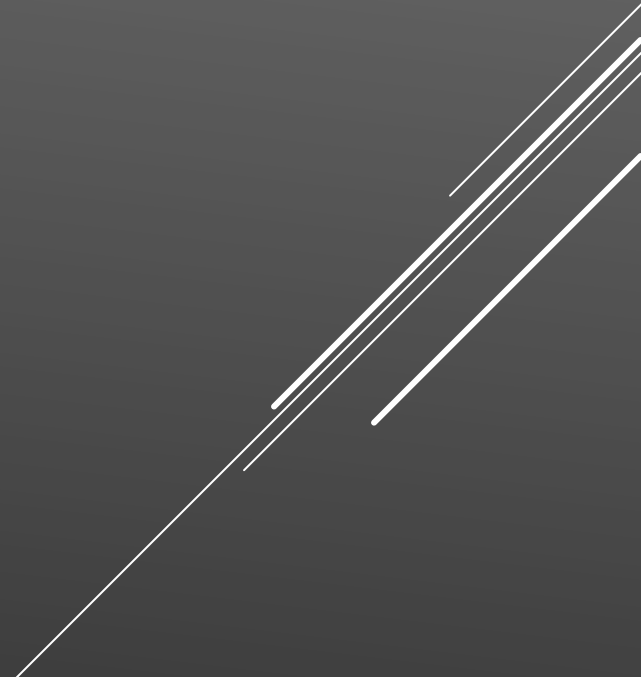


A DEBATE ON THE STRUCTURE OF WATER

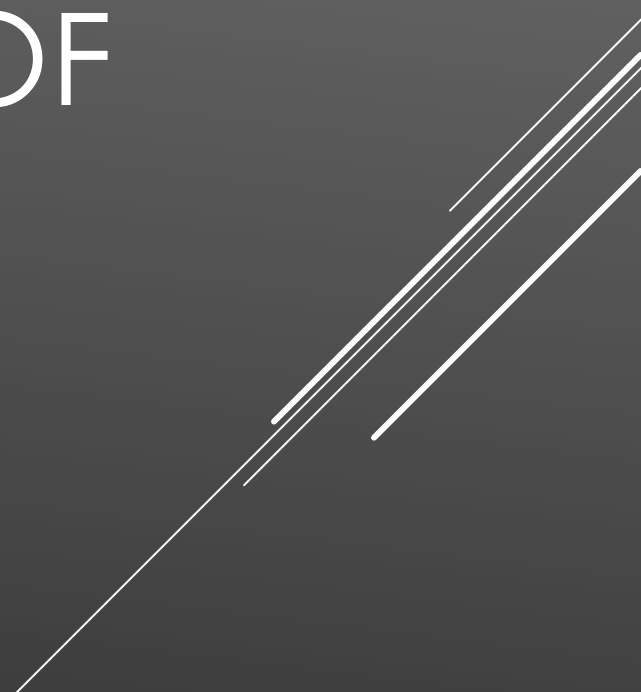
Co-authors: Zachary Wolfe, Erick Holguin

A decorative graphic consisting of several parallel white lines of varying thicknesses, slanted diagonally from the bottom-left towards the top-right, located on the right side of the page.

