Spectral signatures of H-bond networks

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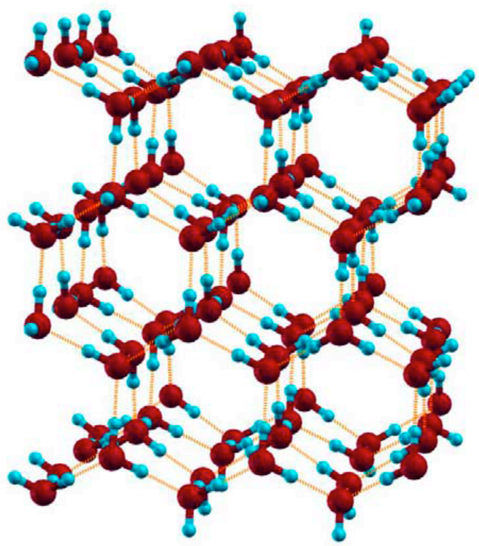
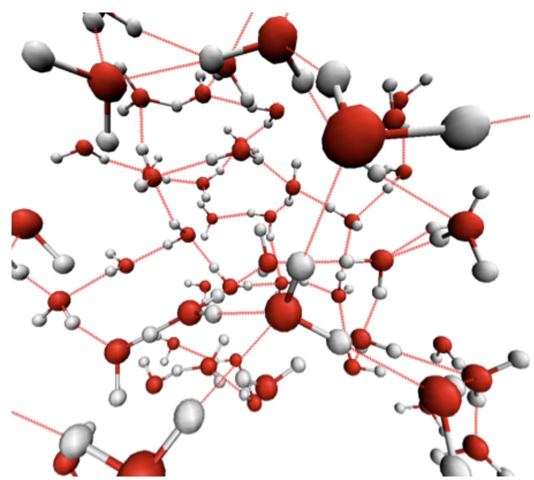
The tetrahedral network of H-bonds in water and ice has characteristic spectral features that can be detected with neutron and x-ray scattering:

What do they tell us about the network structure?

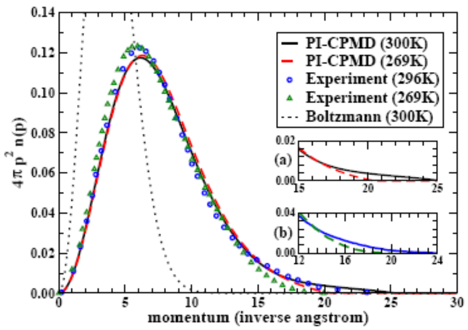


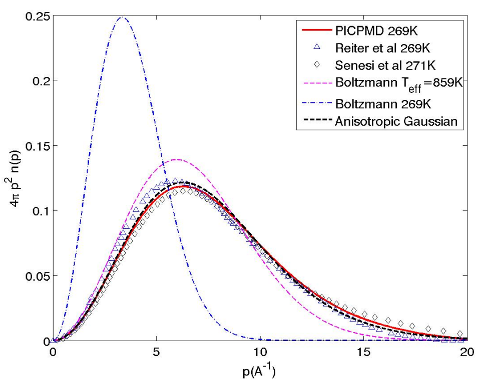
Ice Ih

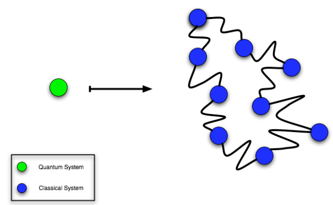


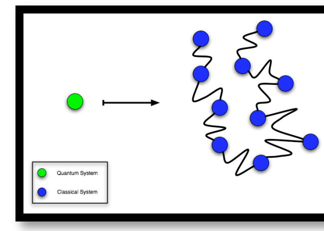
Liquid water

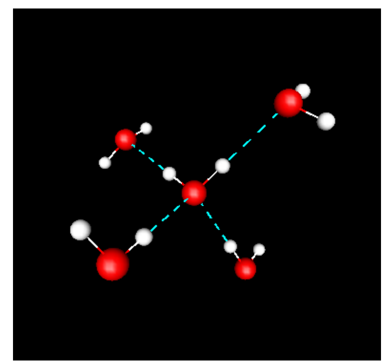
The proton momentum distribution from DINS and PI simulations











