ORDERING OF HYDROGEN BONDS IN HIGH-PRESSURE LOW-TEMPERATURE ICES

The hydrogen bonds linking the water molecules are known to give rise to a rich variety of stable and metastable phases of H_2O under specific temperature and pressure conditions (Fig. 1) [1]. Study of the electronic structure of the hydrogen bonds in various phases of H_2O provides valuable information on the change of hydrogen, covalent and ionic bonding of the H_2O framework that is essential for understanding the icy planetary interiors as well as the physical and chemical properties of organic and biological systems at high pressure. Such information can in principle be obtained from analysis of the near-edge fine structure from X-ray absorption spectroscopy (XAS). For low-Z materials whose core-level electrons are in the soft X-ray region, however, conventional XAS is difficult to perform. An alternative technique, based on the inelastic scattering of hard X-rays (~ 10 keV) by core-level excitations, known as X-ray Raman scattering (XRS), provides the same information as XAS when the momentum transfer of XRS is small enough that the dipole approximation is valid. As our work demonstrated, the inherent bulk sensitivity and good penetration depth of XRS make it especially valuable for studies under extreme conditions such as high pressure.

We have studied the near *K*-edge structure of oxygen in liquid water and ices III, II, and IX at 0.25 GPa and several low temperatures down to 4 K on the Taiwan Inelastic X-ray Scattering Beamline **BL12XU** [2]. The spectra obtained are summarized in Fig. 2, which reveal detailed spectral changes across the various phases that contain important information on the change of the hydrogen bonds of the H_2O framework.

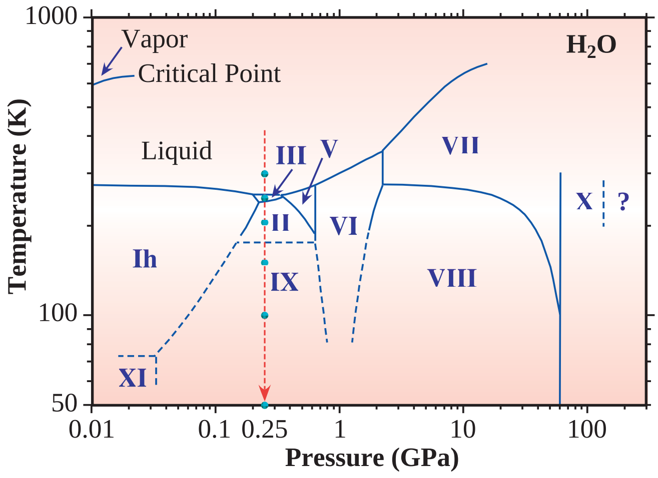

Fig. 1: Phase diagram of H_2O.

The most prominent changes are observed in the pre-edge region (535-537 eV). First-principles density functional calculations (DFT) for liquid water [3] have identified that the pre-edge feature is caused by oxygen 2*p* and 2*s* orbital hybridization in water molecules with an uncoordinated (broken or distorted) donor hydrogen bond. The observed increase of the pre-edge intensity in liquid water upon high-pressure compression at 300 K therefore suggests the increase of the number of uncoordinated hydrogen bonds with pressure.

With decreasing temperature at 0.25 GPa, the H_2O framework undergoes structural changes firstly from liquid to ice III with the ordering of the oxygen network, then from ice III to ices II and IX. Ice IX is the low-temperature proton-ordered phase of ice III with an identical tetragonal crystal structure, whereas ice II has a *completely* proton-ordered rhombohedral lattice. From Fig. 2, the ordering of the oxygen network causes only a small decrease of the pre-edge intensity, whereas the ordering of the proton network, or equivalently the ordering of the hydrogen bonds, dramatically reduces the pre-edge intensity, which can be interpreted as a result of the diminishing number of uncoordinated hydrogen bonds in the proton-ordered lattice of ices II and IX.

