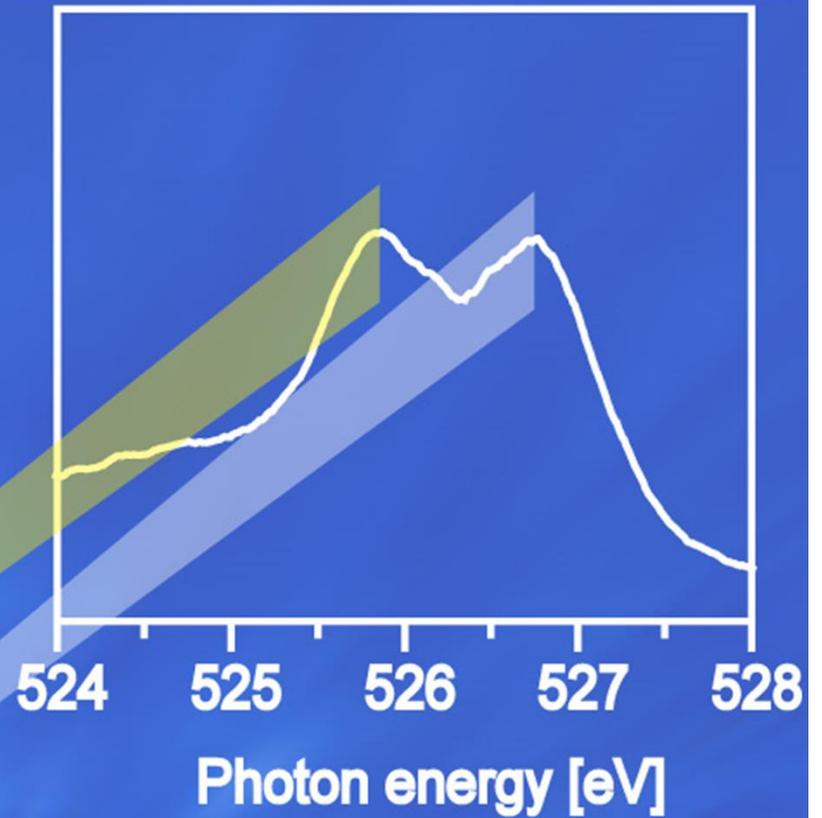


X-ray Spectroscopy and Structure of Water

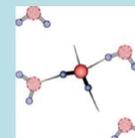


Lars G.M. Pettersson
Stockholm University

"HDL/LDL" Fluctuations in Ambient and Supercooled Water

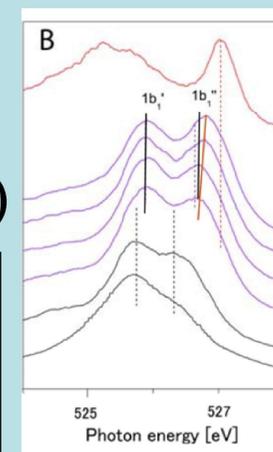
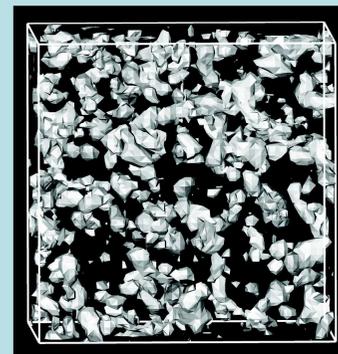
- **XAS** indicates *predominant asymmetrical H-bonding* with fewer H-bonds than in tetrahedral model

Wernet *et al.*, *Science* **304** (2004) 995



- **XES** shows *two motifs*: strongly tetrahedral ("LDL") and very disordered ("HDL"); 25:75

Tokushima *et al.*, *Chem. Phys. Lett.* **460** (2008) 387

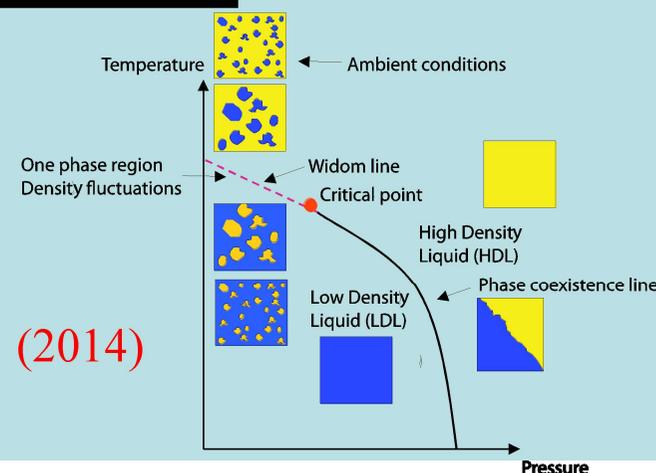


- **SAXS** shows *density fluctuations* Enhanced upon cooling

Huang *et al.*, *PNAS* **106**, 15214 (2009); *JCP* **133**, 134504 (2010)

- **XRD** shows *accelerated transition to LDL* on supercooling to $T \sim 227$ K

LCLS free-electron laser; Sellberg *et al.*, *Nature* **510**, 381 (2014)



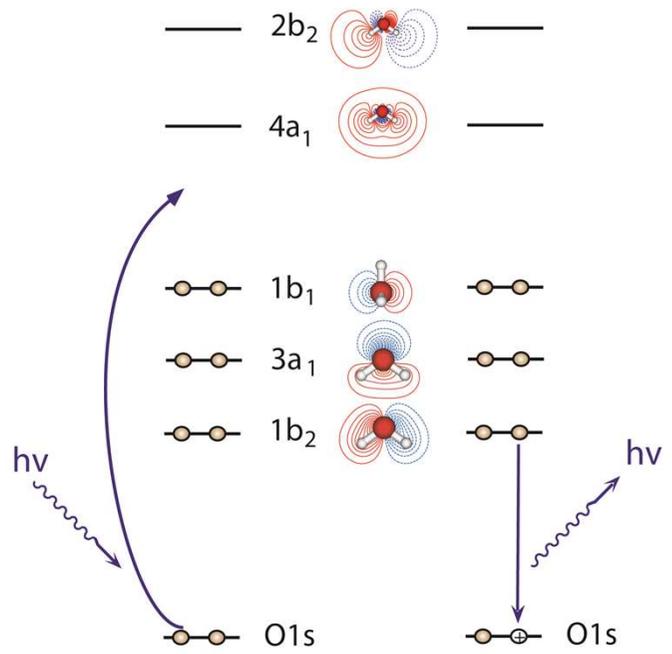
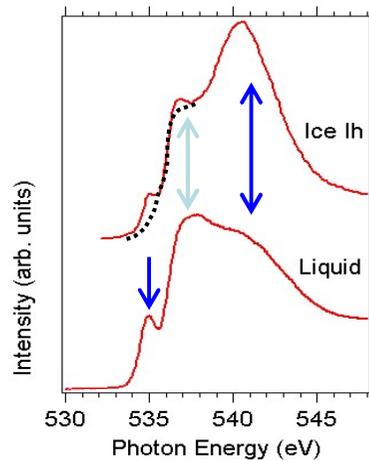
XAS and XES

XAS

X-ray Absorption Spectroscopy

Core electron excited into unoccupied state

Measures unoccupied



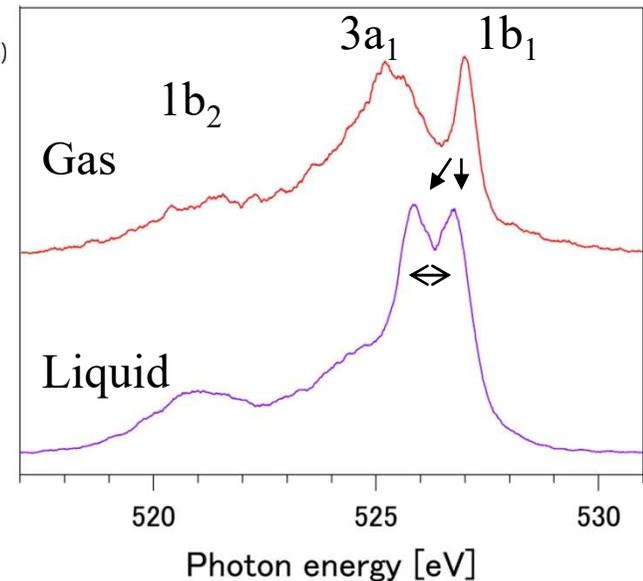
X-ray Absorption Spectroscopy (XAS) X-ray Emission Spectroscopy (XES)

XES

X-ray Emission Spectroscopy

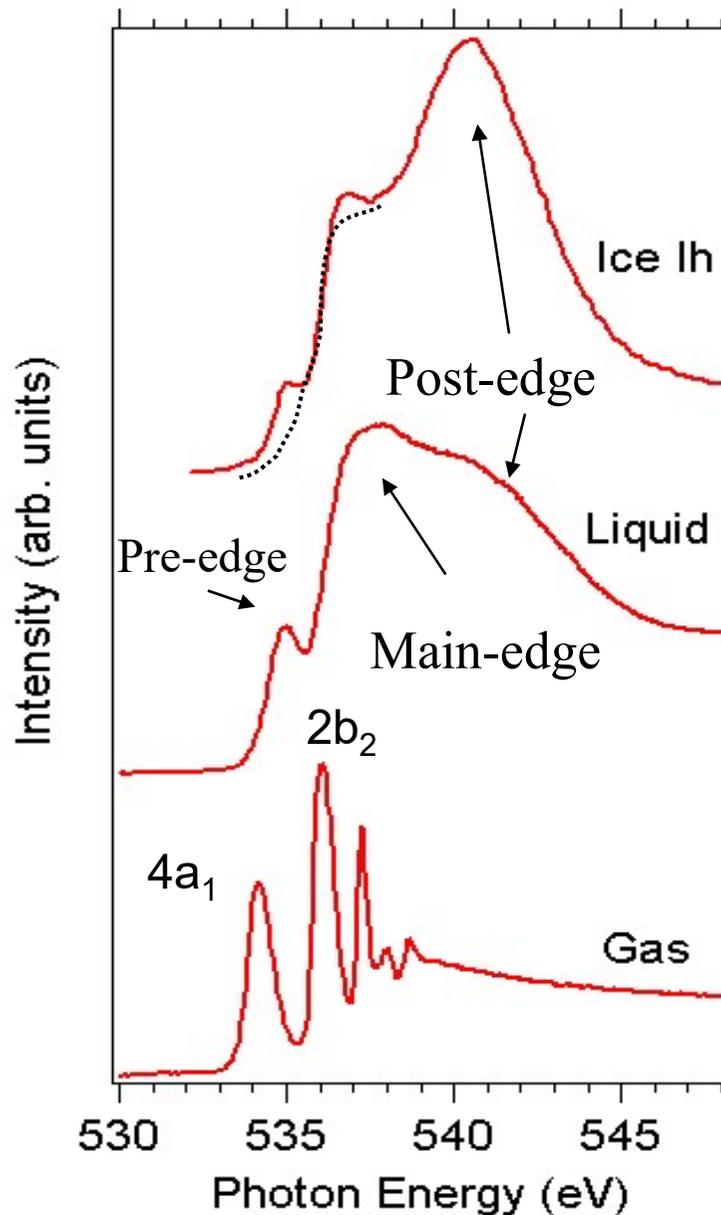
Valence electron decays to fill hole created by XAS

Measures occupied states



~3-4 fsec

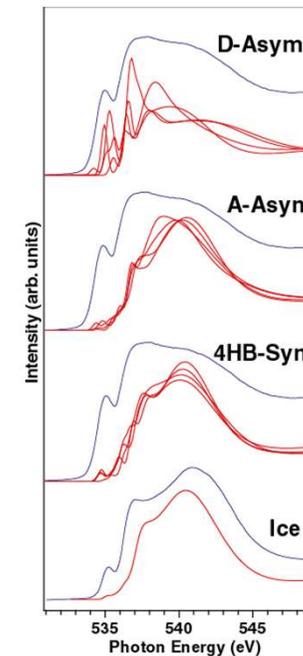
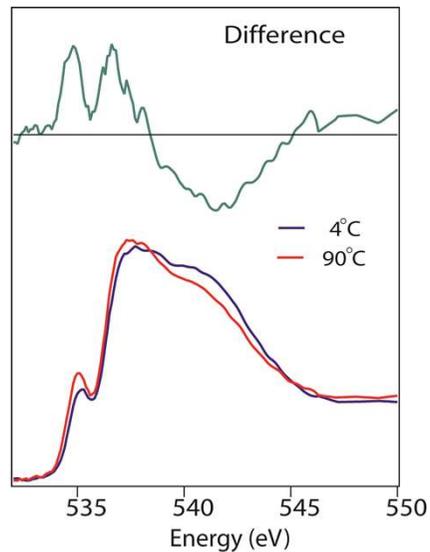
X-ray Absorption Spectroscopy of Water



Wernet *et al.*, *Science* **304** (2004) 995

Myneni *et al.* *J. Phys. Condens. Matter* **14** (2002) 213

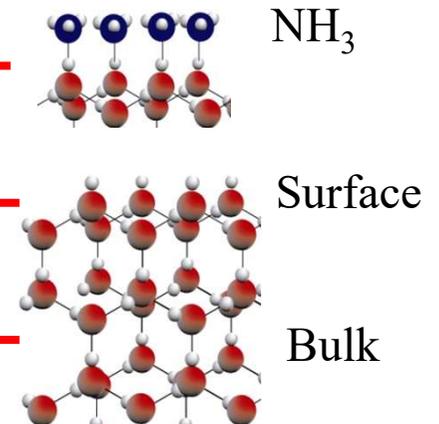
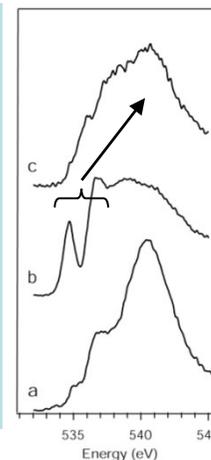
X-ray Raman Scattering High-resolution



Simulations

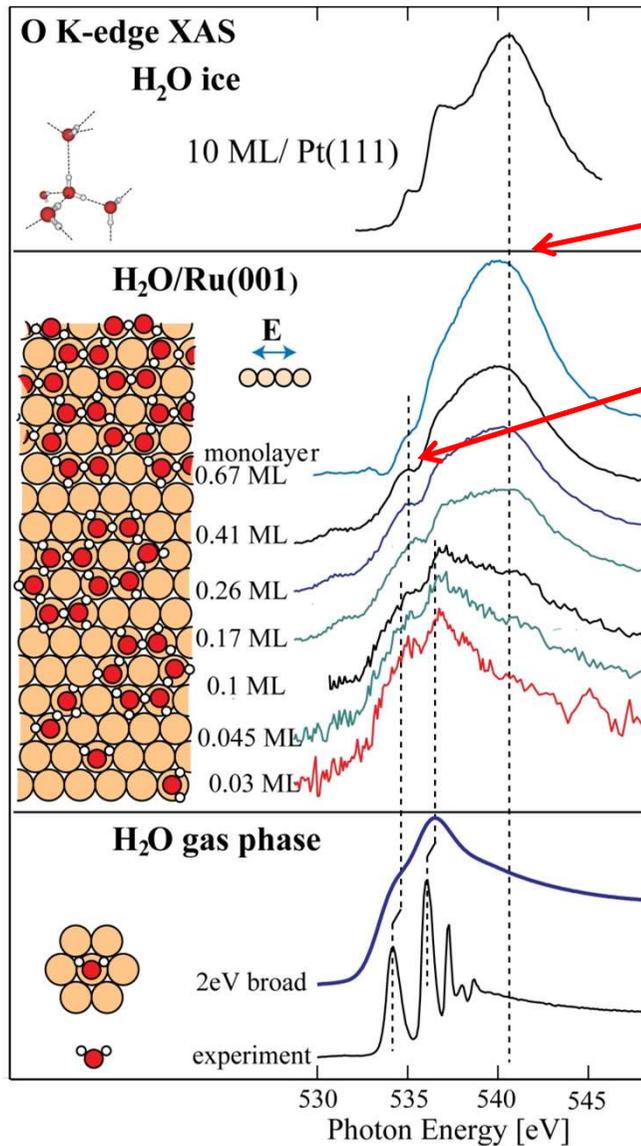
Pre-edge from asymmetric donating H-bonds one broken or distorted

Post-edge: H-bonds



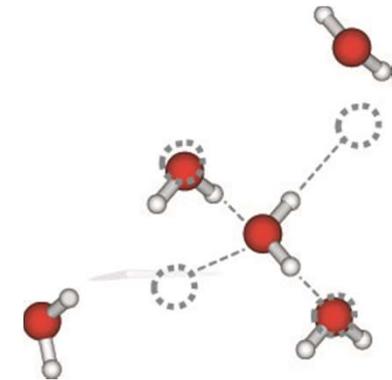
Nilsson *et al.*, *J. Electron Spec. Rel. Phen.* **177**, 99 (2010)