TABLE OF CONTENTS

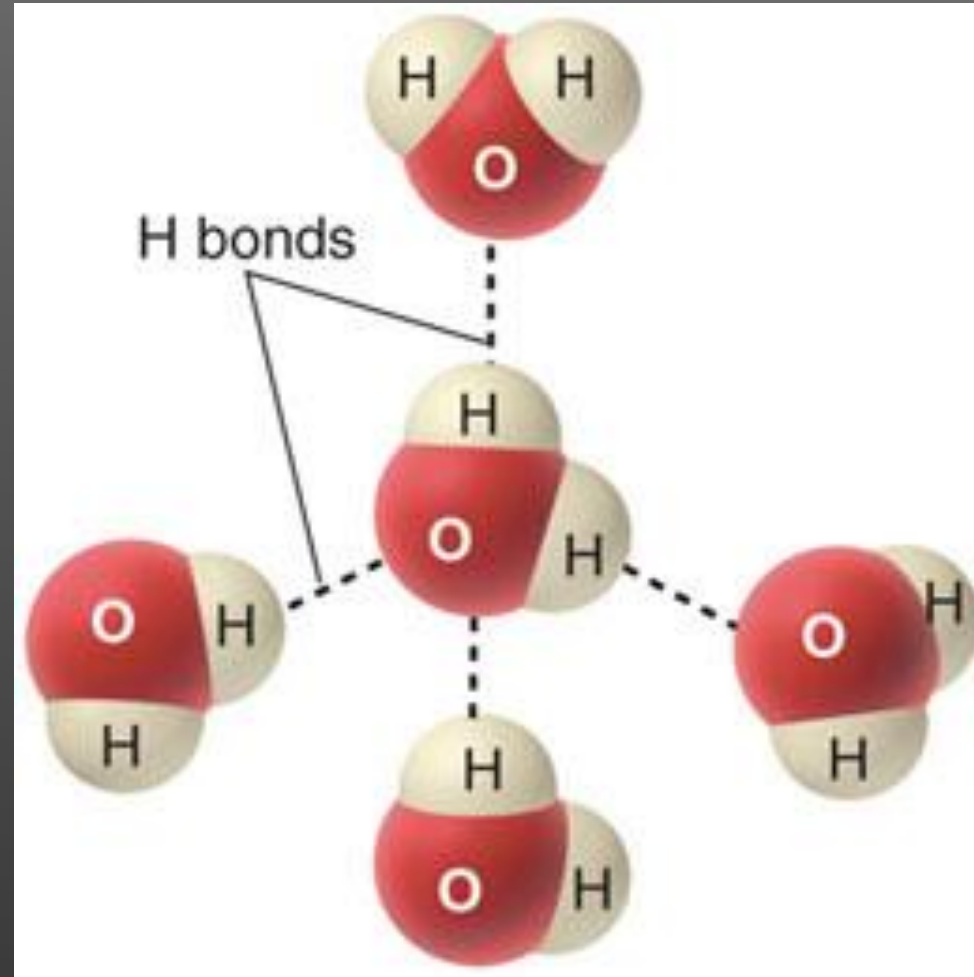
- Review of the solvation structure of water
 - Instrumentation used to determine the structure of water
 - Dr. Wernet's new proposed water structure
 - Introduction of assumption/new viewpoints
 - Computational /Experimental Methodology
 - Conclusion of new water structure
 - Introduce comments by Dr. Smith
 - Overview of methodology
 - Propose Flaws in the Wernet structure
 - Conclude with counterarguments
 - Summary of both perspectives
 - Calculation of H-bond energy
 - References
- 

