Electronic Structure of Hot Dense Water by Inelastic X-ray Raman Scattering

Jung-Fu Lin[1], Nozomu Hiraoka (平岡望)[2], Takuo Okuchi[3], Yong-Qiang Cai (蔡永強)[2,4]

[1]Lawrence Livermore National Laboratory, Livermore, USA
[2]National Synchrotron Radiation Research Center, Hsinchu, Taiwan
[3]Institute for Advanced Research, Nagoya University, Nagoya, Japan
[4]Brookhaven National Laboratory, New York, USA

The properties and phase diagram of H_2O at high pressures and temperatures are of fundamental interest in physics, chemistry, geophysics and biological sciences. The flexibility of hydrogen bonding in H_2O gives rise to a myriad of crystalline, amorphous, and liquid phases with unique physical and chemical properties. In particular, it is predicted that the local structure of liquid H_2O changes from the open four-fold hydrogen bonded structure at ambient pressure and temperature conditions to a nearest-neighbor coordination shell of up to 13 at pressures of 10 GPa (Schwegler *et al.*, 2000; Strässle *et al.*, 2006). This change from low to high density H_2O (LDW to HDW) appears gradually based on neutron diffraction studies up to 400 MPa. In order to shed lights on the local structures of liquid H_2O across the LDW to HDW transition, here we have studied oxygen near K-edge spectra of liquid H_2O at high pressures and temperatures obtained using x-ray Raman scattering in an externally-heated diamond-anvil cell (Fig. 1).

The oxygen near K-edge XRS experiments of compressed liquid H_2O were conducted at the Taiwan Beamline BL12XU at SPring-8. A beryllium gasket, transparent to the incoming and outgoing x-ray, of 3 mm in diameter was pre-indented by a pair of diamonds having culets of 700 μm or 1 mm across to a thickness of 70 μm and a hole of 400 μm in diameter was drilled in it and used as the sample chamber. Distilled liquid H_2O was loaded into the sample chamber of a DAC with a couple of ruby spheres as the pressure calibrant. The XRS spectra were collected using the reverse scan technique: the inelastically scattered x-ray Raman signals were collected at an angle (2θ) of 30° with an array of spherical Si analysers and a Si detector in near back-scattering geometry at a fixed energy of 9.886 keV at BL12XU, while the incident monochromatic x-ray beam (E) from a Si double crystal monochromator was scanned over the energy range of $E-E_0$ from 530 eV to 550 eV. The beamsize was about 15 μm in diameter and the total energy resolution was ~175 meV. Each XRS spectrum took approximately one day to collect.

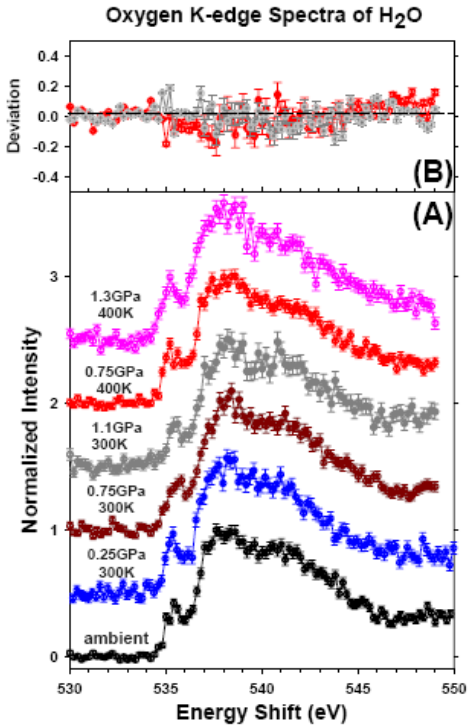

Figure 1. Oxygen K-edge spectra in compressed liquid H_2O by x-ray Raman spectroscopy. The energy resolution of the spectra was ~175 meV. The main feature of the spectra is an pre-edge peak located at ~535-536 eV, whereas the oxygen K-edge is located at 537 eV.

Our XRS spectra over the pressure and temperature conditions of the predicted LDW to HDW transition show that the oxygen K-preedge feature located at ~535-536 eV does not change in intensity nor position, indicating that the strength of the hydrogen bond remains similar in the LDW and HDW water. We are now working with theorists to calculate the local K-edge structures of liquid H_2O in the experimentally determined pressure-temperature range. These results should provide first experimental evidence with unprecedented energy resolution for the local electronic structures of liquid H_2O at high pressures and temperatures.