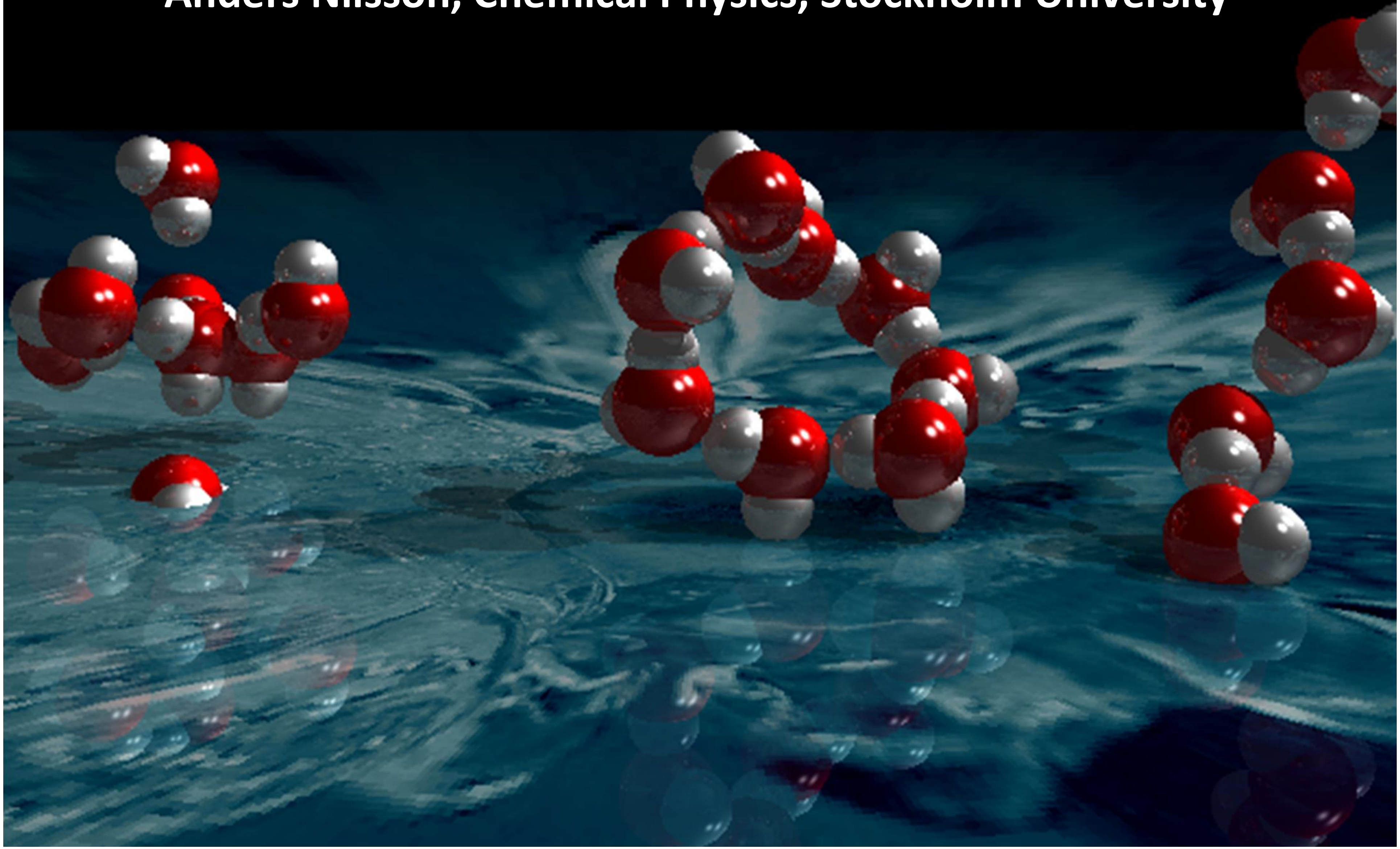
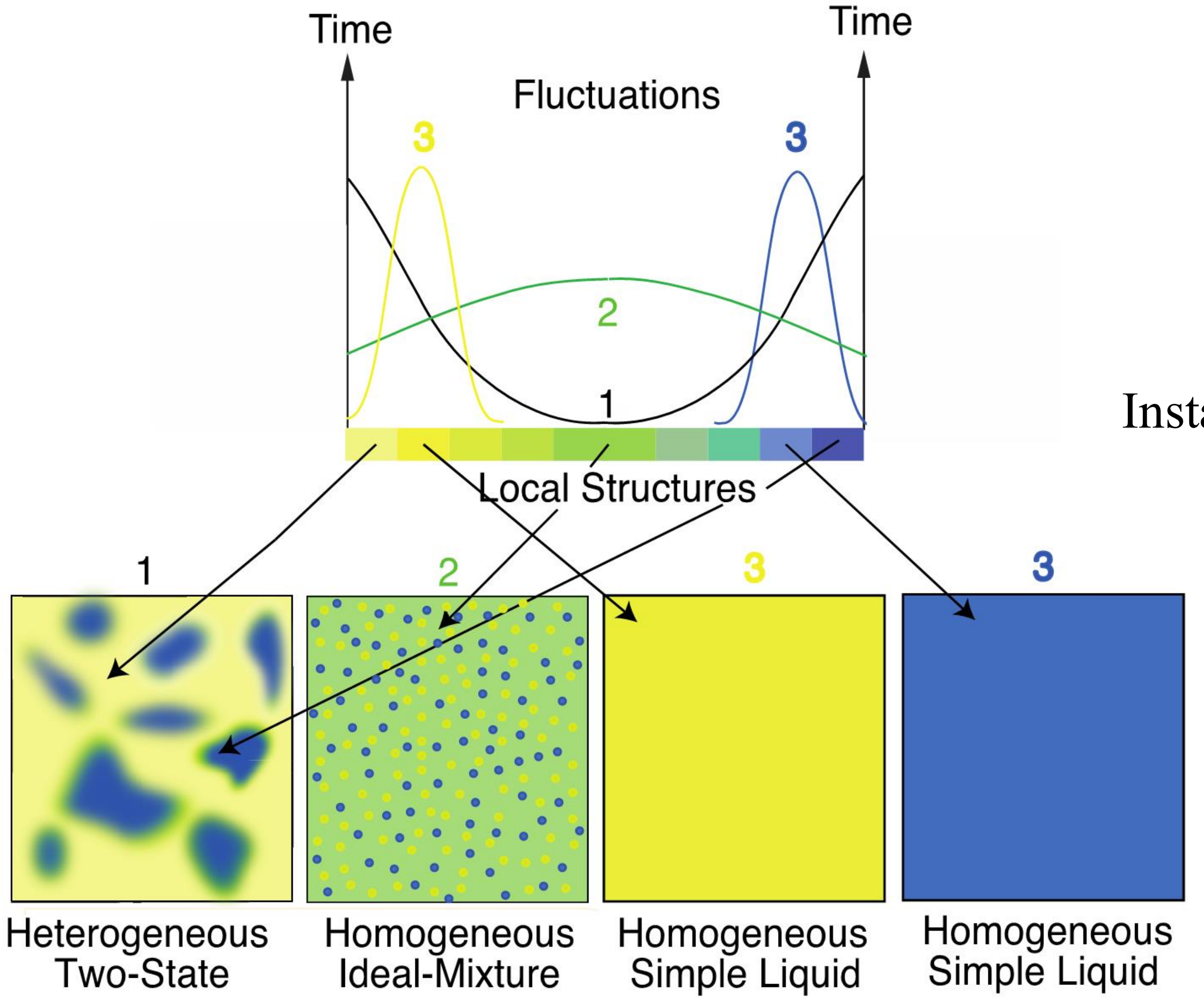
X-ray Spectroscopy Water; Experimental Perspective of Water

Anders Nilsson, Chemical Physics, Stockholm University



Synergy of Mixture and Continuum Models
Fluctuating Heterogeneous Model

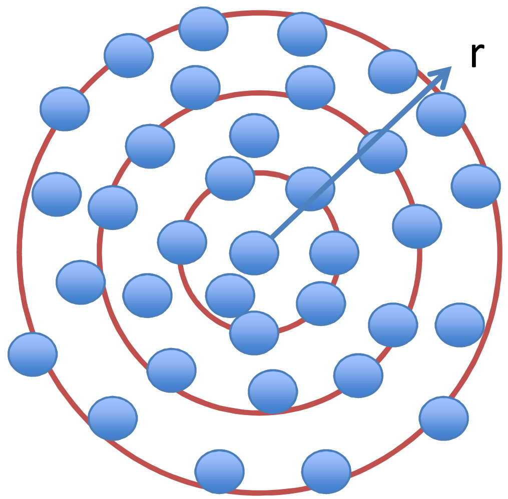


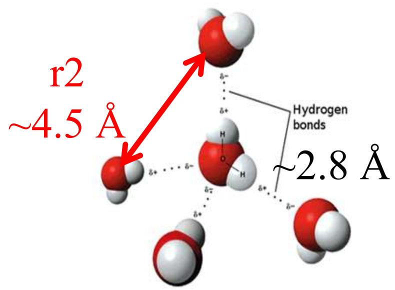
Pendelum

Instantaneous snapshots

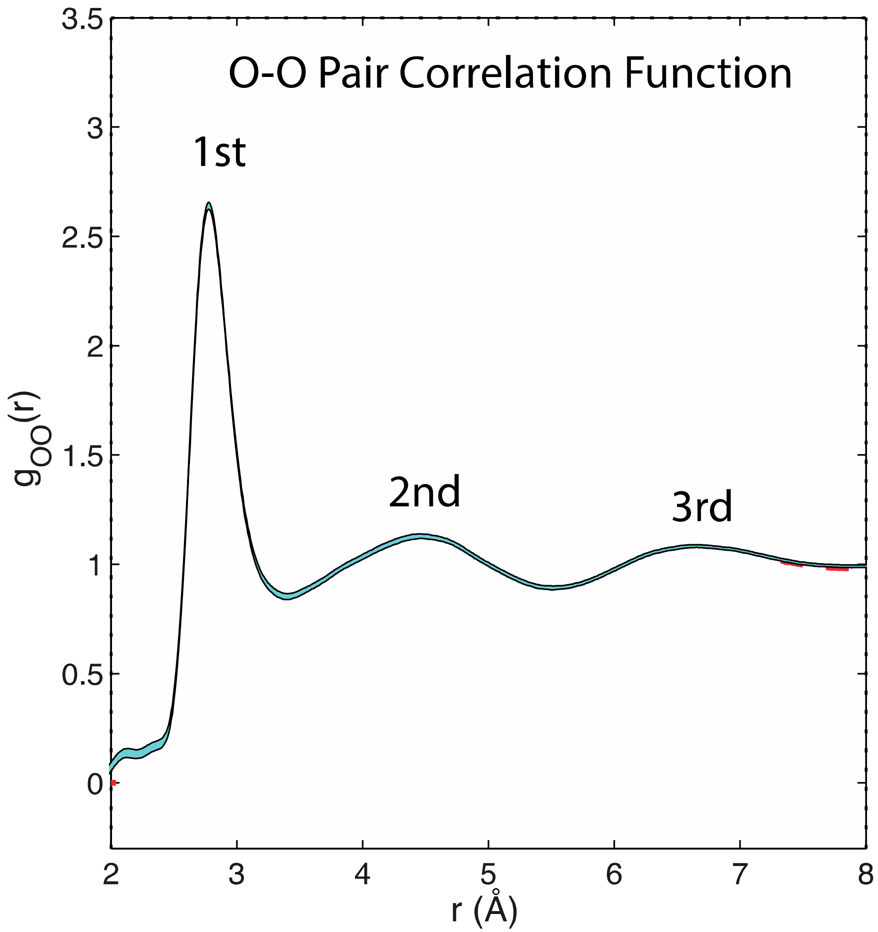
A. Nilsson and L. G. M. Pettersson Nature Communication **6** 8998 (2015)

Pair Correlation Functions





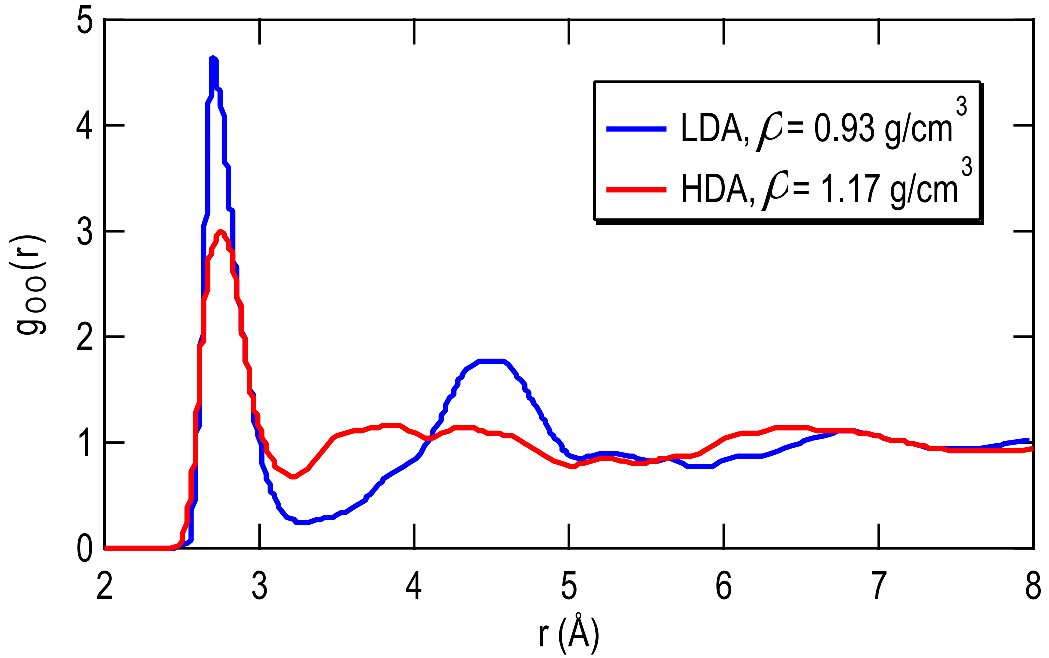
Water at 298 K

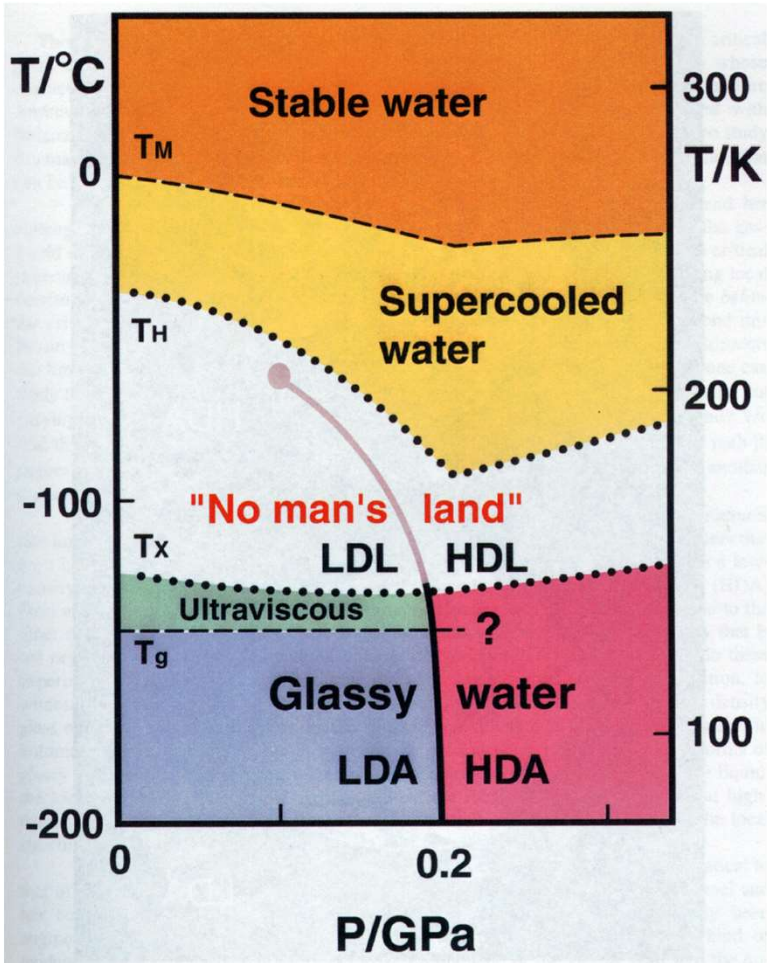


Skinner et al. J. Chem. Phys. **138**, 074506 (2013).

Amorphous Phases of water

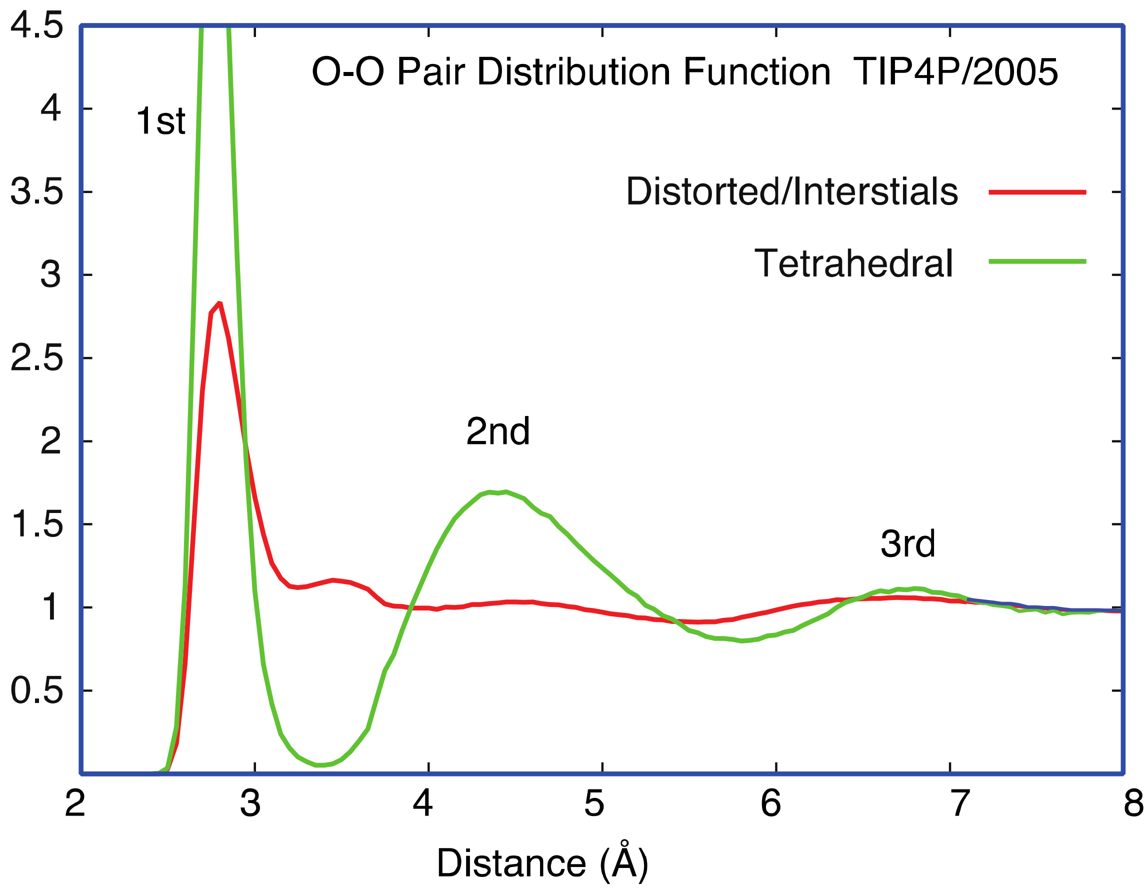
- Polyamorphism
  - Low-density amorphous ice (LDA)
  - High-density amorphous ice (HDA)





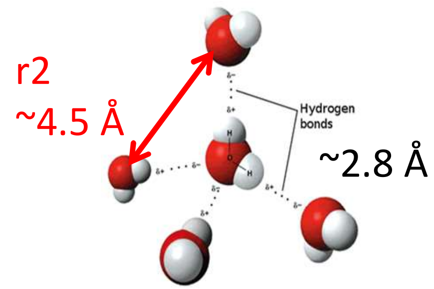
J. L. Finney *et al.*, *Phys. Rev. Lett.* **88**, 225503 (2002)
H. E. Stanley, *Mysteries of Water,* Les Houches Lecture (1998)

Different Liquid Structures in MD

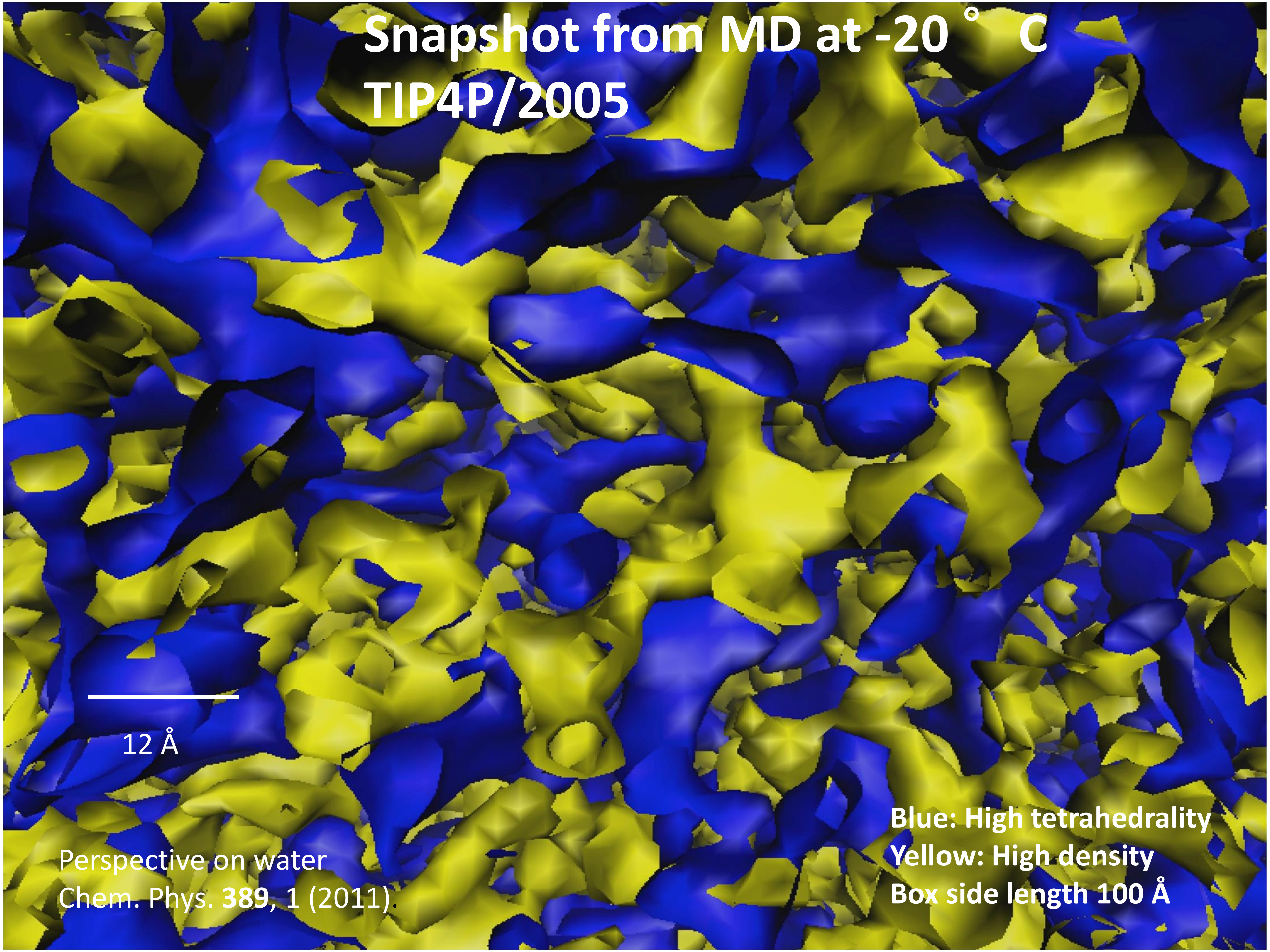


High Density Liquid

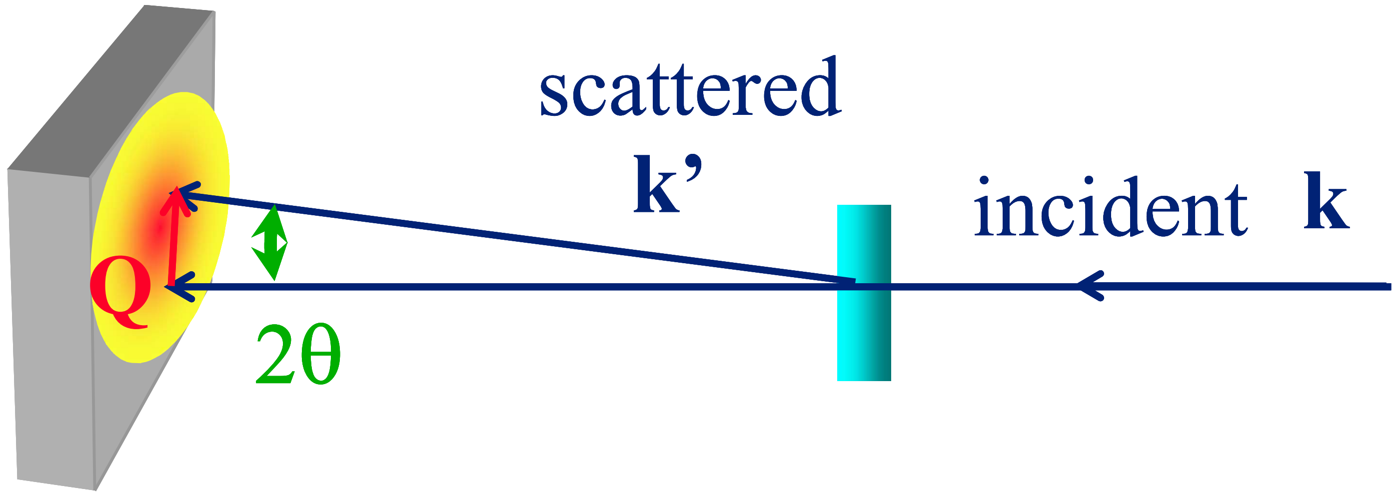
Low Density Liquid

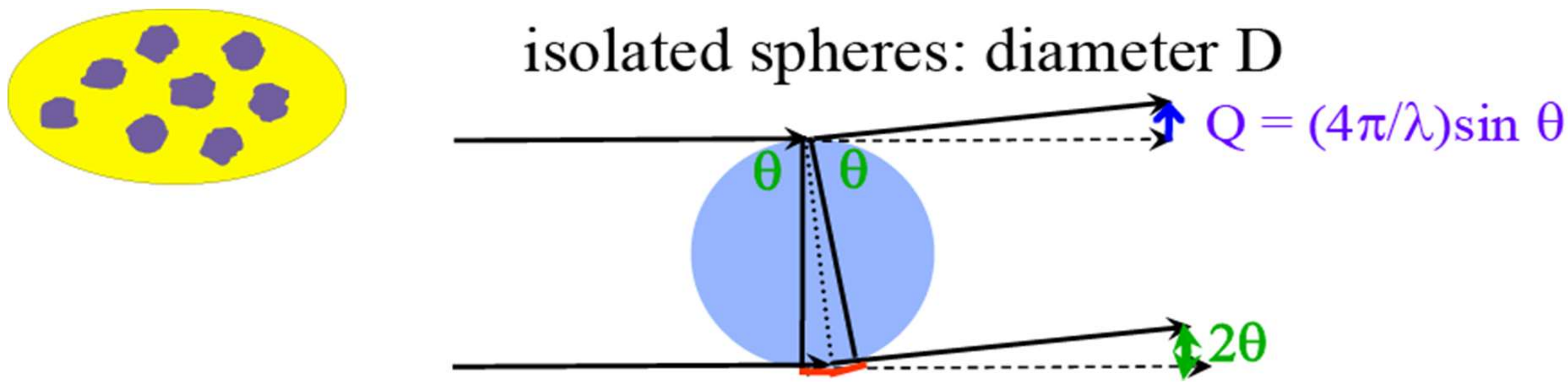


A. Nilsson and L. G. M. Pettersson Nature Communication **6** 8998 (2015)


Snapshot from MD at -20 °C
TIP4P/2005
12 Å
Perspective on water
Chem. Phys. 389, 1 (2011).
Blue: High tetrahedrality
Yellow: High density
Box side length 100 Å