Two-Dimensional Water Structures



H-bond signal

Dangling OH

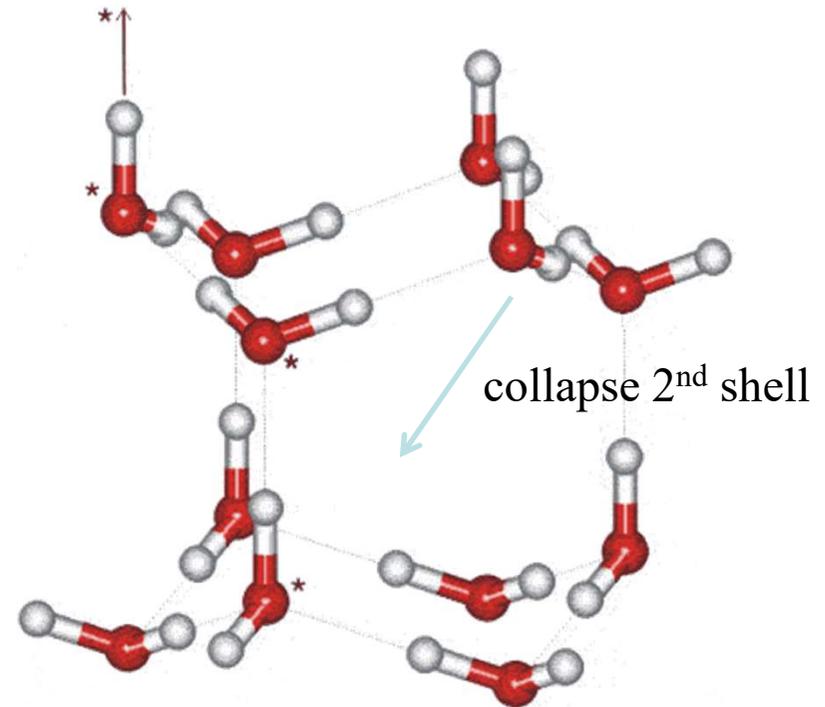
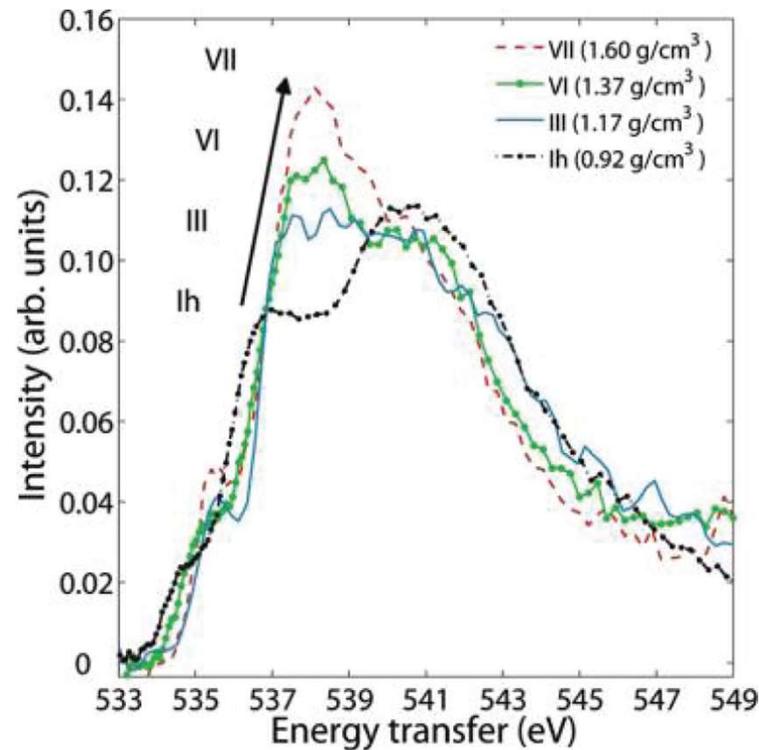


Asymmetrical distortions

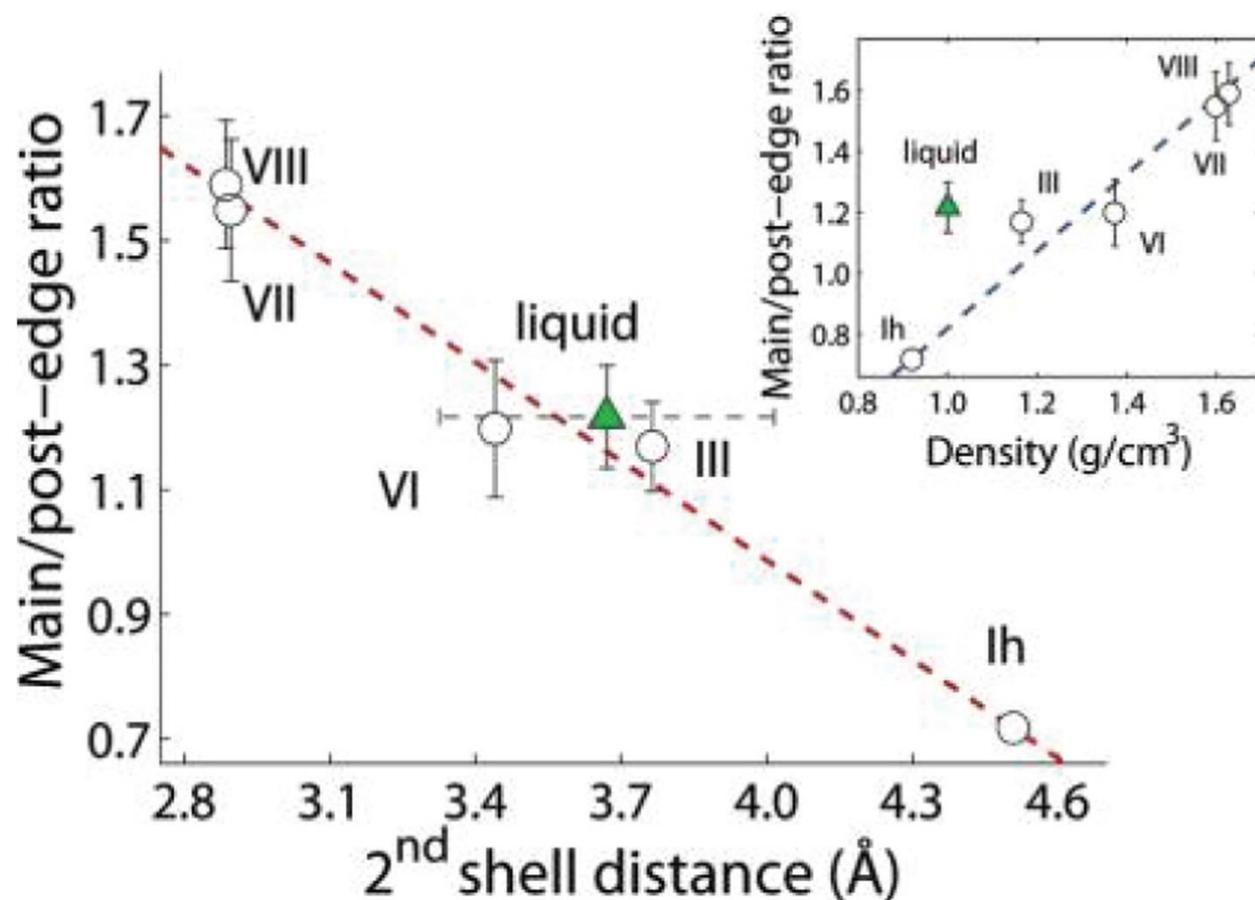
Follow spectrum development for known water structures on Ru(0001)
No donated (ND) to 1 donated (SD) to 2 donated (DD)

Main-edge; Collapse of 2nd Shell High Density Form

X-ray Raman scattering of high pressure ices
Strong increase in main-edge

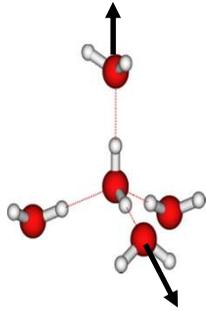


Main-edge; Collapse of 2nd Shell High Density Form

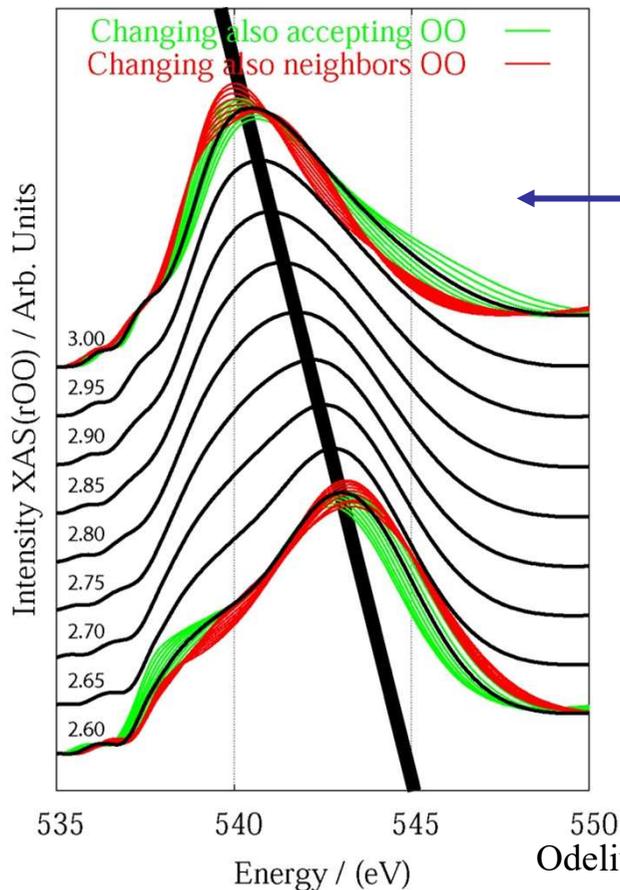


Water should have
a collapsed 2nd
shell
High Density
Liquid (HDL)

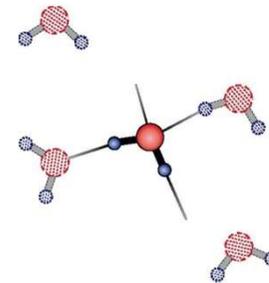
Bondlength with the Ruler



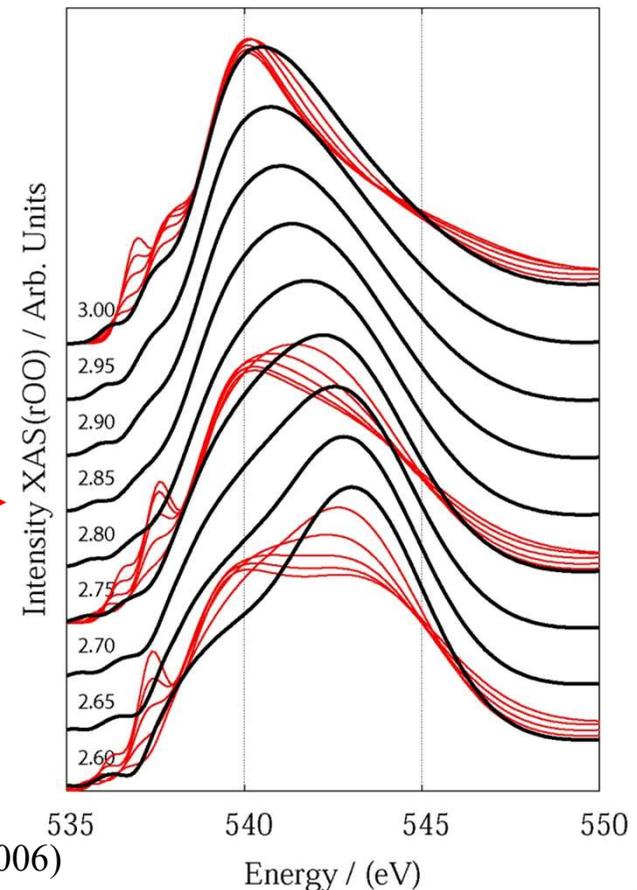
Symmetrical distortions



Effects on spectra from distortions of ice structure

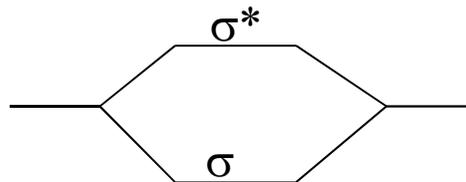


Asymmetrical distortions



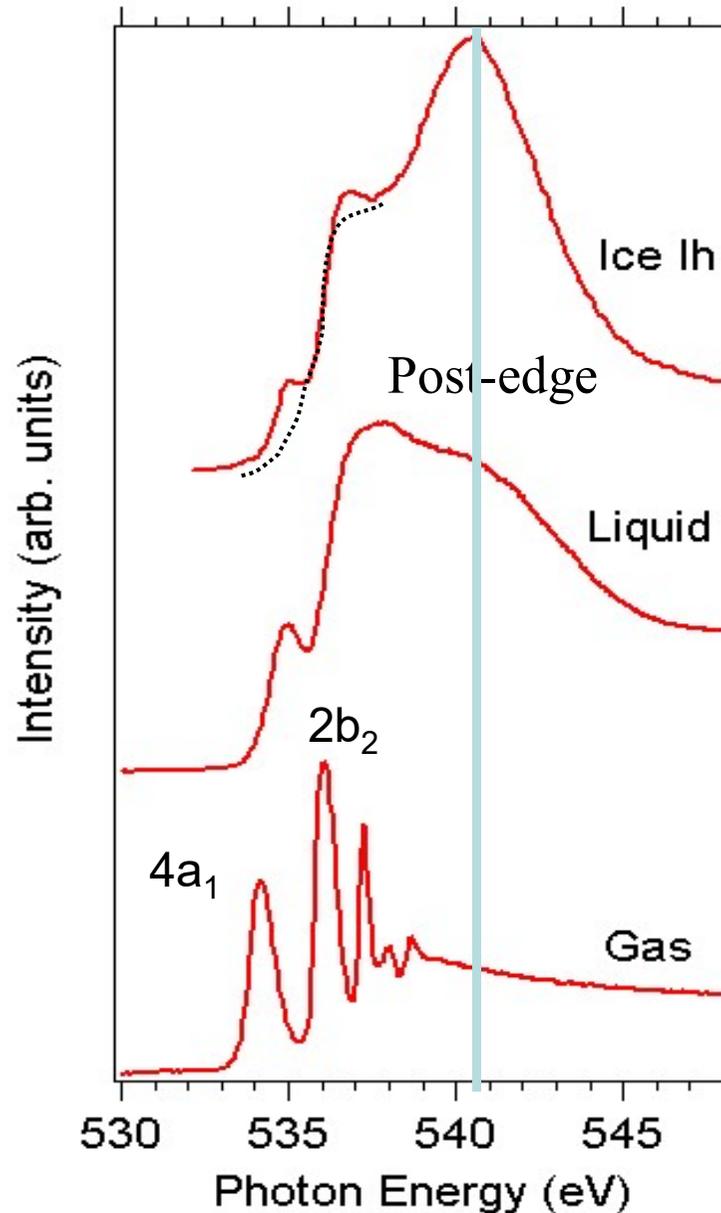
Post-edge position depends on H-bond length (“bondlength with the ruler”) Anti-bonding state

XAS sensitive to asymmetry in H-bonding



Odelius et al, Phys Rev B 73, 024205 (2006)

X-ray Absorption Spectroscopy of Water



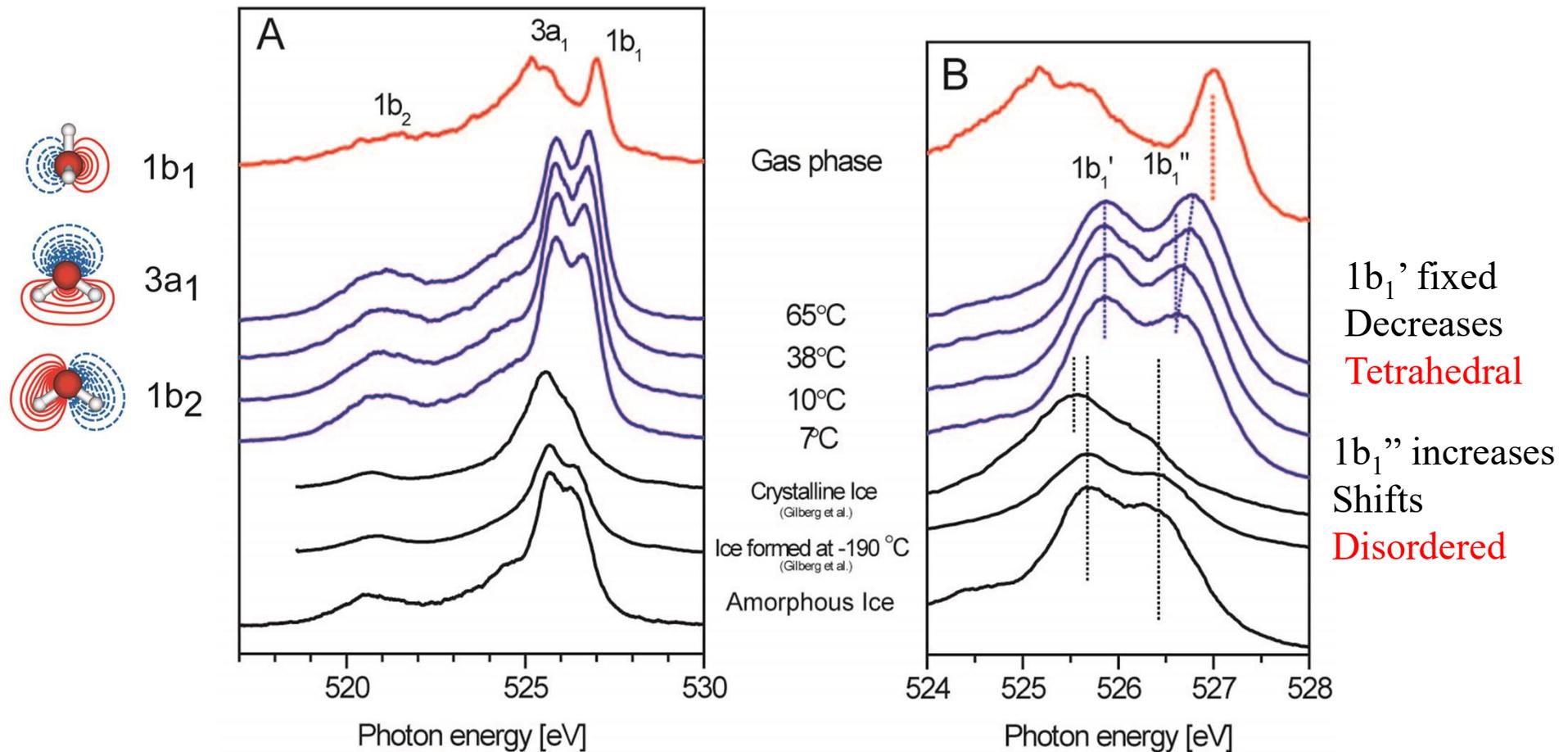
Post-edge shifted to
Higher energy in the liquid

