Ultra-fast core hole induced dynamics in ice and water probed by x-ray emission spectroscopy.

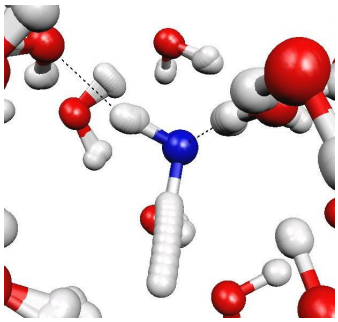
Michael Odelius[a], Dennis Nordlund [a], Hirohito Ogasawara [b], Barbara Brena [c], Oliver Fuchs [d], Lothar Weinhardt [d], Florian Maier [d], Eberhard Umbach [d], Clemens Heske [e], Yan Zubavichus [f], Michael Grunze [f], Jonathan D. Denlinger [g], Lars G. M. Pettersson [a], Anders Nilsson [ab],

[a] Department of Physics, AlbaNova, Stockholm University, S-106 91 Stockholm, Sweden +46-8-55378713, Fax: +46-8-55378442 E-mail: odelius@physto.se, Url: www.physto.se/~xes
[b] Stanford Synchrotron Radiation Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, U.S.A.
[c] Theoretical Chemistry, AlbaNova, Royal Institute of Technology, S-106 91 Stockholm, Sweden
[d] Experimentelle Physik II, Universitat Wurzburg, Am Hubland, 97074 Wurzburg, Germany
[e] Department of Chemistry, University of Nevada, Las Vegas, NV 89154-4003.
[f] Angewandte Physikalische Chemie, Universitat Heidelberg, INF 253, 69120 Heidelberg, Germany
[g] Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720.

Oxygen K-edge X-ray emission (XE) spectra were measured for normal and deuterated water. In a combination of experimental and theoretical techniques, we show that the oxygen K-edge x-ray emission spectrum (XES) contains information on the ultra-fast photo-induced processes.

Using x-ray emission and photoemission spectroscopies to measure the occupied valence levels in a thin crystalline ice film, we resolve the ionization-induced dissociation of water in ice on a femtosecond time scale [1]. Isotope substitution confirms proton transfer during the core-hole lifetime in spite of the nonresonant excitation. Through ab initio molecular dynamics on the core-ionized state, the dissociation and spectrum evolution are followed on a femtosecond time-scale. The theoretical simulations confirm the experimental analysis and allow for a detailed study of the dissociative reaction path.

In liquid water, the isotope effect in the x-ray emission spectrum was measured at different excitation energies [2]. The isotope effect and the difference between selective and non-selective core-excitations are modeled using ab initio molecular dynamics and spectrum simulations. The isotope effect in the XES is direct evidence of femto-second dynamics in the core-excited state. Comparison to theoretical simulations shows that even the excitation-energy dependence in the XES is mainly related to differences in core-excited state dynamics.



Femto-second molecular dynamics is simulated for a core-exciton in water. For the resonant excitation of partially hydrogen bonded molecules, the core-exciton localizes around the uncoordinated OH group which consequently undergoes ultrafast dissociation in the core-excited state. In contrast, the non-resonant excitation results in a dissociation of the hydrogen bonded OH group. These mechanisms are of fundamental importance for the understanding of radiation damages in aqueous solution, and for the interpretation of XE spectra.

[1] B. Brena, D. Nordlund, M. Odelius, H. Ogasawara, A. Nilsson, and L. G. M. Pettersson. "Ultra-fast molecular dissociation of water in ice." *Phys. Rev. Lett.*, **2004**, 93:148302.

[2] M. Odelius, H. Ogasawara, D. Nordlund, O. Fuchs, L. Weinhardt, F. Maier, E. Umbach, C. Heske, Y. Zubavichus, M. Grunze, J. D. Denlinger, L. G. M. Pettersson, and A. Nilsson. "Ultra-fast core hole induced dynamics in water probed by x-ray emission spectroscopy." *Submitted to Phys. Rev. Lett.*, **2004**.