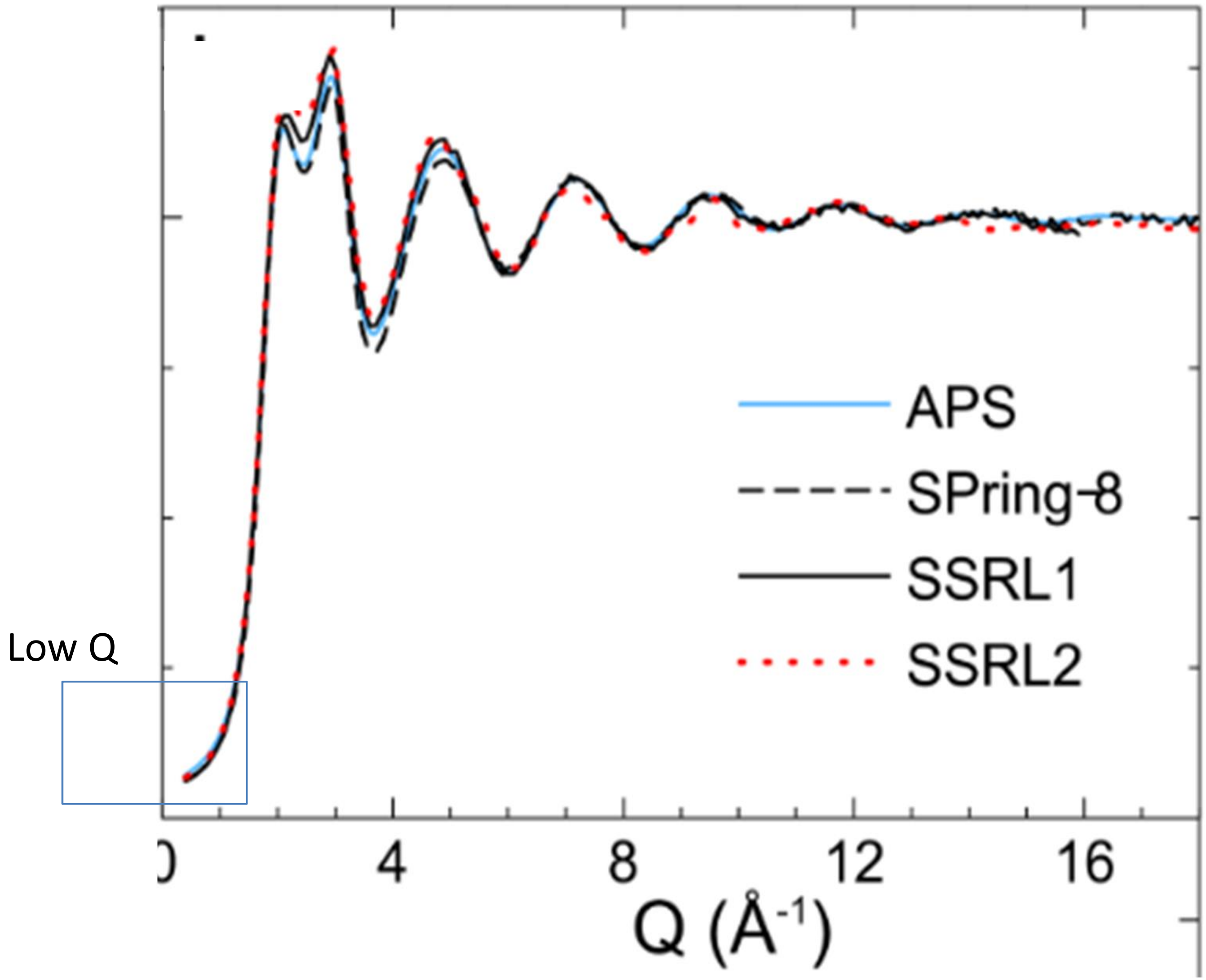
Small Angle X-ray Scattering (SAXS)



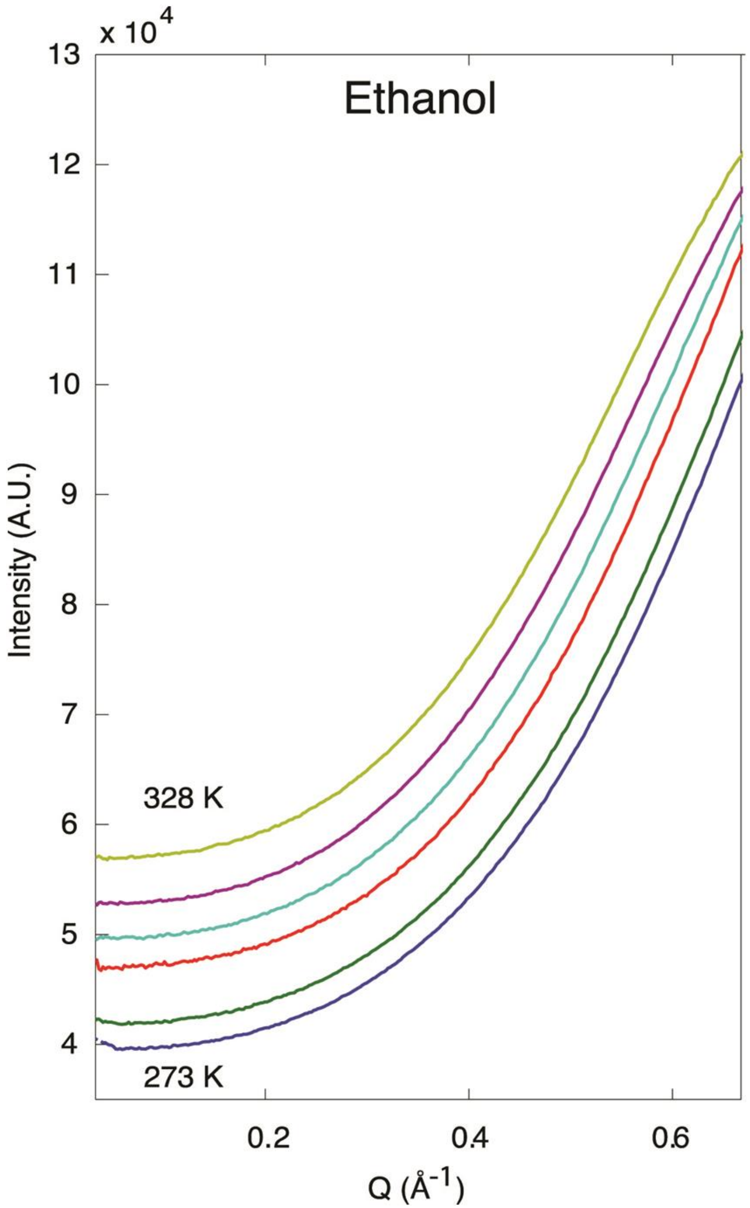


Courtesy Mike Toney

Structure Factor



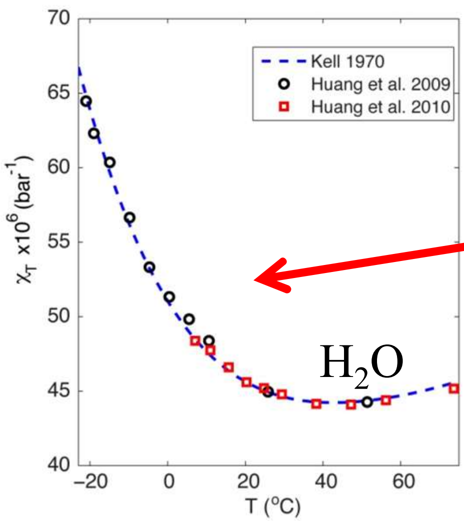
SAXS: Normal Liquid vs Water



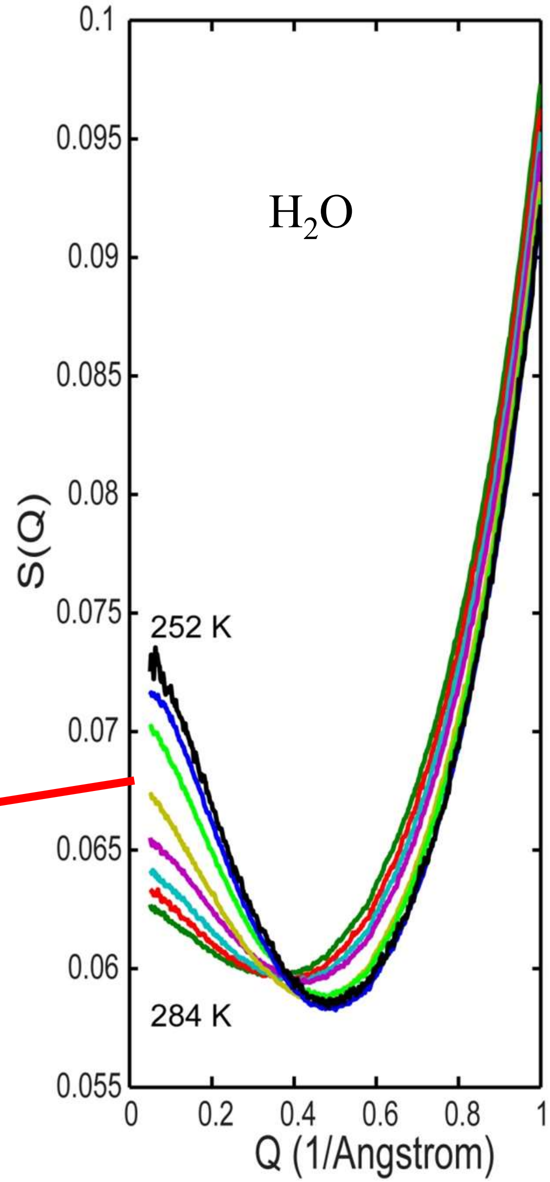
Normal liquid

The isothermal compressibility χ_T

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



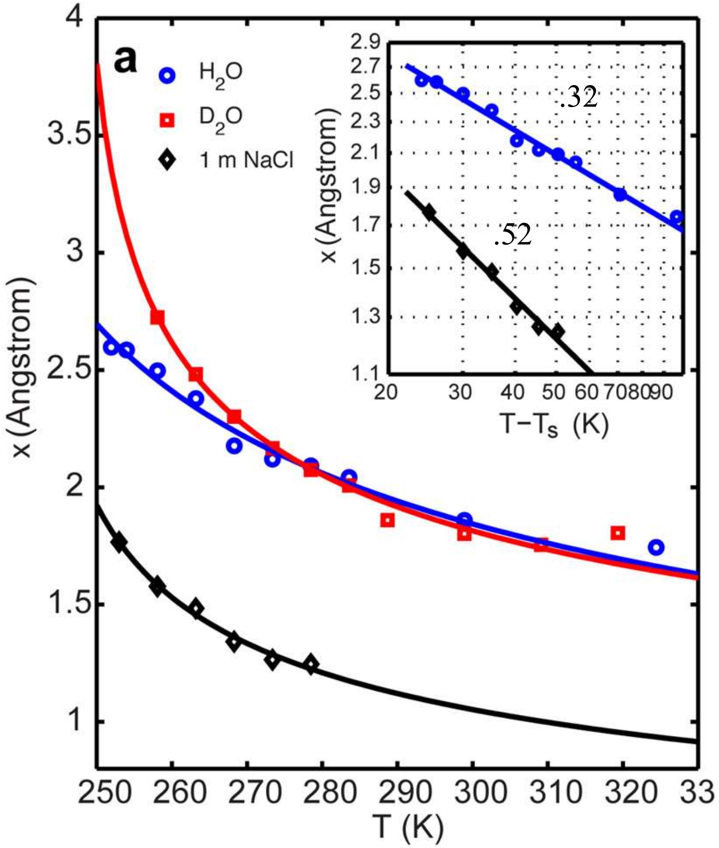
χ_T



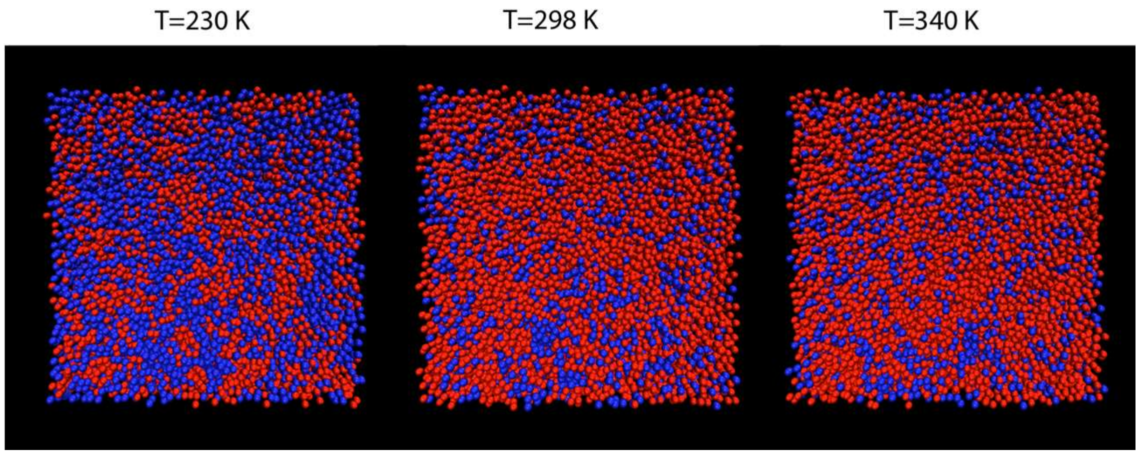
Huang et al. JCP **133**, 134504 (2010)
Nilsson et al. Mol. Liq. **176**, 2 (2012)

Apparent Power Law

Critical phenomena characterized by power laws with critical exponents



2nd critical point scenario
Fluctuations between HDL/LDL
Poole *et al*., *Nature* **360**, 324 (1992)



TIP4P-2005 simulations
Blue LDL Red HDL
based on inherent structure

Fit ζ to (apparent) powerlaw

$$\xi = \xi_0 \varepsilon^{-\nu}$$

with

$$\varepsilon = T / T_s - 1$$

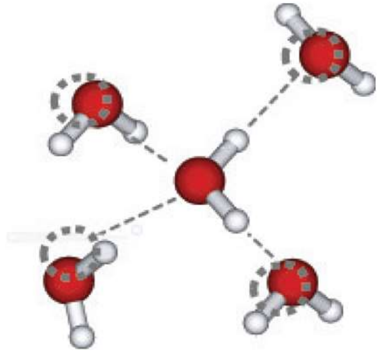
Huang et al. JCP **133**, 134504 (2010)

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

Hypothesis Two Local Structures

Low Density Liquid (LDL)

is connected to strong tetrahedral coordination



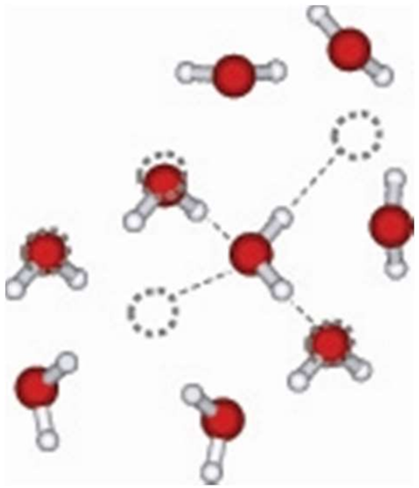
Bond Energy

High Density Liquid (HDL)

is connected to species with higher coordination with the expense of breaking hydrogen bonds

Asymmetrical species

Importance of van der Waals interactions



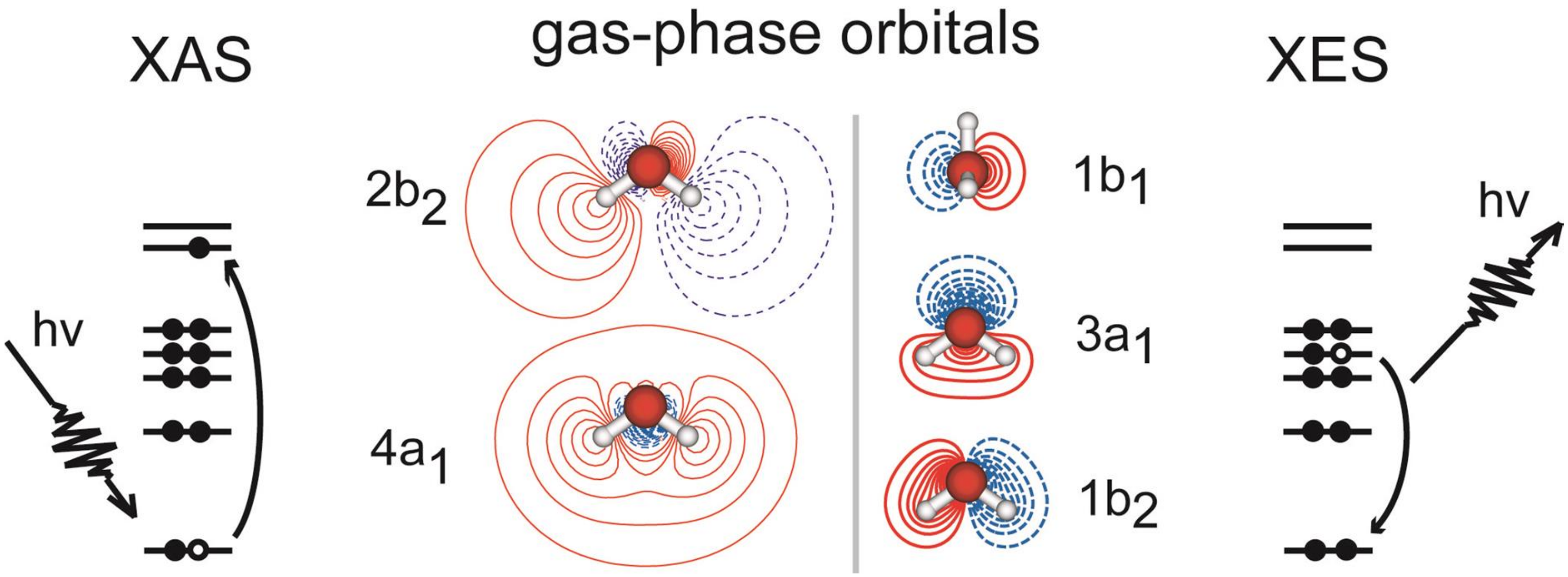
Dominates at RT!!!!

Entropy

Probing Valence Electrons

The hydrogen bond is directional

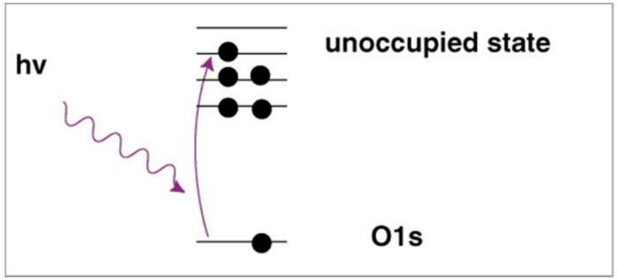
Probing of valence electrons



X-ray Absorption Spectroscopy
Probes Unoccupied Orbitals

X-ray Emission Spectroscopy
Probes Occupied Orbitals

X-ray Absorption Spectroscopy (XAS)

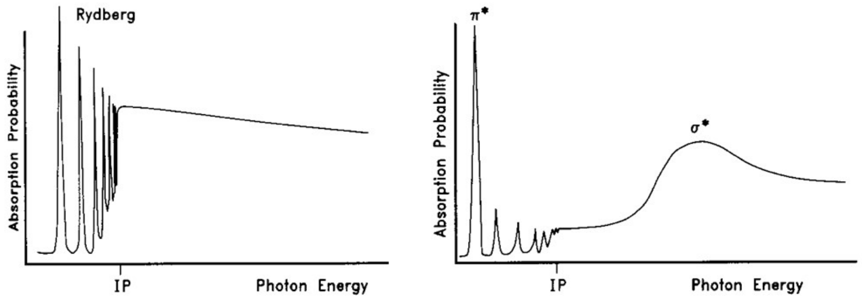


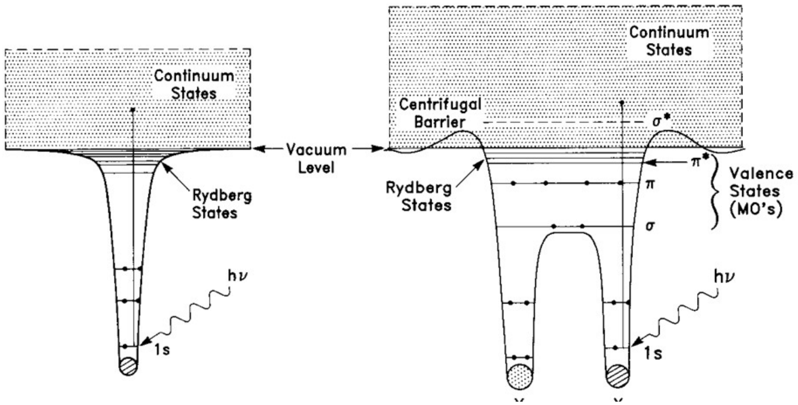
Dipole selection rule $\Delta l = \pm 1$