Shorter H-bond distances

Wernet *et al.*, *Science* **304** (2004) 995

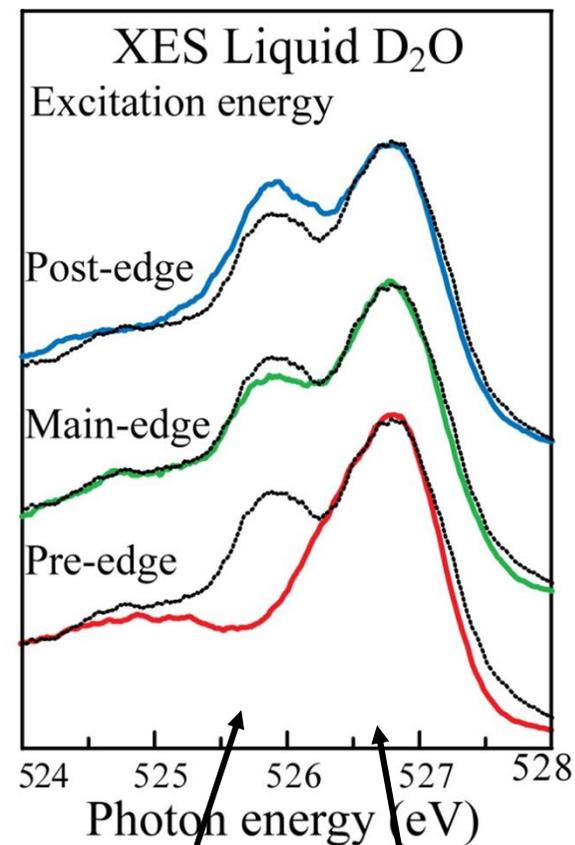
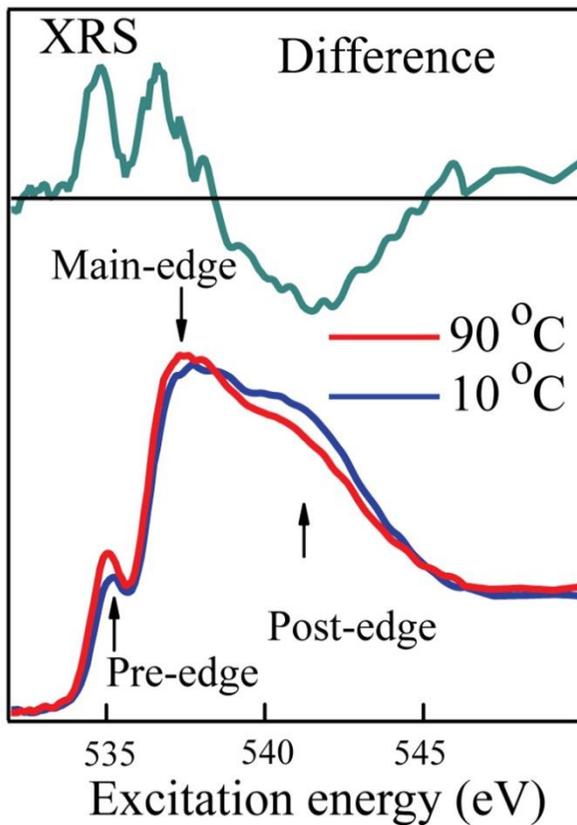
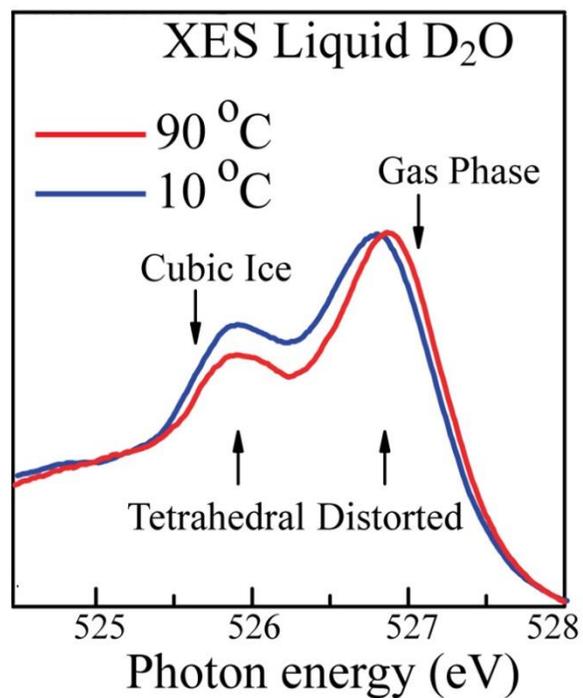
Myneni *et al.* *J. Phys. Condens. Matter* **14** (2002) 213

XES H₂O: Temperature dependence

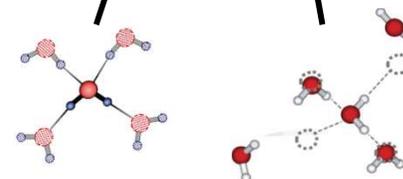


- Intensity transferred from 1b₁' to 1b₁'' as temperature is increased (**fewer H-bonds**)
- NO broadening, NO new peaks: **Either tetrahedral OR very disordered**

Connection between XAS/XRS and XES

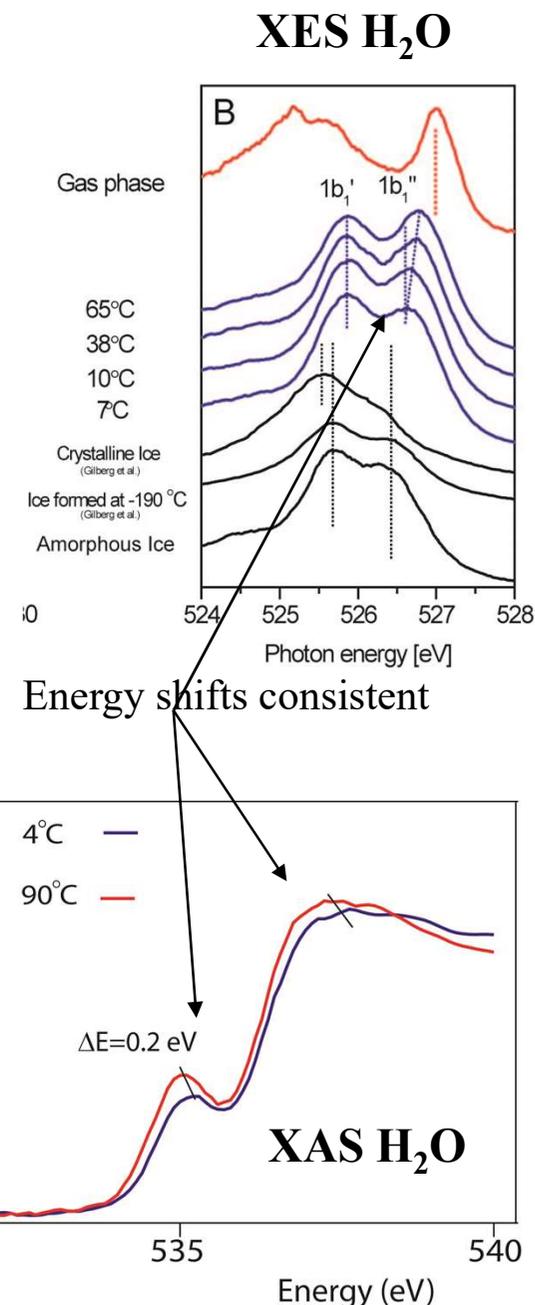


* XRS = X-ray Raman Scattering



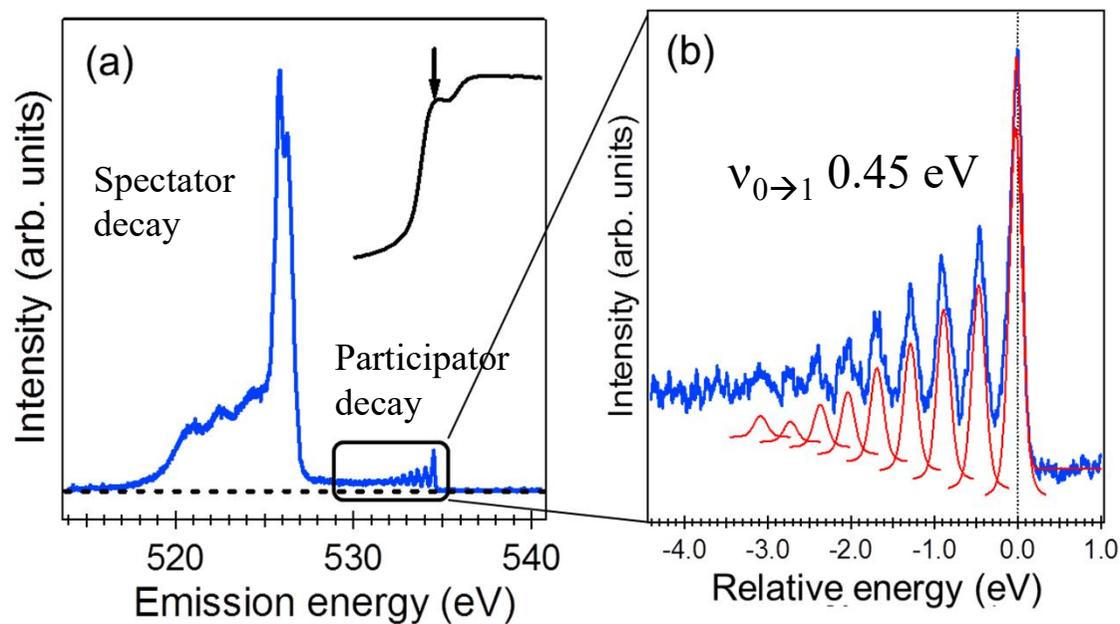
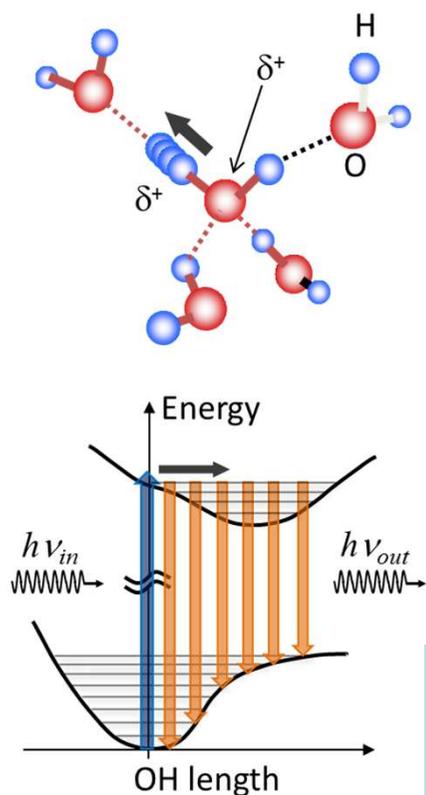
Two Local Structures: Enthalpy vs. Entropy

- **Tetrahedral loses intensity** with temperature, but peak at fixed energy
- **Distorted gains intensity and disperses** with temperature in both XES and XAS
- **Energy taken up through:**
 - Thermal excitation of distorted species
 - Breaking up a fraction of tetrahedral species



Participant Decay in XES

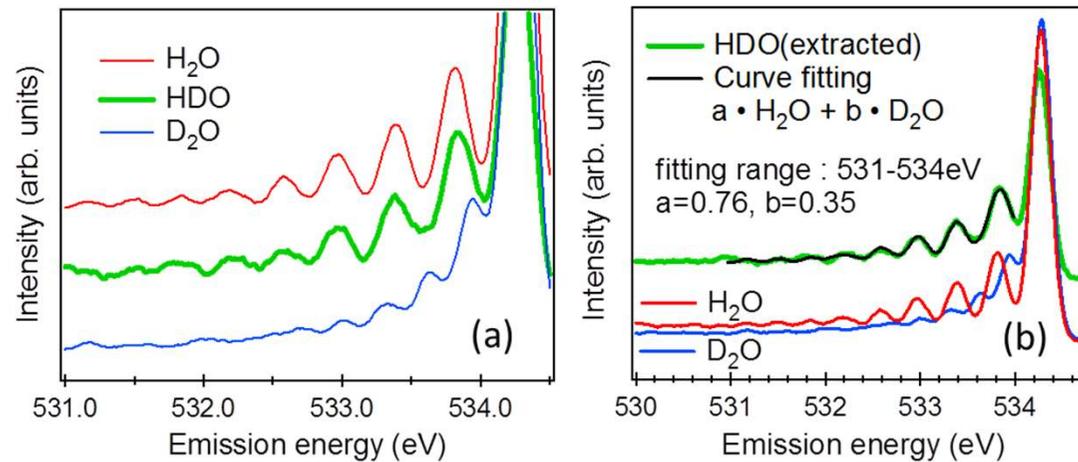
Experimental evidence of broken H-bonds



When exciting on the pre-edge the excited electron stays localized
 Excited electron may decay back – Participant decay
 Similar energy emitted – Vibrational losses
 OH stretch $\nu_{0 \rightarrow 1}$ 0.45 eV *close to gas phase symmetric* 0.453 eV
 and asymmetric $\nu_{0 \rightarrow 1}$ (0.465 eV) \rightarrow weakly interacting
 Liquid IR band peak position 0.422 eV

Harada et al., PRL
111, 193001 (2013)

Isotope Effects: In HDO OH Preferentially "Broken"



Ratio 1.50 ± 0.2
OH/OD "broken"

In HDO in H₂O or D₂O preferentially OH is broken/weakly interacting
Femtosecond pump-probe vibrational spectroscopy may not sample all situations

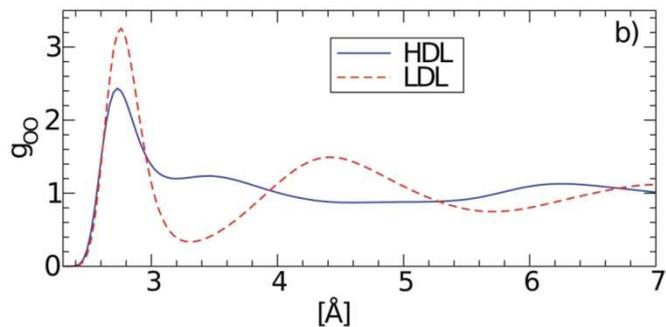
Bimodality in Simulations?

Local Structure Index (LSI)

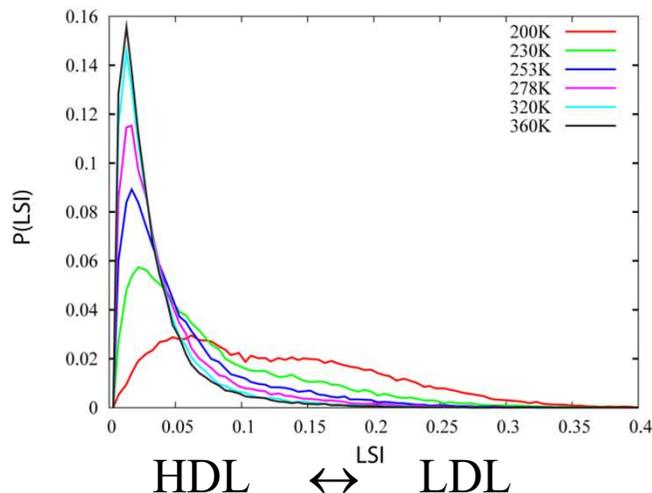
Order molecules according to distance from molecule i as

$$r_1 < r_2 < r_3 < \dots < r_{n(i)} < 3.7 \text{ \AA} < r_{n(i)+1}$$

where $n(i)$ is the number of molecules that are within 3.7 Å from molecule i



Soper & Ricci PRL **84** (2000) 2881



Define: $\Delta(j; i) = r_{j+1} - r_j$

Average: $\bar{\Delta}(i)$ is the average of $\Delta(j; i)$ over all neighbors j of molecule i within cutoff

LSI:
$$I(i) = \frac{1}{n(i)} \sum_{j=1}^{n(i)} [\Delta(j; i) - \bar{\Delta}(i)]^2$$

Measures degree of order

Shiratani & Sasai *J Chem Phys* **104**, 7671 (1996)

Shiratani & Sasai *J Chem Phys* **108**, 3264 (1998)

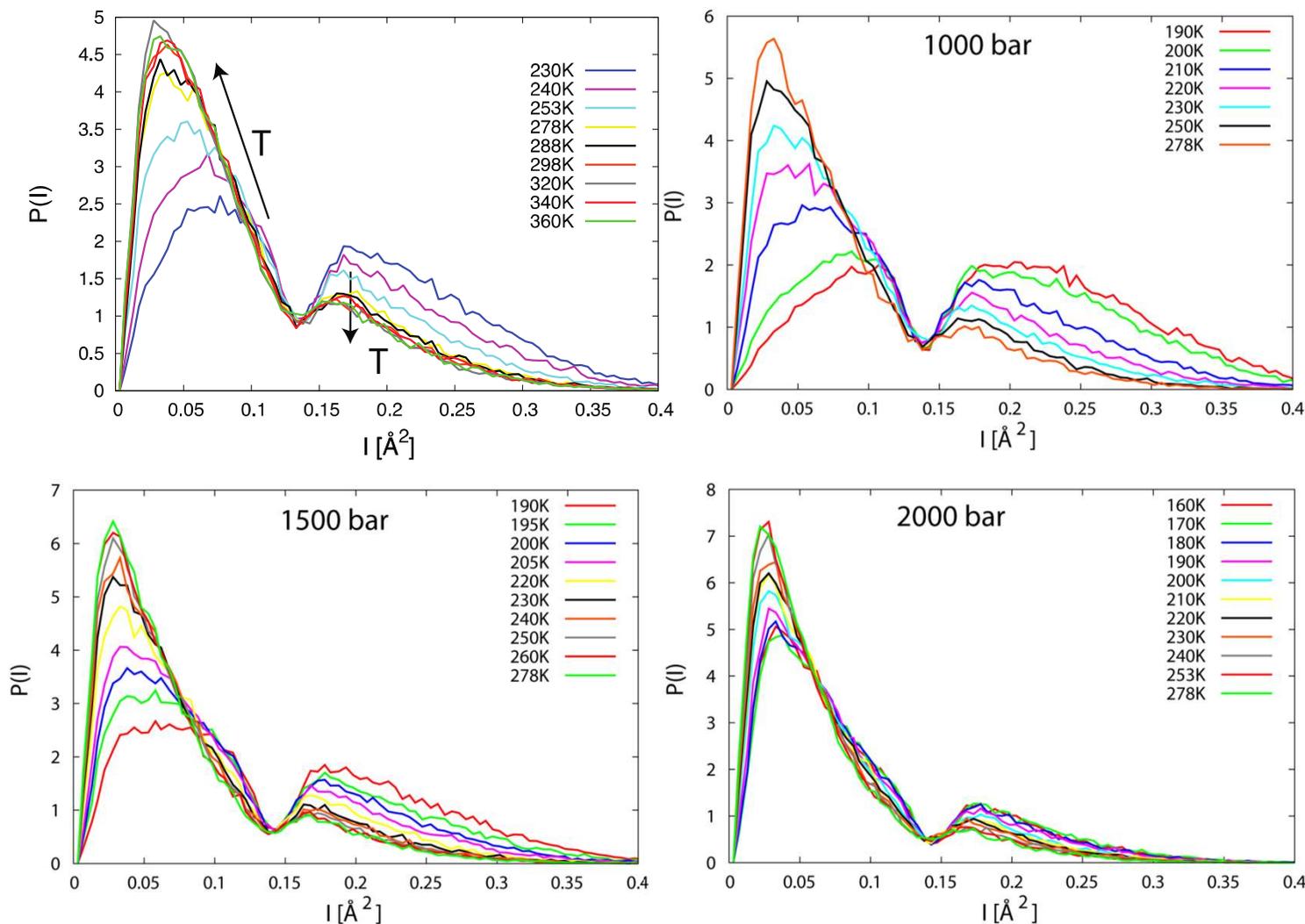
Appignanesi et al. *Eur. Phys. J. E* **29**, 305 (2009)

Accordino et al. *Eur. Phys. J. E* **34**, 48 (2011)