REVIEW:
THE SOLVATION STRUCTURE OF
WATER

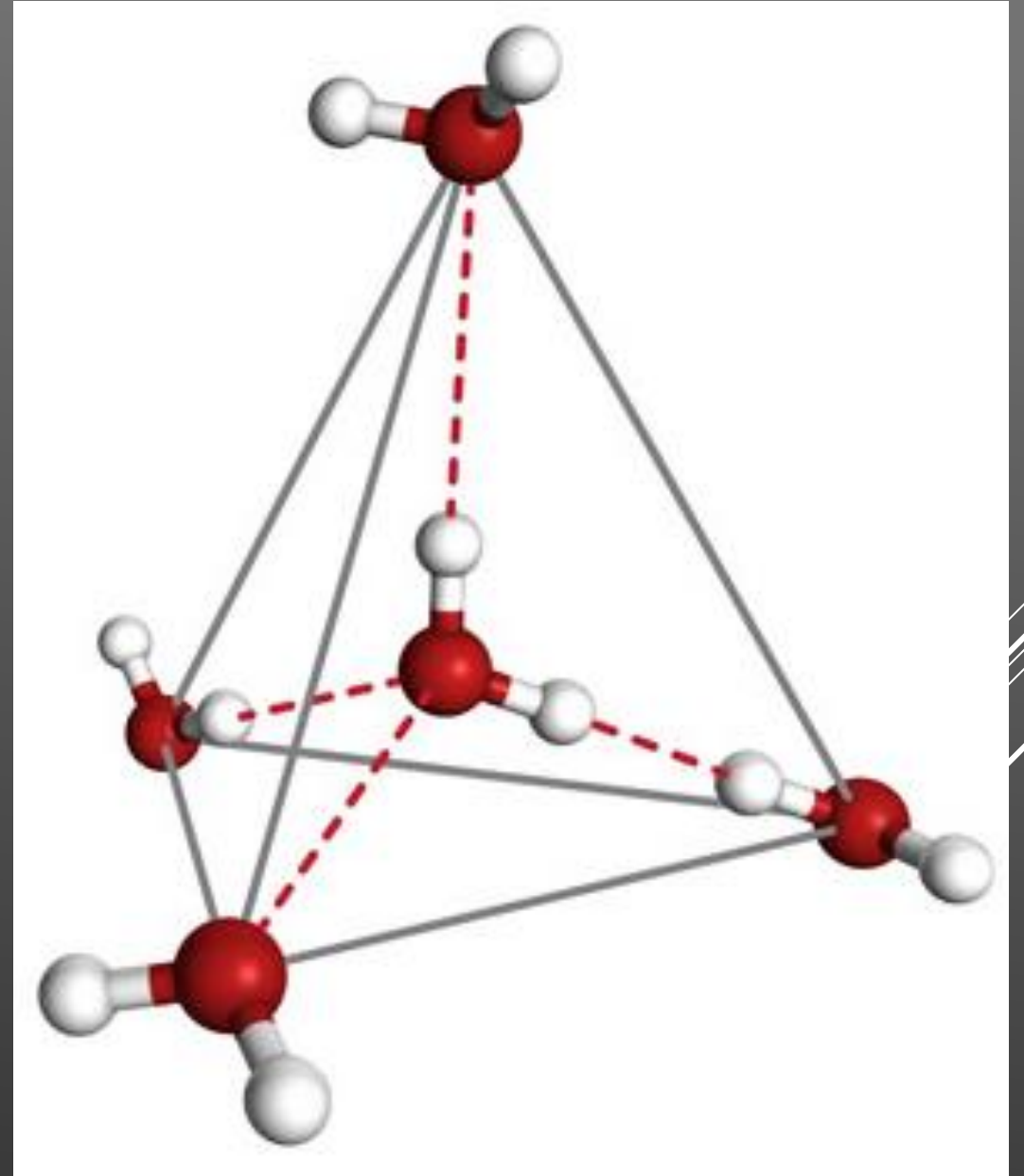


BONDING IN WATER

- Fundamental bonding in water is hydrogen bonding and polar-covalent bonding
- The H-bonds in liquid water are constantly breaking and reforming with neighboring water molecules.
- Unlike crystals (ice), liquid water is a constant state of flux.
- Results in the local density constantly changing, unable to directly observe the density.

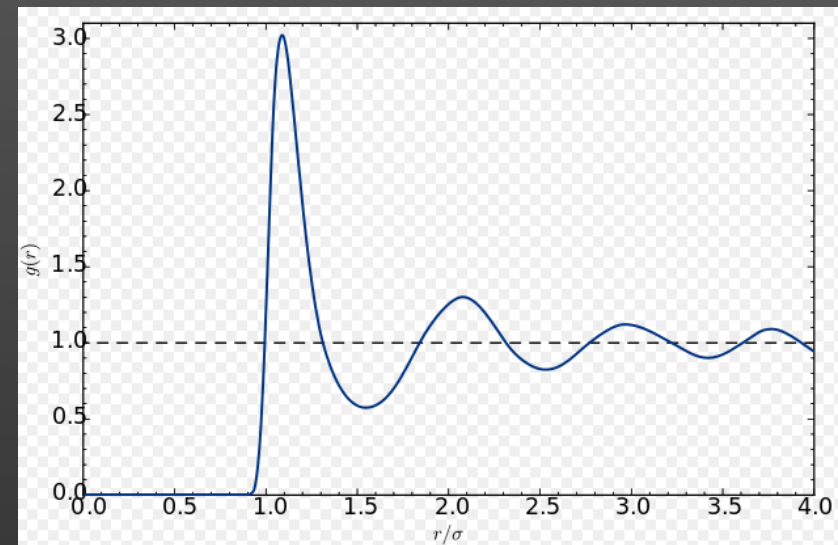
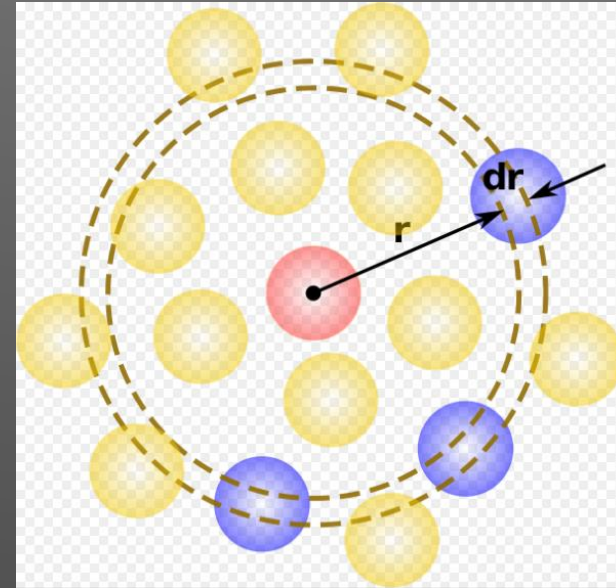


- Any one water molecule will form up to four hydrogen bonds with its neighbors.
- These bonds form a tetrahedral shape and is the first solvation shell from the center molecule.
- These neighbors form more H bonds forming the 2nd shell, and so forth.
- In ice, this leads to a crystal arrangement with hexagonal symmetry.