1s $\rightarrow$ 2p

Molecular orbital or scattering picture

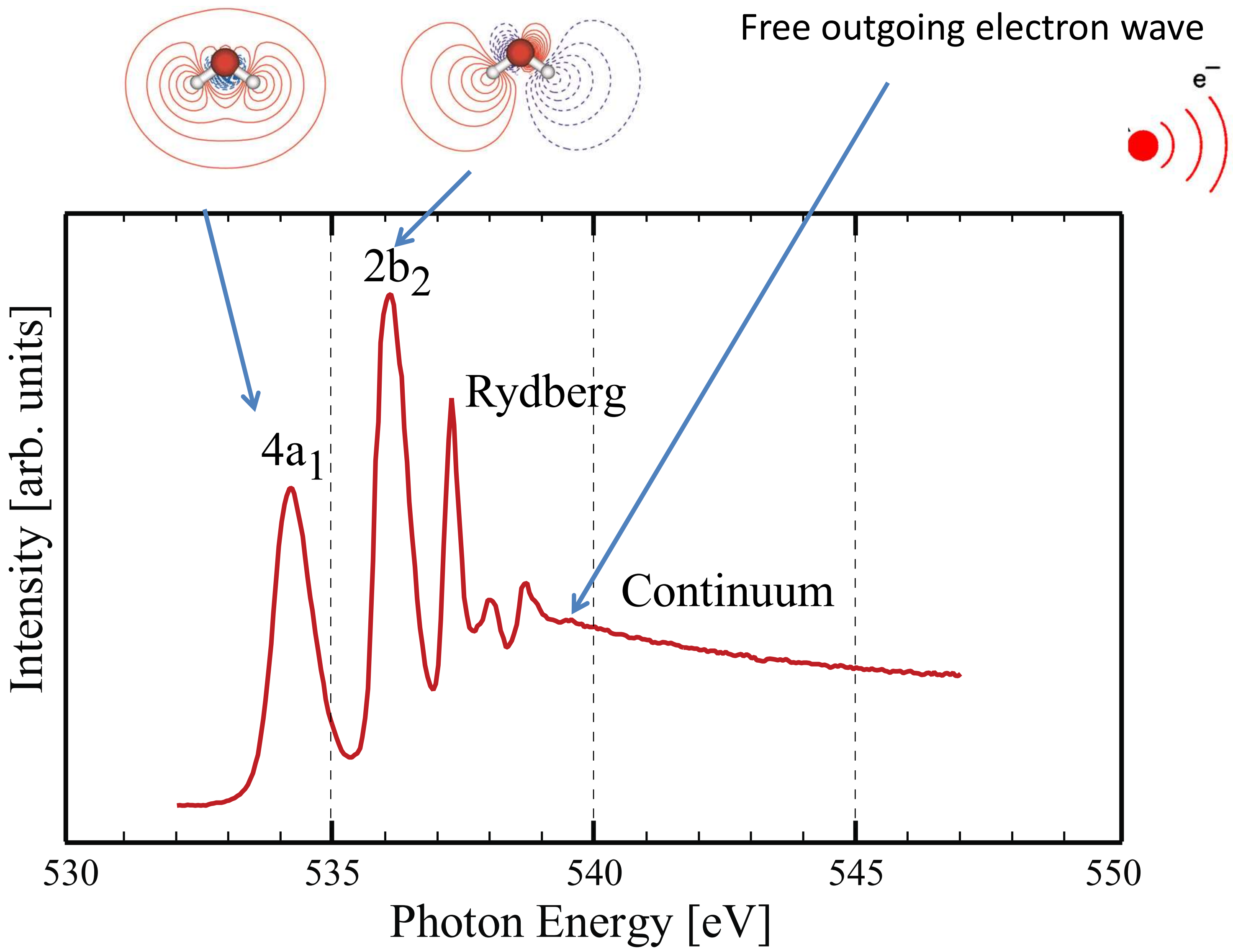
NEXAFS or XANES



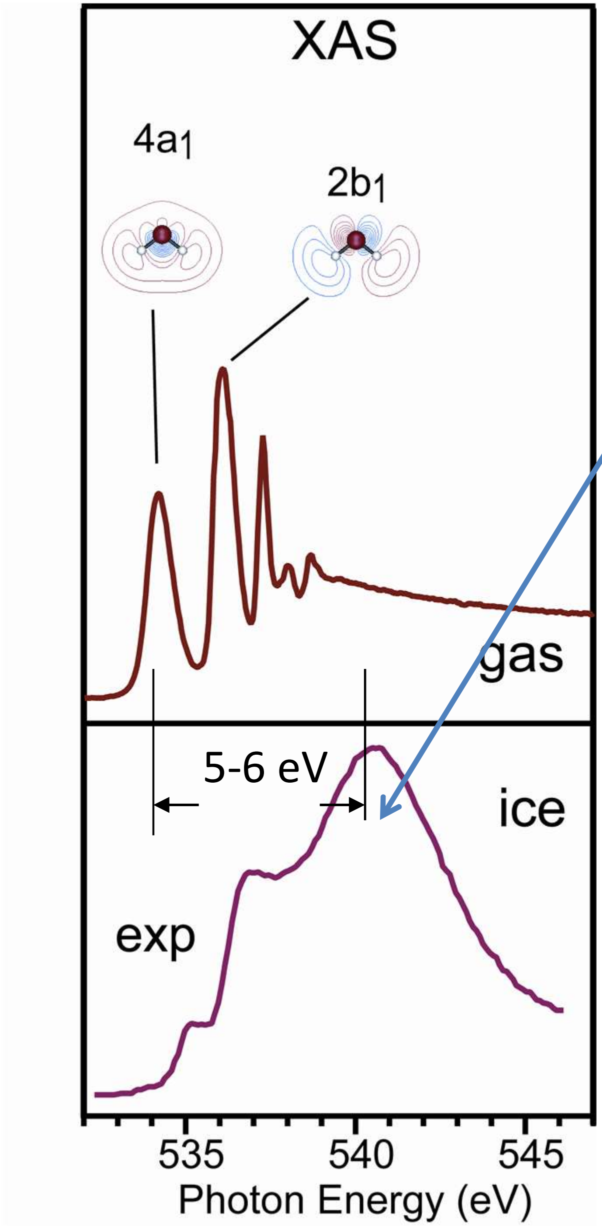


Stöhr, NEXAFS spectroscopy

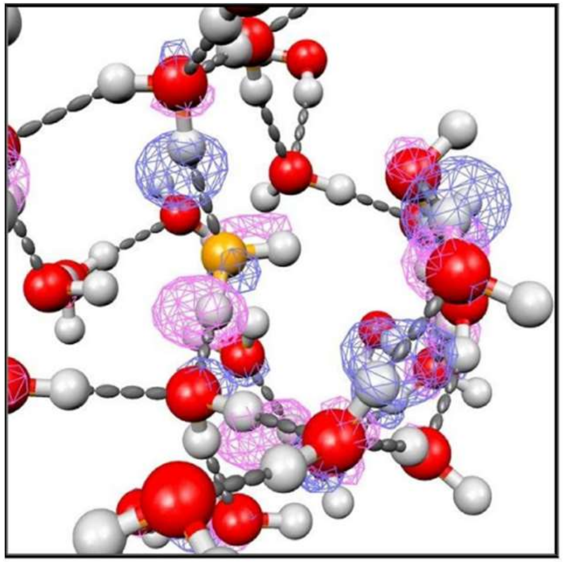
XAS Gas Phase Water



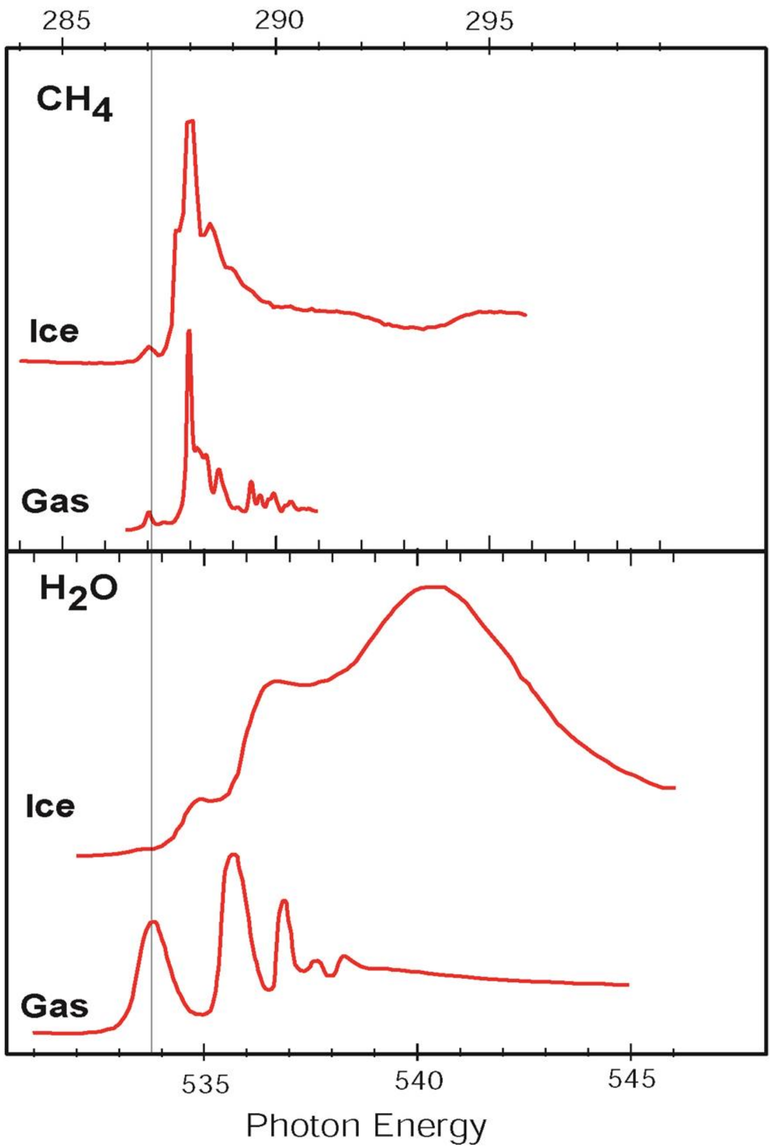
XAS of Ice



Denoted Post-Edge
Conduction band in Ice
Delocalized states



Water and Methane

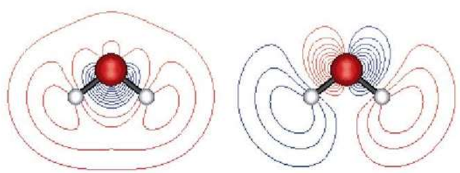


C-C distance in solid methane 4.2Å

No change between gas-solid

O-O distance in ice 2.75 Å

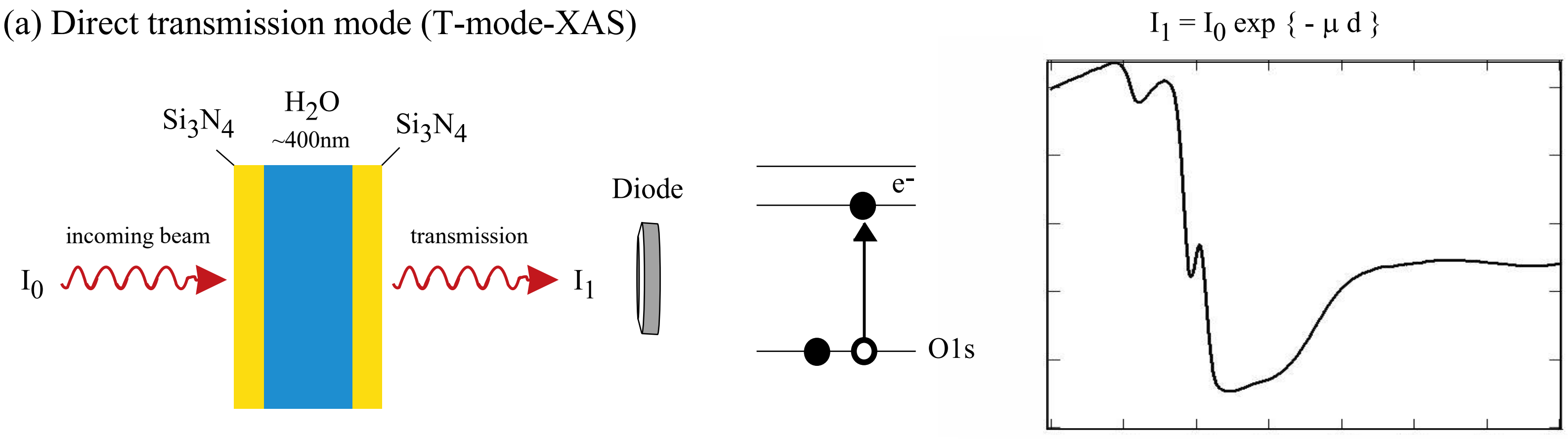
Large change between gas-solid



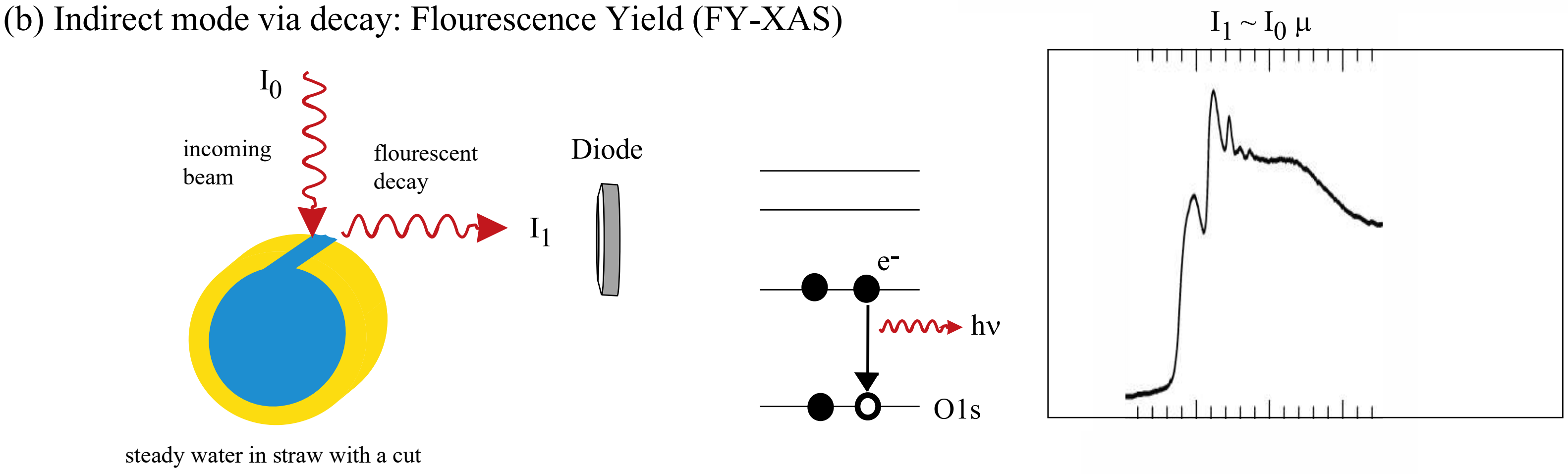
Nilsson et.al. J. El. Spec. Rel. Phen. **177**, 99 (2010)

Liquid Water XAS measurements

(a) Direct transmission mode (T-mode-XAS)



(b) Indirect mode via decay: Flourescence Yield (FY-XAS)

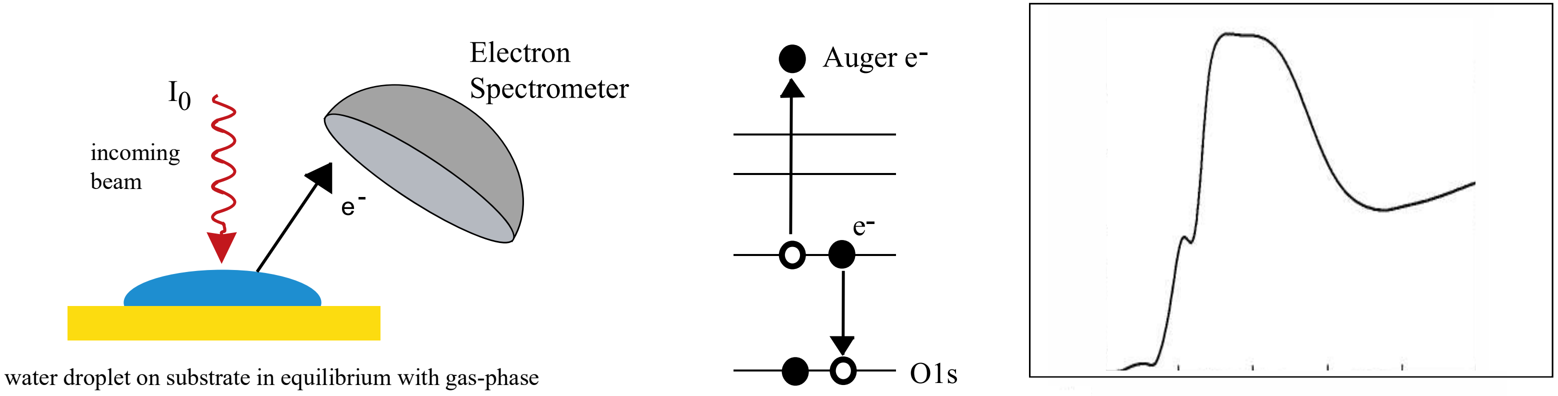


Nilsson et.al. J. El. Spec. Rel. Phen. **177**, 99 (2010)

Liquid Water XAS measurements II

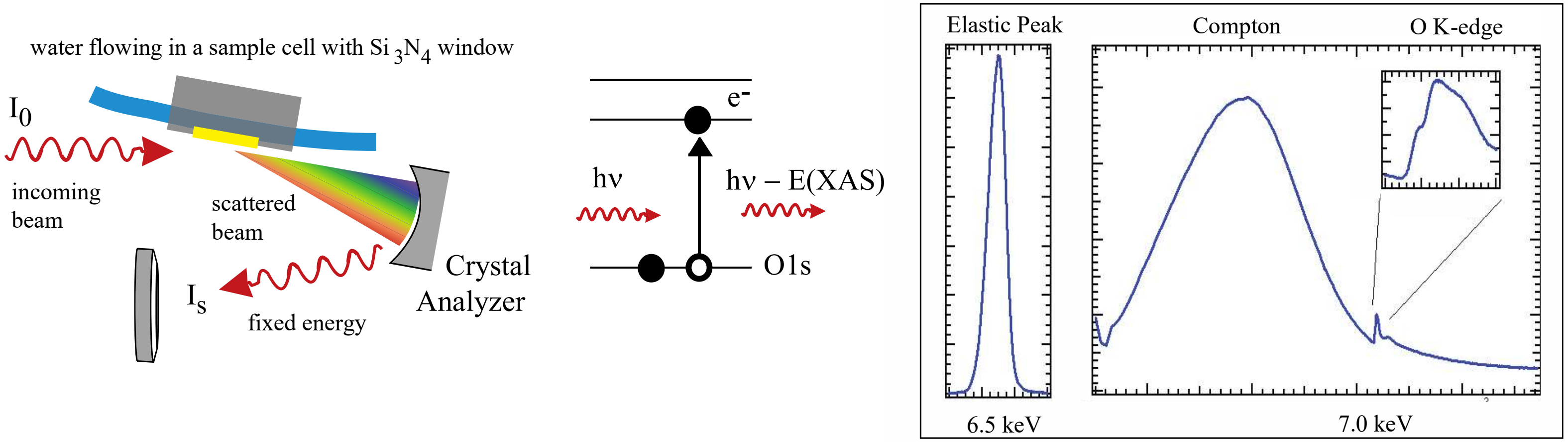
(c) Indirect mode via decay: Auger Electron Yield (AEY-XAS)

$I_1 \sim I_0\,\mu$



(d) Indirect mode via energy loss: X-ray Raman Scattering (XRS)

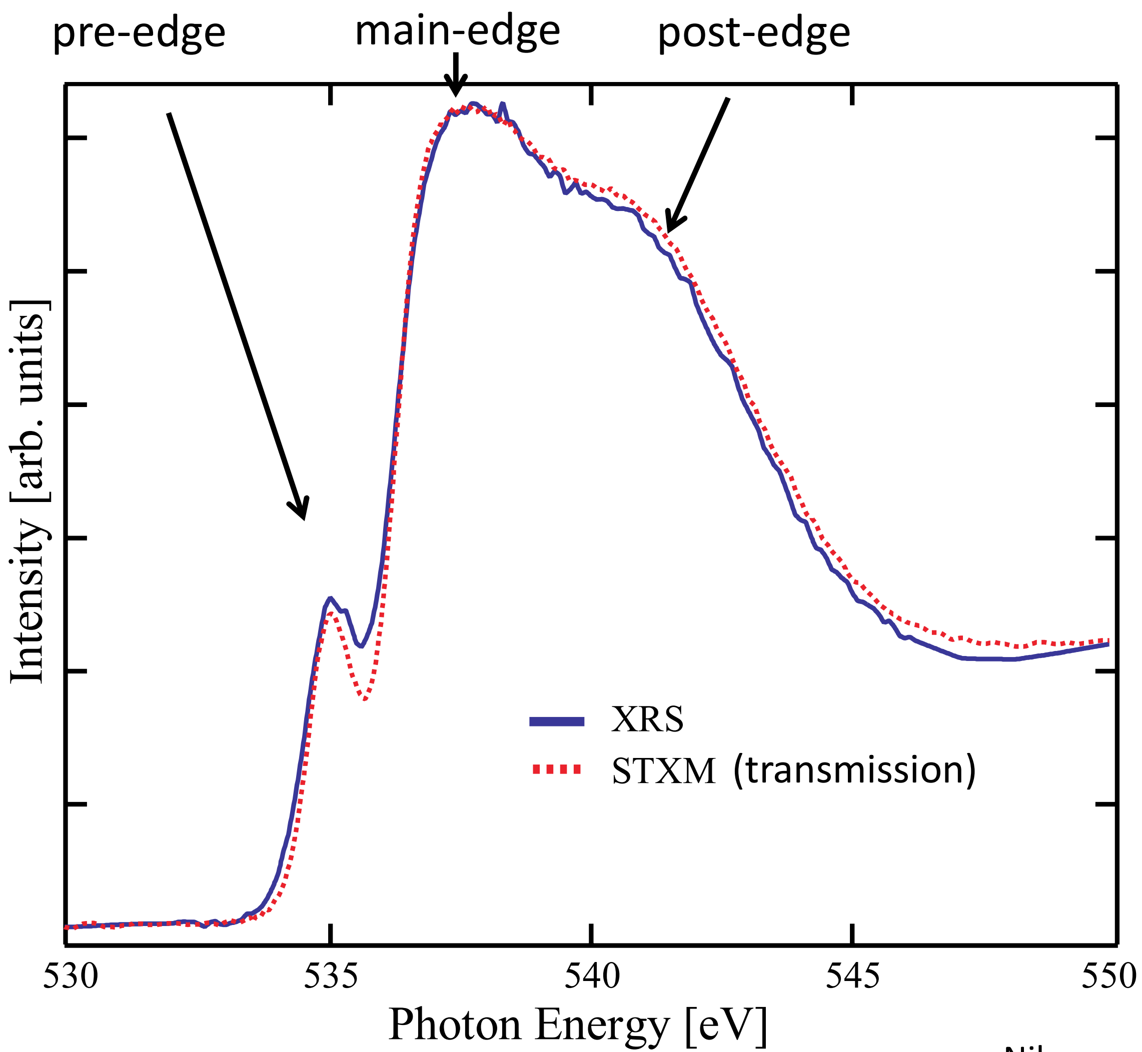
$I_s \sim I_0\,\mu$



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

Final XAS Water

3 major resolved spectral features

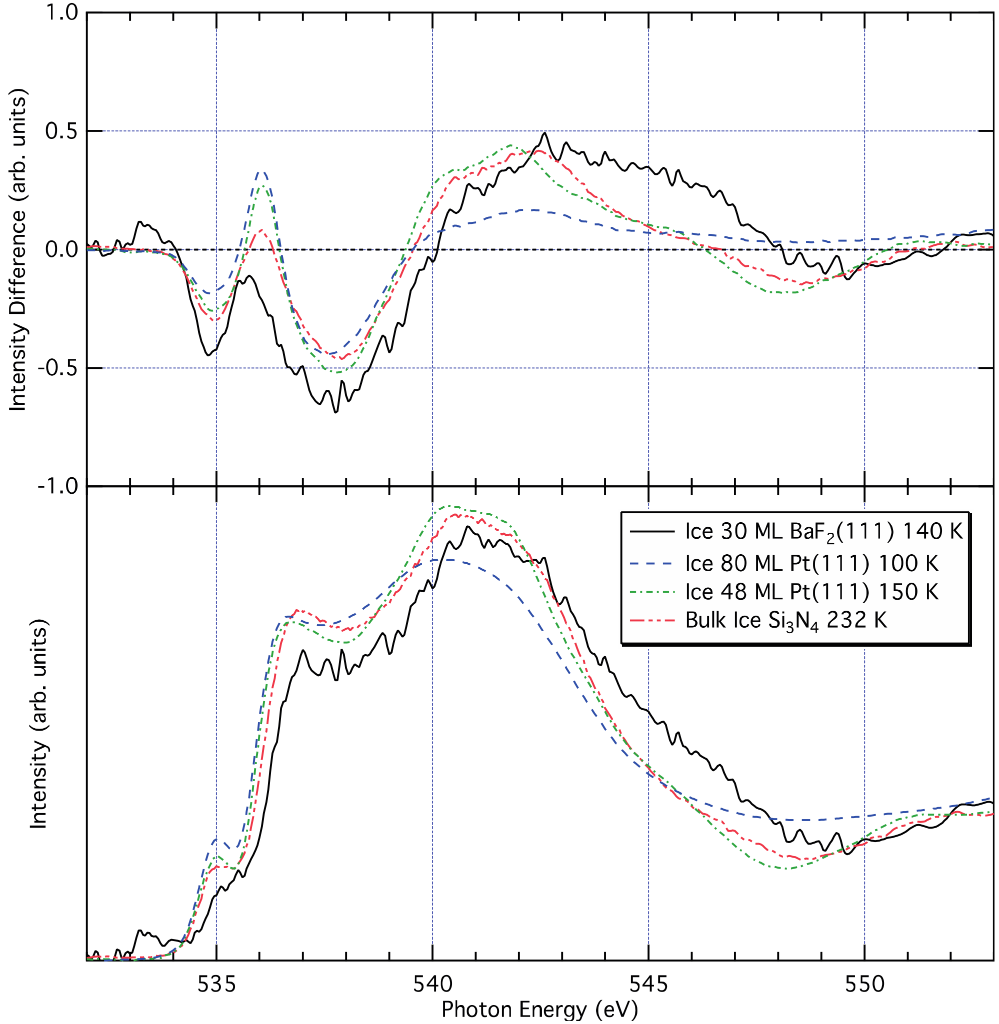


Difference is energy resolution
XRS ≈ 0.5 eV
XAS ≈ 0.1 eV

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

Ice

Different ice preparations gives different spectra!!

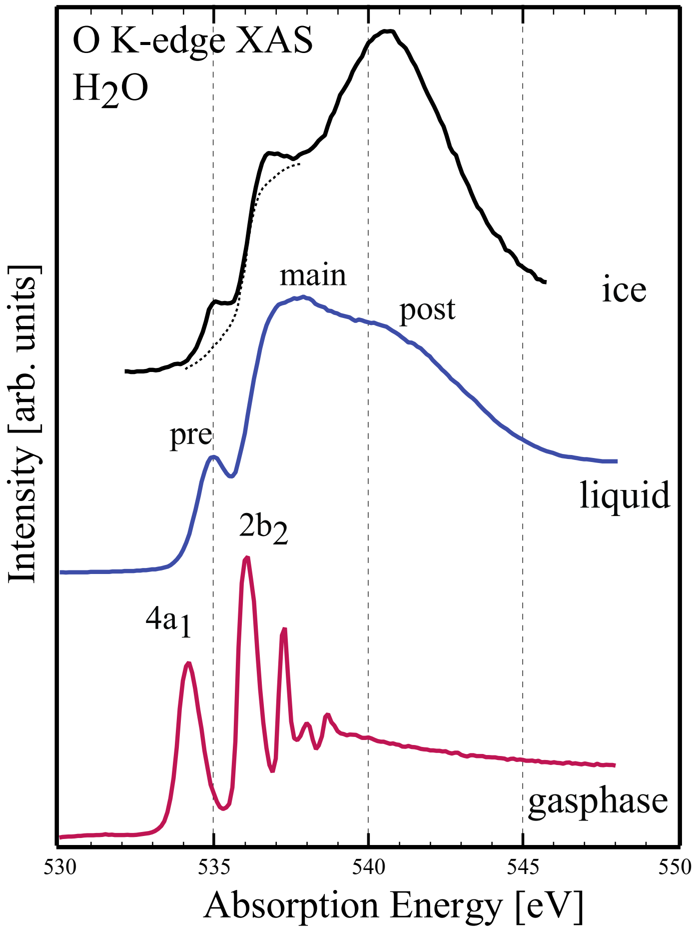


Difference with Water

Attempt to grow ice on BaF2 with less nucleation sites

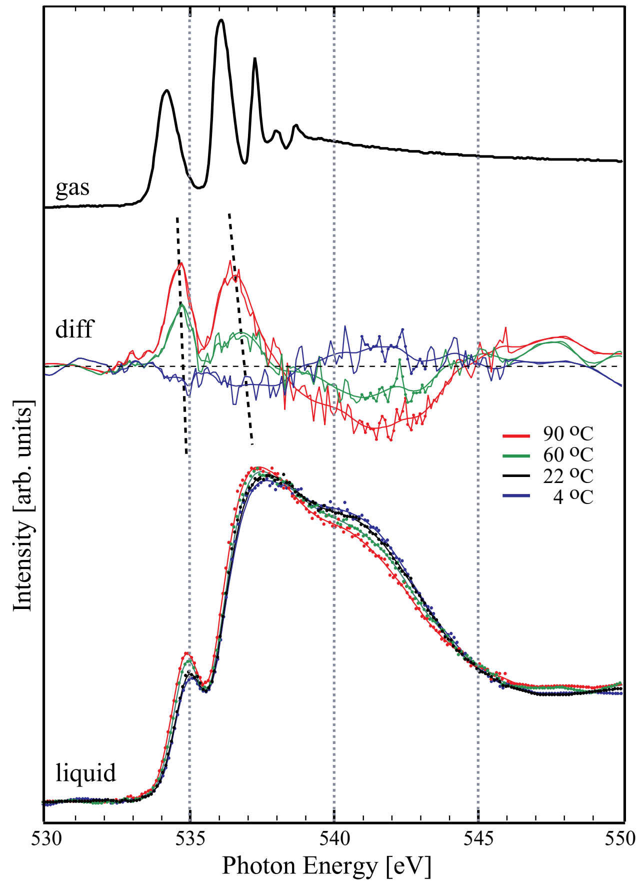
Shifted post-edge and less pre-edge

X-ray Absorption Spectroscopy of Water (XAS)



Intense debate

temperature dependence
X-Raman Scattering

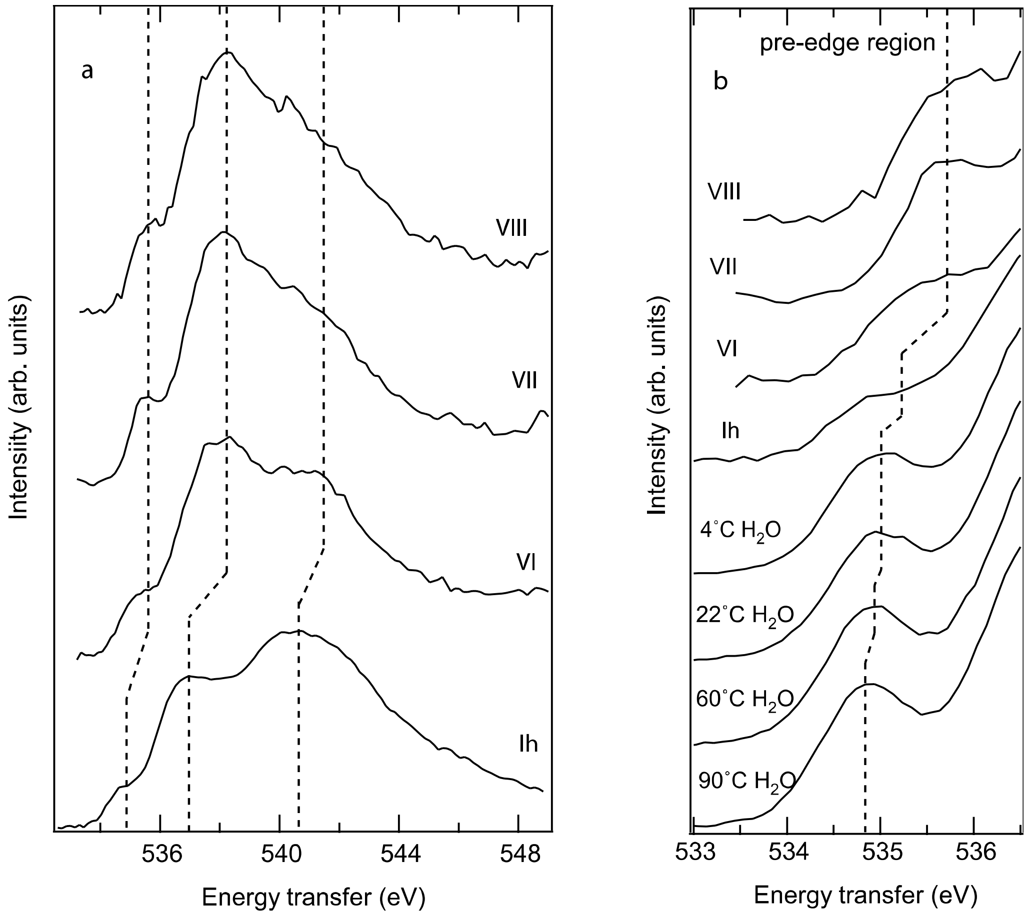


Wernet et al, *Science* **304** (2004) 995
Myneni et.al. *J. Phys. Condens. Matter* **14** (2002) 213