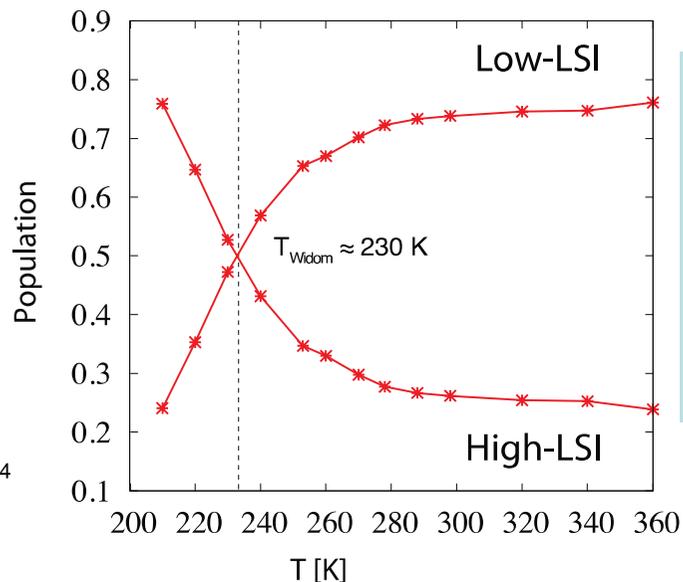
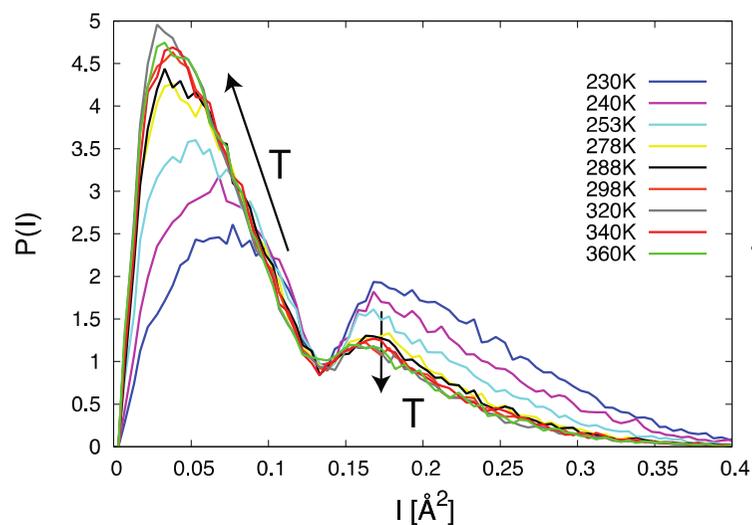
Wikfeldt et al., PCCP **13**, 19918 (2011)

Bimodality in *Inherent* Structure

Inherent structure obtained by energy minimization



Bimodality in *Inherent* Structure



Inherent Structure:
Quench to 0 K, i.e.
minimize the energy
for each dump

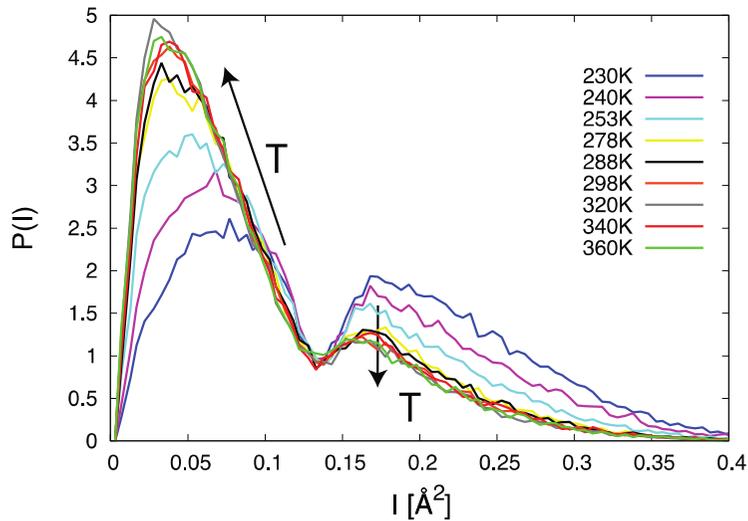
Bimodal

LSI inherent structure
High LSI fixed (LDL)
Low LSI disperses (HDL)

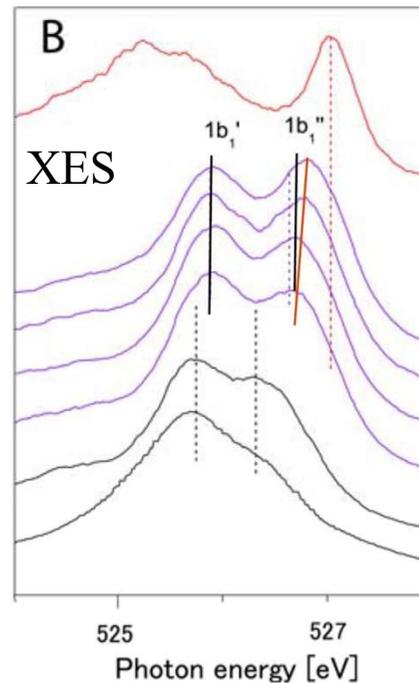
Ambient conditions:
~75% HDL, 25% LDL
(\equiv XAS, XES)

Widom line:
50% HDL, 50% LDL
Maximum fluctuations
(κ_T, C_P)

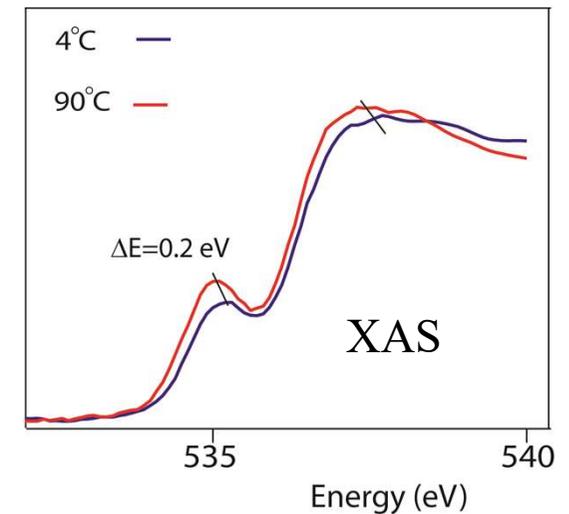
Temperature Dependence LSI vs XES/XAS



LSI inherent structure
 High LSI fixed (LDL)
 Low LSI disperses (HDL)



XES/XAS
 "LDL"-like fixed
 "HDL"-like disperses

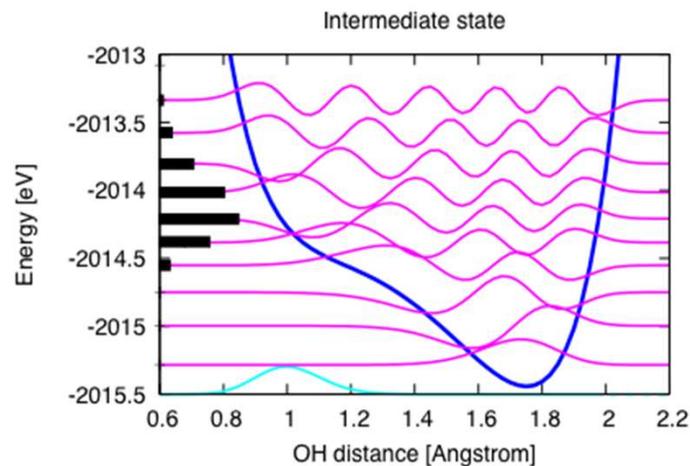
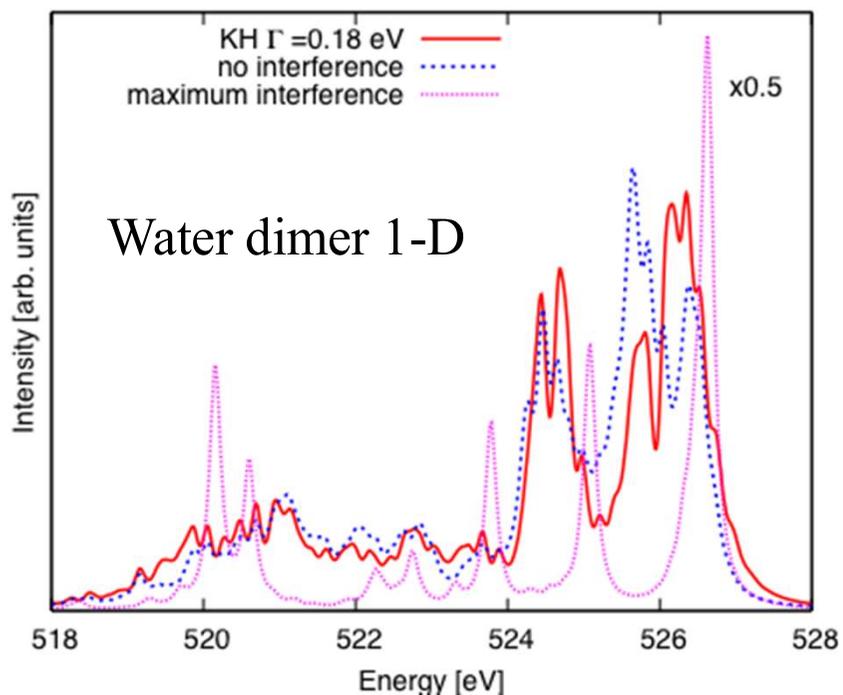


Bimodality with similar temperature dependence
 in LSI inherent structure and in XES/XAS

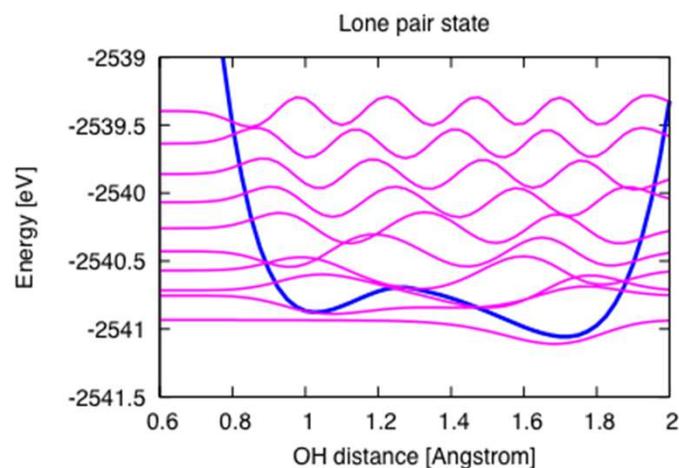
Smeared out in real structure

Kramers-Heisenberg

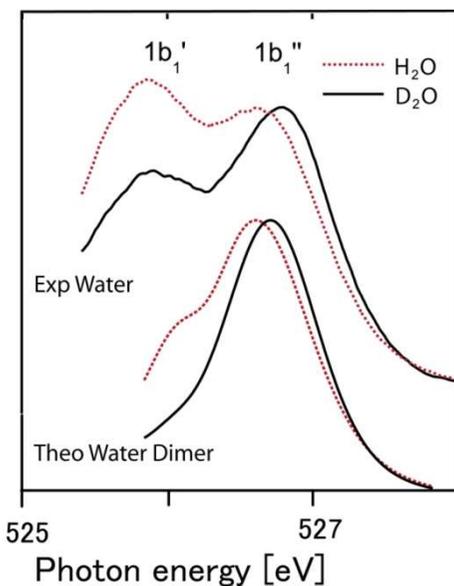
$$\sigma(\omega') \propto \sum_f \left| \sum_n \frac{\langle f | D'_{FN} | n \rangle \langle n | D_{NI} | i \rangle}{\omega' - (E_n - E_f) + i\Gamma} \right|^2$$



CH state



l.p. state



Isotope difference simply more interference for D₂O making 1b₁ peak symmetric

Core-shifted second component on either asymmetric or symmetric background

Dissociation not possible
Only delocalized vibrational states accessible

Dynamics

Semiclassical Approximation

Need reliable technique to compute XES including life-time vibrational interference for large clusters with many degrees of freedom

- treat the nuclear degrees of freedom in the time domain
- sum over classical trajectories with QM initial conditions

$$\sigma^{class}(\omega') = \sum_{traj} \sum_F |D_F^{+class}(\omega')|^2$$

- approximate nuclear Hamiltonians with corresponding electronic energy

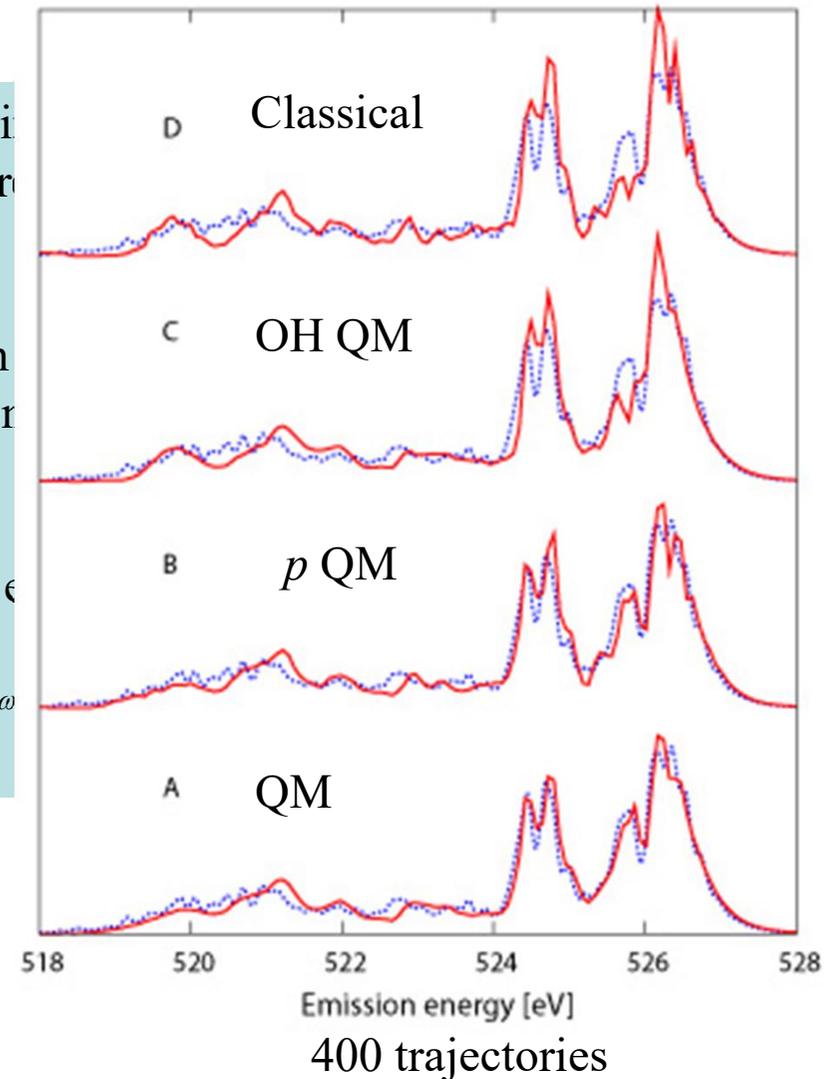
$$D_F^{+class}(\omega') = \int_0^\infty dt D_{NI}^+(0) D_{FN}^+(t) e^{-i \int_0^t (E_F(\tau) - E_N(\tau)) d\tau} e^{-\Gamma t'} e^{-i\omega t}$$

Sample structure model

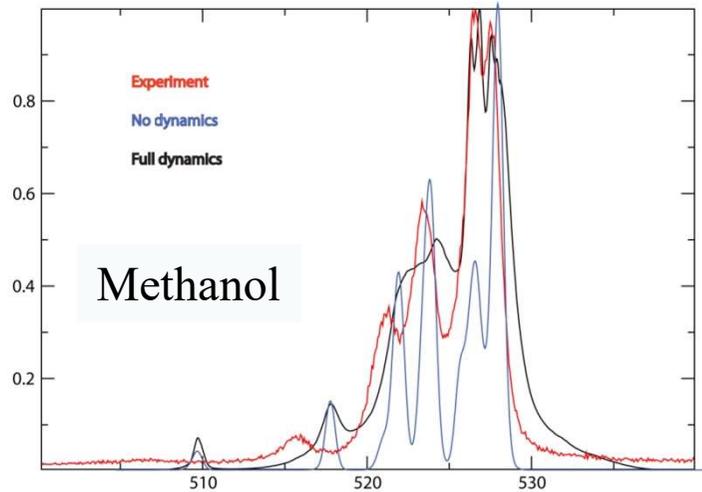
Sample QM O-H and momentum distributions for the two hydrogens

Run trajectories and sum to get one spectrum

Sample many to get spectrum for the model...

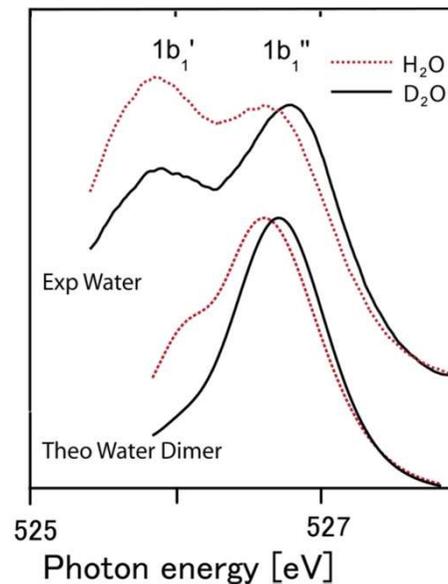
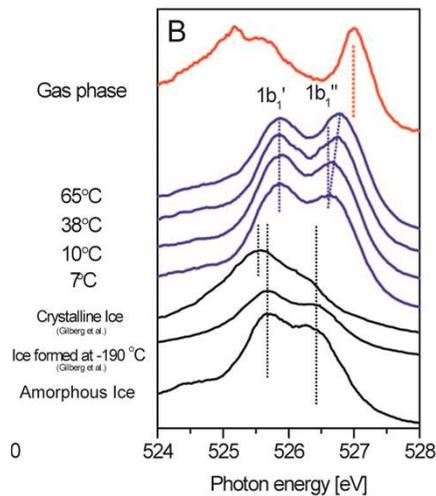


Computed XES



$$\sigma(\omega') \propto \sum_f \left| \sum_n \frac{\langle f | D'_{FN} | n \rangle \langle n | D_{NI} | i \rangle}{\omega' - (E_n - E_f) + i\Gamma} \right|^2$$

Kramers-Heisenberg expression:
Interference – or dynamical – effects modify intensity distribution – but do not give new features



Isotope difference
simply more interference
for D₂O making 1b₁ peak
symmetric

Core-shifted second
component on either
asymmetric or symmetric
background

Background - TDDFT

- Linear response TDDFT
- In its simplest form (Tamm-Dancoff) approximation:

$$\mathbf{A} \mathbf{X} = \omega \mathbf{X}$$

where

$$\mathbf{A} = \delta_{ij} \delta_{ab} (\varepsilon_a - \varepsilon_i) + K_{ia,jb}$$

$$K_{ia,jb} = \iint \psi_i^*(\mathbf{r}_1) \psi_a^*(\mathbf{r}_1) \left(\frac{1}{r_{12}} + \frac{\partial^2 E_{xc}}{\partial \rho(\mathbf{r}_1) \partial \rho(\mathbf{r}_2)} \right) \psi_j(\mathbf{r}_2) \psi_b(\mathbf{r}_2)$$

TDDFT for XES

- Extension to X-ray emission spectroscopy

1 Perform SCF calculation on core ionized state

2 Perform TDDFT calculations and X-ray emission transitions appear as negative eigenvalues

Can we build TDDFT model as accurate as EOM-CCSD?