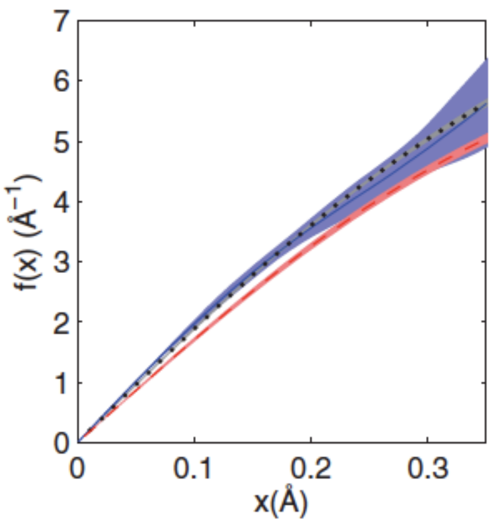
Principal frequencies in ice from PI-CPMD:

2639+/-60, 1164+/-25, 775+/-20 cm-1

The distribution is quasi-harmonic but anisotropic

G. Reiter et al. *Braz. J. Phys.* 2004
JA Morrone, RC, *PRL* 2008; L Lin, JA Morrone, RC, M Parrinello, *PRL* 2010 and *PRB* 2011;
D. Flammini et al. *JCP* 2012

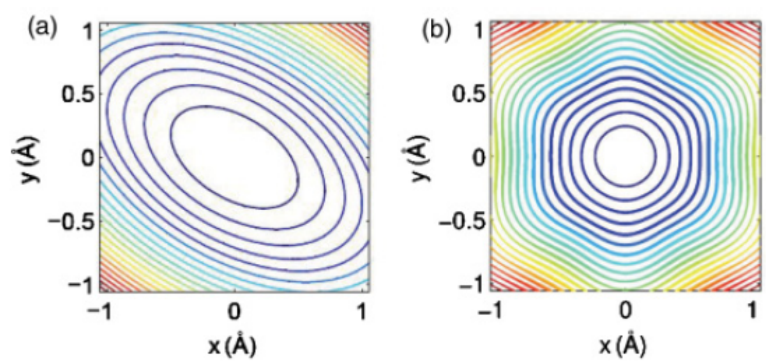
Directional and spherically averaged "momentum distribution" in ice Ih



The "mean force" to open the Feynman paths is directly related to the Compton profile

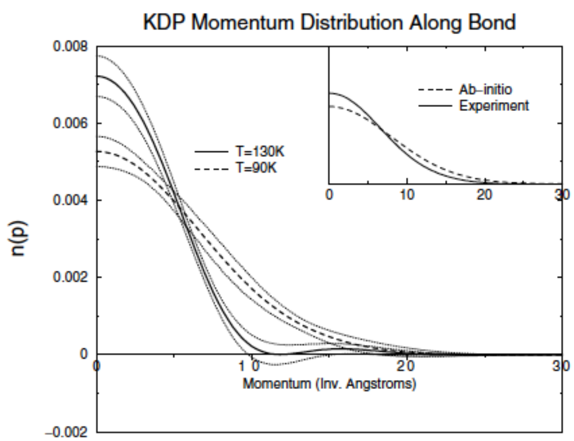
$$f(x) = -\frac{Mx}{\beta\hbar^2} + \frac{\int_0^\infty dy\ y \sin(xy/\hbar)\bar{J}_{IA}(y)}{\hbar \int_0^\infty dy\ \cos(xy/\hbar)\bar{J}_{IA}(y)}$$

"Hexagonal" protons: what an experiment with super high resolution would detect from the directional distribution of the protons projected in the basal plane of ice Ih



Only zero-point motion so far; what about tunneling?

Two experiments



Proton tunneling in KDP. From G. Reiter et al. *PRL* 2002

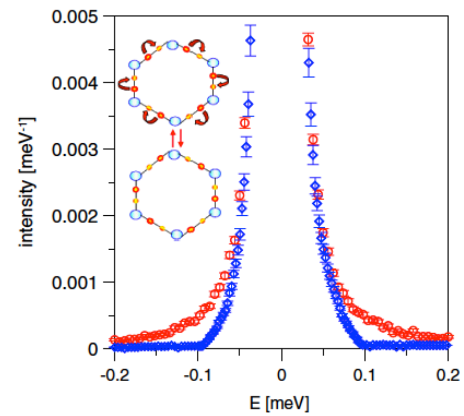
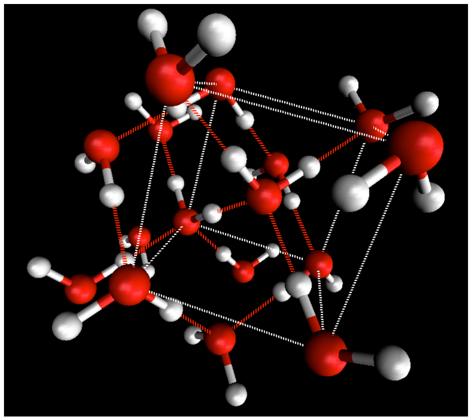