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

Main-edge; Collapse of 2nd shell High density form

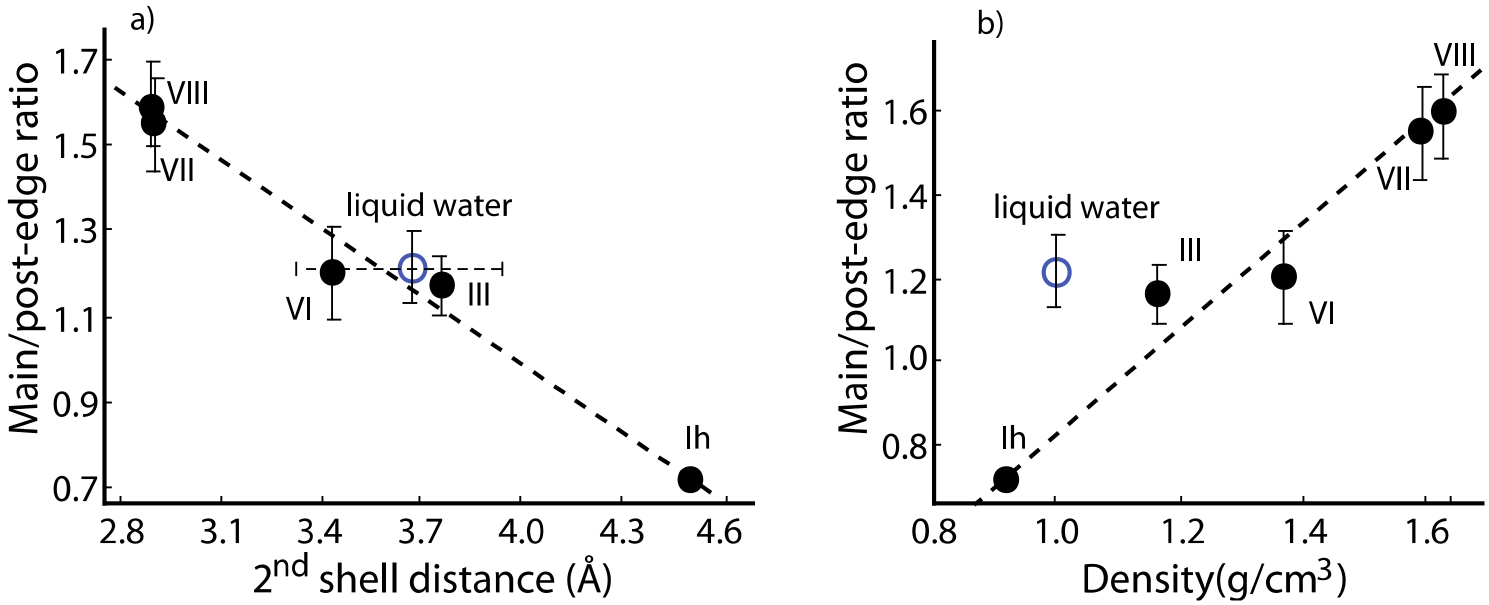
X-ray Raman scattering of high pressure ices
Strong increase in main-edge
pre-edge shifts to higher energy



VII (1.60 g/cm^3)
VI (1.37 g/cm^3)
III (1.17 g/cm^3)
Ih (0.92 g/cm^3)

Pylkkänen et al. *J. Phys. Chem. B 2010,* ***114****, 3804*

Main-edge; Collapse of 2nd shell
High density form



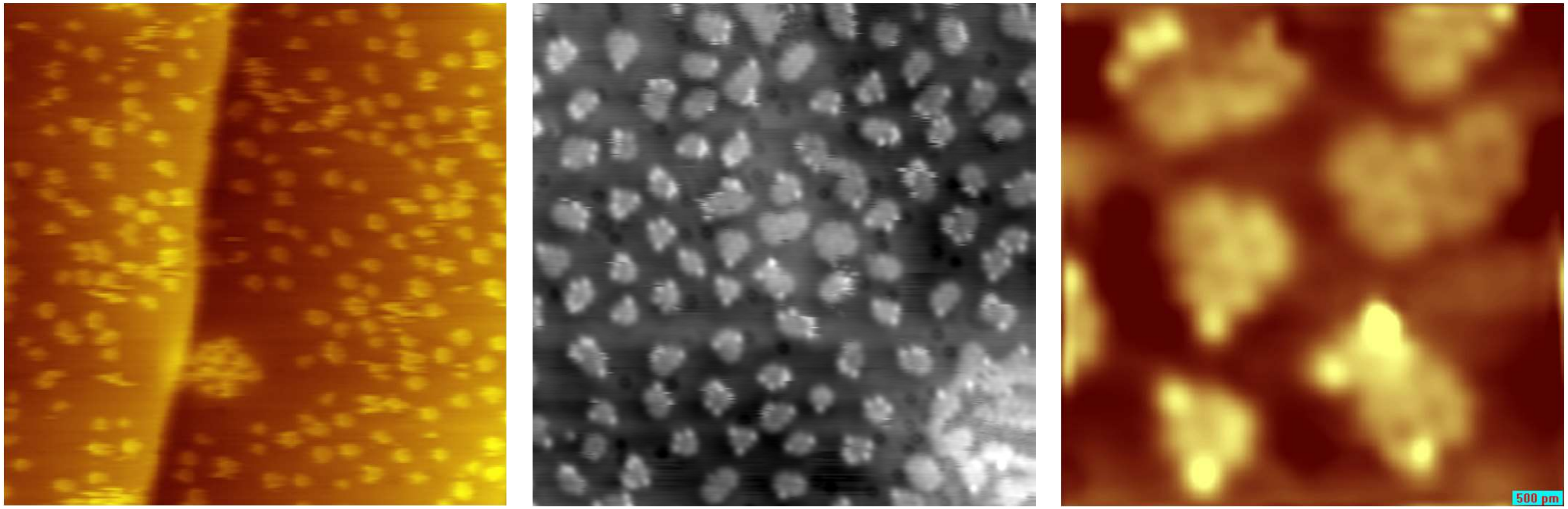
Water should have a collapsed 2nd shell
High Density Liquid
To low density indicating thermal distortions

Pylkkänen et al. *J. Phys. Chem. B 2010,* ***114****, 3804*

Water Clusters on Surfaces

Scanning Tunneling Microscopy (STM) of Water on Ru(0001)

Nordlund et al. Phys. Rev. B **80**, 233404 (2009)



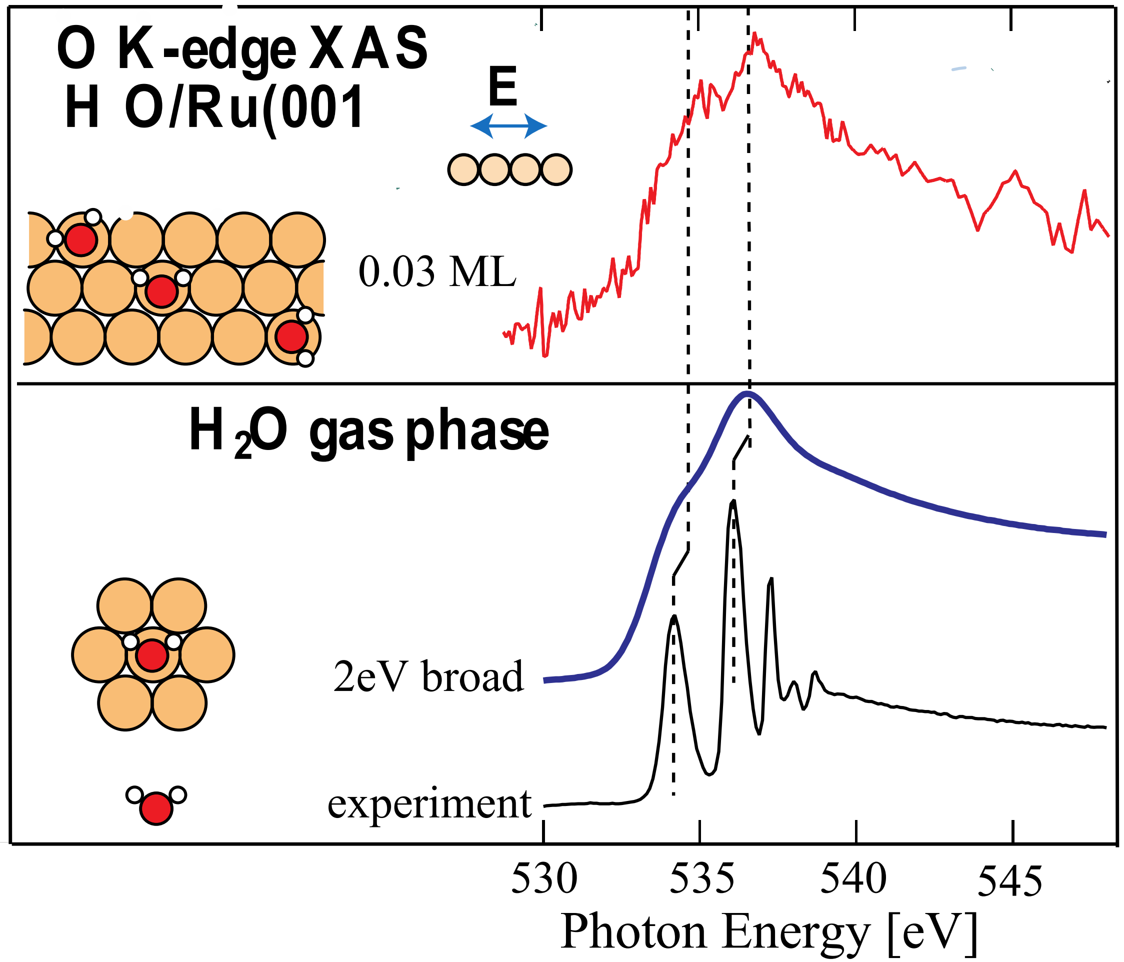
Deposited at 50 K

Annealed to 130 K imaged at 50 K

IR shows that water molecules are adsorbed flat with the HOH plane parallel to the surface

A. Hodgson et.al. unpublished

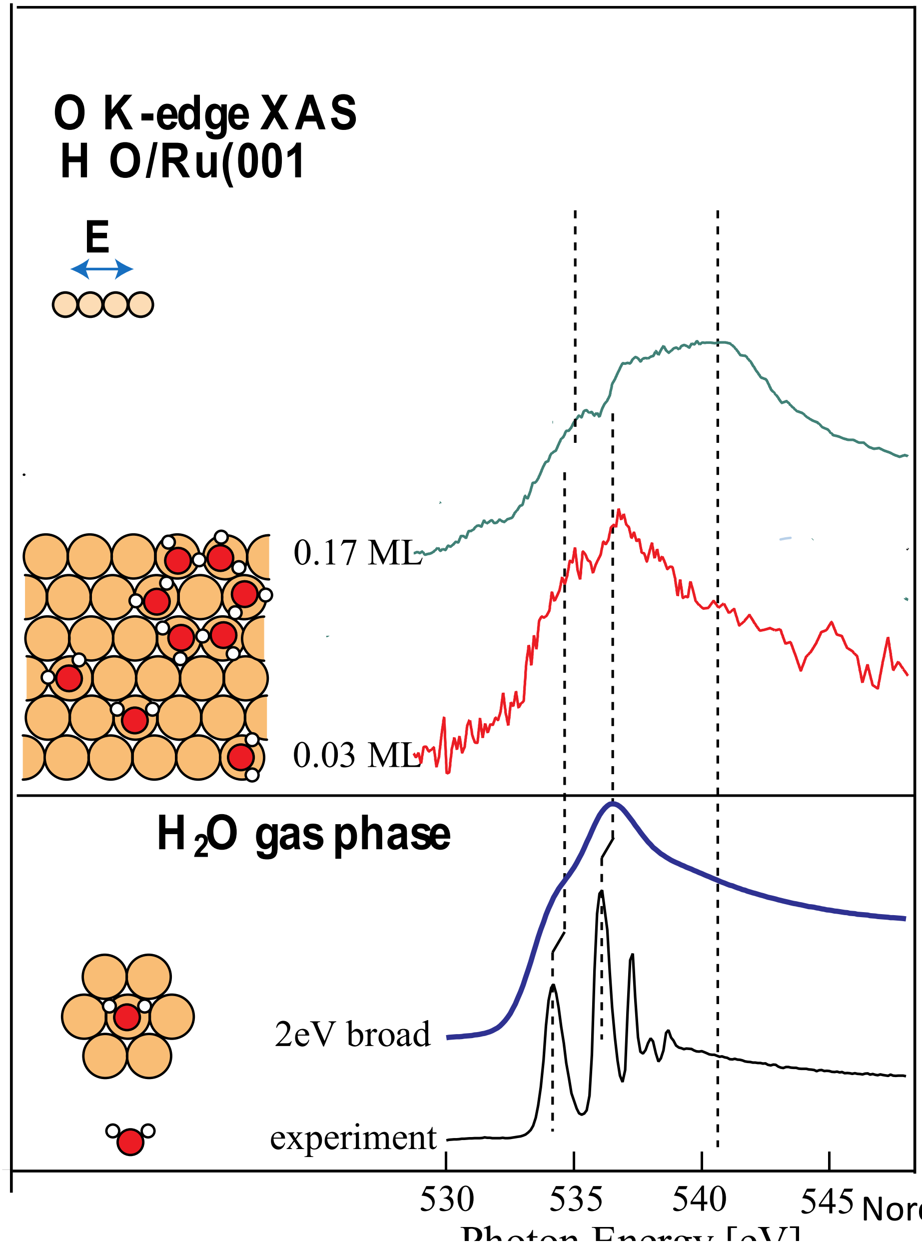
Isolated Water



Like Gas Phase water

Nordlund et al. Phys. Rev. B **80**, 233404 (2009)

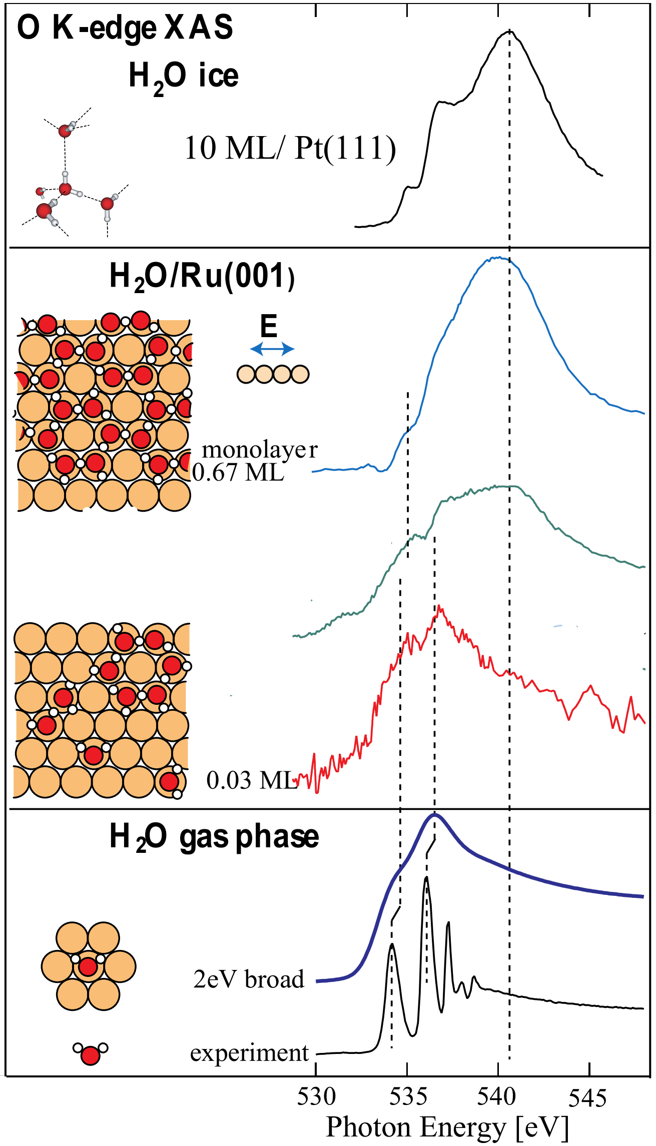
Small Clusters



Nordlund et al. Phys. Rev. B **80**, 233404 (2009)

One **strong** and one **broken** donor H-bond

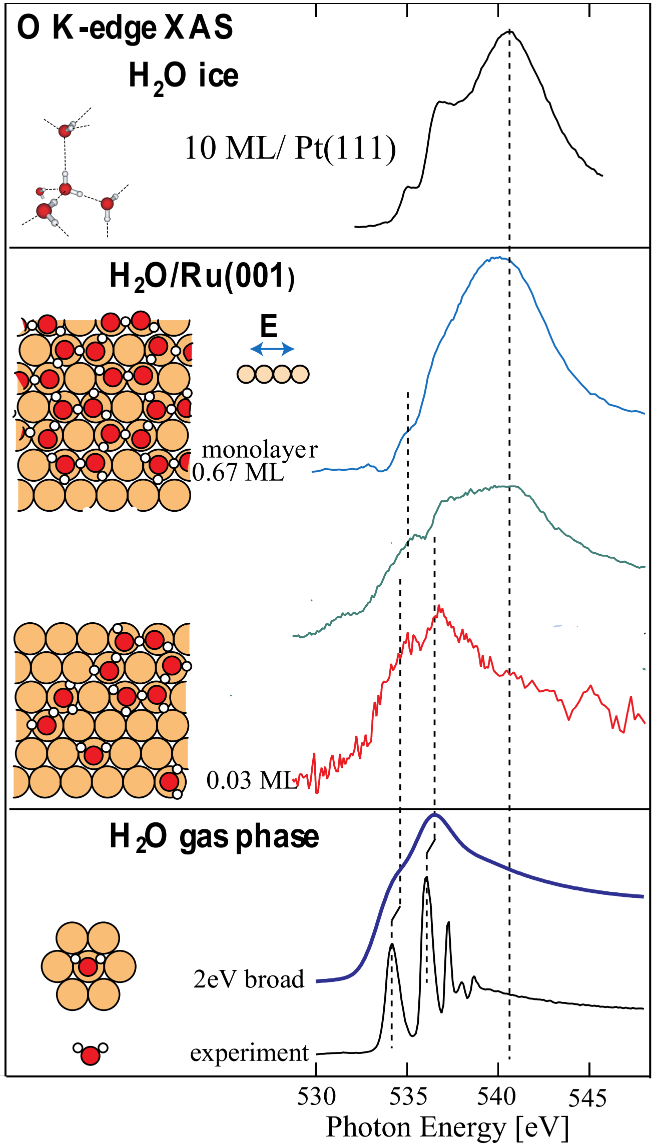
Two dimensional Monolayer



Complete H-bond layer spectrum
similar to ice

Nordlund et al. Phys. Rev. B **80**, 233404 (2009)

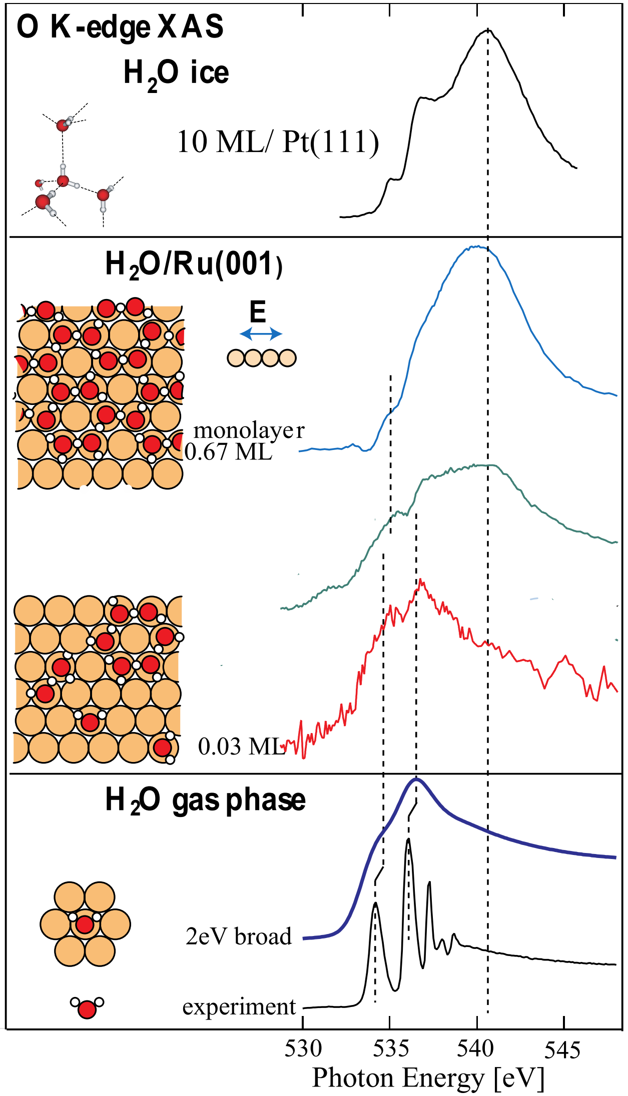
Two dimensional Monolayer

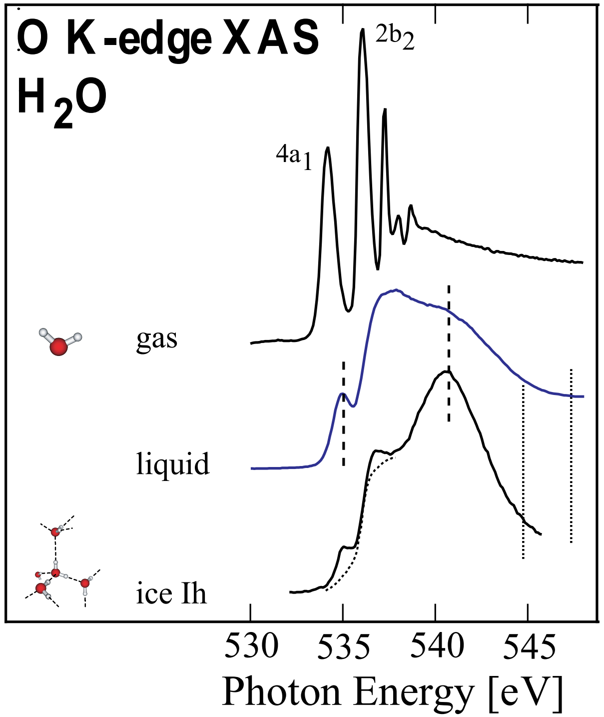


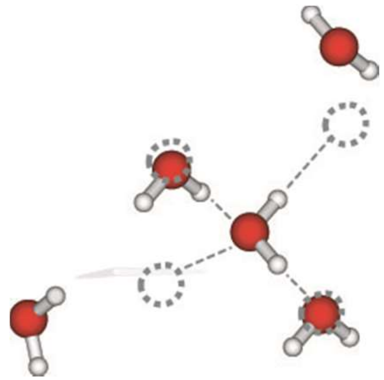
Complete H-bond layer spectrum **similar to ice**

Nordlund et al. Phys. Rev. B **80**, 233404 (2009)

Two Dimensional Water Structures



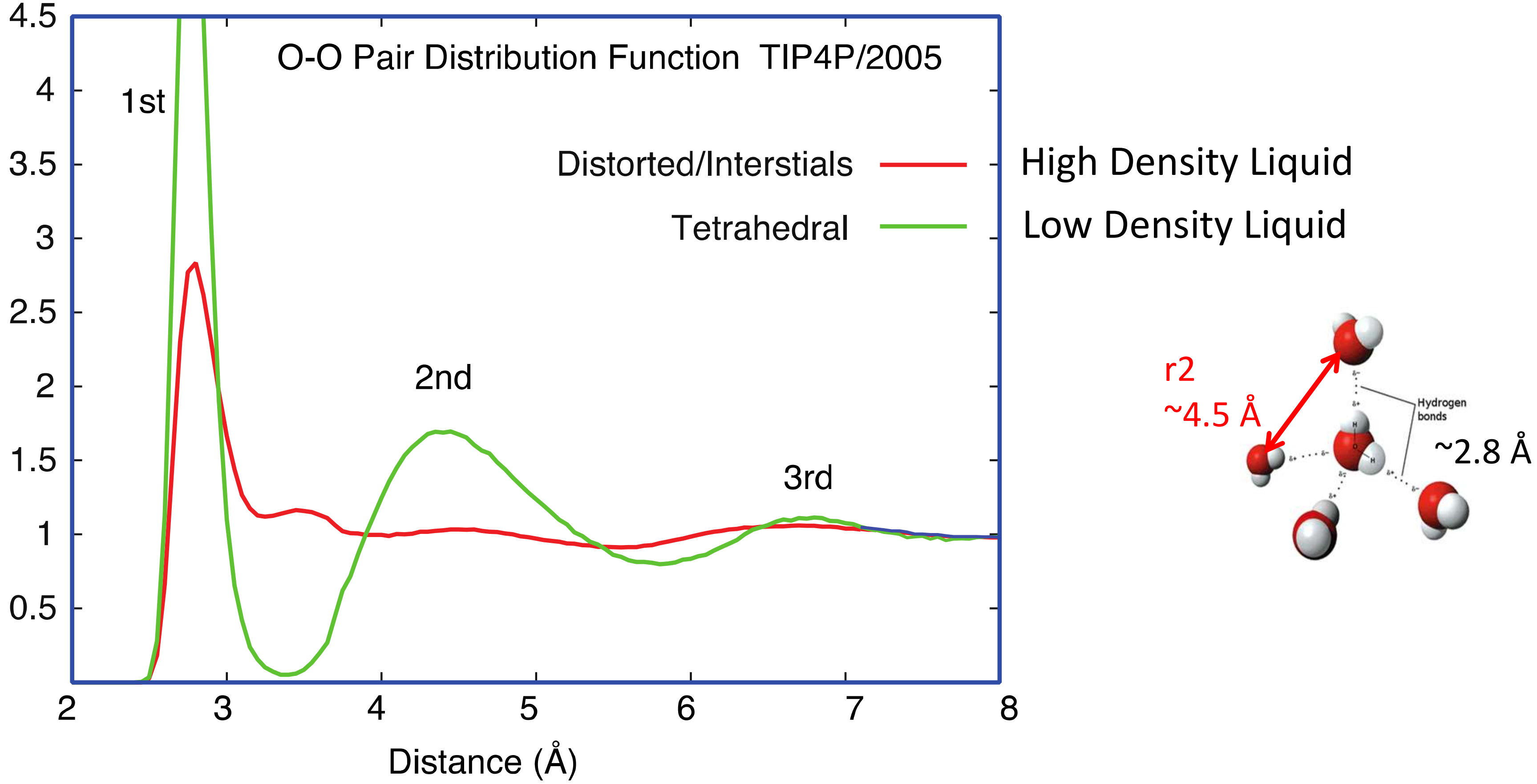




Asymmetrical distortions

Nordlund et al. Phys. Rev. B **80**, 233404 (2009)