Modification of Functionals

Best results from modification of a hybrid functional:

$$B^X\text{LYP} = X \text{ HF} + (0.92 - X) \text{ B} + 0.08 \text{ S} + 0.19 \text{ VWN} + 0.81 \text{ LYP}$$



Optimize the fraction of HF exchange:
fitted to EOM-CCSD data

optimum value is 66%: $B^{66}\text{LYP}$

Wadey & Besley, JCTC, 10, 4557 (2014)

Courtesy Nick Besley

Improved Transition Energies

Excitation	EXP. / eV	B3LYP / eV	B ⁶⁶ LYP / eV
CH ₄ 1t ₂ →1a ₁	276.3	282.7	276.4
NH ₃ 2a ₁ →1a ₁	395.1	401.9	395.3
H ₂ O 1b ₂ →1a ₁	527.0	535.3	527.6
CH ₃ OH 2a''→1a'	527.8	535.9	527.7
HF 1π→1σ	678.6	687.3	678.5

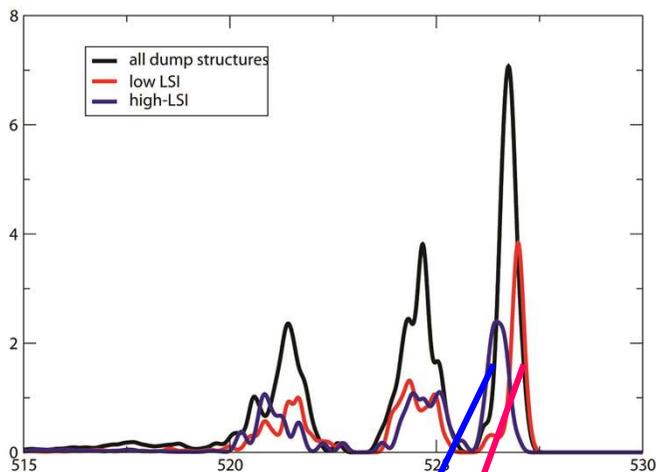
u6-311G** basis set

- Much closer agreement with experiment

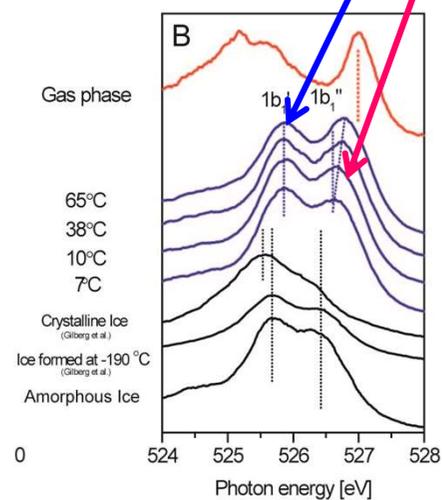
Wadey & Besley, *JCTC*, 10, 4557 (2014)

Courtesy Nick Besley

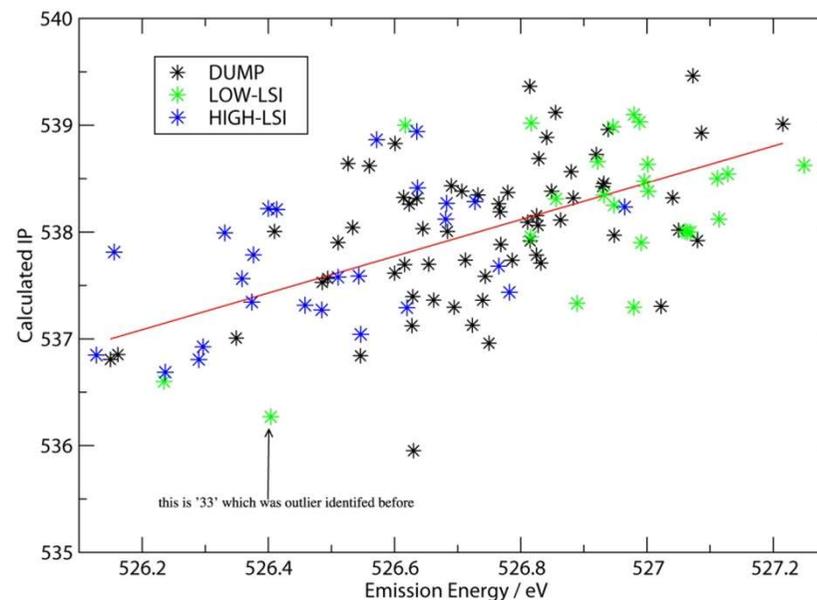
TDDFT Computed XES



XES (no dynamics) computed from an optPBE-vdW PIMD dump *gives one peak*, but high and low LSI structures reproduce the experimental split

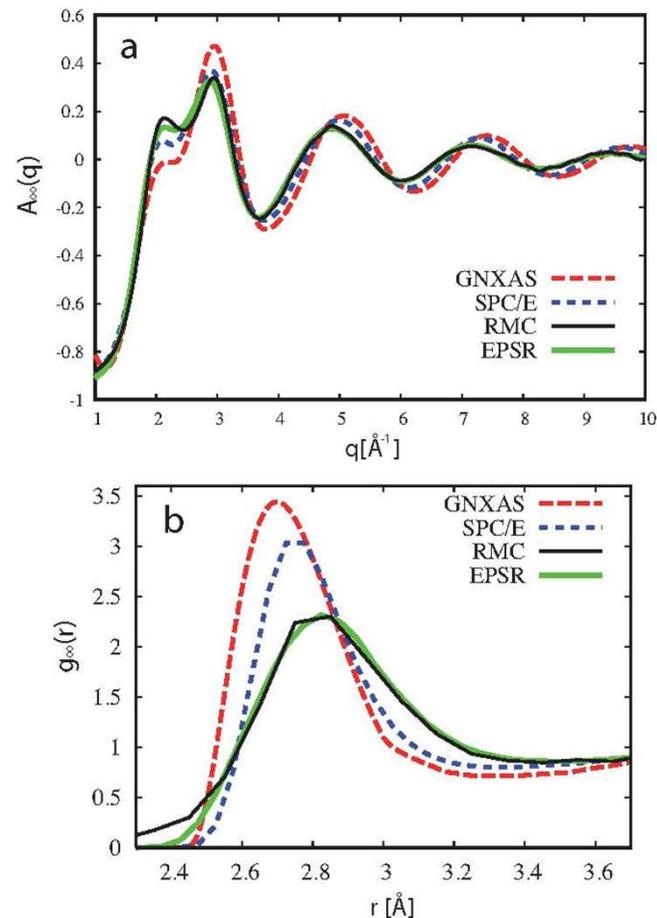


Connection between IP and XES peak position



Besley & Pettersson, unpublished

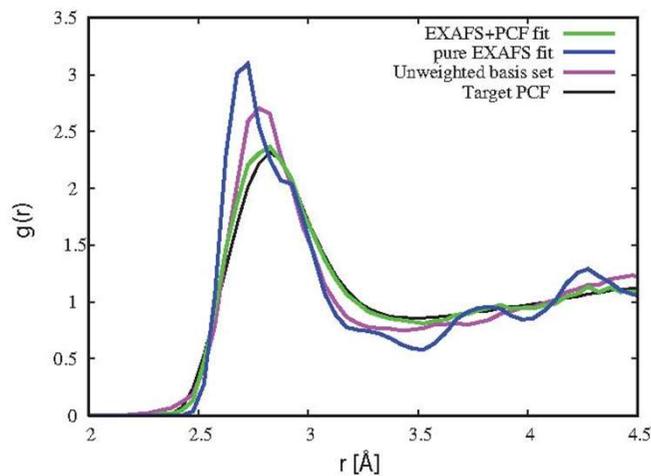
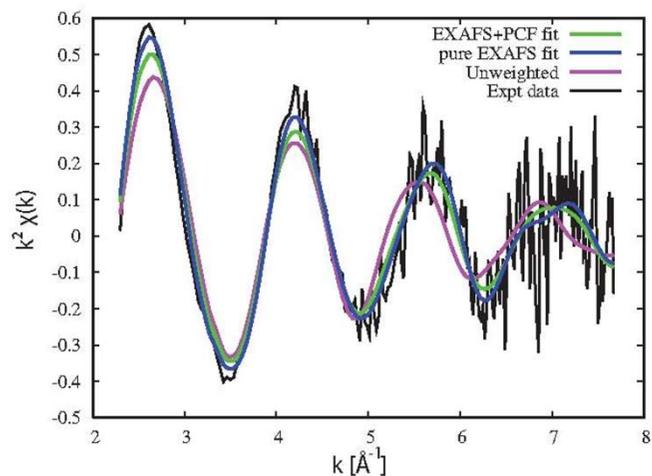
O-O Pair-Correlation from EXAFS



Structure factor determined by Bergmann et al. J. Chem. Phys. **128**, 089902 (2008) from EXAFS wiggles in X-ray Raman Spectroscopy of water.

The derived PCF was highly peaked towards short distances compared to RMC and EPSR fits to neutron data (Soper) and x-ray data (Hura et al.)

Combine XRD+ND with EXAFS



Fit simultaneously EXAFS signal and PCF

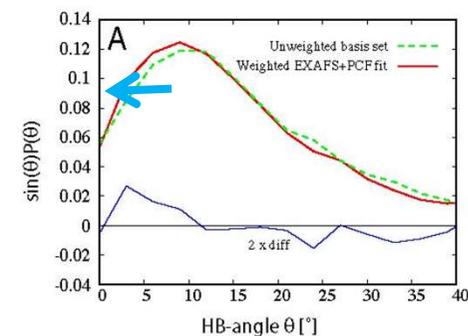
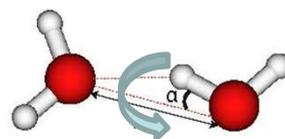
Joint solution possible