FIG. 4 (color online). Quasielastic contribution in hydrogenated ice I*h* (○) compared with partially deuterated (◇), both at 5 K. Inset: a sketch of the proposed concerted tunneling of the hydrogen atoms in the ordered loops.

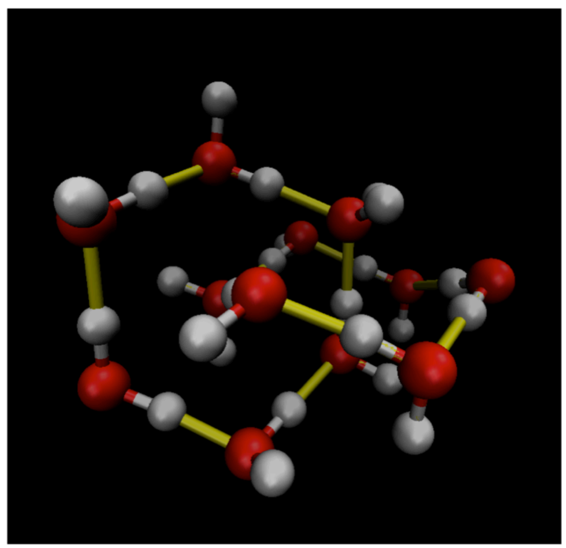
Anomalous proton dynamics in ice: collective tunneling? From L.E. Bove et al. *PRL* 2009

Concerted proton tunneling in simulations on ice VII

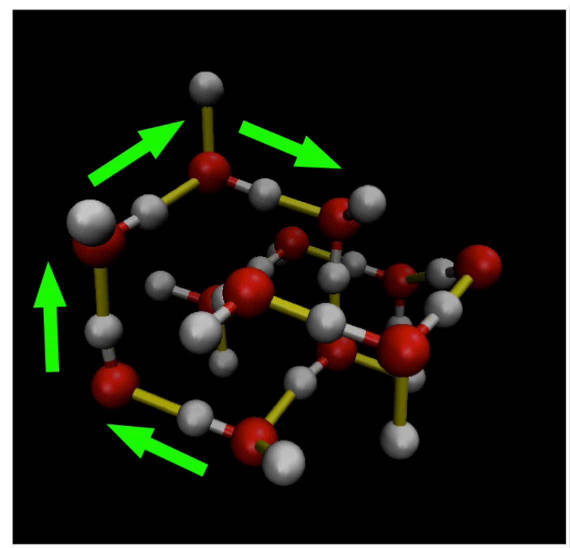


Molecular structure of ice VII (and VIII neglecting tetragonal distortions)

Entangled (interpenetrating) molecular rings

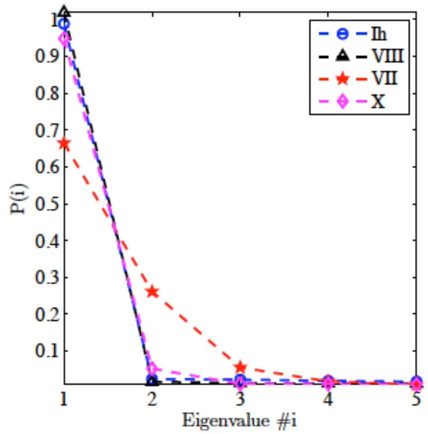


Ice VIII (Antiferroelectric)



Ice VII (Paraelectric)

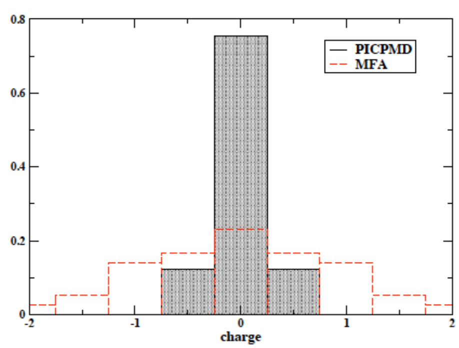
Entangled protons: why and how entanglement affects the momentum distribution