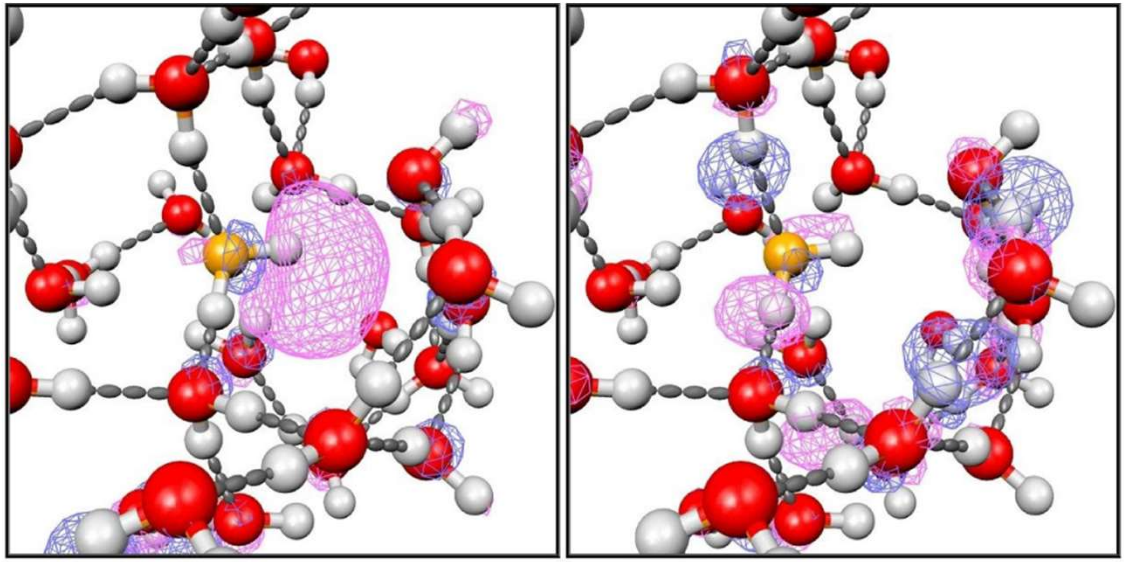
Different Liquid Structures in MD



A. Nilsson and L. G. M. Pettersson Nature Communication **6** 8998 (2015)

Interpretation of Water XAS Spectrum

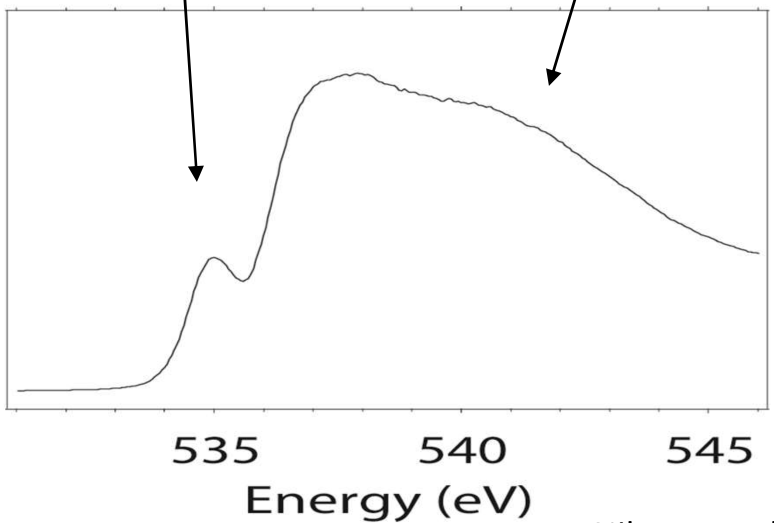
Pre-edge
and partly
Main-edge



Post-edge

Localized
on free OH

Distortion in
High Density

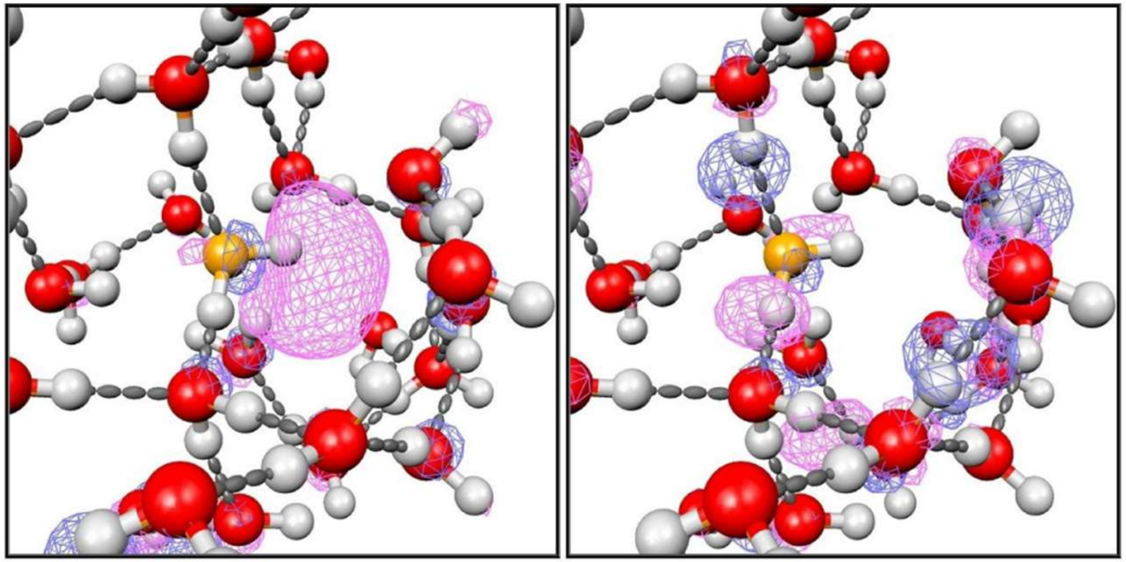


Delocalized
along the H-bond
network

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

Interpretation of Water XAS Spectrum

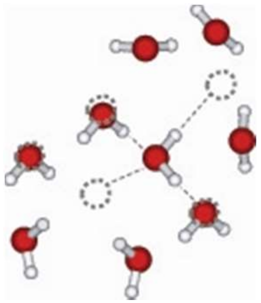
Pre-edge
and partly
Main-edge

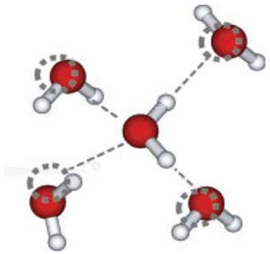


Post-edge

Distorted
High Density

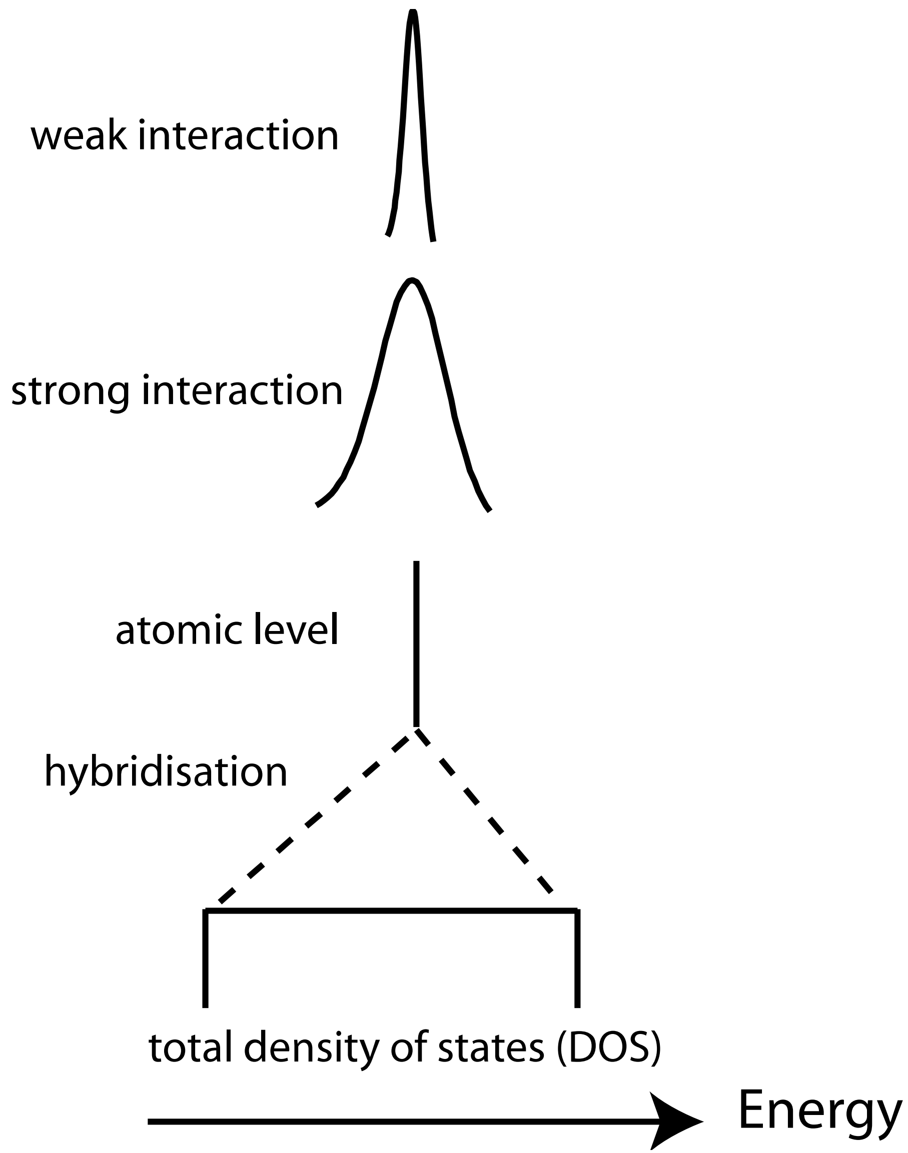
Strong H-bonds
Tetrahedral





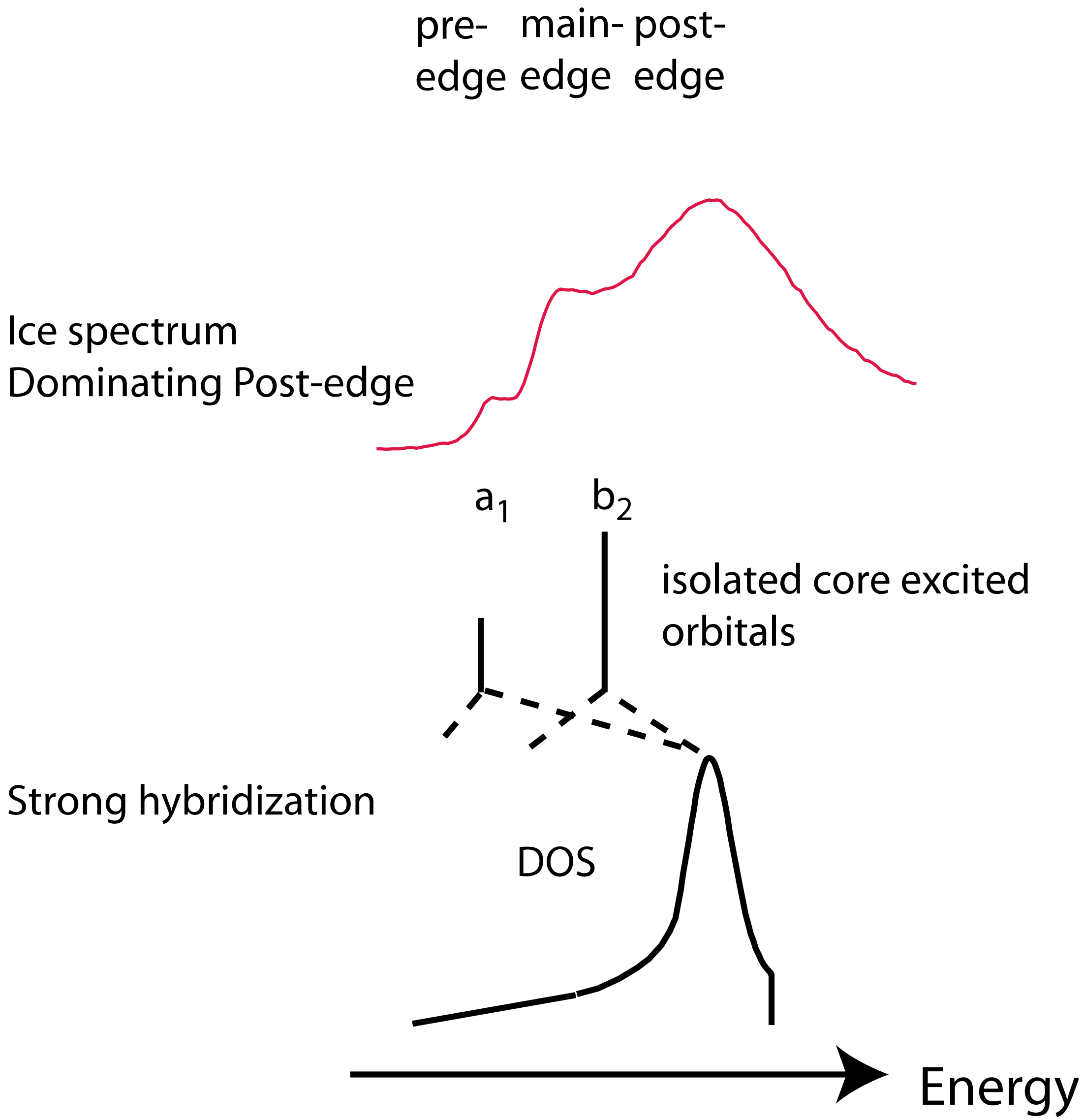
Nilsson et.al. J. El. Spec. Rel. Phen. **177**, 99 (2010)

Anderson Impurity Model



Nilsson and Pettersson, Chem. Phys. **389**, 1 (2011)

Anderson Impurity XAS Model; Ice

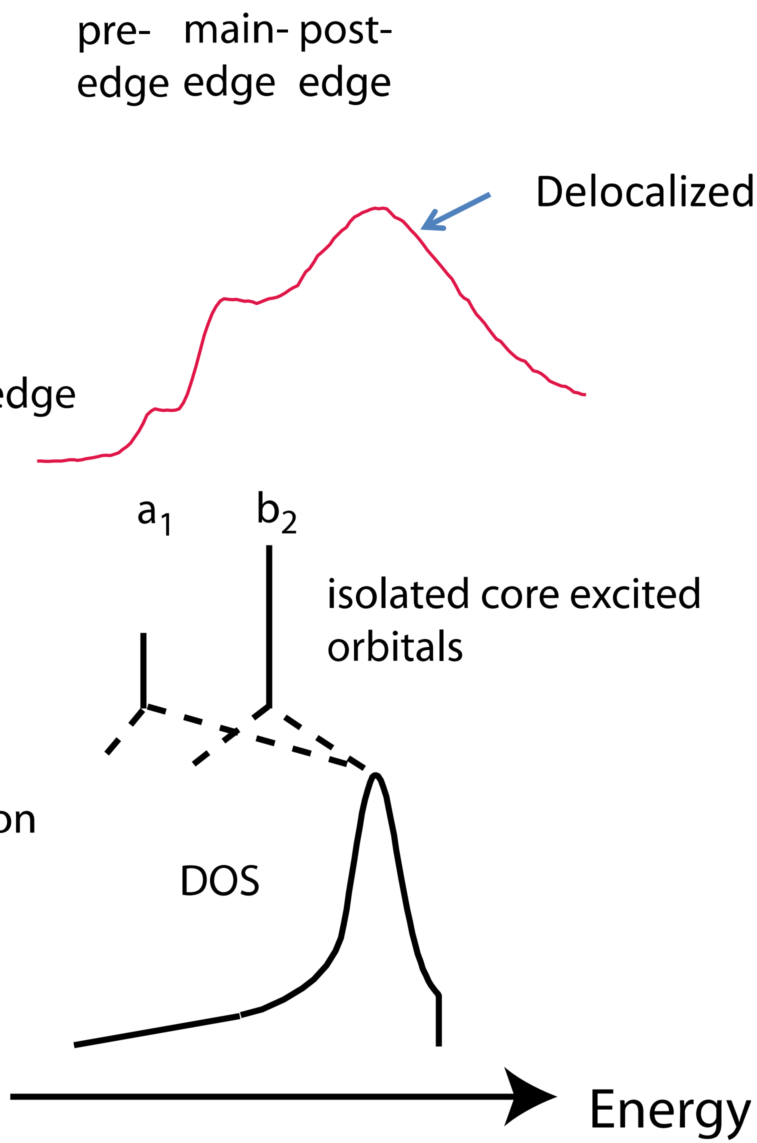


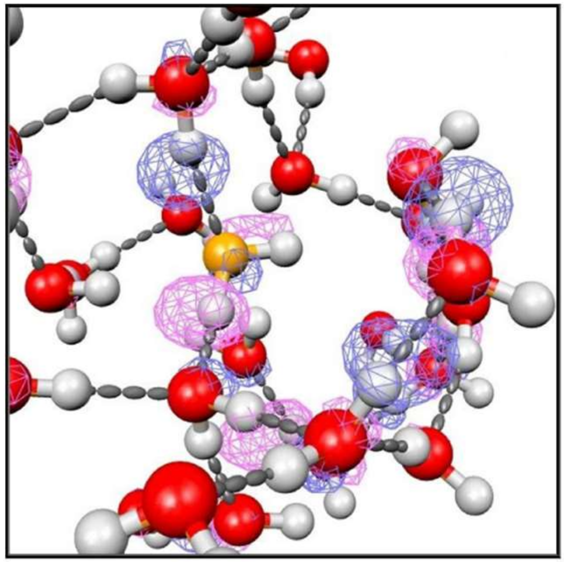
Nilsson and Pettersson, Chem. Phys. **389**, 1 (2011)

Anderson Impurity XAS Model; Ice

Ice spectrum
Dominating Post-edge

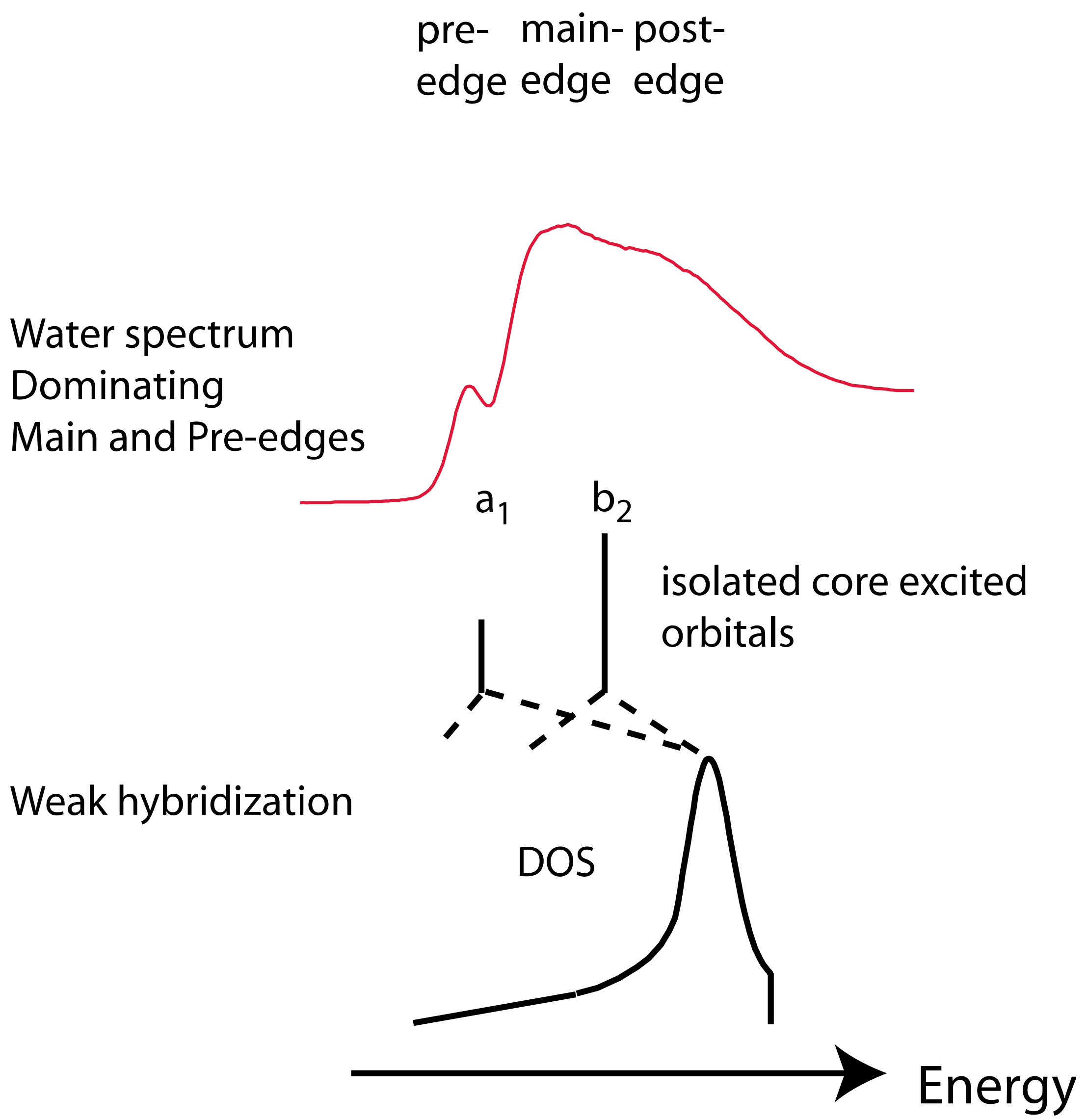
Strong hybridization





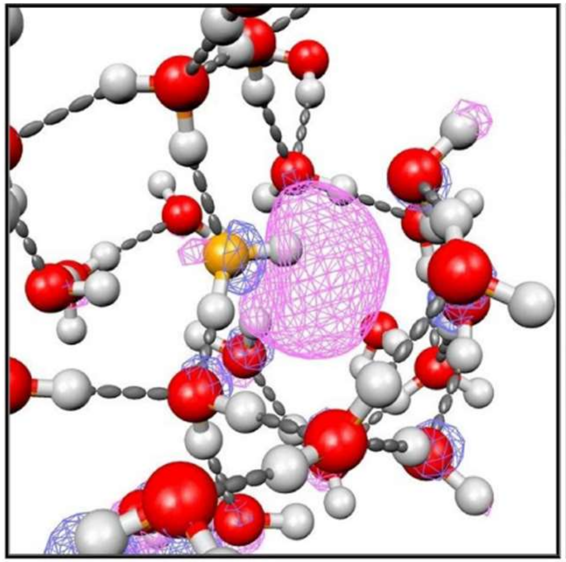
Nilsson and Pettersson, Chem. Phys. **389**, 1 (2011)

Anderson Impurity XAS Model; Water

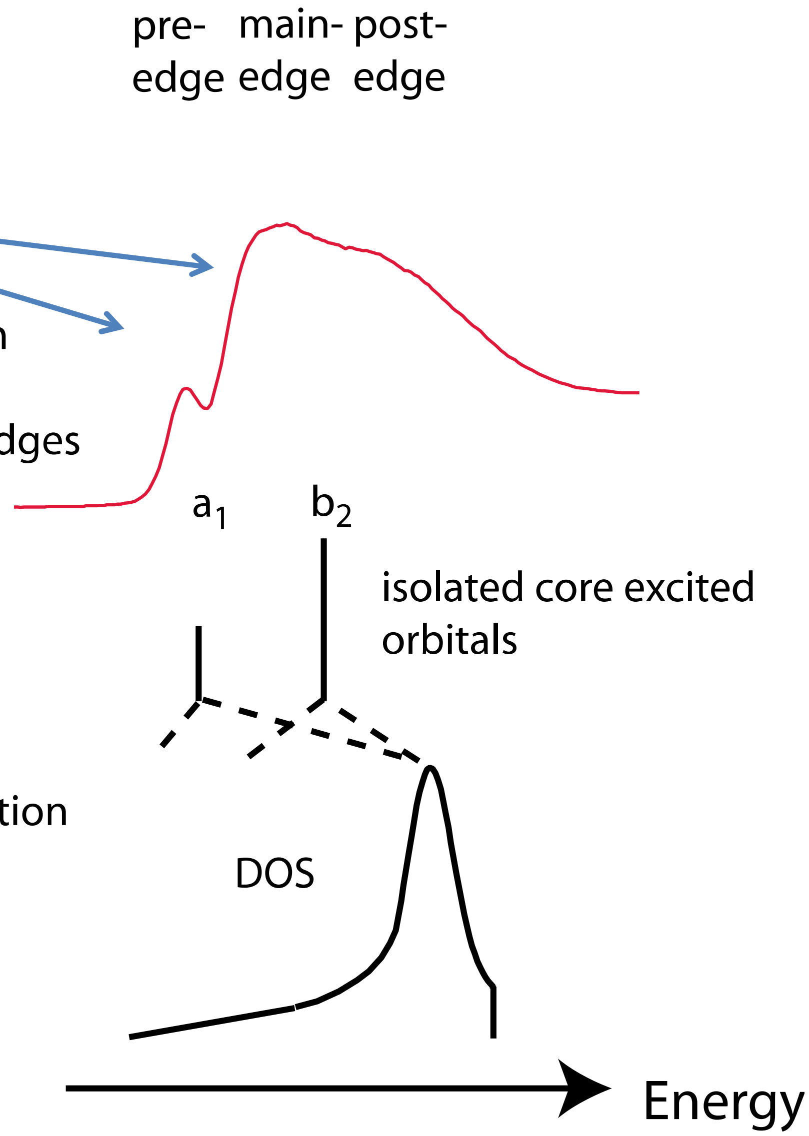


Nilsson and Pettersson, Chem. Phys. **389**, 1 (2011)

Anderson Impurity XAS Model; Water



Water spectrum
Dominating
Main and Pre-edges

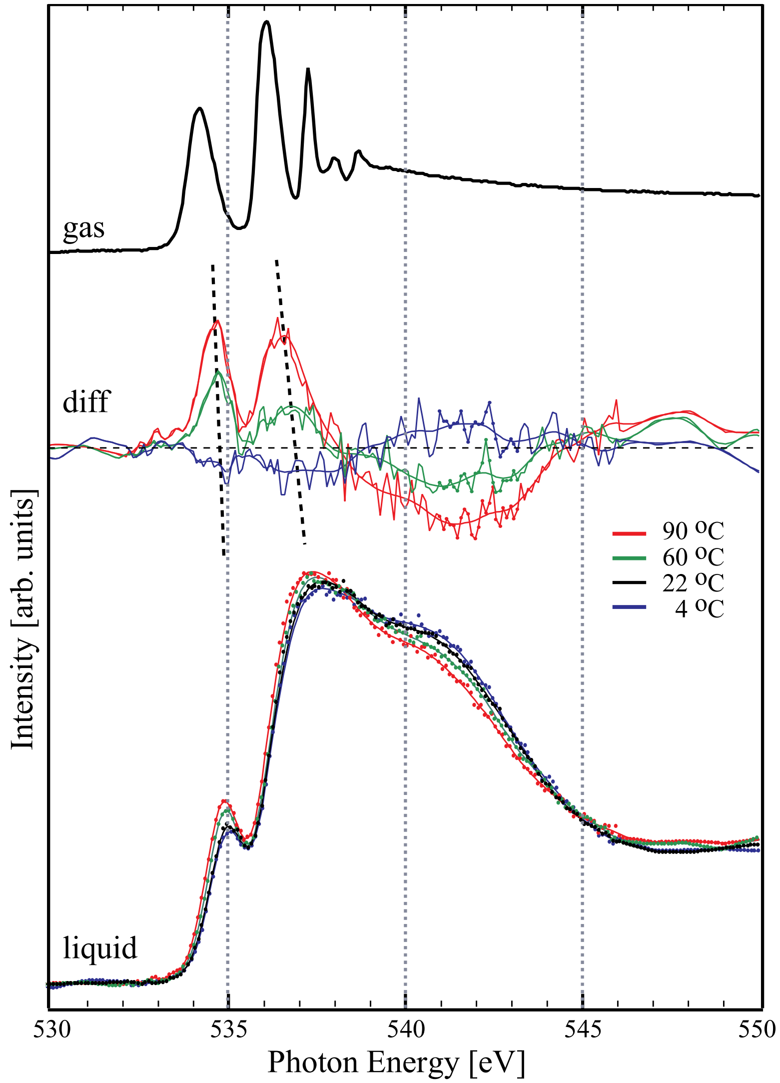


Weakened H-bond
2^{nd} shell collapse
Local bond distortion

Weak hybridization

Nilsson and Pettersson, Chem. Phys. **389**, 1 (2011)

