excited-state dynamics and result in a larger isotope

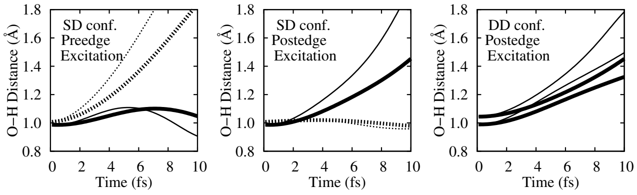

FIG. 3. The O-H-bond dynamics for a single H-bond donor (SD) configuration in liquid water in the excited state upon preedge (left) and postedge (middle) core excitations. Full lines correspond to the H-bonded OH group, dashed lines pertain to the uncoordinated OH group. Thin and thick lines denote normal and deuterated liquid water, respectively. For a DD configuration in normal liquid water (right), both OH groups dissociate and the excited-state dynamics exhibits no energy dependence (not shown).

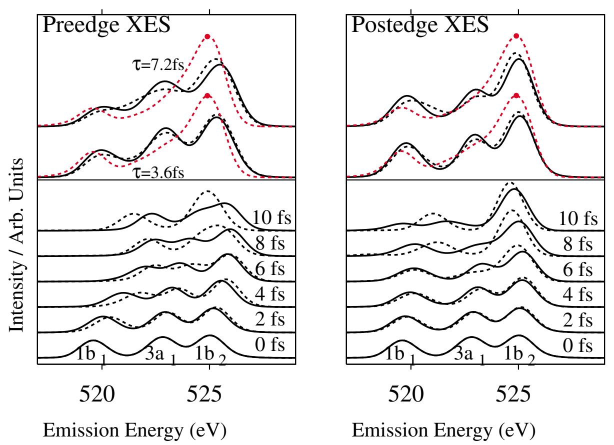

FIG. 4 (color online). X-ray emission spectra, calculated for structures along the core-excited-state dynamics. Deuterated (full lines) and normal (dashed lines) liquid water as modeled by the SD configuration used in Fig. 3. The lifetime averaged spectra for a double H-bond donor configuration (dashed lines with a circle) is included for comparison. Narrow excitations on the Franck-Condon profile leading to a faster dissociation is simulated by averaging with a longer lifetime, which results in a further shift of $3a_1$ intensity towards the main $1b_2$ peak.

effect in the liquid. Mainly, SD species contribute to the XAS preedge, whereas DD species have an enhanced cross section in the postedge. Hence, for postedge excitations the DD species will contribute as much as the SD species even if DD species are in the minority. Therefore we cannot extract any reliable quantitative information on the distribution of species present in the liquid. The sharpness of the preedge peak in XAS for liquid water indicates the existence of somehow rather structurally well defined species, which when probed in the preedge XES shows a smaller dependence on isotope substitution for the $1b_2$ peak.

In conclusion, experimental XES for normal and deuterated liquid water has been analyzed against the background of AIMD simulations. We give an explanation of the excitation-energy dependence in the XES data based on differences in excited-state dynamics. Because of the different inertia of the hydrogen and deuterium, excited-state dynamics on the same time scale as the decay of the core-excited state will result in an isotope effect in the XES. The experimentally observed isotope effect is the key to resolve this problem, but theoretical simulations were essential for proving the feasibility of the proposed mechanism.

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[1] A. Nilsson and L. G. M. Pettersson, Surf. Sci. Rep. **55**, 49 (2004).
[2] S. Kashtanov, A. Augustsson, Y. Luo, J.-H. Guo, C. Såthe, J.-E. Rubensson, H. Siegbahn, J. Nordgren, and H. Ågren, Phys. Rev. B **69**, 024201 (2004).
[3] J.-H. Guo, Y. Luo, A. Augustsson, J.-E. Rubensson, C. Såthe, H. Ågren, H. Siegbahn, and J. Nordgren, Phys. Rev. Lett. **89**, 137402 (2002).
[4] S. Myneni *et al.*, J. Phys. Condens. Matter **14**, L213 (2002).
[5] P. Wernet *et al.*, Science **304**, 995 (2004).
[6] B. Brena, D. Nordlund, M. Odelius, H. Ogasawara, A. Nilsson, and L. G. M. Pettersson, Phys. Rev. Lett. **93**, 148302 (2004).
[7] CPMD, Copyright IBM Corp 1990-2004, Copyright MPI für Festkörperforschung Stuttgart 1997-2001, http://www.cpmd.org/.
[8] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[9] J. VandeVondele, F. Mohamed, M. Krack, J. Hutter, M. Sprik, and M. Parrinello, J. Chem. Phys. **122**, 014515 (2005).
[10] J. Ireta, J. Neugebauer, and M. Scheffler, J. Phys. Chem. A **108**, 5692 (2004).
[11] K. Hermann *et al.*, computer code STOBE, http://w3.rz-berlin.mpg.de/~hermann/StoBe/, 2002.
[12] M. Cavalleri, M. Odelius, A. Nilsson, and L. G. M. Pettersson, J. Chem. Phys. **121**, 10 065 (2004).
[13] D. Nordlund, H. Ogasawara, M. Nagasono, L. G. M. Pettersson, and A. Nilsson (to be published).
[14] C. Kolczewski *et al.*, J. Chem. Phys. **115**, 6426 (2001).
[15] F. Gel'mukhanov, H. Ågren, M. Neeb, J.-E. Rubensson, and A. Bringer, Phys. Lett. A **211**, 101 (1996).
[16] I. Hjelte *et al.*, Chem. Phys. Lett. **334**, 151 (2001).
[17] O. Takahashi, M. Odelius, D. Nordlund, A. Nilsson, and L. G. M. Pettersson (to be published).