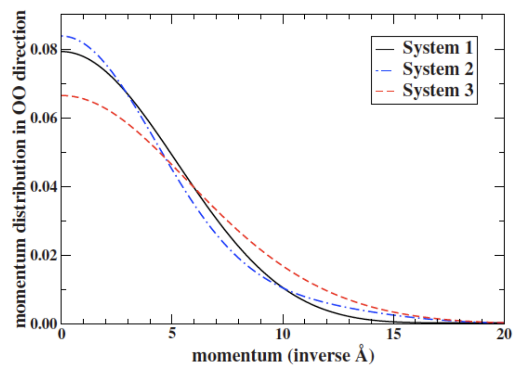
$$\rho = \sum_i |\phi(i)\rangle P(i) \langle \phi(i)| \qquad S = -\mathrm{Tr}[\rho \log \rho]$$

S is essentially 0 in ice Ih and VIII

$S = 0.60$ in ice VII and $S = 0.20$ in ice X

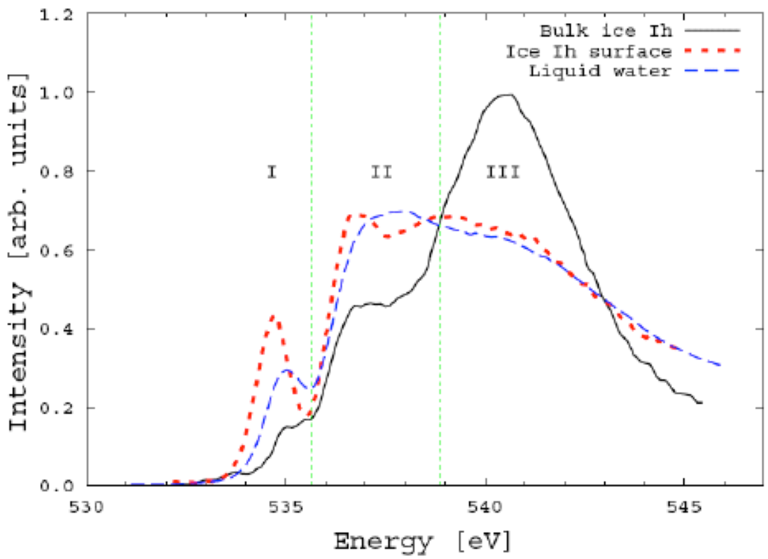


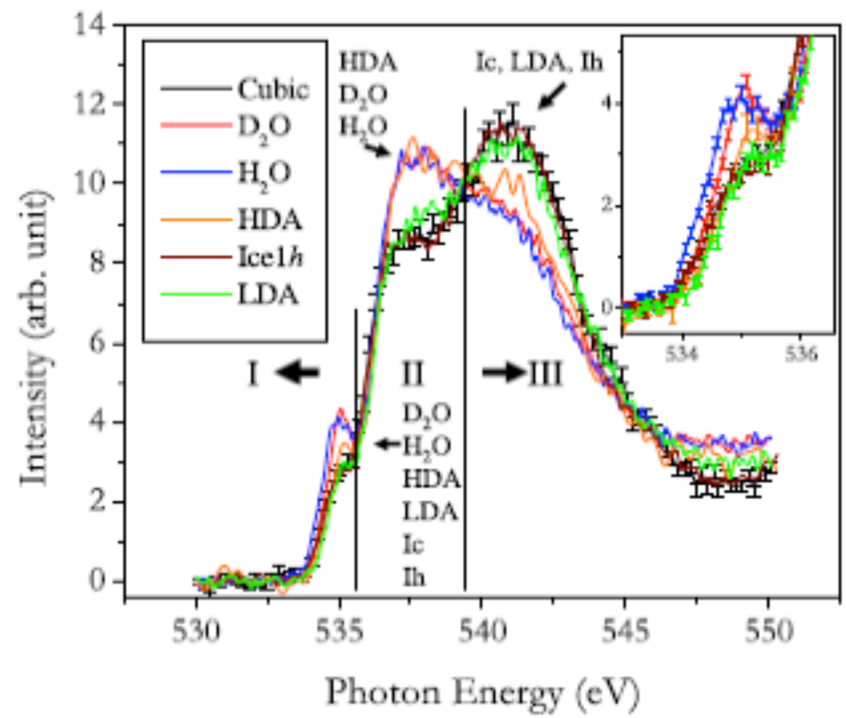
From L. Lin, J.A. Morrone, R.C. (JSP, 2011)