Temperature Dependence



With increasing temperature

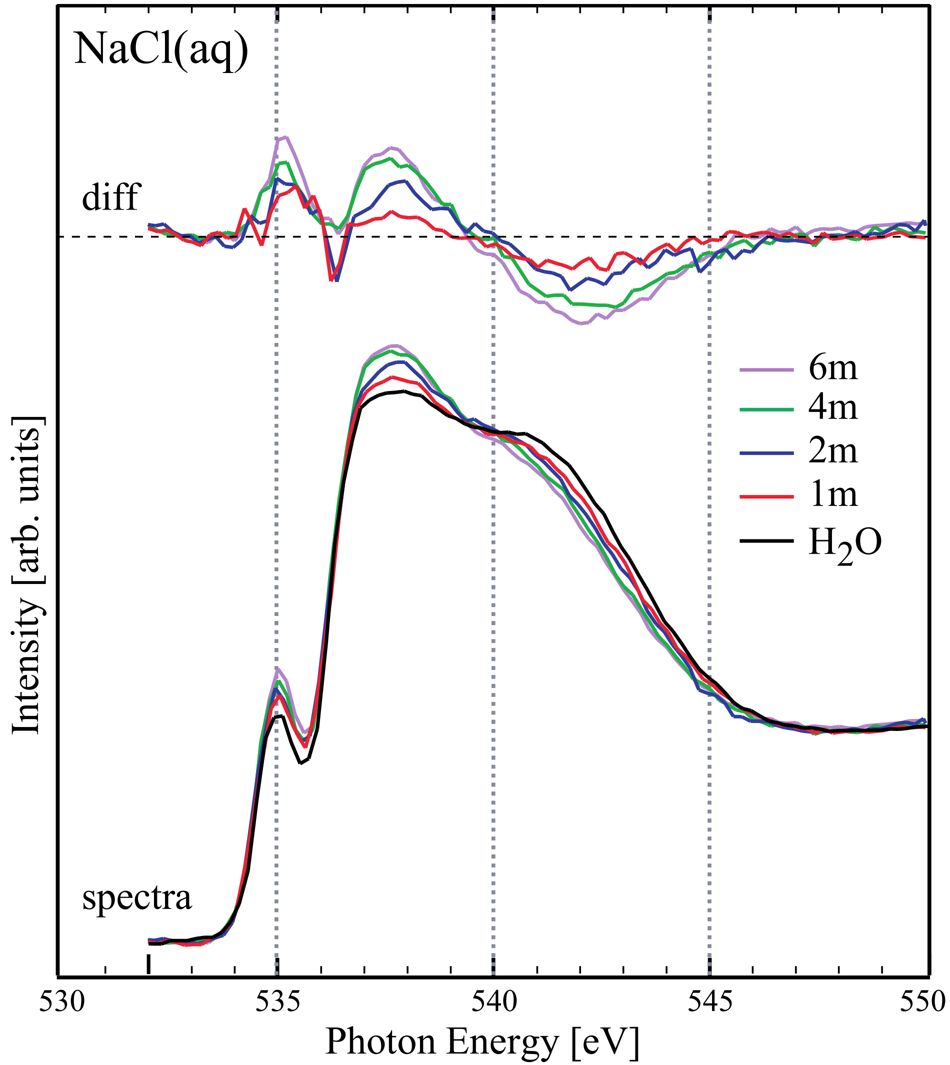
- Increase in pre- and main-edge
- decrease in post-edge

- Similar to difference between water and ice

- Shift of resonances towards gas phase

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

NaCl Concentration Dependence



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Similar trend as with temperature but without shift

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

Main-edge; Collapse of 2nd shell
High density form

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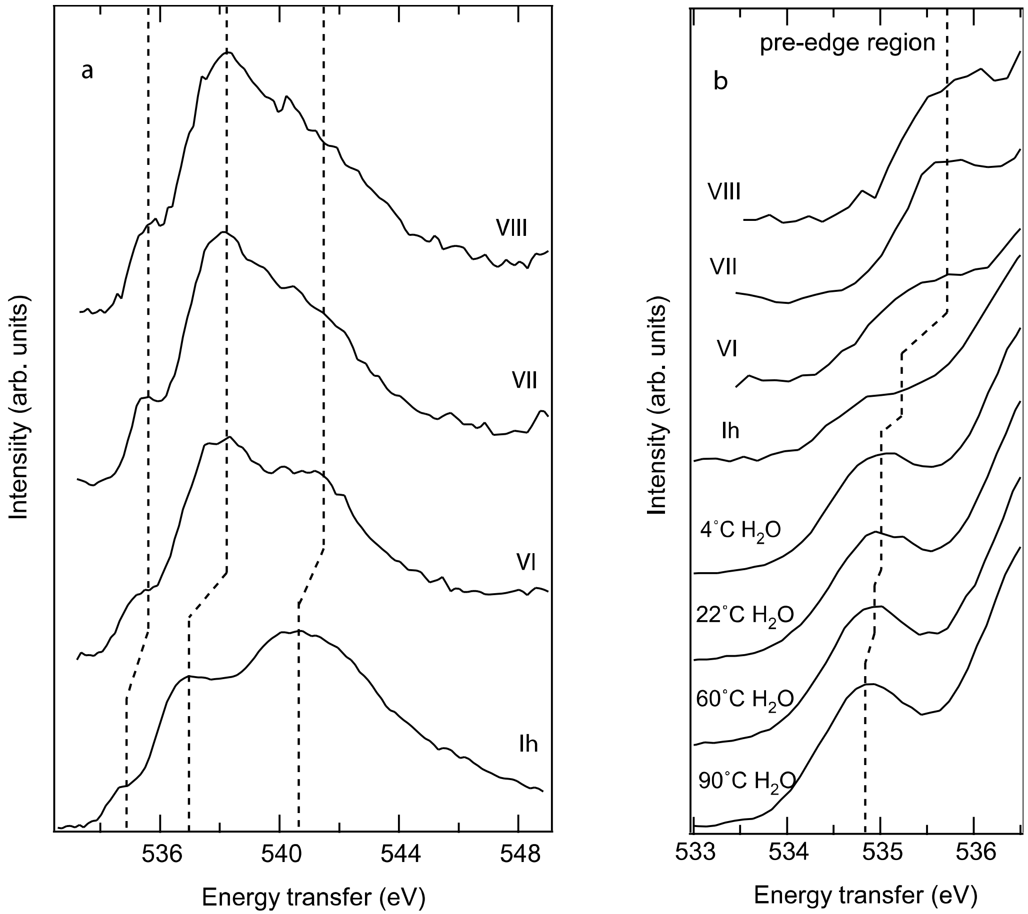

VII (1.60 g/cm^3)
VI (1.37 g/cm^3)
III (1.17 g/cm^3)
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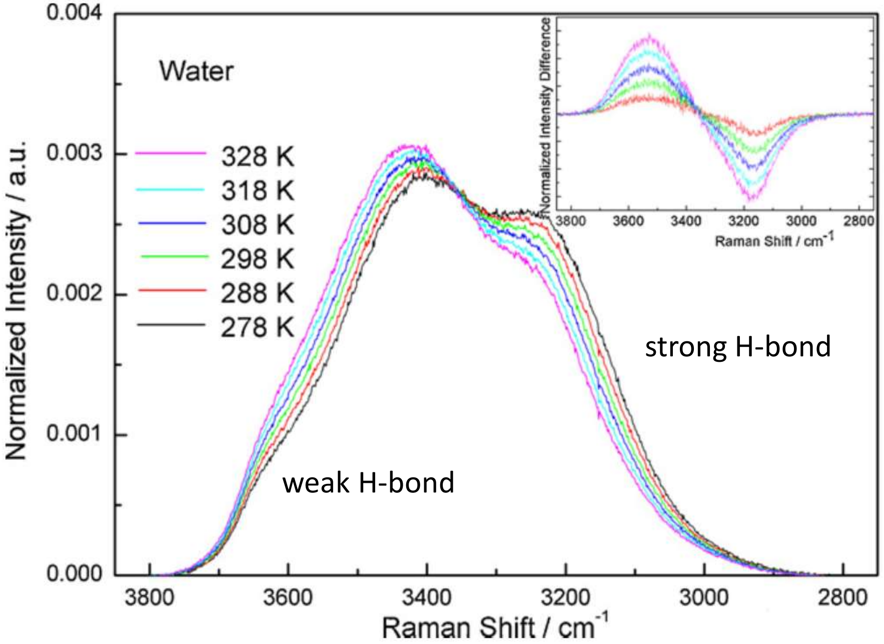
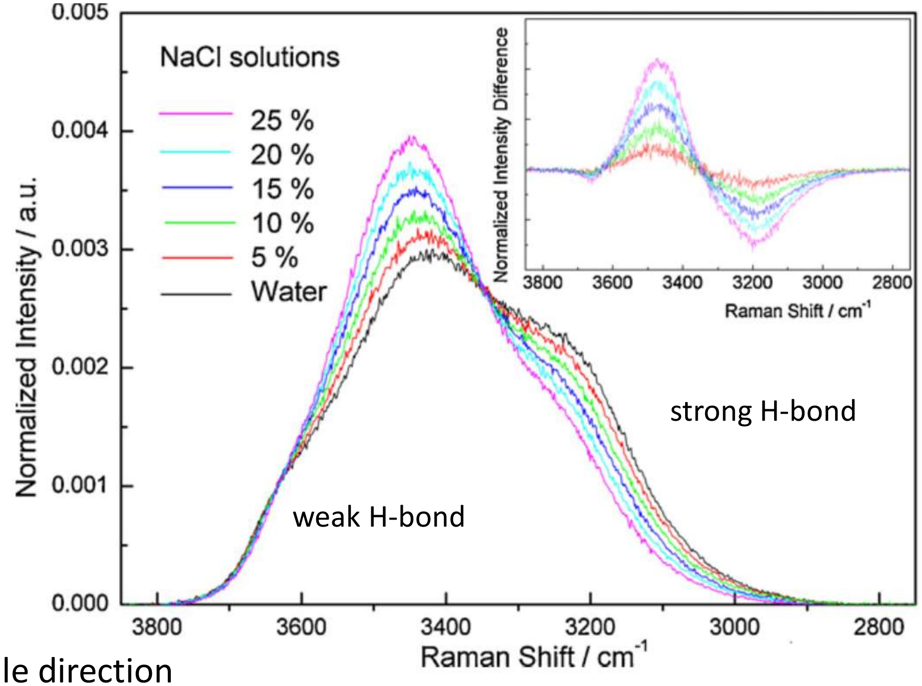
Pylkkänen et al. *J. Phys. Chem. B 2010*, ***114***, *3804*

Raman OH spectroscopy of H_2O

Temperature Dependence



NaCl Concentration Dependence



note energy scale direction

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- Decrease in post-edge
- Shift of weak bond towards gas phase

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- Increase in weak H-bond
- Decrease in strong H-bond
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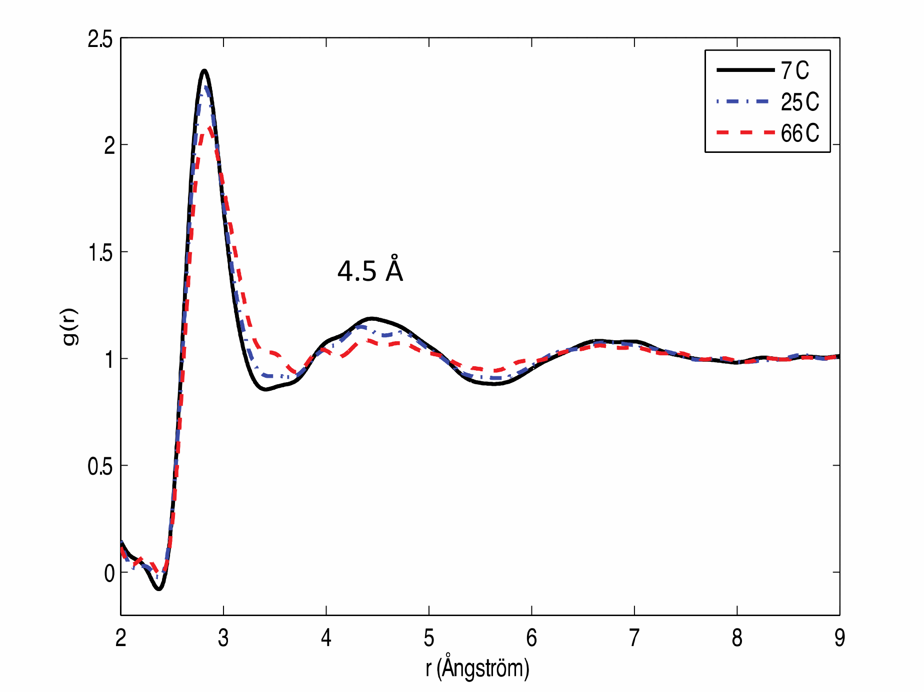
Similar trend as with temperature but without shift

Q. Sun, Vibrational Spectroscopy *62 (2012) 110– 114*

O-O Pair Correlation Function

Temperature Dependence

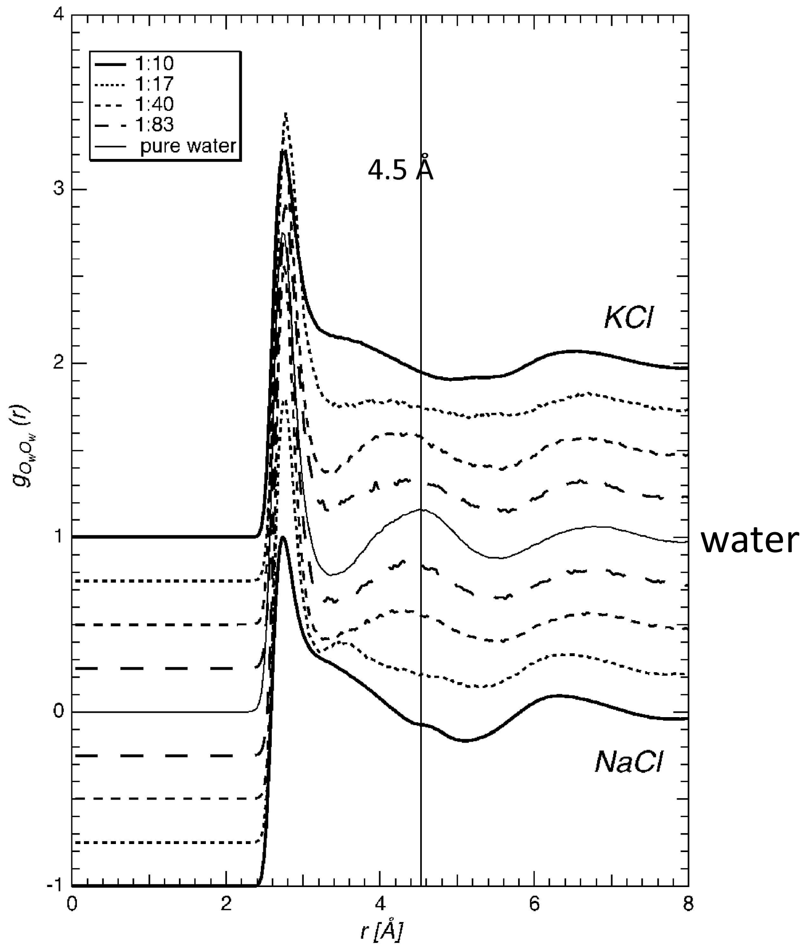


Decreasing 4.5 Å Tetrahedral

Consistent change in terms of the tetrahedral component between T and NaCl concentration

Huang et al. PCCP **13**, 19997 (2011)

NaCl Concentration Dependence

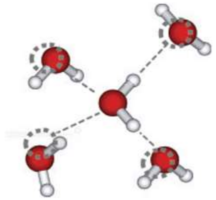


Disapparence of 4.5 Å Tetrahedral

Mancinelli et al. PCCP **9**, 2559 (2007)

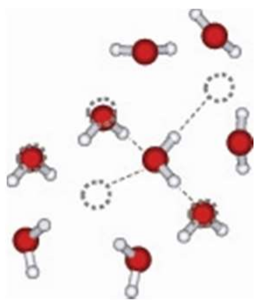
Summary XAS

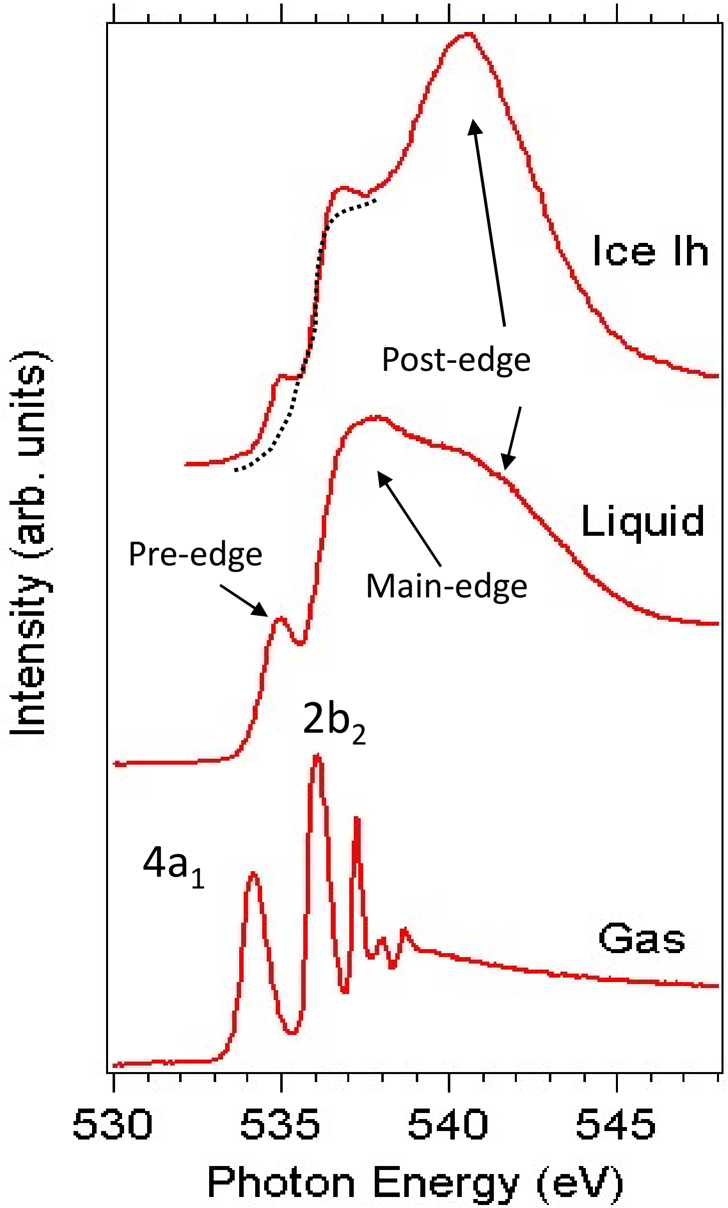
Post-edge is related to directed H-bonds
Position shifts with H-bond length
Tetrahedral structures in water at similar H-bond length in water



Pre-edge is related to weaken/broken H-bonds
Intensity and energy position changes depends on distortions

Main-edge intensity is related to collapse of 2^{nd} shell
High density liquid structures

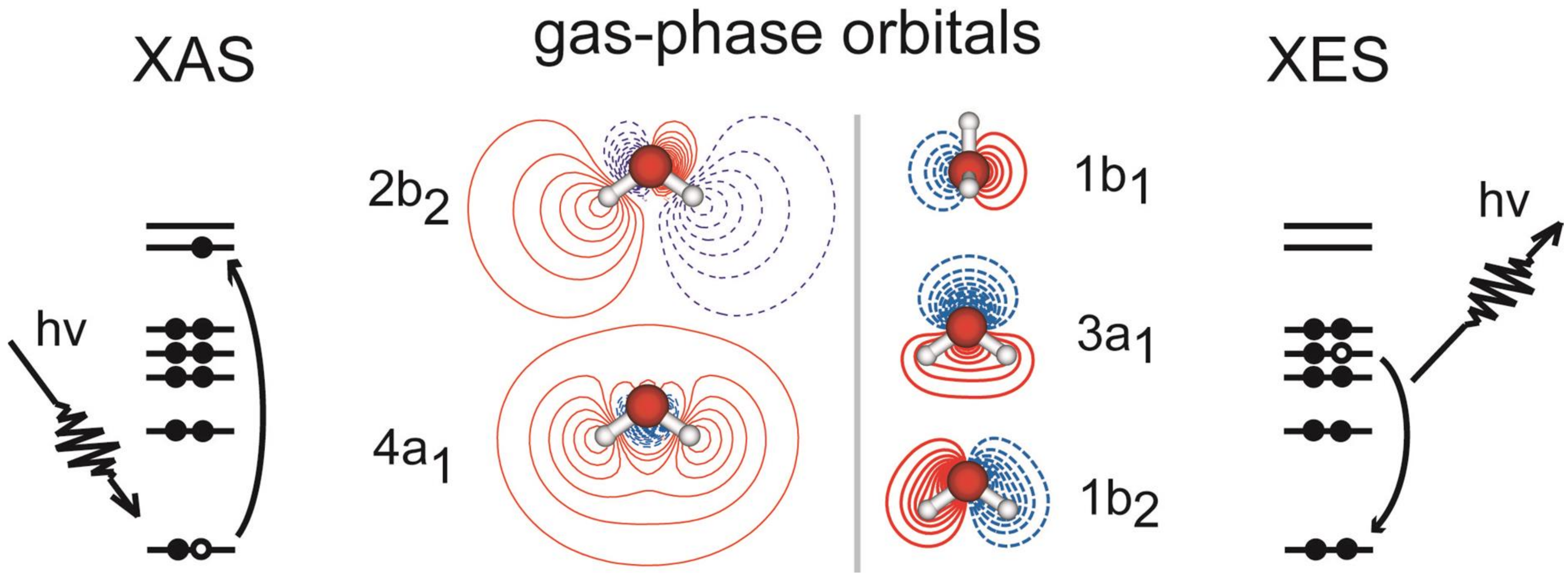




Probing Valence Electrons

The hydrogen bond is directional

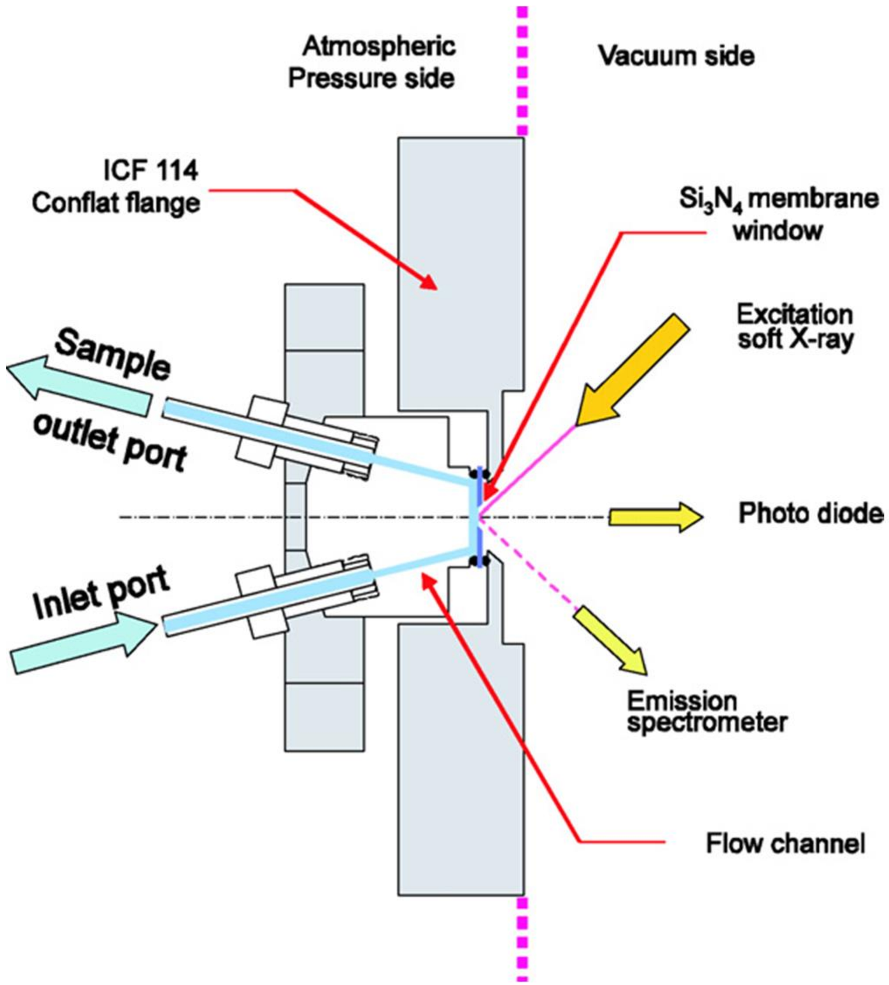
Probing of valence electrons

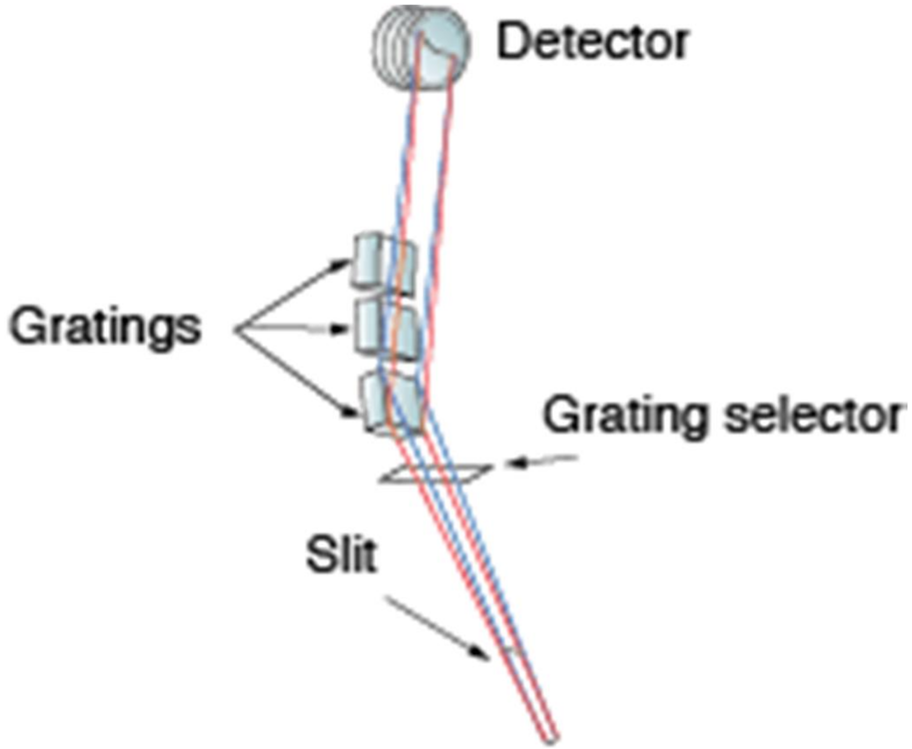


X-ray Absorption Spectroscopy
Probes Unoccupied Orbitals

X-ray Emission Spectroscopy
Probes Occupied Orbitals

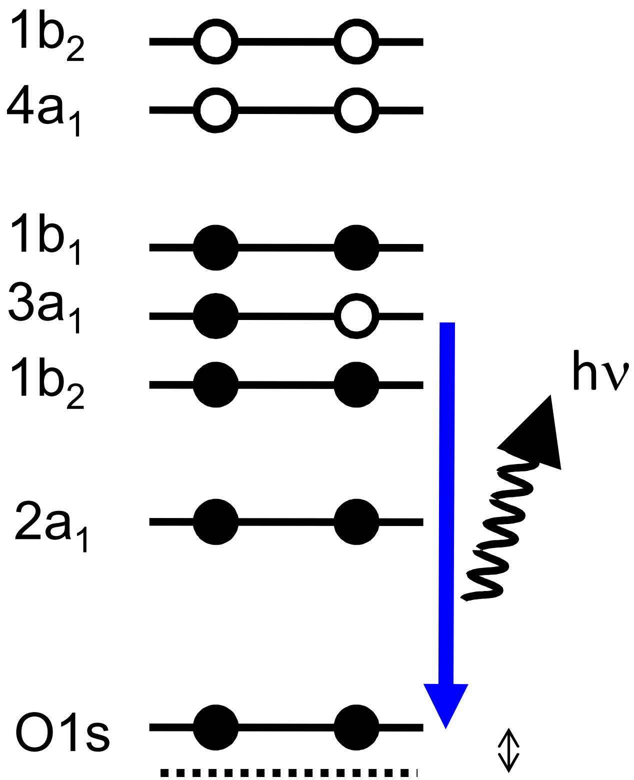
Liquid Water XES measurements

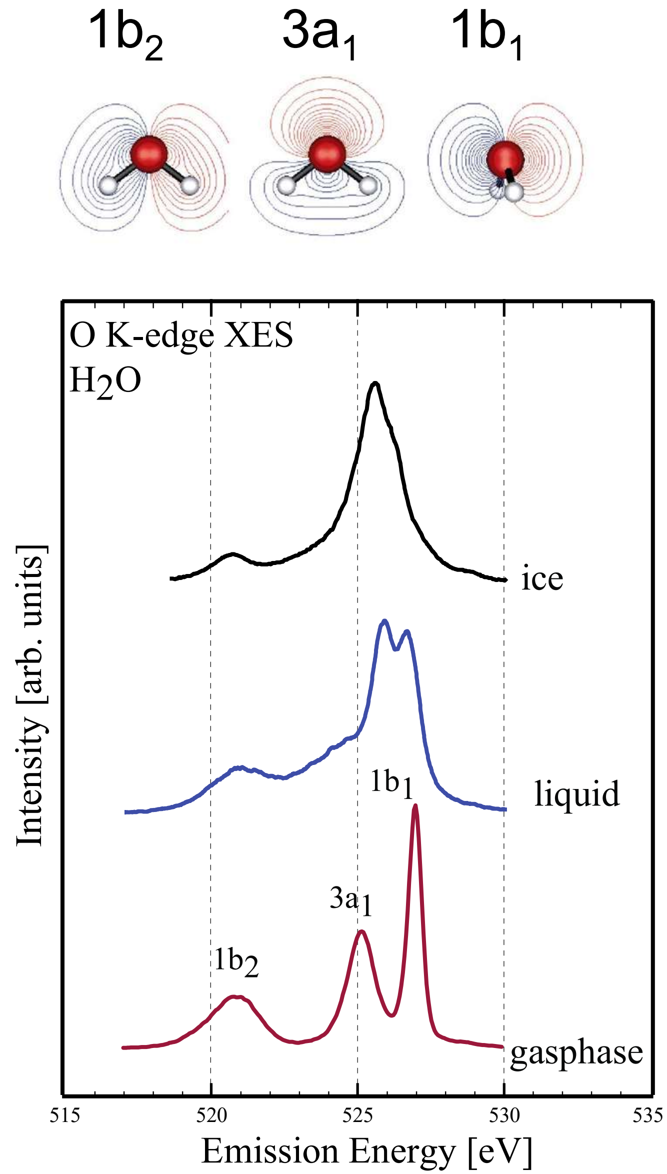




X-ray Emission Spectroscopy of Water (XES)

