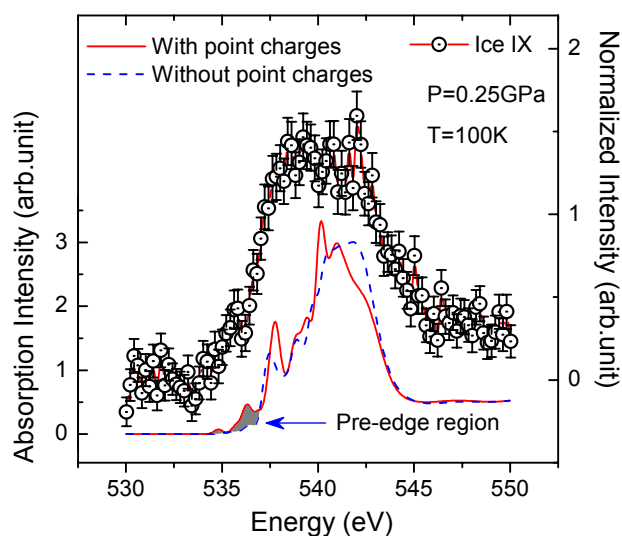


**Fig. 2:** Near K-edge spectra of the oxygen in various phases of H<sub>2</sub>O. The total energy resolution was (a) 305 and (b) 175 meV at the analyzer energy of 9884.7 eV. The phases and the pressure and temperature conditions are indicated.

With decreasing temperature at 0.25 GPa, the ordering of the oxygen network associated with the phase transition from liquid to ice III causes only a small decrease of the pre-edge intensity, whereas the increased ordering of the hydrogen bonds in ices II and IX, dramatically reduces the pre-edge intensity, which can be interpreted as a result of the diminishing number of uncoordinated hydrogen bonds in the lattice of ices II and IX. One also notices that, for the completely hydrogen-bond ordered ice II, the pre-edge intensity is smallest. The main-edge (537–540 eV) and post-edge (540–545 eV) features are also best resolved among all the phases investigated.

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. Figure 3 shows the comparison of the experimental spectrum for ice IX and the DFT-calculated XAS spectra. The influence of the Madelung potential was estimated by point charges placed at the hydrogen and oxygen periodic lattice positions. The calculation including the point charges reproduces qualitatively the major features of the experimental spectrum. We therefore conclude that the Madelung potential of the hydrogen-bond ordered lattice causes the remaining pre-edge intensity. This is in contrast to



**Fig. 3:** Comparison of near K-edge spectra of ice IX with DFT calculations. The shaded area indicates the difference in the pre-edge region of the calculation with and without the point charges.

liquid water where the near-edge structure is determined pre-dominantly by the first coordination shell of the water molecules. These results however can be reconciled by considering that the ordered hydrogen bonds creates a long-range anisotropy in the H<sub>2</sub>O framework and introduces the necessary orbital asymmetry in the hydrogen bonds of the water molecules, causing the observed pre-edge intensity. A randomly distributed hydrogen-bond 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 in turn suggest substantial changes of the H<sub>2</sub>O framework and the formation of a possible new ice phase in this largely unexplored P-T region. Further structural characterization is however required to confirm this finding.

**BEAMLINE**

SP12U Inelastic X-ray Scattering beamline

**EXPERIMENTAL STATION**

Inelastic X-ray scattering spectrometer end station

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