From JA Morrone, L Lin, RC (JCP 2009)

Two x-ray experiments





Wernet et al. (*Science*, 2004) interpreted XAS solely in terms of SRO (broken H-bonds): they attributed the stronger pre-edge in the liquid to a large fraction of broken bonds, and the weaker post-edge to a less extended H-bond network

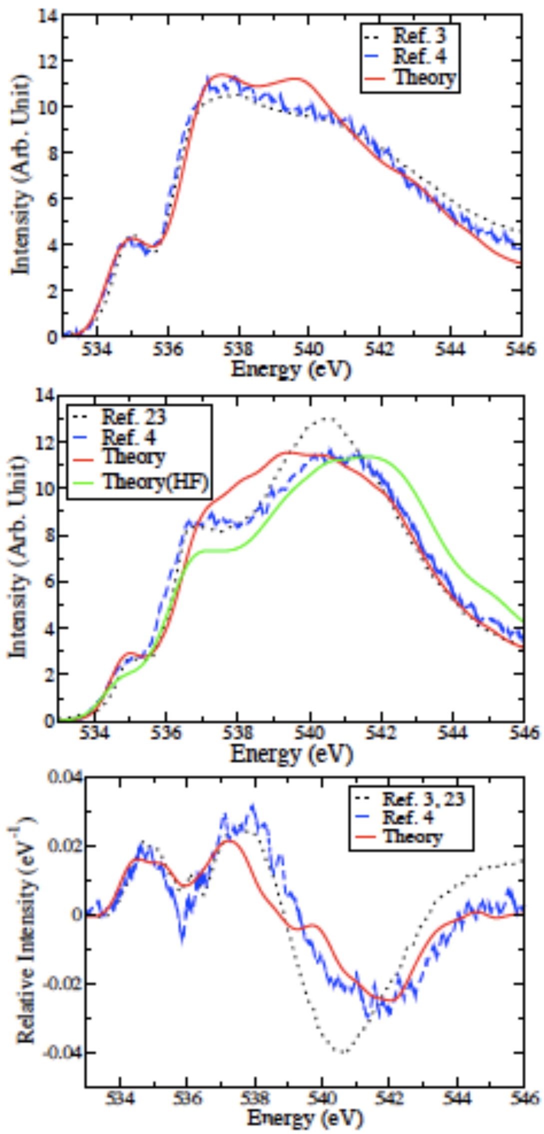
XRS experiments by Tse et al. (*PRL*, 2008) showed that IRO is important. Notice the similarity between HDA and water, and between LDA and ice. Both HDA and LDA have negligible broken bond fractions and equally extended networks

Modeling theoretically XAS, XRS experiments is challenging: (a) the spectral features are associated to core excitons, and (b) the spectra are highly sensitive to the adopted model of atomistic disorder

Our group showed that accurate spectral calculations are possible using the static Coulomb-hole and screened exchange approximation for the self-energy of the excited electron in the field of a frozen screened core hole (W. Chen, X. Wu, R. C., *PRL*, 2010)

In combination with good models of disorder this approach leads to spectra that are not only qualitatively but also quantitatively in good agreement with experiment (L. Kong, X. Wu, R. C., *PRB*, 2012)

Quantum disorder due to zero-point motion is important to achieve almost quantitative agreement



Upper panel: water at 300K

Middle panel: ice Ih (proton disordered) at 269K

Lower panel: difference spectrum (water – ice)