XES

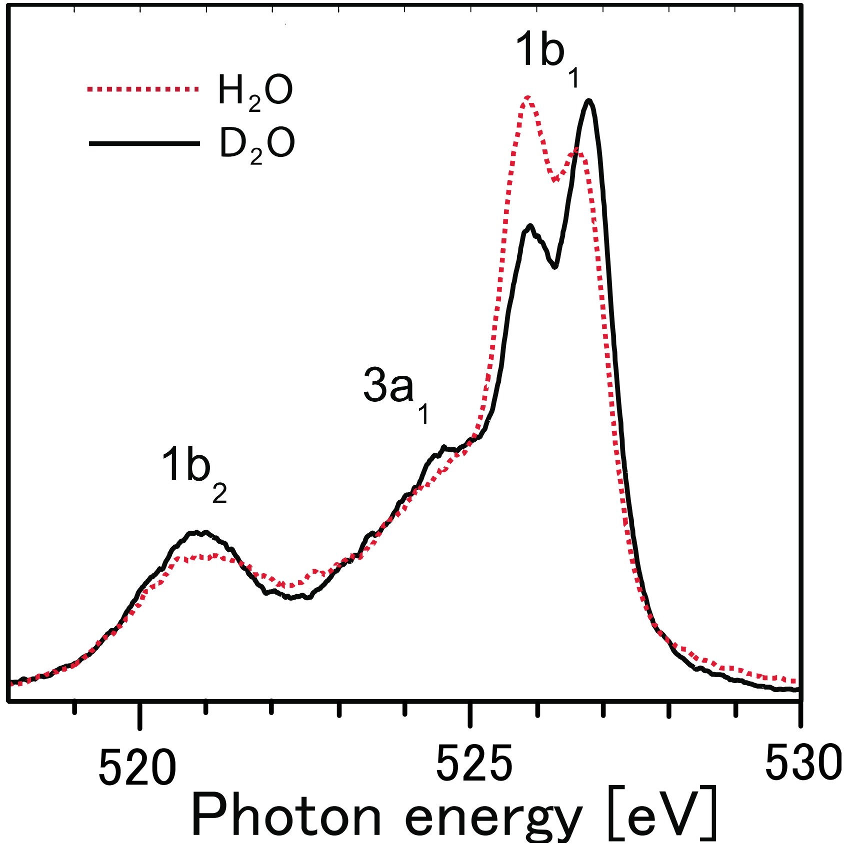




Tokushima *et al.*, Chem. Phys. Lett. **460** (2008) 387

Isotope effect in XES of water

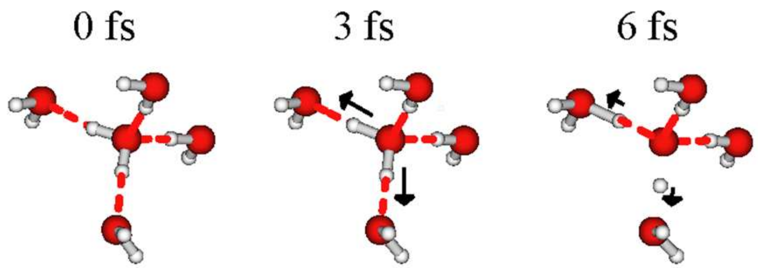
Split lone pair peak



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

Isotope dependent line shape

Two different Interpretations



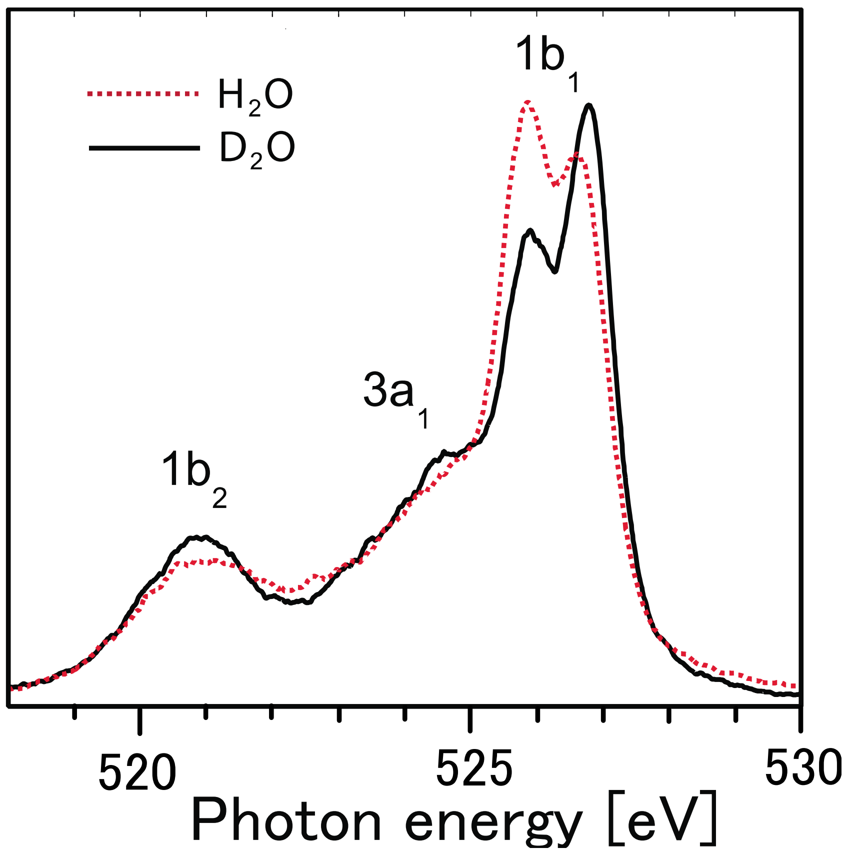
Ultrafast Dissociation

Intact water
Dissociated water

Fuch *et al*.,Phys. Rev. Lett. **100** (2008) 027801

Isotope effect in XES of water

Split lone pair peak



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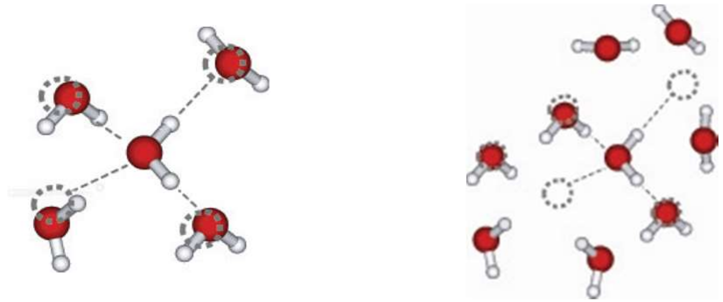
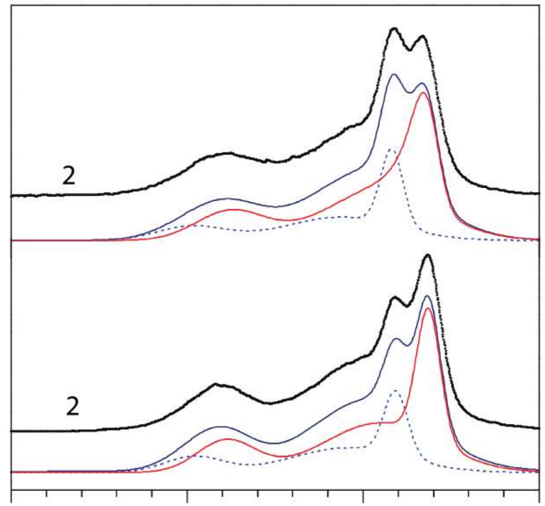
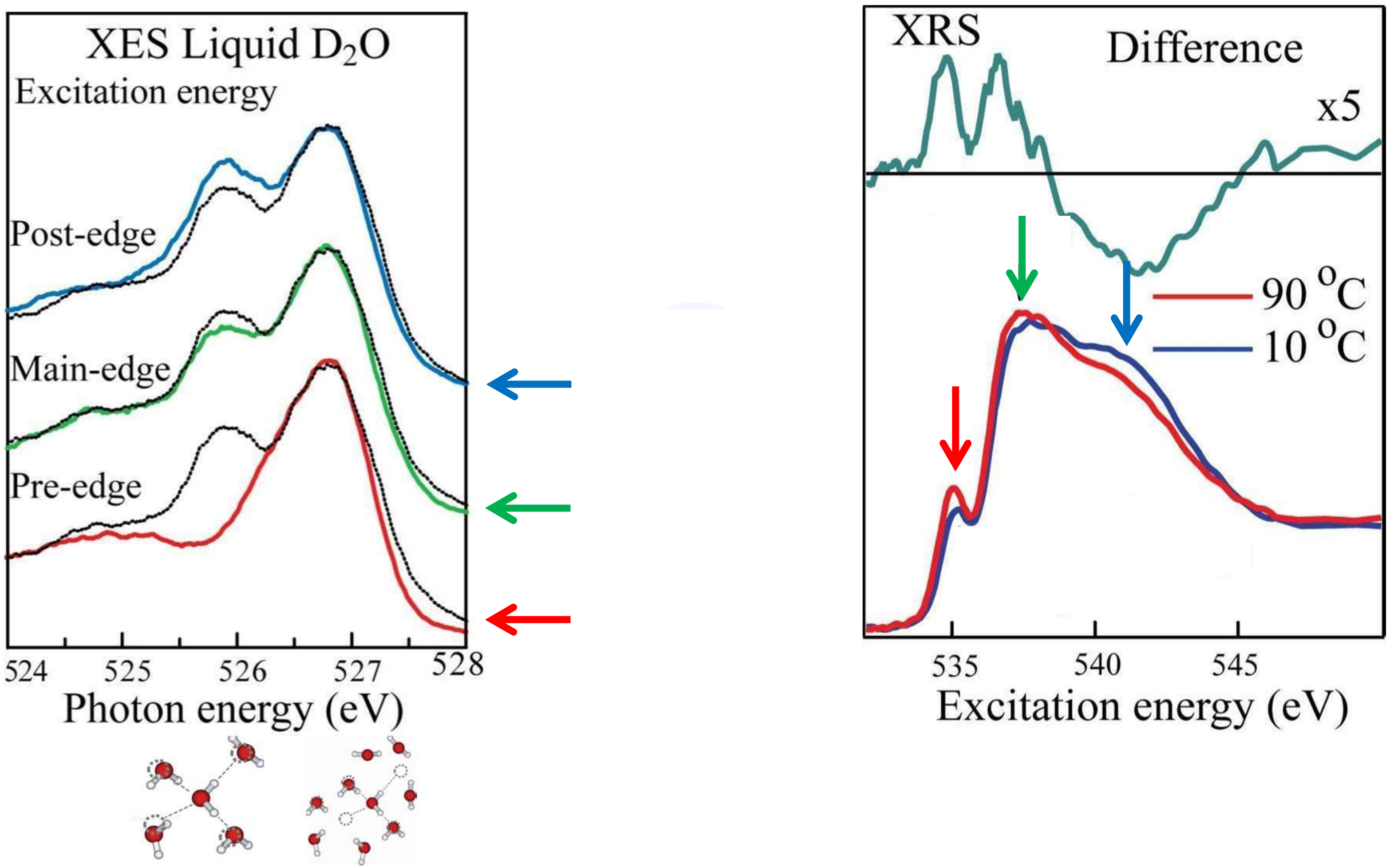


Two distinct local environments

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



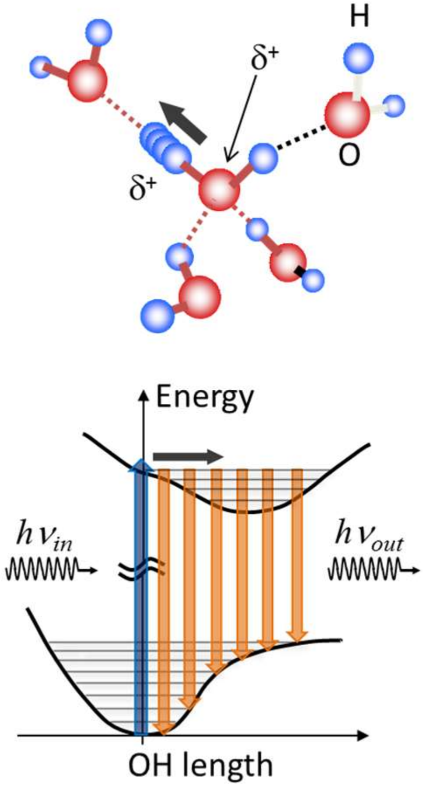
Connection XAS and XES

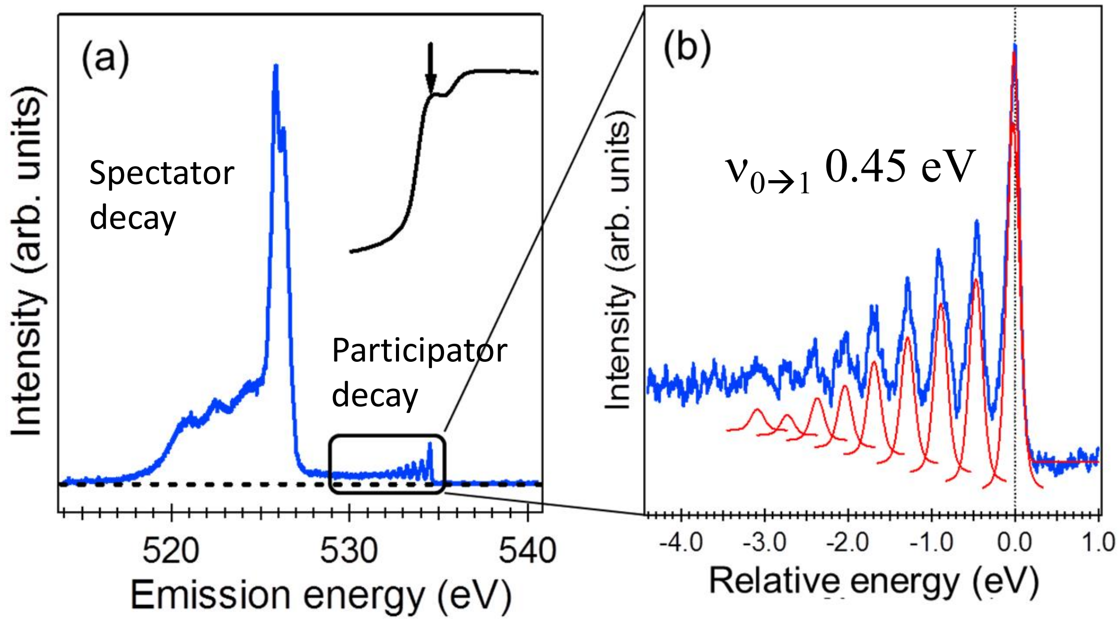


C. Huang et al. Proc. Natl. Acad. Sci. USA **106** (2009) 15214

Participator Decay in XES/RIXS
Vibrations

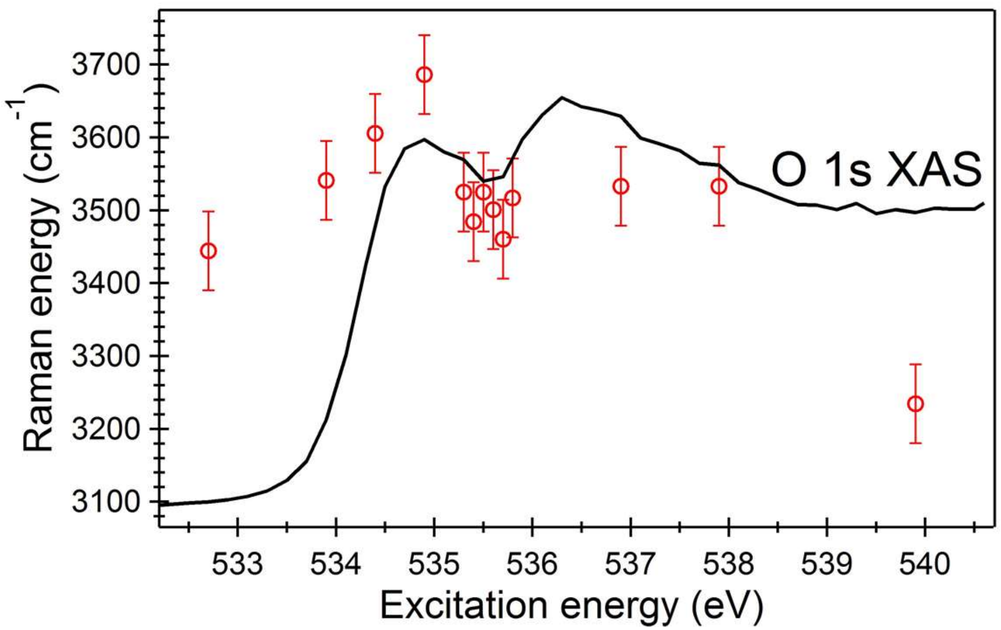
Pre-edge excitation
Strongly antibonding orbital

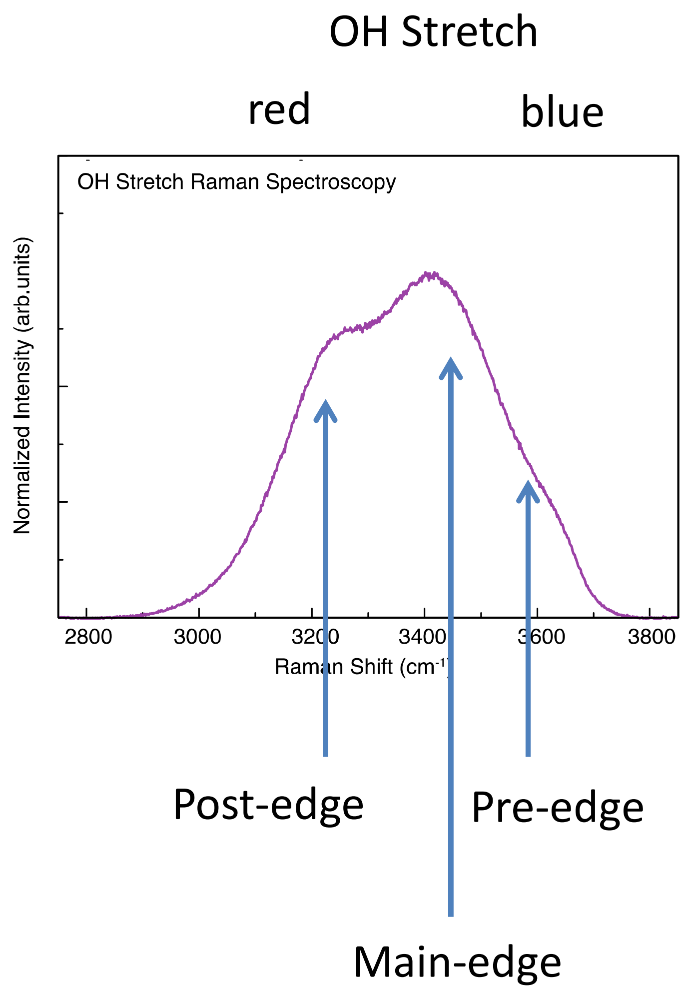




Y. Harada et al. Phys. Rev. Lett. **111**, 193001 (2013)

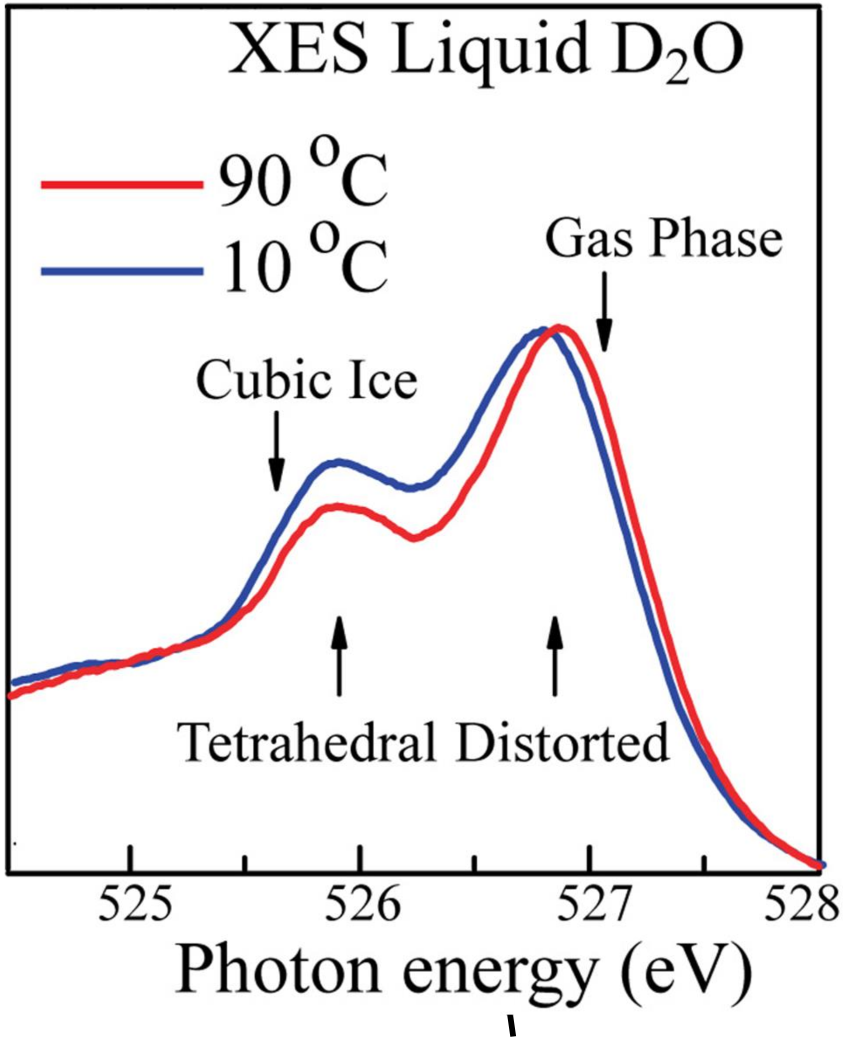
Excitation Dependence in Vibrations





Y. Harada et al. Unpublished

Temperature Dependence



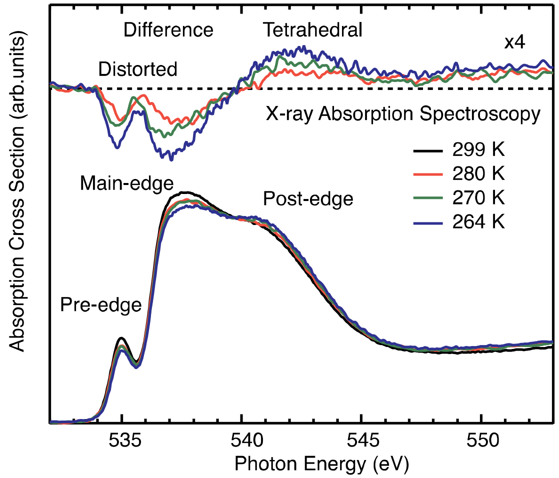
- Intensity transferred tetrahedral to disordered as temperature is increased (fewer H-bonds)

- NO broadening, NO new peaks: Either tetrahedral *OR* very distorted

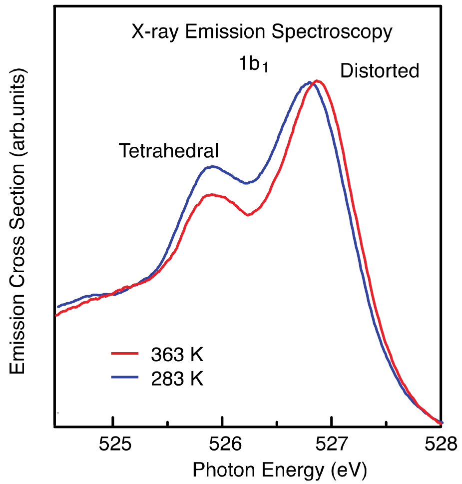
Tokushima *et al*., Chem. Phys. Lett. **460** (2008) 387
Huang *et al*., PNAS. **106** (2009) 15214