EXAFS very sensitive to strong, directional H-bonds

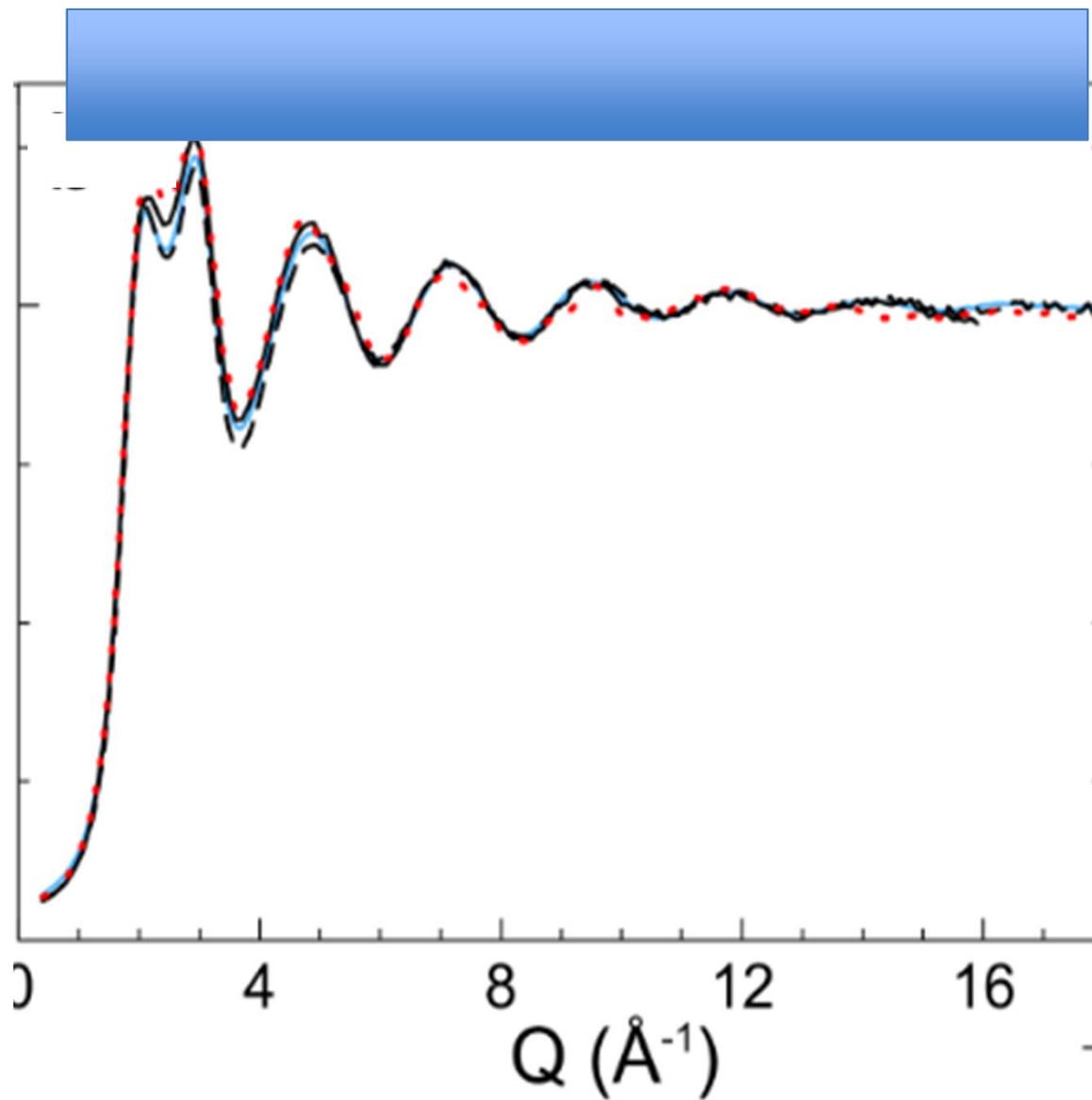
XRD+ND sees all situations

EXAFS enforces a subclass of structures with well-defined H-bonds

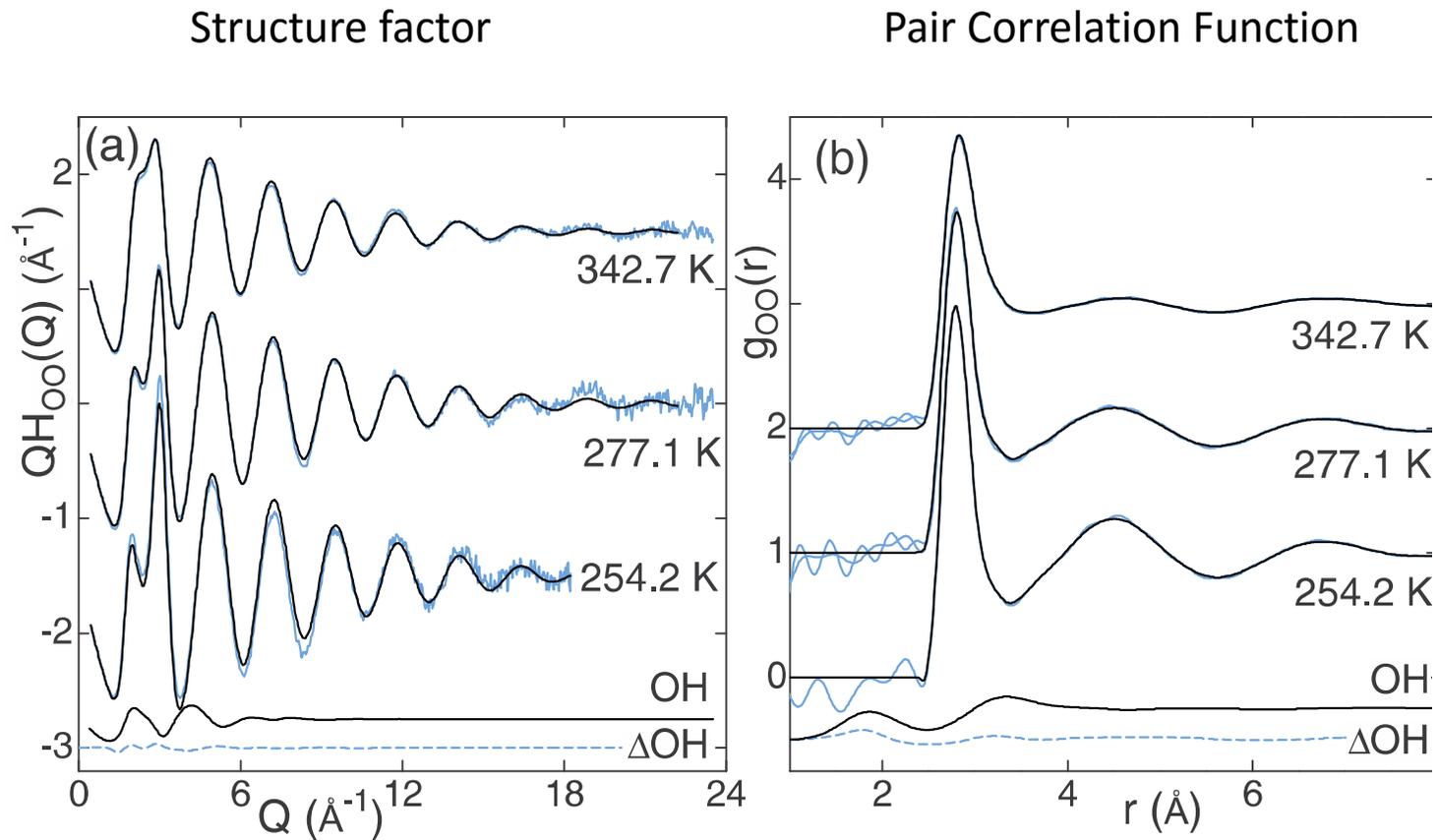
Complementary information

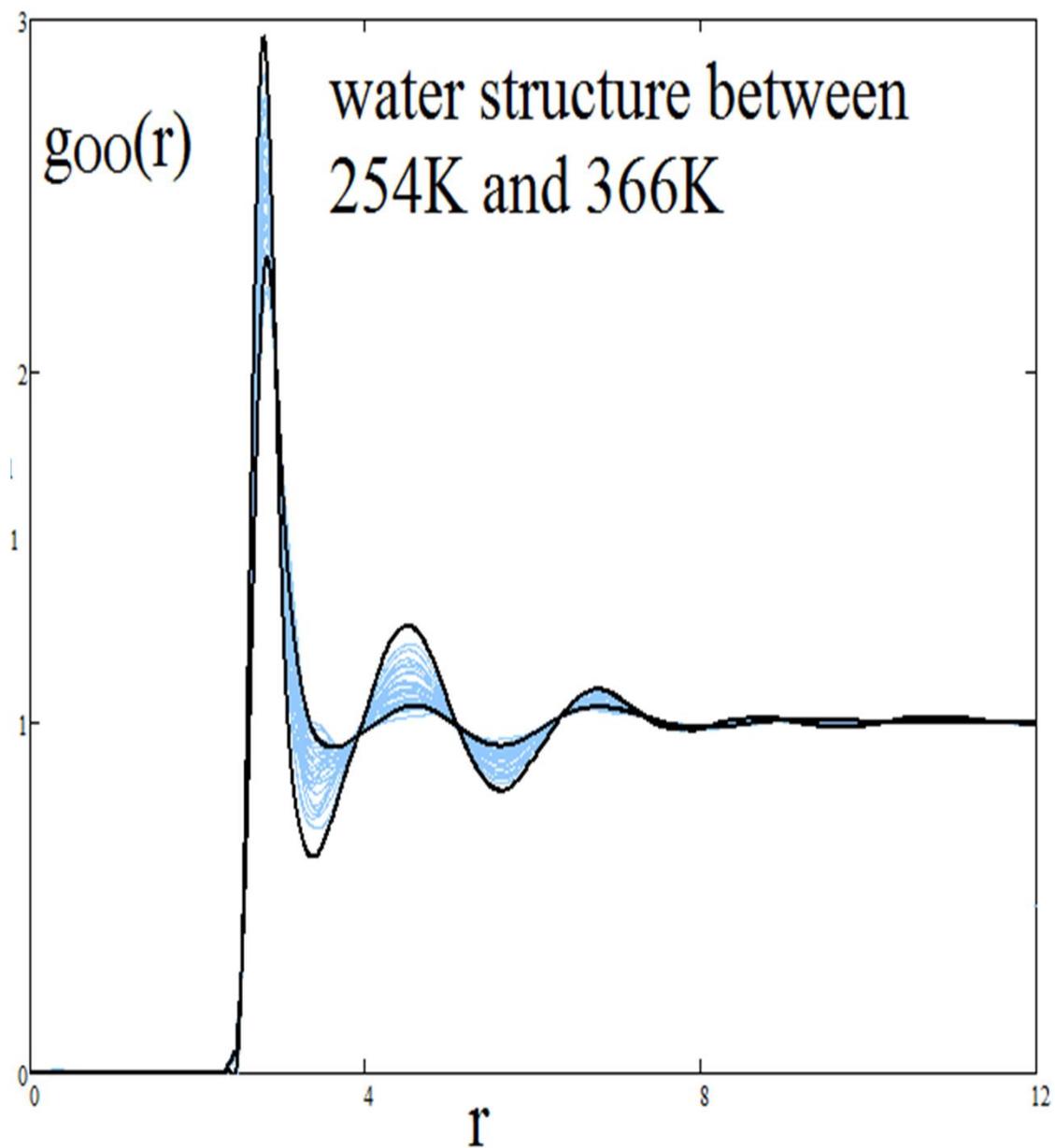


Wide Angle Region $Q > 0.5 \text{ \AA}^{-1}$



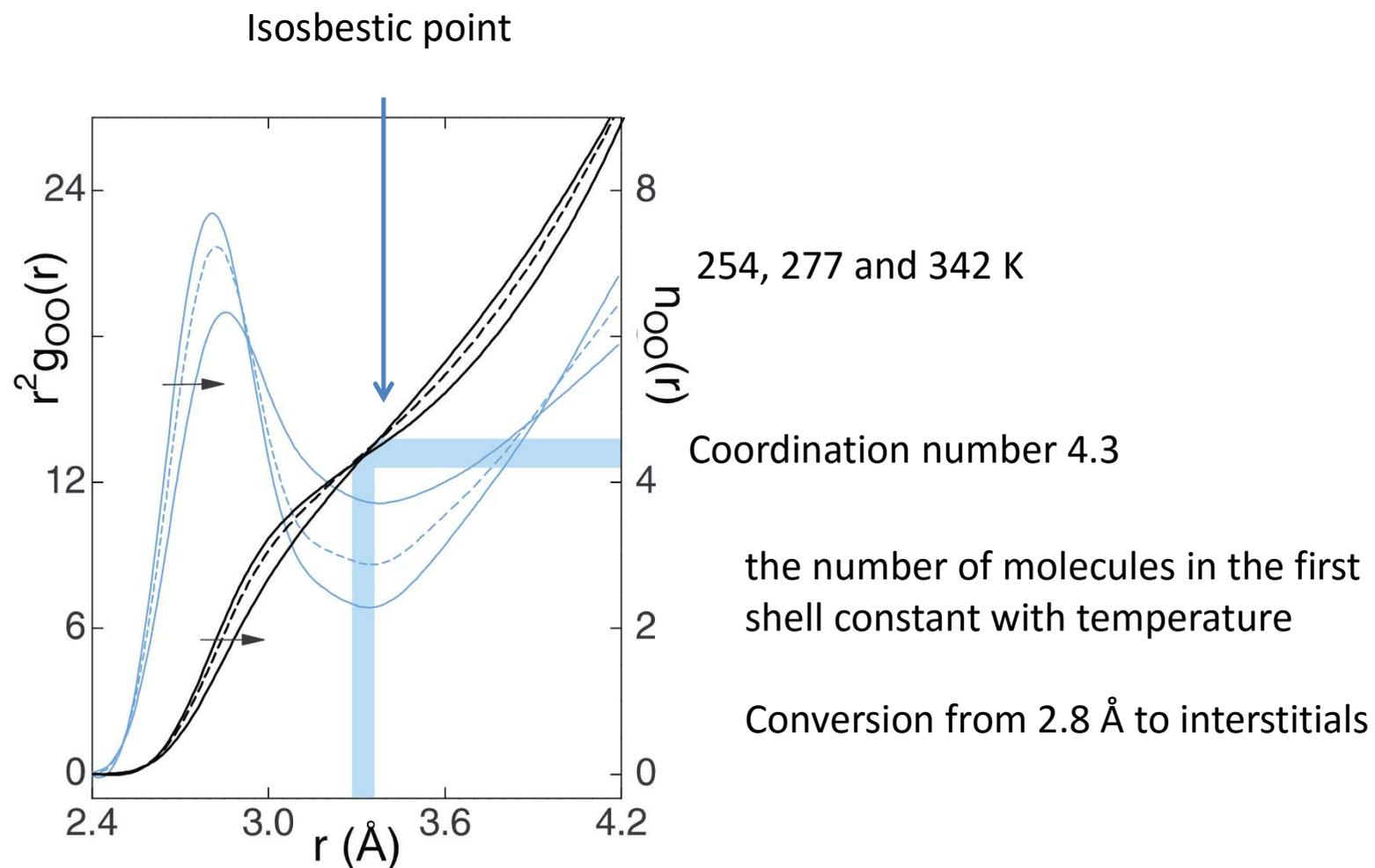
Temperature Dependence



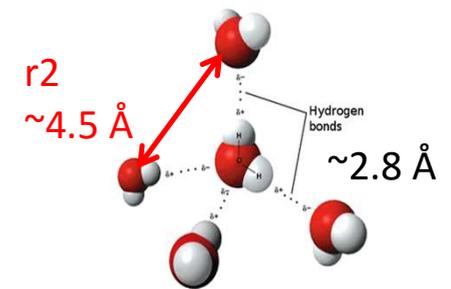
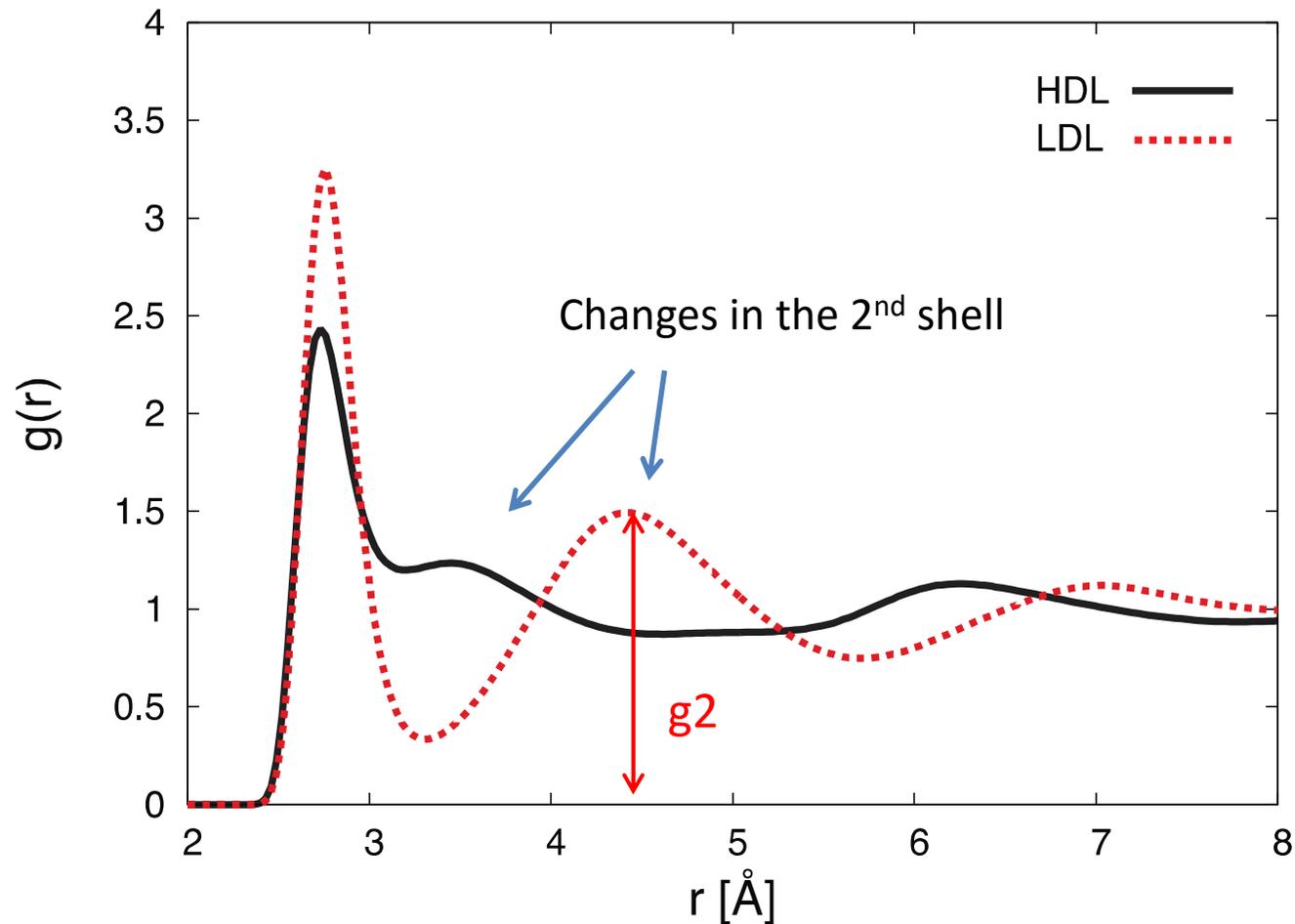


L. Skinner et al. J. Chem. Phys. **141**, 214507 (2014)

Number of molecules in first shell

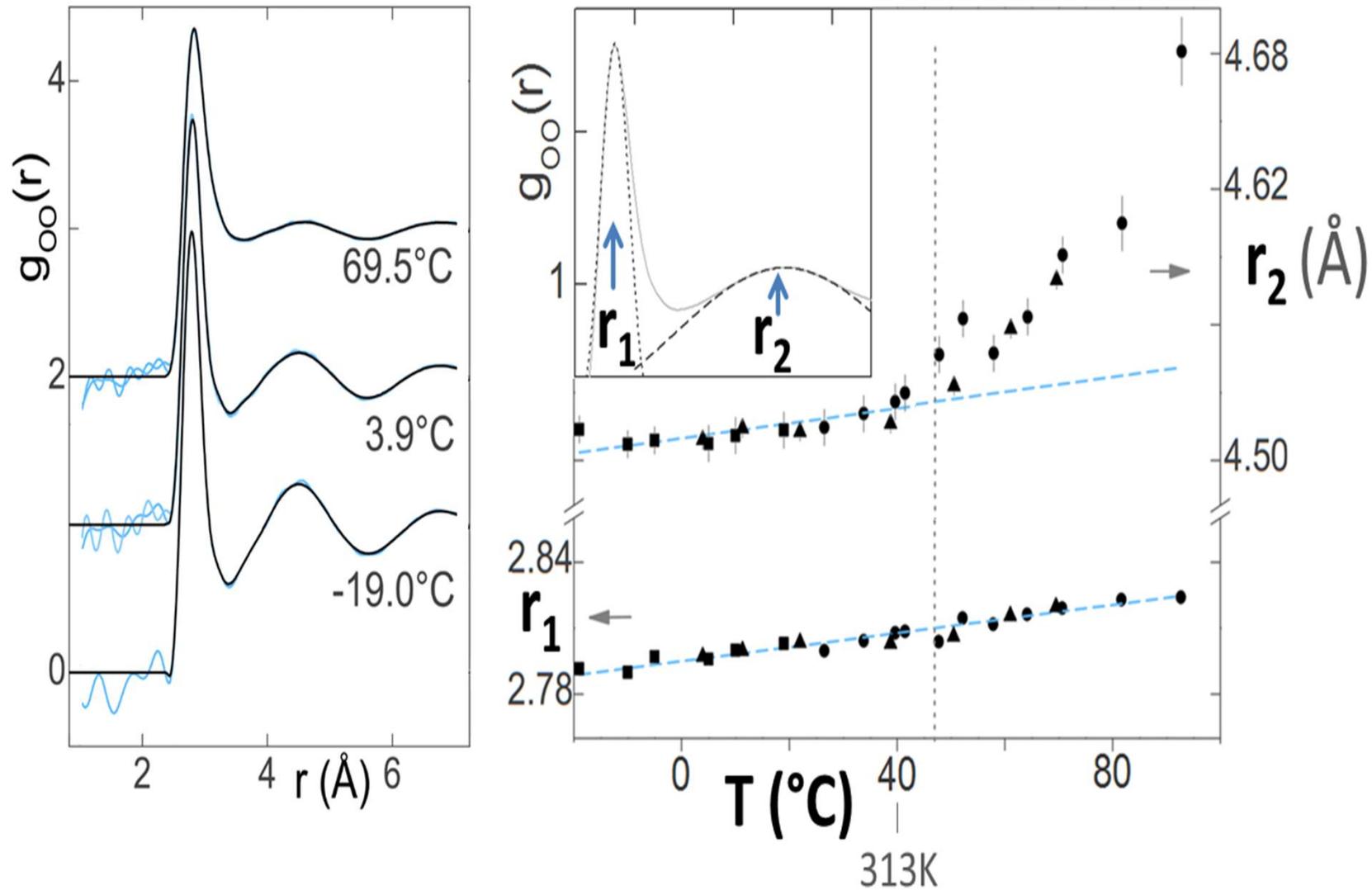


Structure models

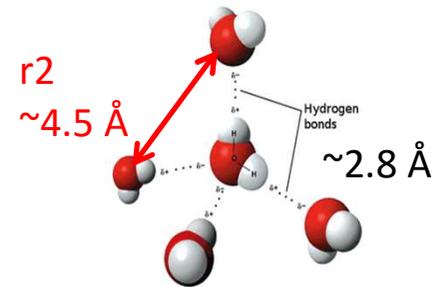
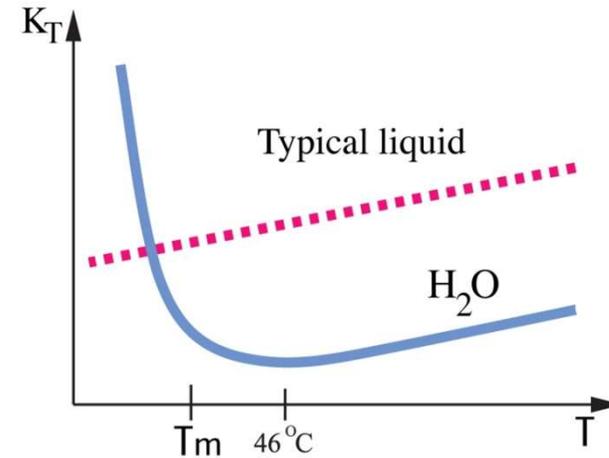
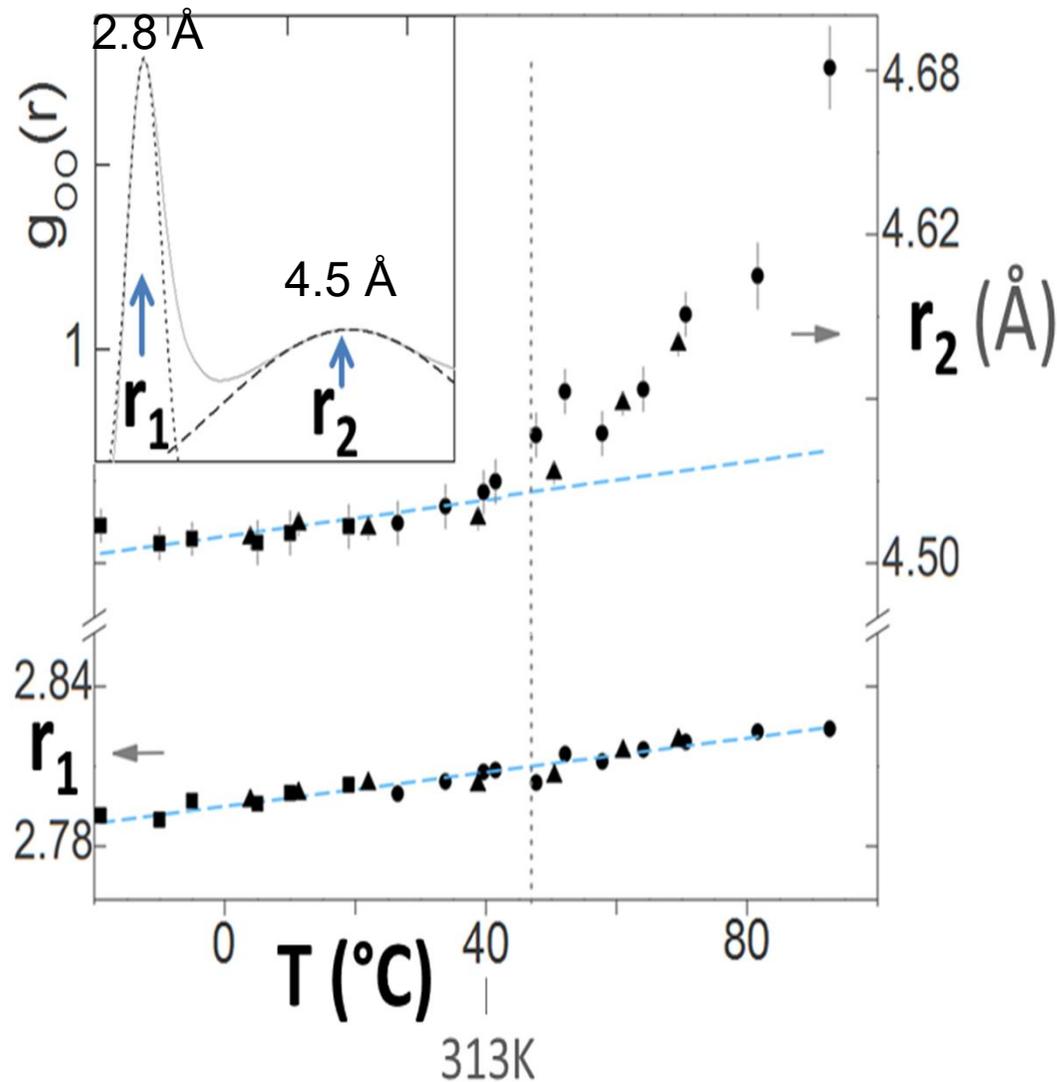


g_2 height of 2nd shell in the O-O Pair Correlation function
Directly related to amount and ordering of tetrahedral water (LDL)