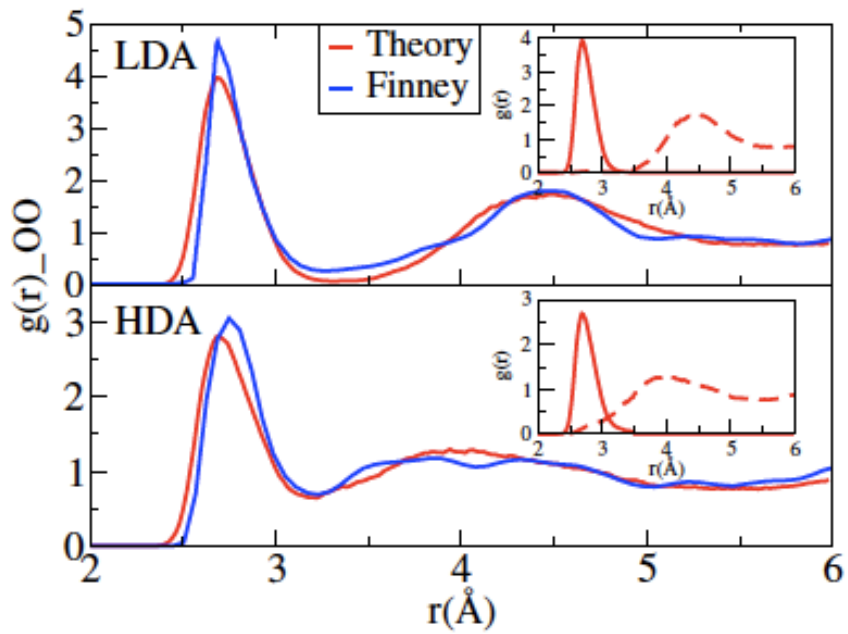
Spectra aligned at onset and normalized by area

Theory: molecular configurations from path integral AIMD (BLYP) (J.A. Morrone and R.C., *PRL*, 2008), static GW screening with HL local density approximation

Experiments: 1 - Wernet et al (*Science* 2004); 3 - Tse *et al.* (*PRL* 2008); 12 - Nilsson et al. *(JCP* 2005)

From L. Kong, X. Wu, and RC (PRB, 2012)

Model amorphous ice structures are useful to understand the spectral role of network changes (IRO)



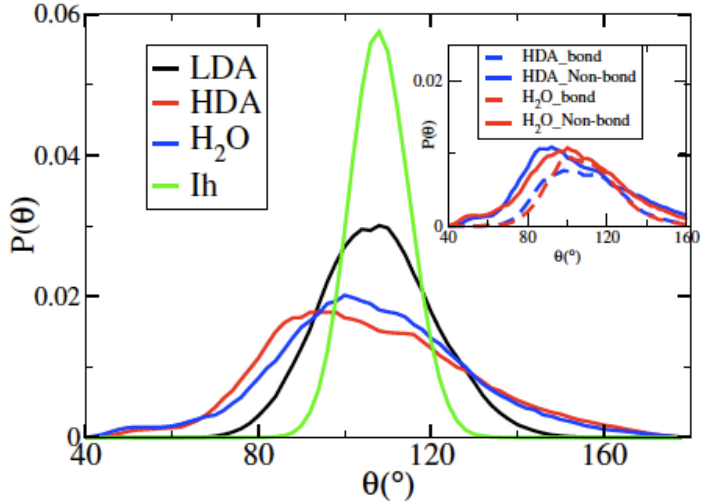
LDA and HDA structures generated with the WWW bond switching scheme followed by refinement with AIMD (PBE) with colored noise (Ceriotti, Bussi, Parrinello, *PRL*, 2009) to include quantum zero-point disorder

Experiment: Finney et al. (*PRL,* 2002)

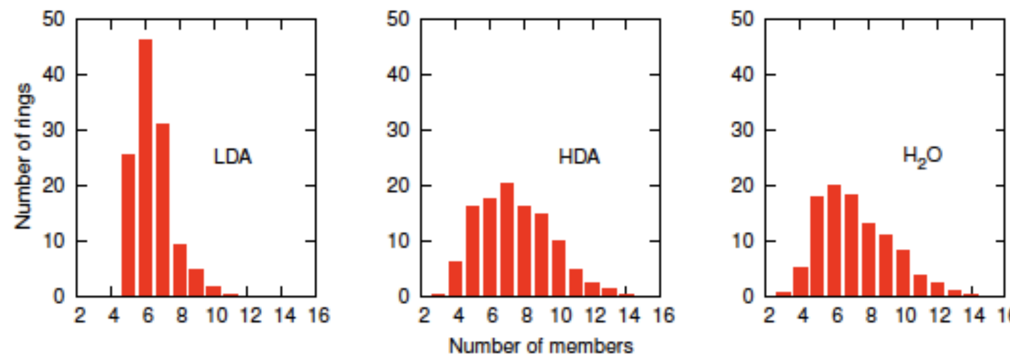
Notice the collapse of the 2nd shell of neighbors in HDA

From L. Kong and R. C. (2013)

