Investigating liquid water with X-ray emission spectroscopy using XFEL

V. Utrio Lanfaloni[1], A. Mondal[1], M. Harder[2], L. Mercadier[2], Y. Chang[3], T. Balciunas[1], B. van Kuiken[2], S. Serkez[2], M. Teichmann[2], L. Adriano[2], A. De Fanis[2], J. Valerio[2], R. J. Ugalino[4], N. Kurahashi[4], N. Gerasimova[2], S. Parchenko[2], N. Ghoradi[2], R. Carley[2], M. Agaker[5], A. Scherz[2], J.-E. Rubensson[5], L. Pettersson[6], J.-P. Wolf[3], Y. Harada[4], K. Ueda[1,7], H. J. Wörner[1,†], Z. Yin[2,8]*

[1]Laboratorium für Physikalische Chemie, ETH Zürich, Switzerland
[2]European XFEL, Germany
[3]GAP-Biophotonics, Université de Genève, Switzerland
[4]Institute for Solid State Physics, The University of Tokyo, Japan
[5]Department of Physics and Astronomy, Uppsala University, Sweden
[6]FYSIKUM, AlbaNova University Center, Stockholm University, Sweden
[7]Department of Chemistry, Tohoku University, Japan
[8]International Center for Synchrotron Radiation Innovation Smart, Tohoku University, Japan
zhong.yin.e2@tohoku.ac.jp

The complexity of the hydrogen-bond network makes understanding the bulk water structures and properties an unsolved problem. For example, currently, water is assumed as a dynamical mixture of two local structures (high-density (HDL) and low-density (LDL) liquid) near the liquid-liquid critical point [1]. However, direct observations of these motifs under ambient conditions are still missing. We present here high-resolution resonant inelastic X-ray scattering (RIXS) experiments of liquid jet water as proof of the two local structures under ambient conditions. The experiments have been performed at the SCS beamline of European XFEL that delivers pulses of <15 fs duration, around the oxygen K-edge. Figure **1A** shows the RIXS spectra at the pre- (533 eV, blue) and post- (550 eV, orange) edge excitation. In both emission spectra, features attributed to the three outer valence orbitals of water are visible: the $1b_2$ at ~520.8 eV, the $3a_1$ at ~524.8 eV, and the $1b_1$ at ~526 eV [2,3]. While below the pre-edge excitation, the $1b_1$ presents one emission, with the post-edge excitation, the $1b_1$ splits in two bands, attributed to the HDL and LDL motifs [2]. Fluence-dependent measurements for post-edge excitation, reported in figure **1B**, shows a relative decrease in intensity of the LDL peak compared to the HDL peak with increasing FEL fluence. Previous works on heated water explain this effect as a temperature-induced morphology change [2], which are unlikely in our case, due to the ~15 fs XFEL pulses. Preliminary interpretations predict this as an ultrafast effect from ionized neighbouring molecules resulting in complex hydrogen bond interactions.

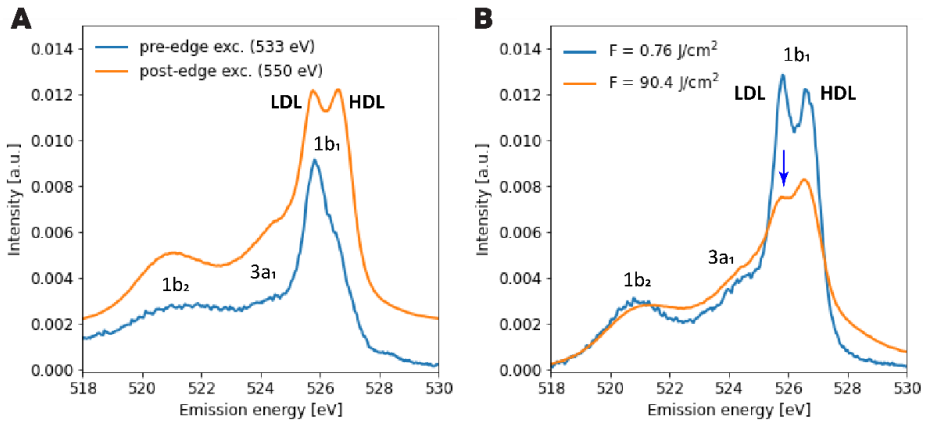

Fig. 1. **A)** RIXS spectra at 533 eV (blue) and 550 eV excitation (orange). **B)** RIXS spectra at 550 eV excitation at 0.76 J/cm^2 (blue) and 90.4 J/cm^2 (orange) fluence.

References

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