Temperature dependence of $g_{OO}(r)$

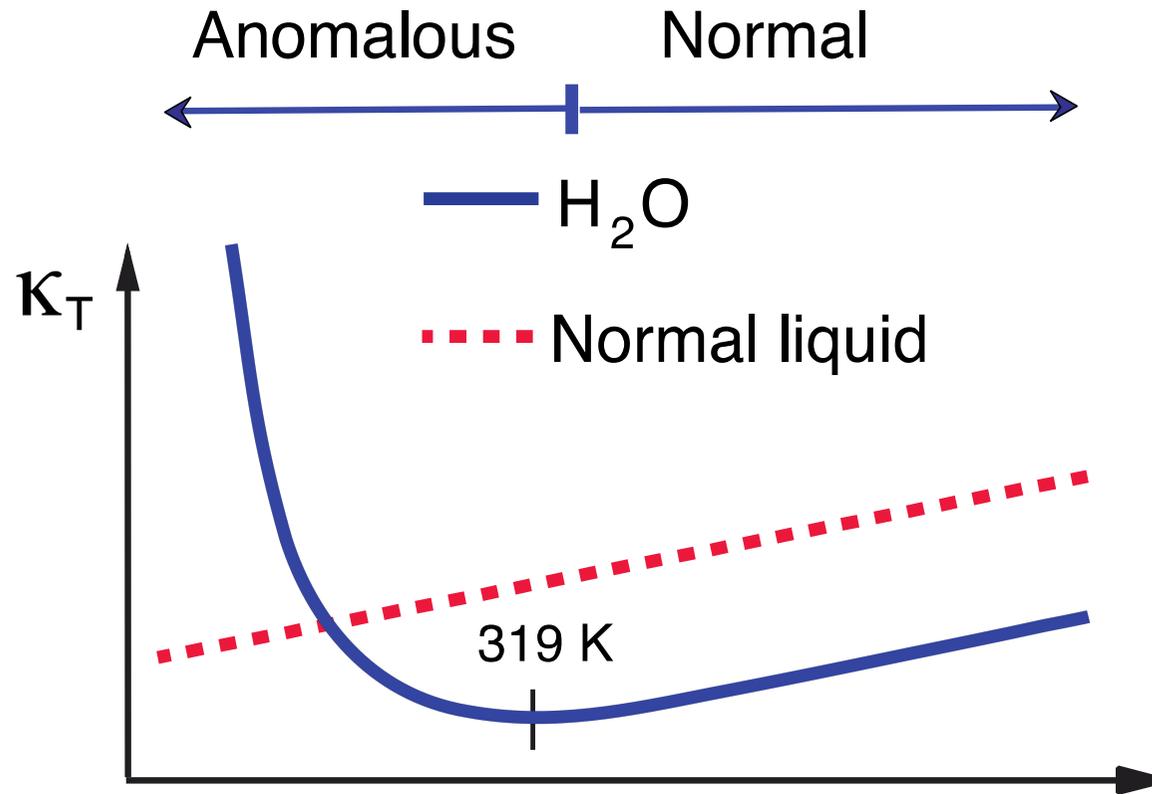


Temperature dependence of $g_2(r)$: Tetrahedrality not important above 46 °C



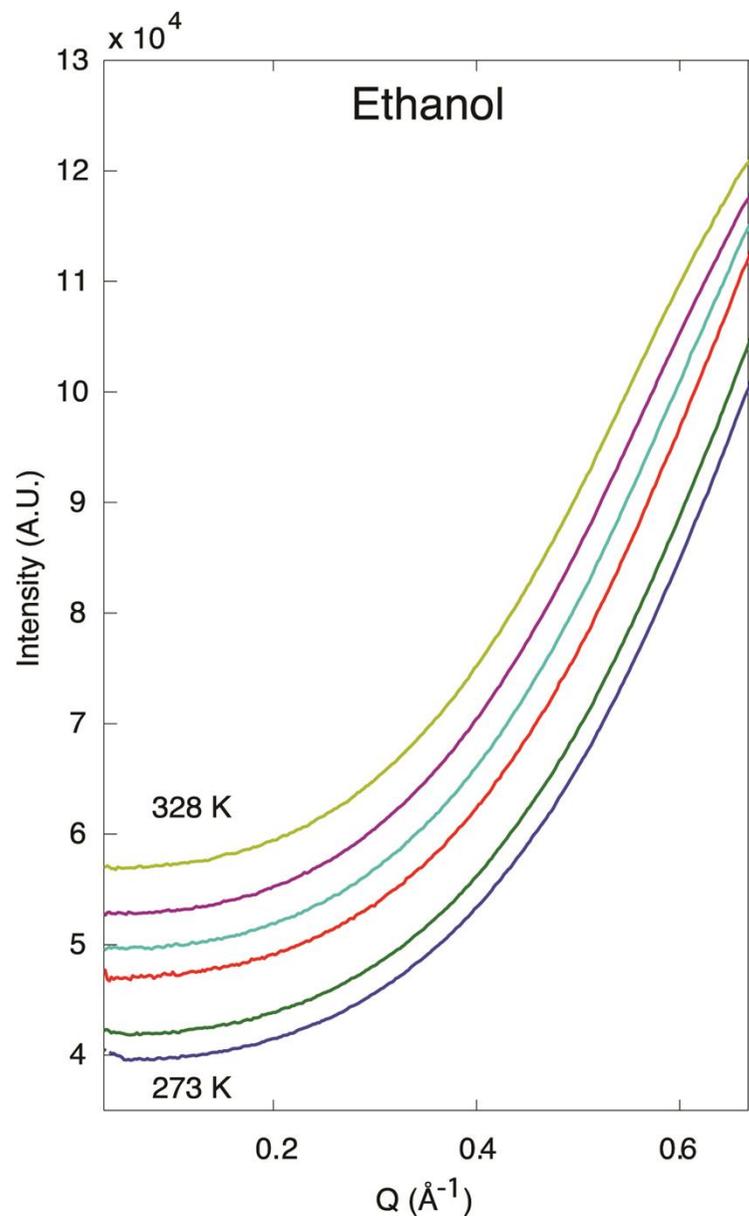
Things begin to happen around 46 °C...

Compressibility

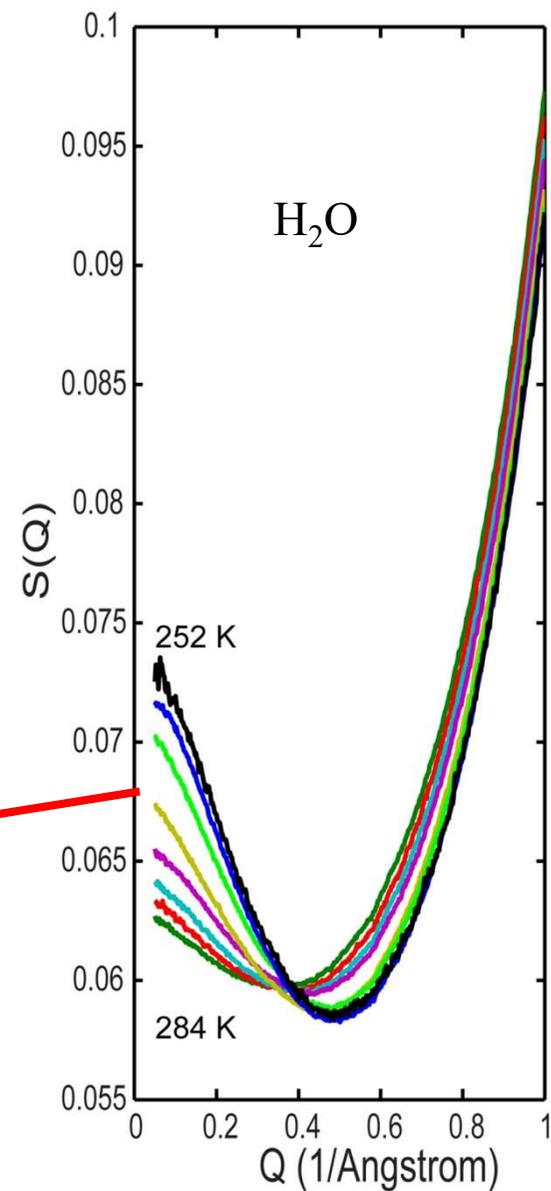
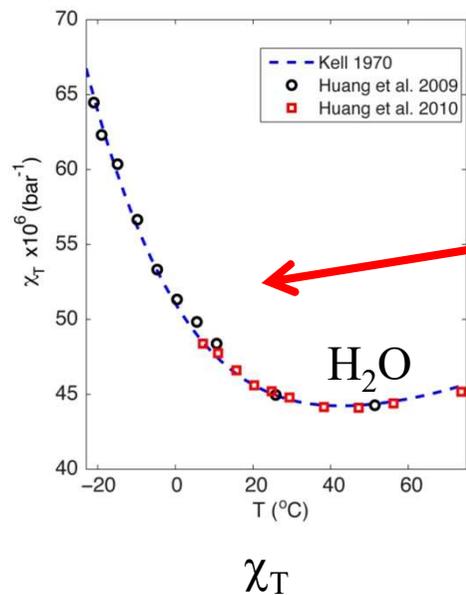


2nd shell well defined when water becomes anomalous

SAXS: Normal Liquid vs Water

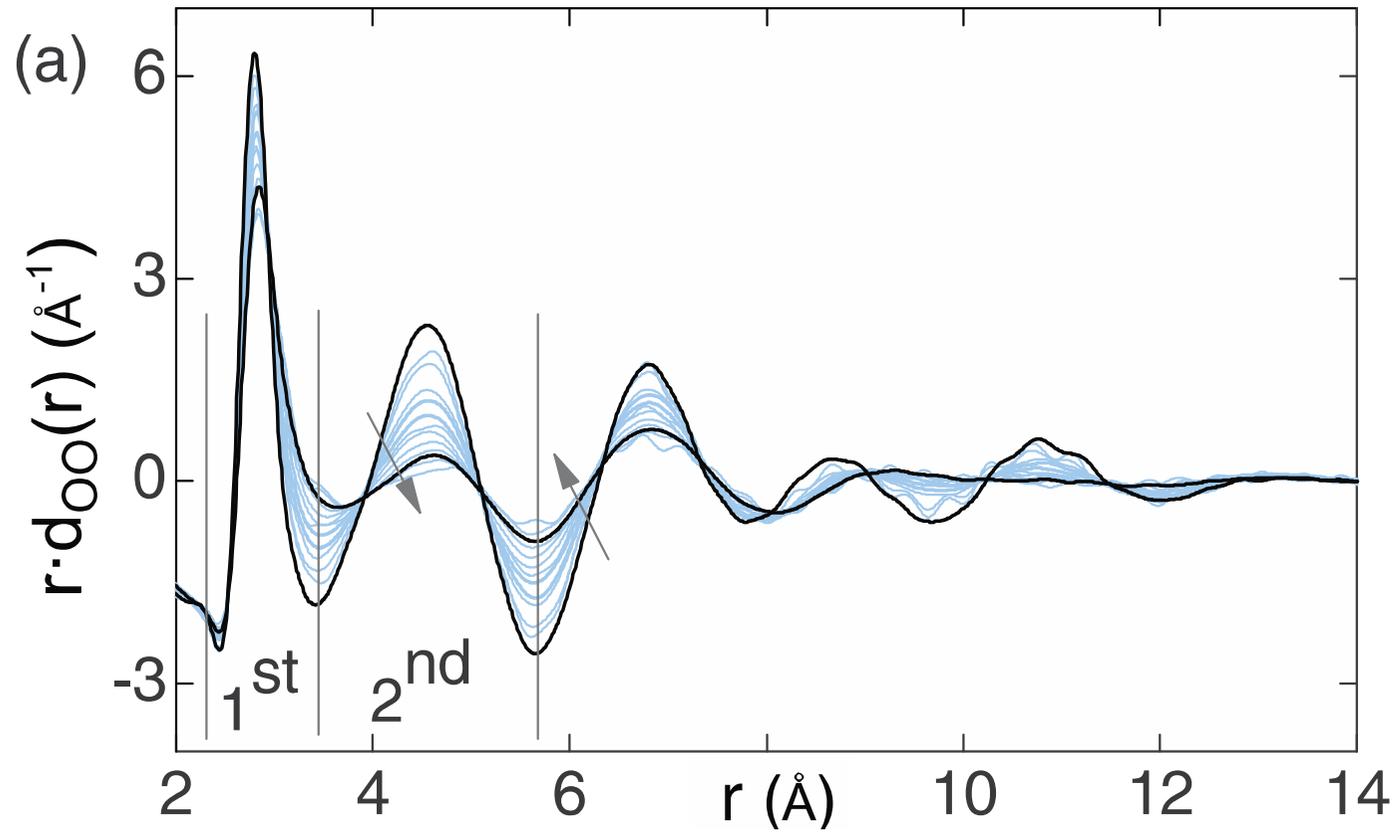


The isothermal compressibility χ_T

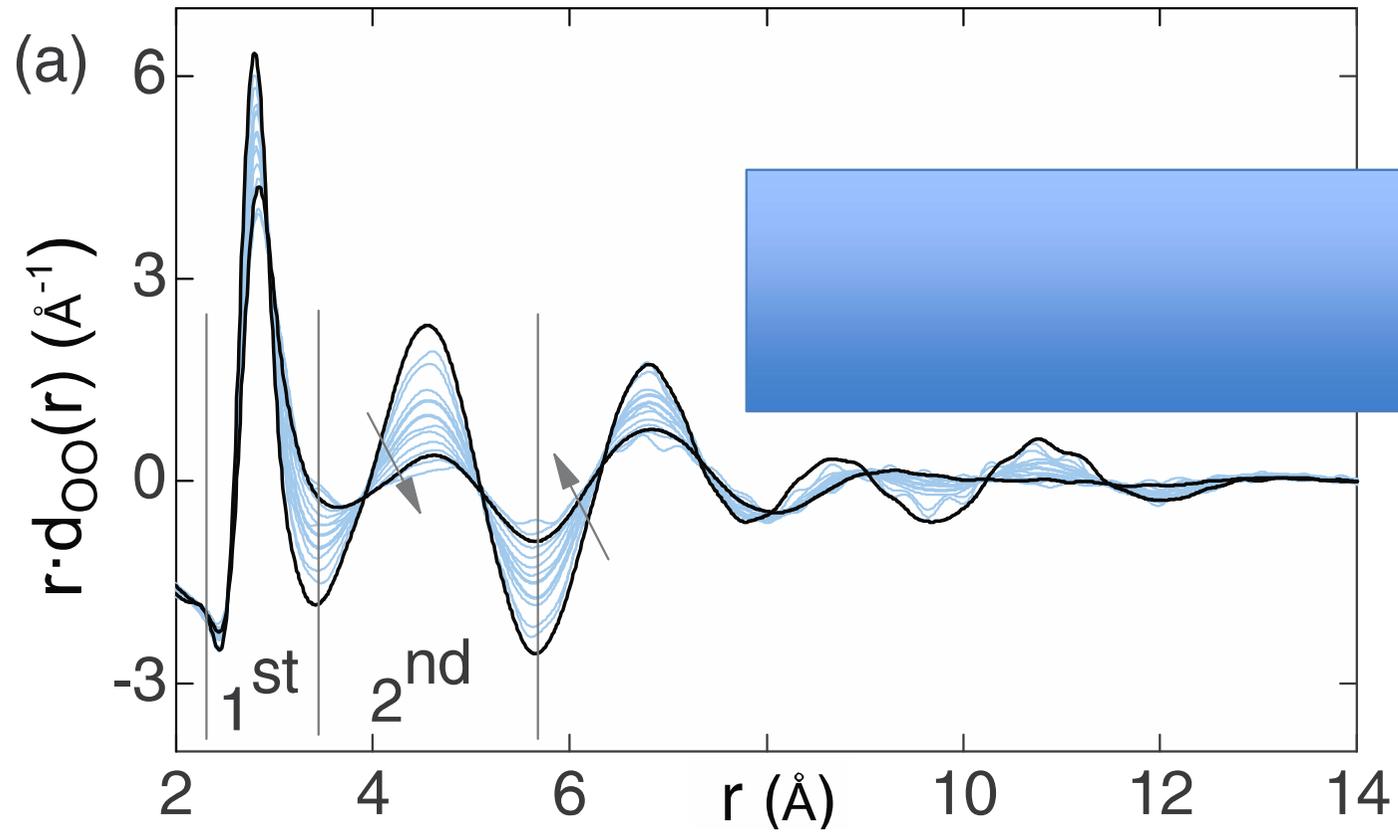
$$S(0) = k_B T n \chi_T$$


Normal liquid

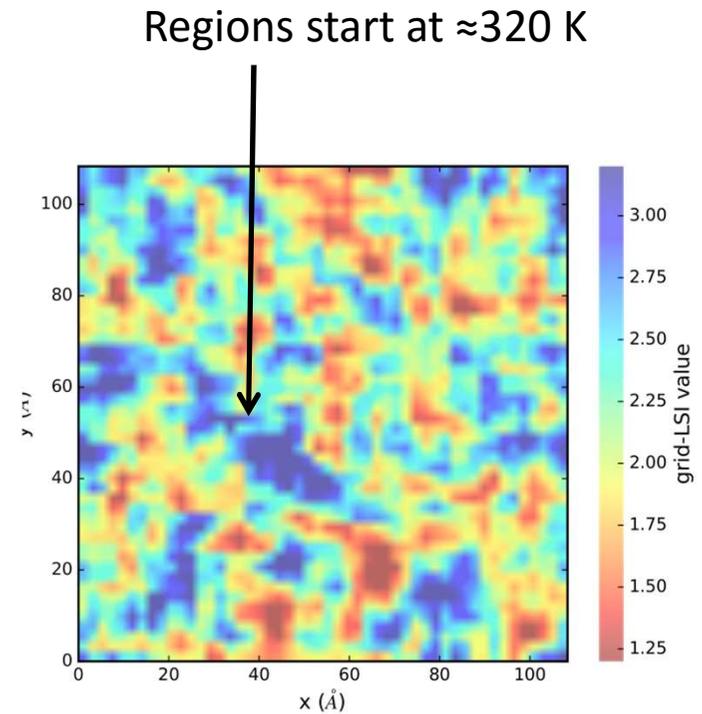
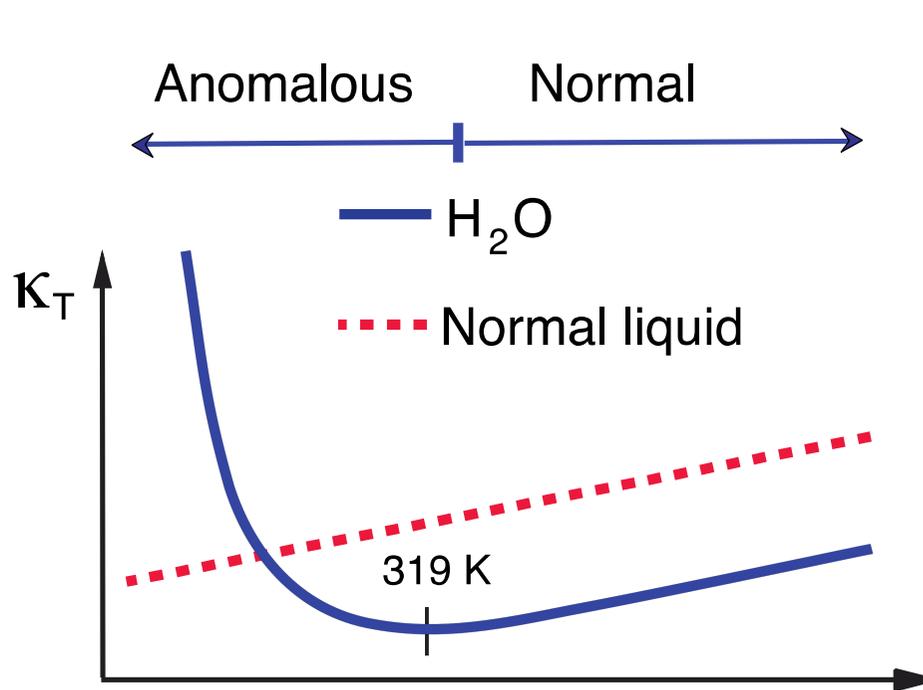
Long Range Correlations