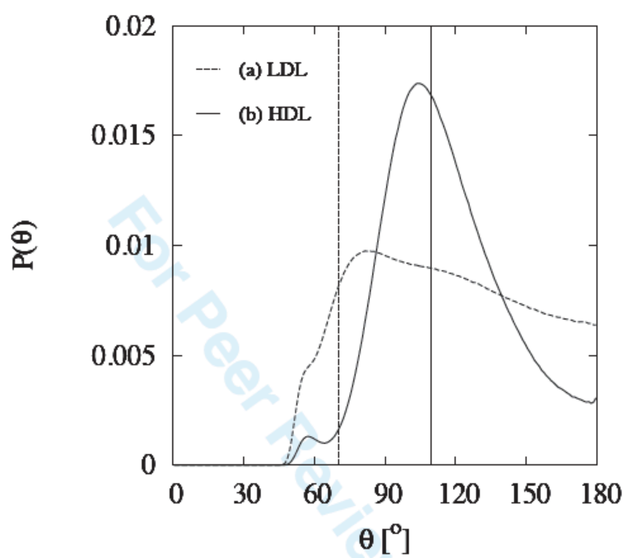
Assessing SRO and IRO of amorphous ices and liquid water



O-O-O bond angle distributions in simulated models

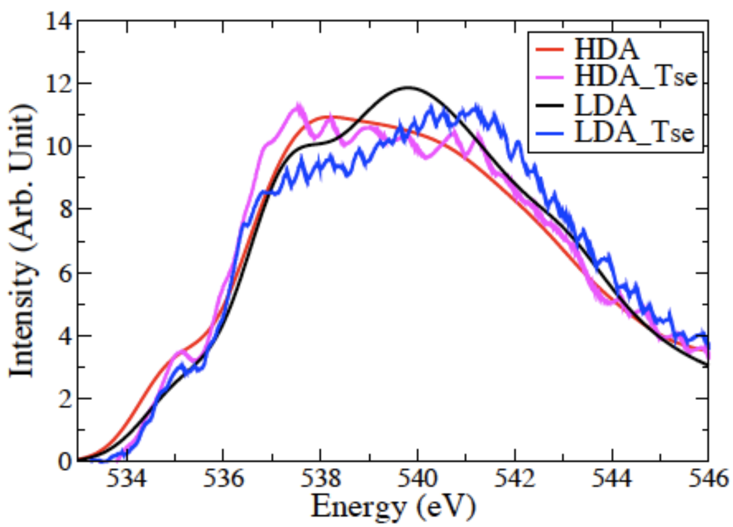


Ring distribution in LDA, HDA ices and liquid water



O-O-O bond angle distributions extracted from experiments (A. Soper, *Mol. Phys.* 2008)

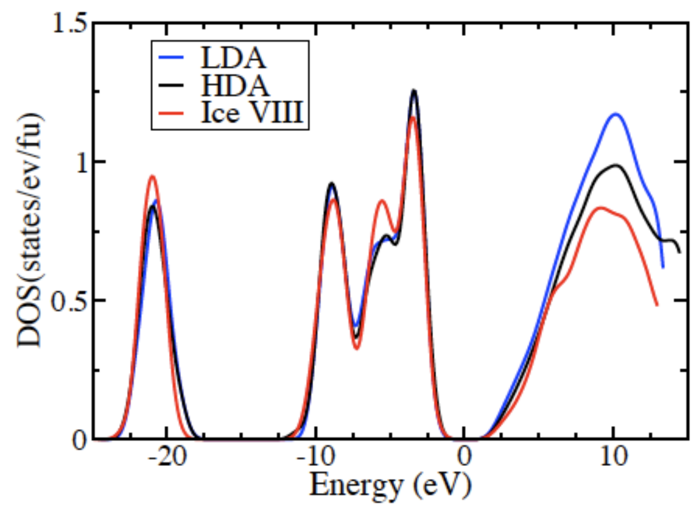
XRS spectra: comparison theory-experiment



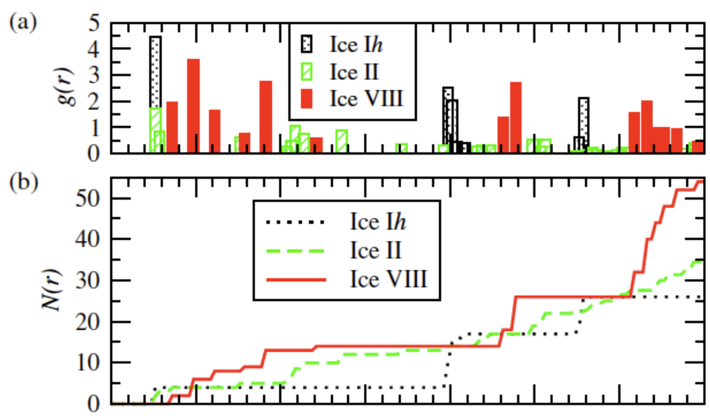
Experiment: J. Tse *et al.* (*PRL,* 2008) Theory: L. Kong, and RC (2013)