The remaining pre-edge intensities observed in ices II and IX are, however, unexpected as all (most) of the water molecules in the proton-ordered lattice of ice II (IX) are fully coordinated with symmetric hydrogen bonds, which should lead to a diminishing pre-edge intensity. Our DFT calculations of the near-edge XAS spectrum for ice IX indicate that the remaining intensity may be due to the influence of the local electronic structure by the Madelung potential of the crystal lattice, estimated by point charges placed at the hydrogen and oxygen periodic lattice positions. The calculated XAS spectrum including the point charges reproduces qualitatively the major features of the experimental spectrum (Fig. 3). We therefore conclude that the Madelung potential of the proton-ordered lattice causes the remaining pre-edge intensity. This is in contrast to liquid water where the near-edge structure is determined pre-dominantly by the first coordination shell of the water molecules [4]. These results can be reconciled, however, by considering that the ordered proton network creates a long-range anisotropy in the H_2O framework and introduces the necessary orbital asymmetry in the hydrogen bonds of the water molecules, causing the observed pre-edge intensity. A randomly distributed proton network smears out the anisotropy, and the pre-edge intensity is dominated by uncoordinated donor hydrogen bonds.

At temperatures between 4 and 50 K, substantial spectral changes from ice IX are observed, which suggest substantial changes of the H_2O framework in this *P-T* regime and the formation of a possible new ice phase. Further structural characterization is however required to confirm this finding.

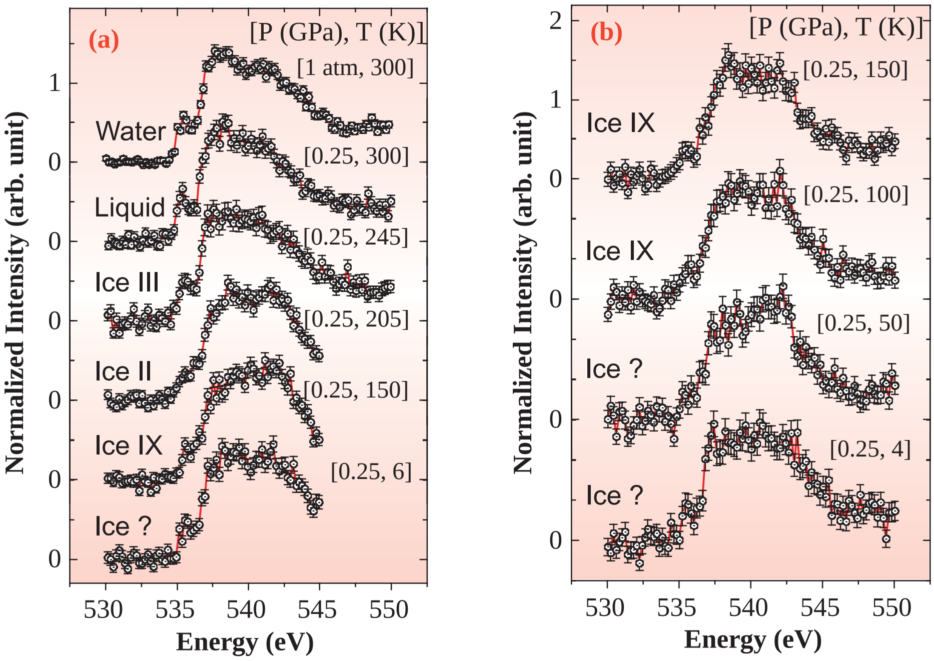

Fig. 2. Near *K*-edge spectra of the oxygen in various phases of H_2O obtained with a total energy resolution of 305 **(a)** and 175 meV **(b)** at E_0 = 9884.7 eV. The pressure and temperature conditions are indicated.

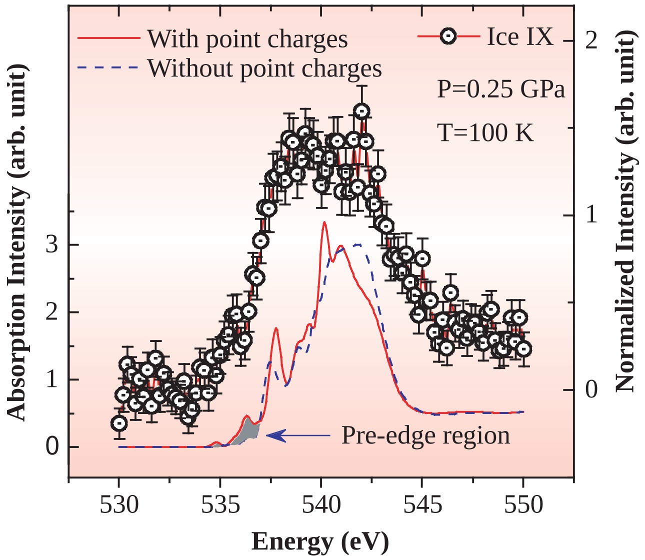

Fig. 3. Comparison of the near *K*-edge spectrum of ice IX with DFT calculations.

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