Long Range Correlations



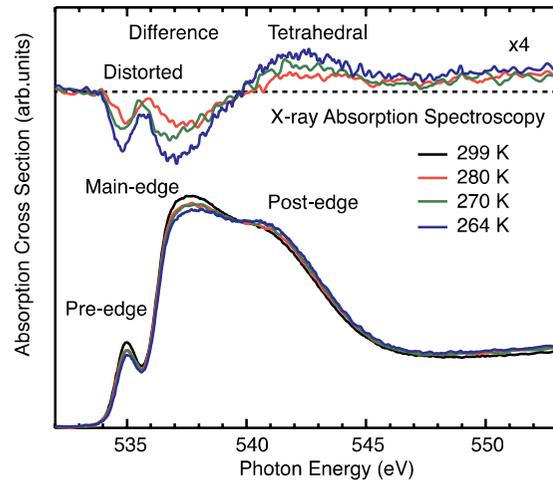
Compressibility and Structure



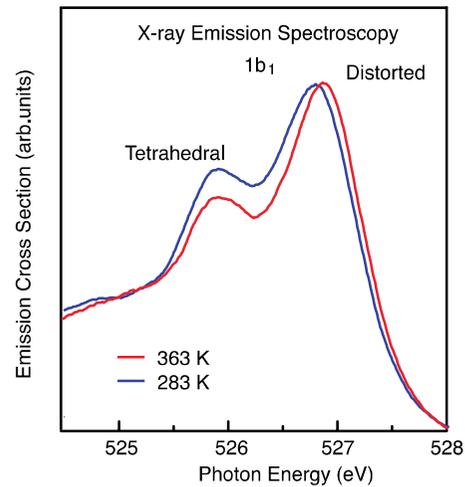
Simulation at 298 K

Two Structural Environments

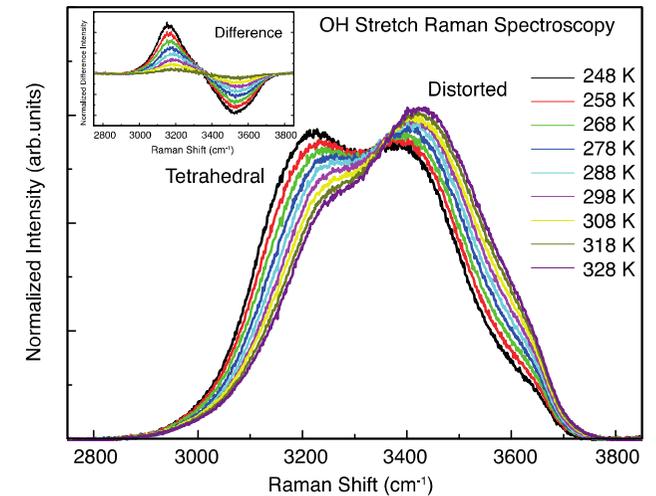
X-ray Absorption



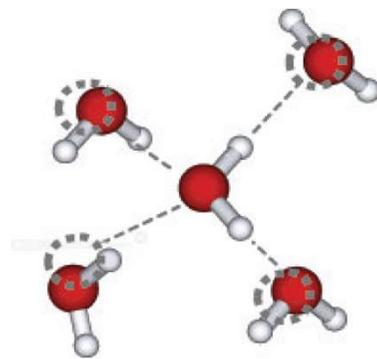
X-ray Emission



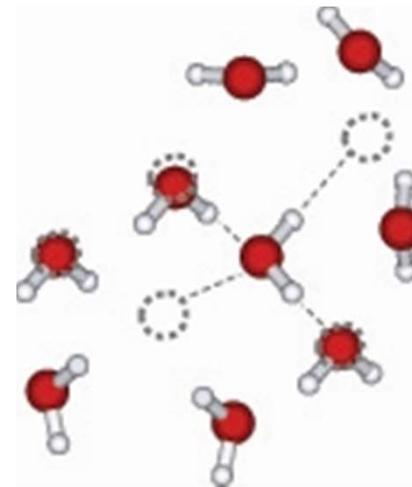
OH Stretch Vibrational



≈ 20%

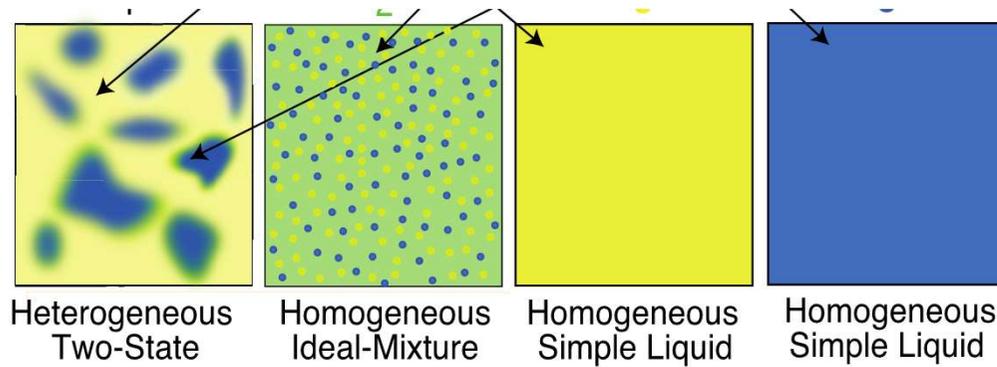


At 300 K



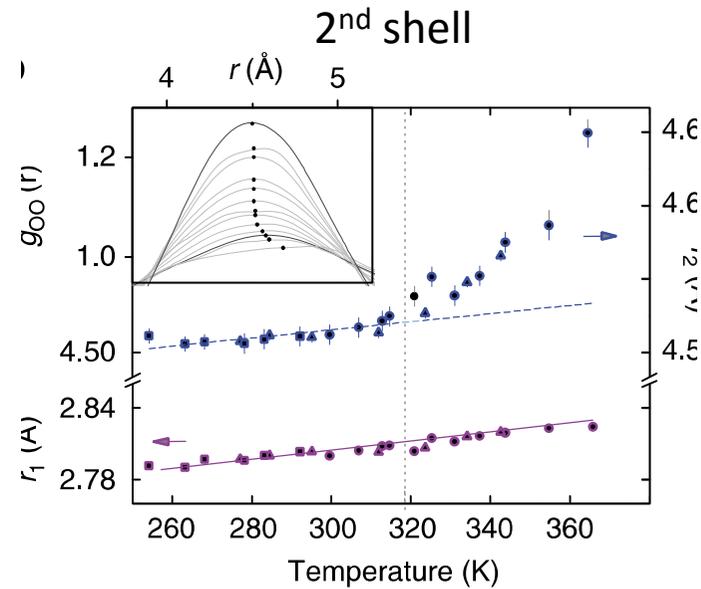
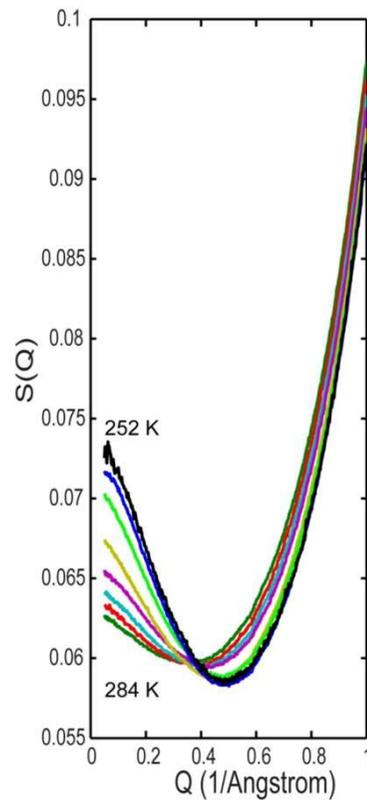
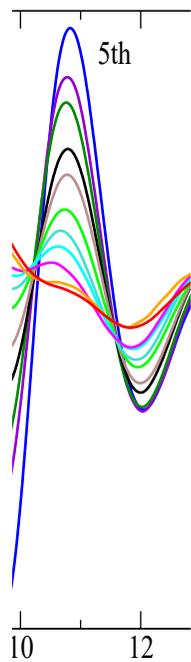
≈ 80%

Long range correlations of two structures

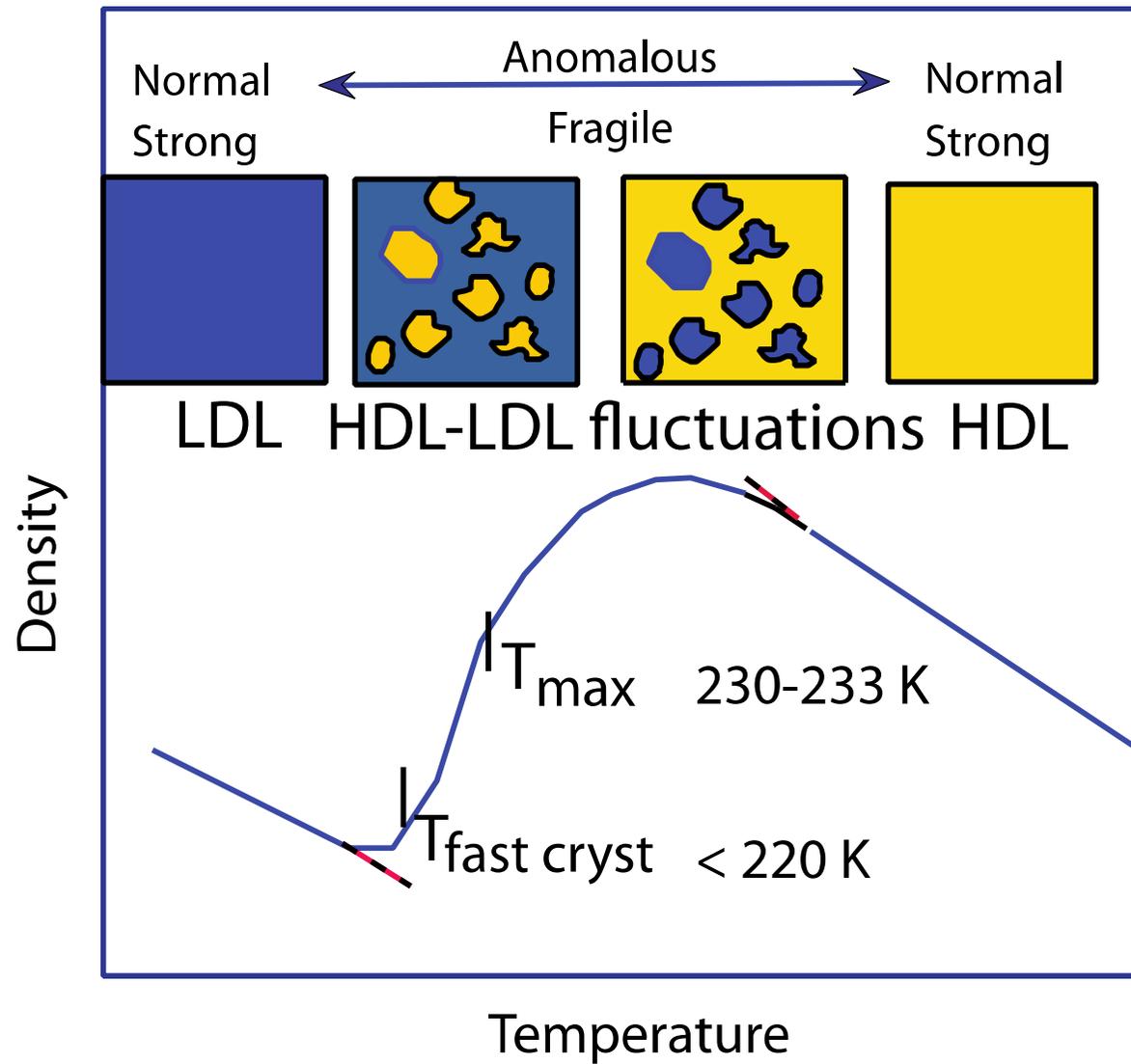


Long range 5th shell

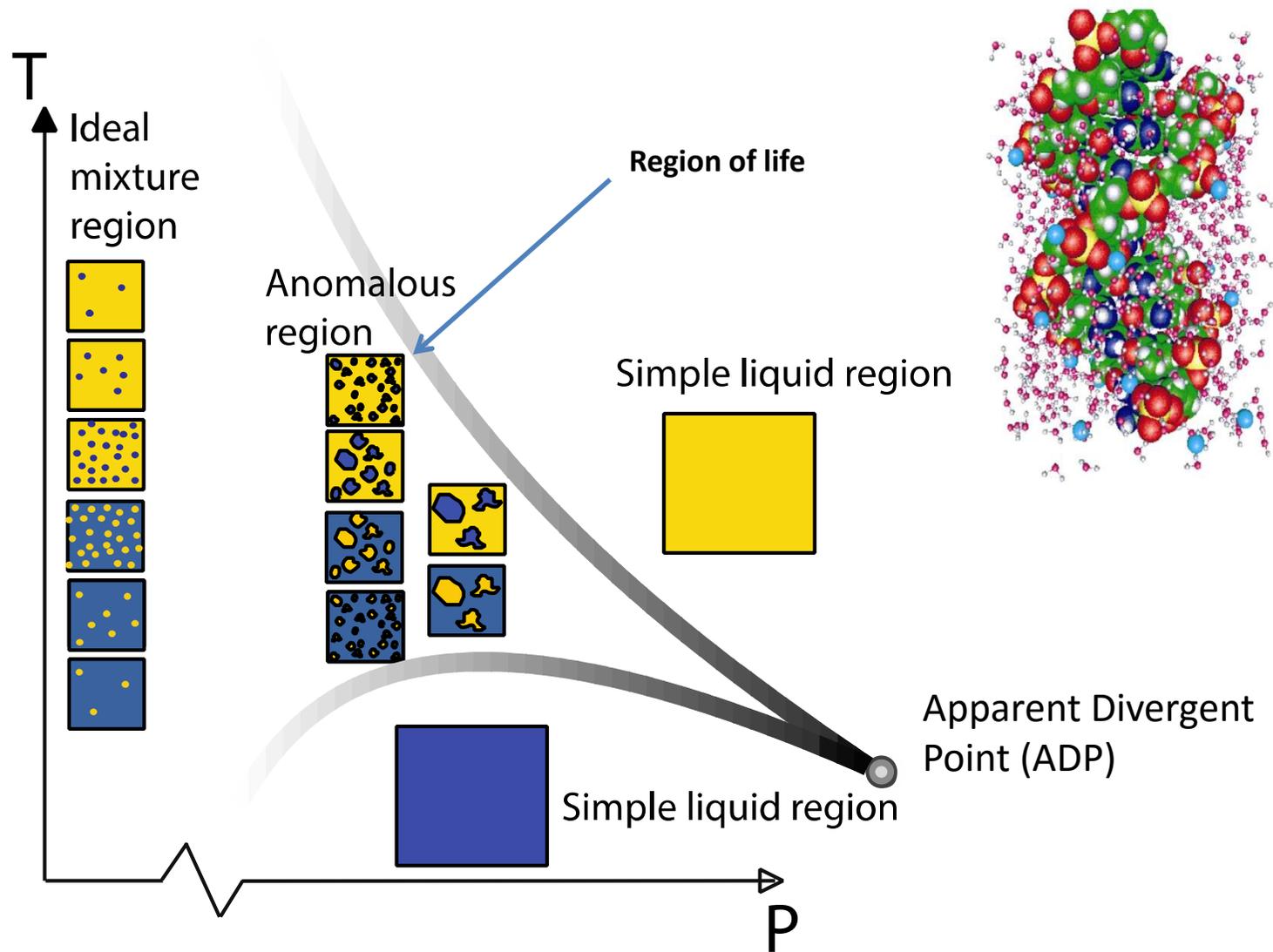
SAXS



Water is a correlated material below 320 K



We live in the “funnel” of an ADP



Challenges

Character of ADP

Dynamics within H-bonds

Breaking and forming H-bonds

Dynamics in long-length-scale fluctuations

Fragile to Strong Transition

Potential long-range coupling with dynamics

Para and Ortho Water