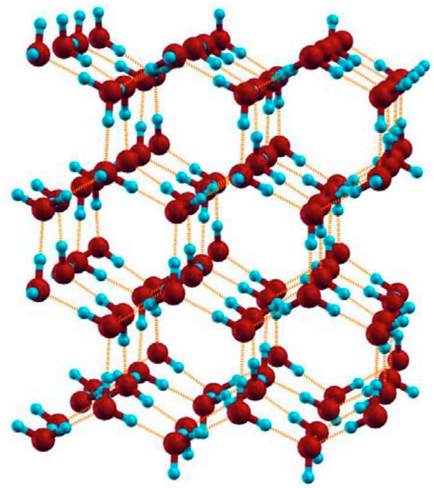
Notice post-edge reduction main-edge enhancement in HDA vs LDA

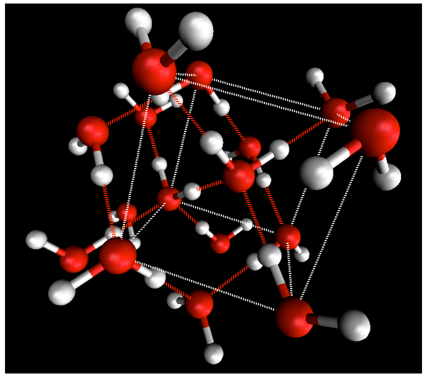
The effect on the post-edge correlates with the behavior of the electronic DOS (right panel) as suggested by W. Chen, X. Wu and RC (*PRL,* 2010) who found that *non-bonded* molecules in the range of the first coordination shell broaden the conduction band feature at ~10 eV. Ice VIII, a high pressure form of crystalline ice, is an extreme case of collapse of the 2nd neighbor shell to accommodate the density increase.

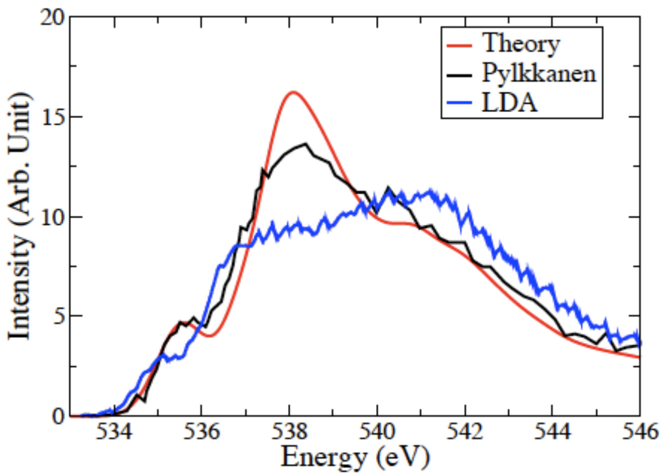


Ice VIII: an extreme case of collapse of the 2nd shell of neighbors









Experiment: T. Pylkkannen et al. (*J. Phys. Chem. B*, 2010) Theory: L. Kong and RC (2013)

Spectral effects similar to those that were assigned to H-bond breaking in l-water can be ascribed entirely to SRO, IRO changes due to changes in the network topology promoted by density changes

Concluding remarks

• The topology of extended tetrahedral networks is largely independent of the chemistry details (H vs. covalent bonds) but H-bonds have specificities that stem from the asymmetric character of the bond and from the role of zero-point motion and tunneling

• Modeling quantum dynamics effects is challenging, so far we have been limited to statics

• Modeling experiments that probe the local order is challenging and, in view of the underlying topological structure, attributing observations made with local probes to purely local effects is dangerous as SRO and IRO are strongly intertwined due to the network topology

• Spectral calculations (XAS, XRS) are also challenging because they depend on the accuracy of the underlying structure ***and*** of the excitation cross-section calculation. The latter depends on non trivial electronic many body effects

Acknowledgement

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