Two Structural Environments

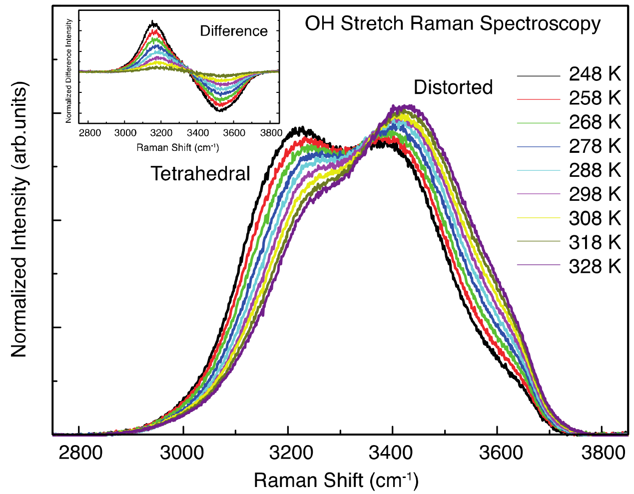
X-ray Absorption



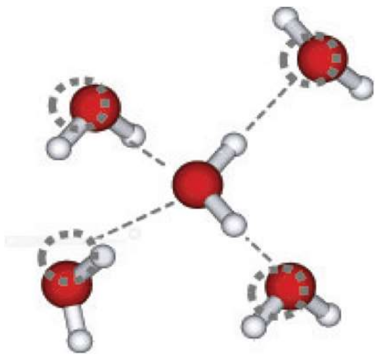
X-ray Emission



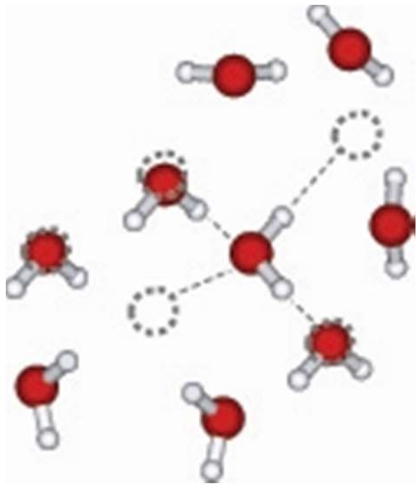
OH Stretch Vibrational



≈ 20%



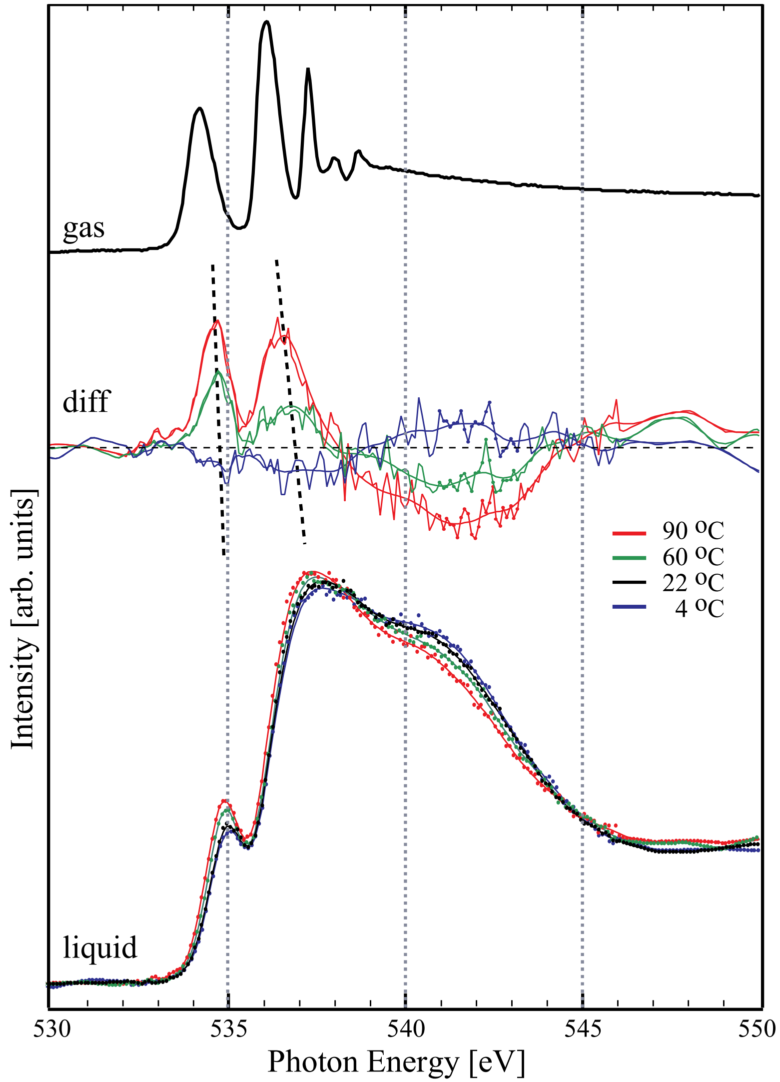
At 300 K



≈ 80%

A. Nilsson and L. G. M. Pettersson Nature Communication **6** 8998 (2015)

Temperature Dependence



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

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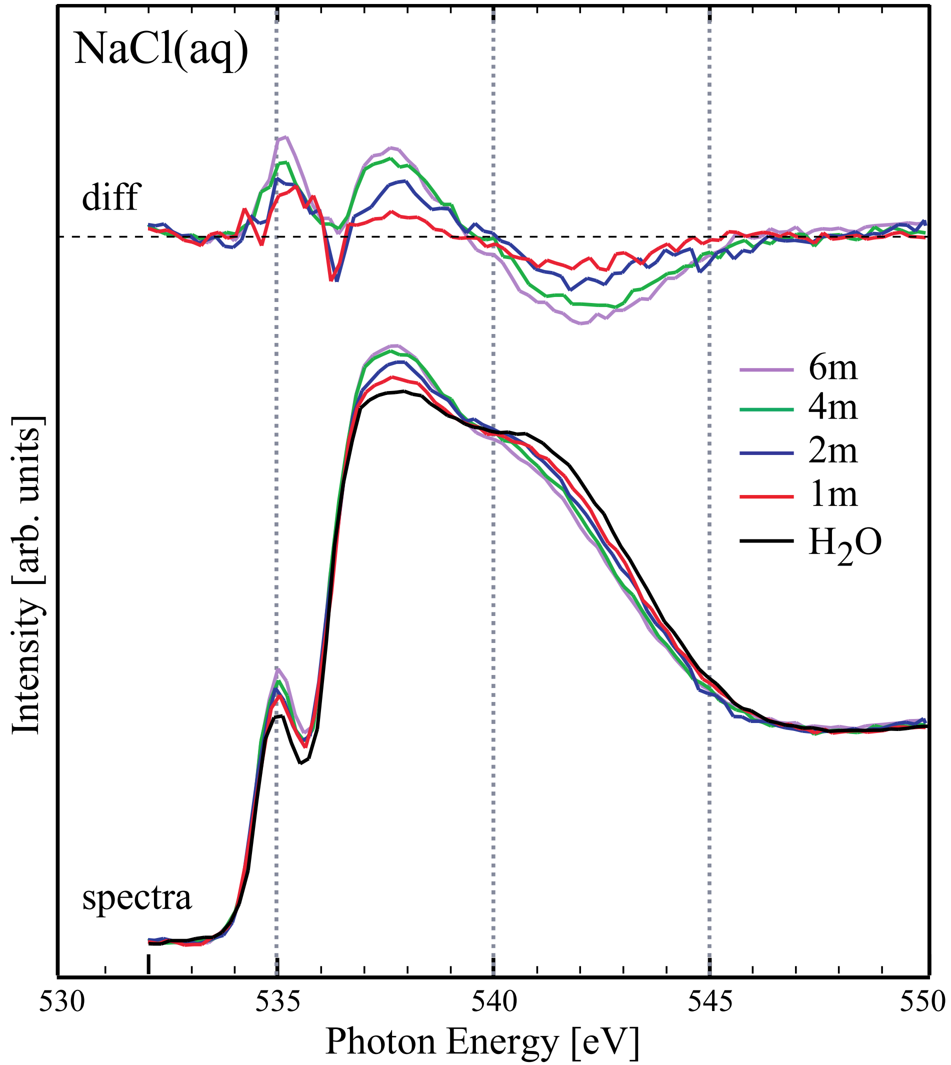

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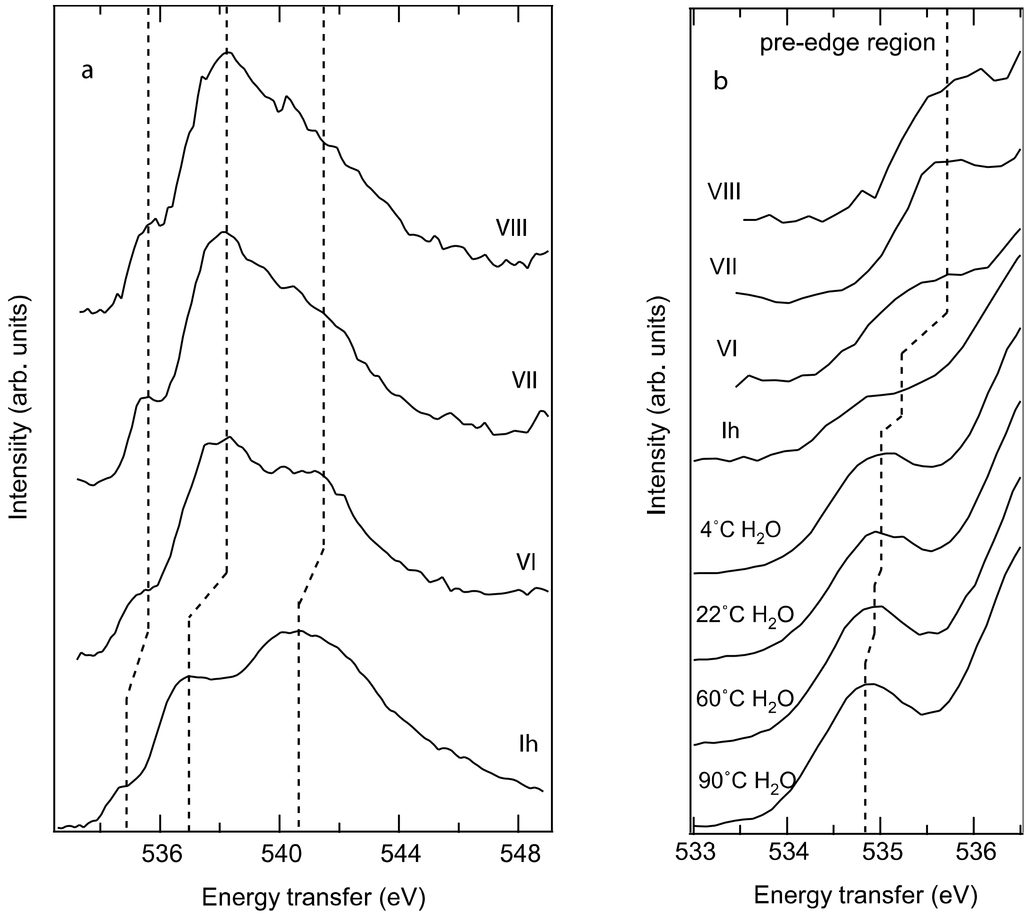

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Pylkkänen et al. *J. Phys. Chem. B 2010*, ***114***, *3804*

Raman OH spectroscopy of H_2O

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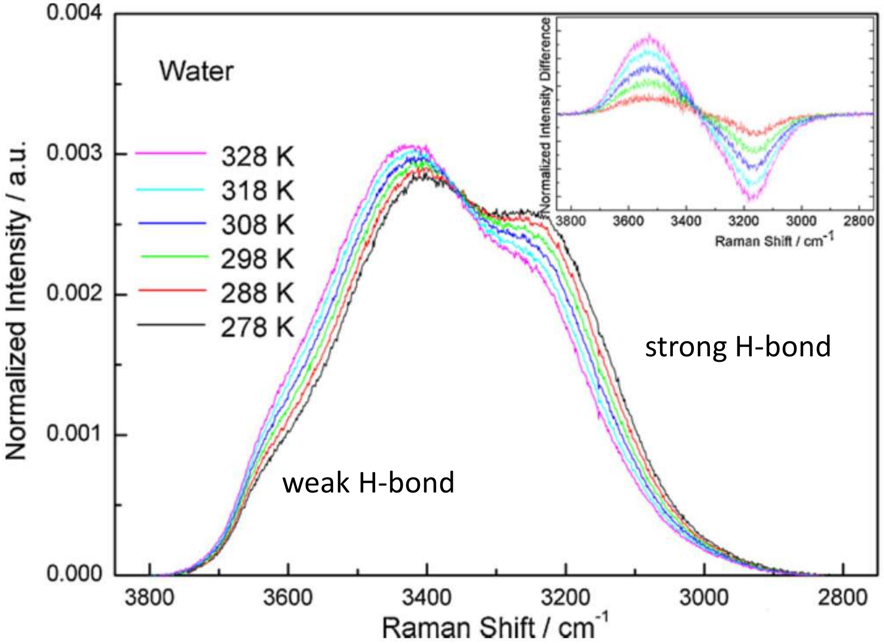

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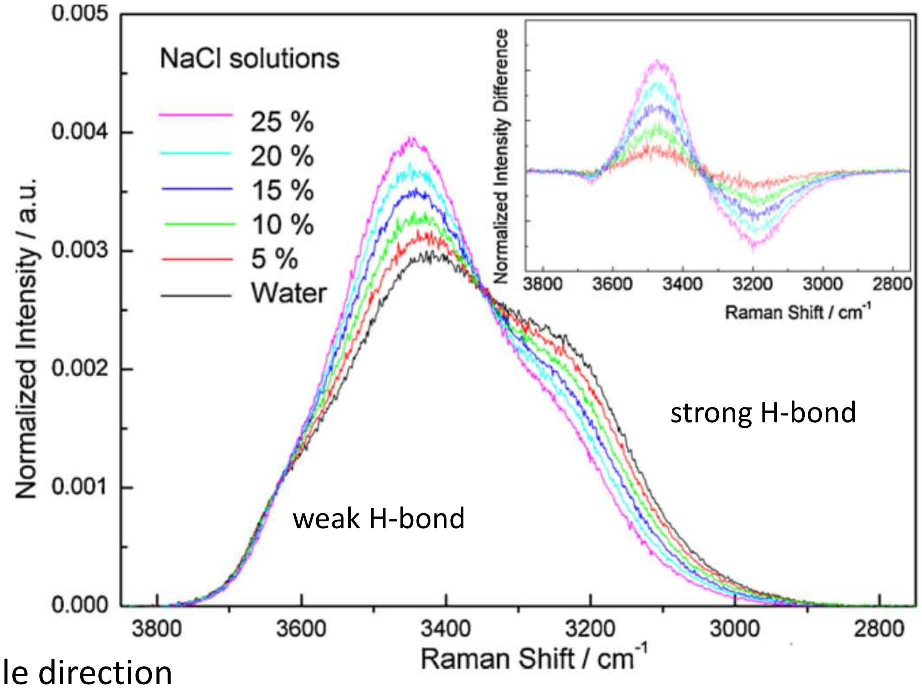

note energy scale direction

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- Shift of weak bond towards gas phase

Q. Sun, Vibrational Spectroscopy *62 (2012) 110– 114*

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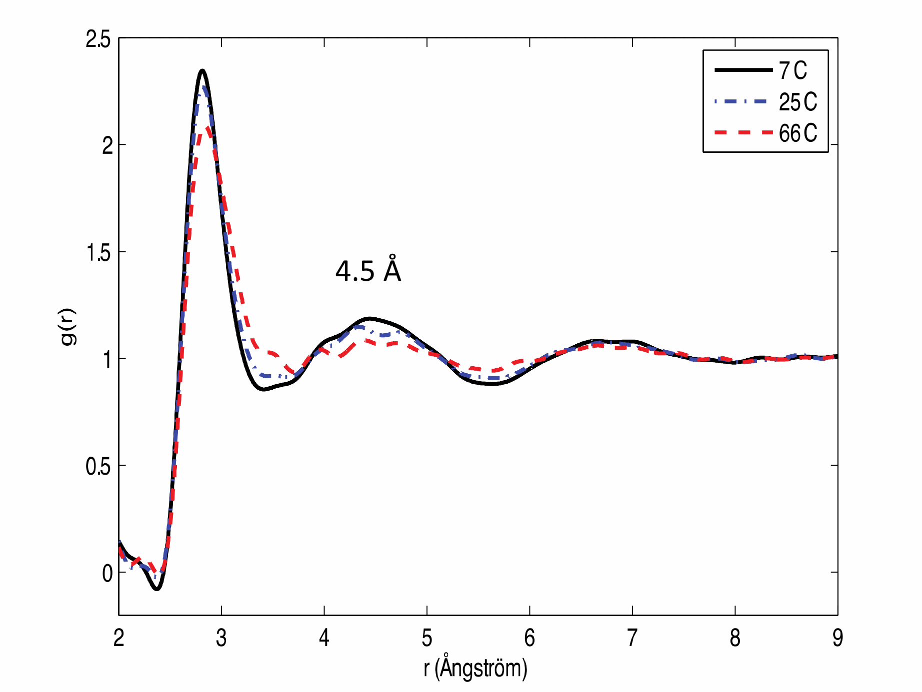
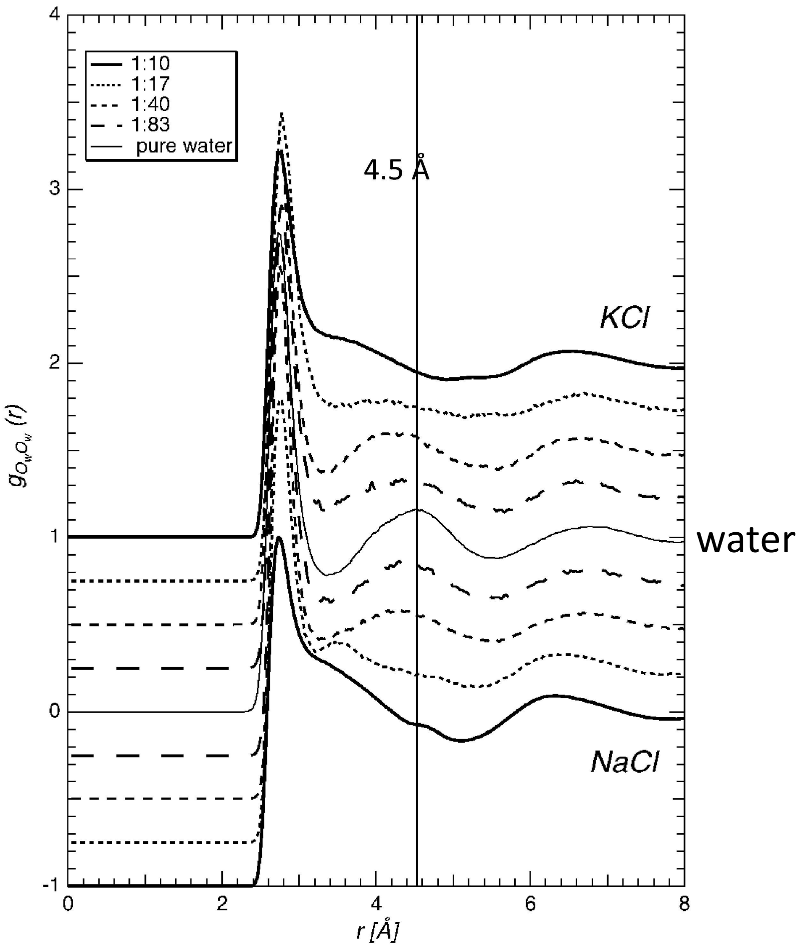


Decreasing 4.5 Å Tetrahedral

NaCl Concentration Dependence



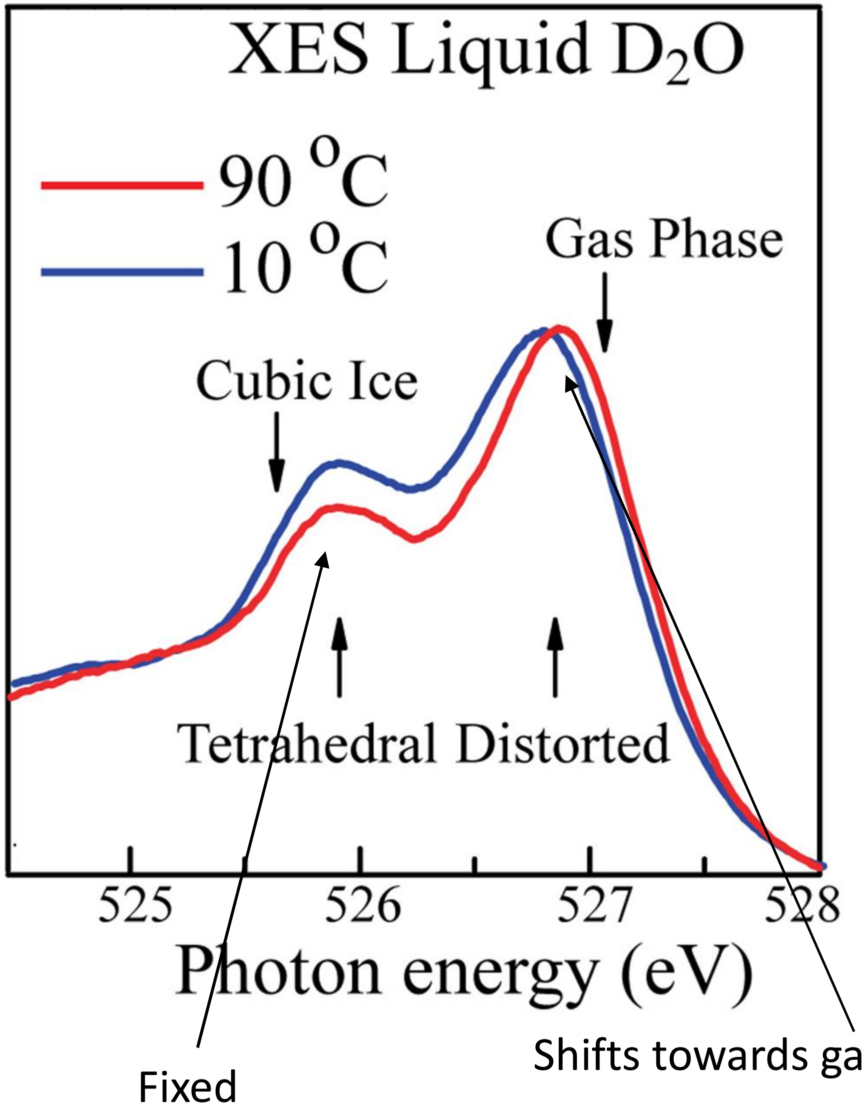
Disapparence of 4.5 Å Tetrahedral

Consistent change in terms of the tetrahedral component between T and NaCl concentration

Huang et al. PCCP **13**, 19997 (2011)

Mancinelli et al. PCCP **9**, 2559 (2007)

Temperature Changes of Distorted Component

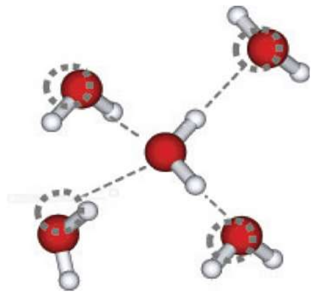


- Distorted species changes with temperature
- Tetrahedral fixed

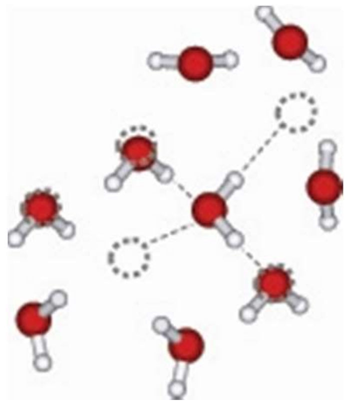
Huang *et al.*, PNAS. **106** (2009) 15214

Summary X-ray Emission Spectroscopy

- Bimodal structural distribution
- Tetrahedral loses intensity with temperature, but peak at fixed energy
- Distorted gains intensity and disperses with temperature
- Energy taken up through:
  - Thermal excitation of distorted species
  - Breaking up a fraction of tetrahedral species



20-30 %



70-80 %

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

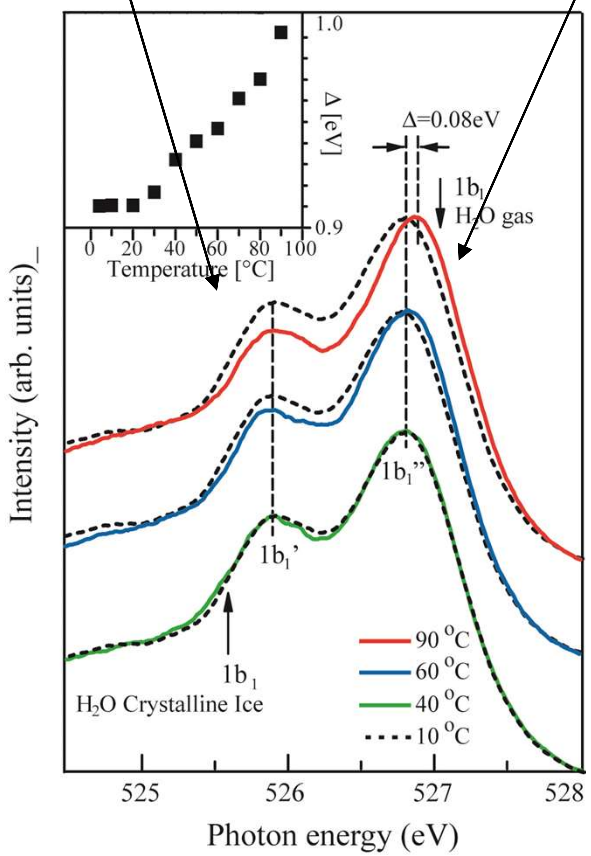
Huang *et al*., PNAS. **106** (2009) 15214

Temperature Changes of Distorted Component

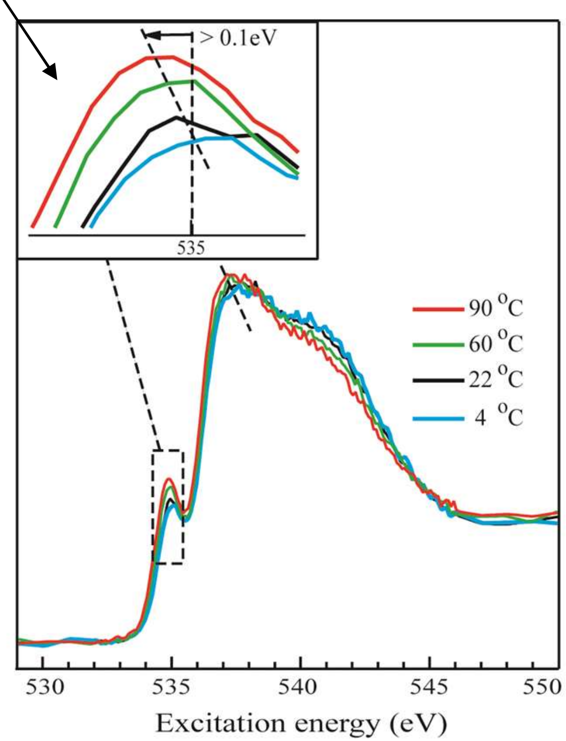
Shifts towards gas phase with increasing temperature

Fixed

XES D_2O



XAS H_2O



Distorted species changes with temperature
Tetrahedral fixed

Huang *et al.*, PNAS. **106** (2009) 15214

Coworkers and Funding Stanford/Sweden

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Ningdong Huang/SSRL

Ira Waluyo/SSRL

Dennis Nordlund/SSRL

Lars Åke Näslund/SSRL

Hirohito Ogasawara/SSRL

Sarp Kaya/SUNCAT

Tomas Weiss/SSRL

Trevor Mcqueen/SUNCAT

Chen Chen/SUNCAT

Jonas Sellberg/SUNCATL

Philippe Wernet/(SSRL/BESSY)

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Matteo Cavalleri/Stockholm

Michael Odelius/Stockholm

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Mathias. Ljungberg/Stockholm

Thor Wikfeldt/Stockholm

Lars Ojamäe/Linköping

Daniel Schlesinger/Stockholm

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Hiroshima University

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