RADIAL DISTRIBUTION FUNCTIONS

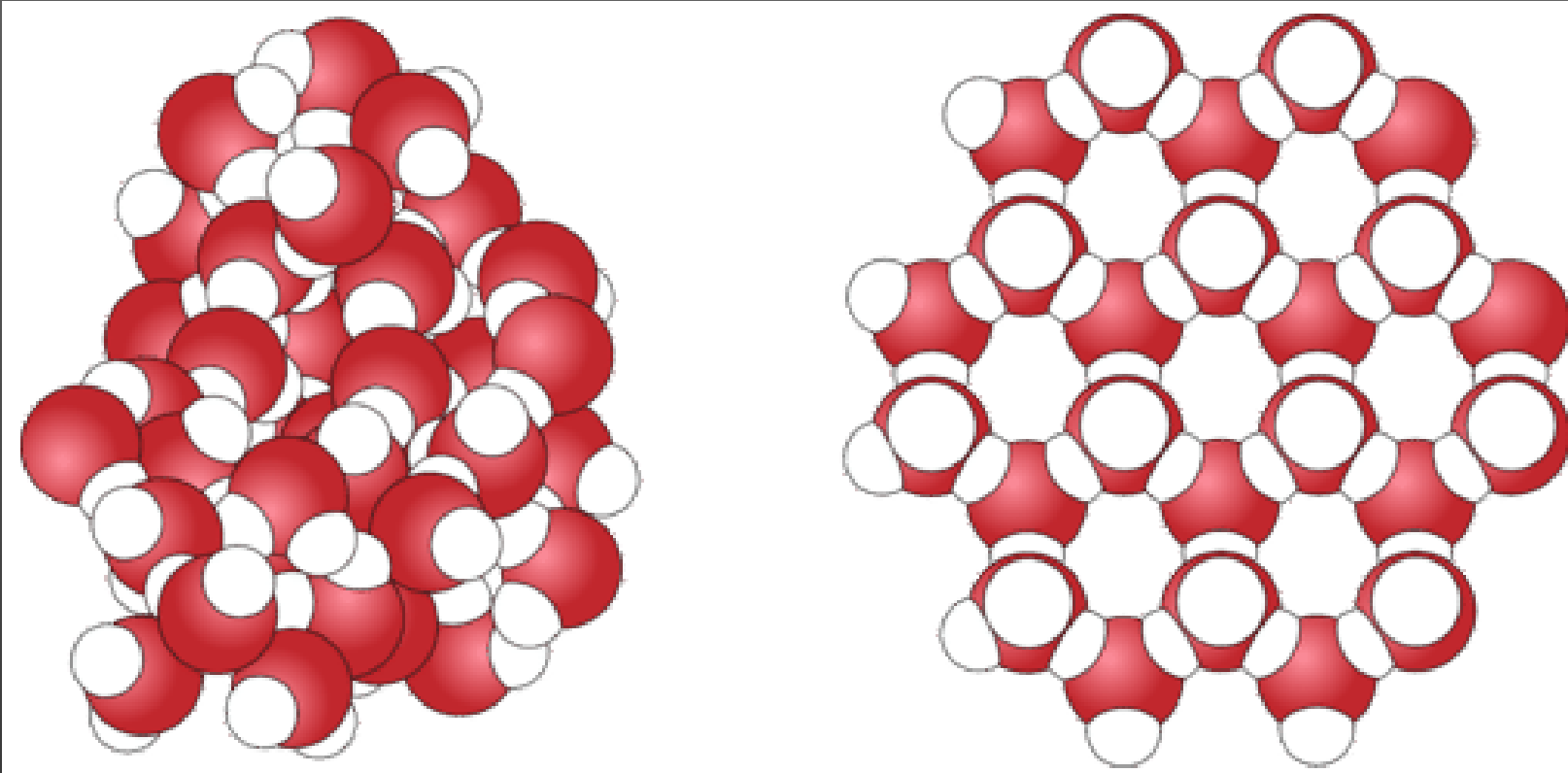
- These functions describe how the density varies as a function of distance, three functions in total for water.
- *In effect*, We sit on an atom and count all the other atoms that we find in a given displacement from that atom.
- These local densities are then averaged over all the atoms in the system.



INSTRUMENTATION



HOW DO WE CURRENTLY ANALYZE THE STRUCTURE OF WATER?

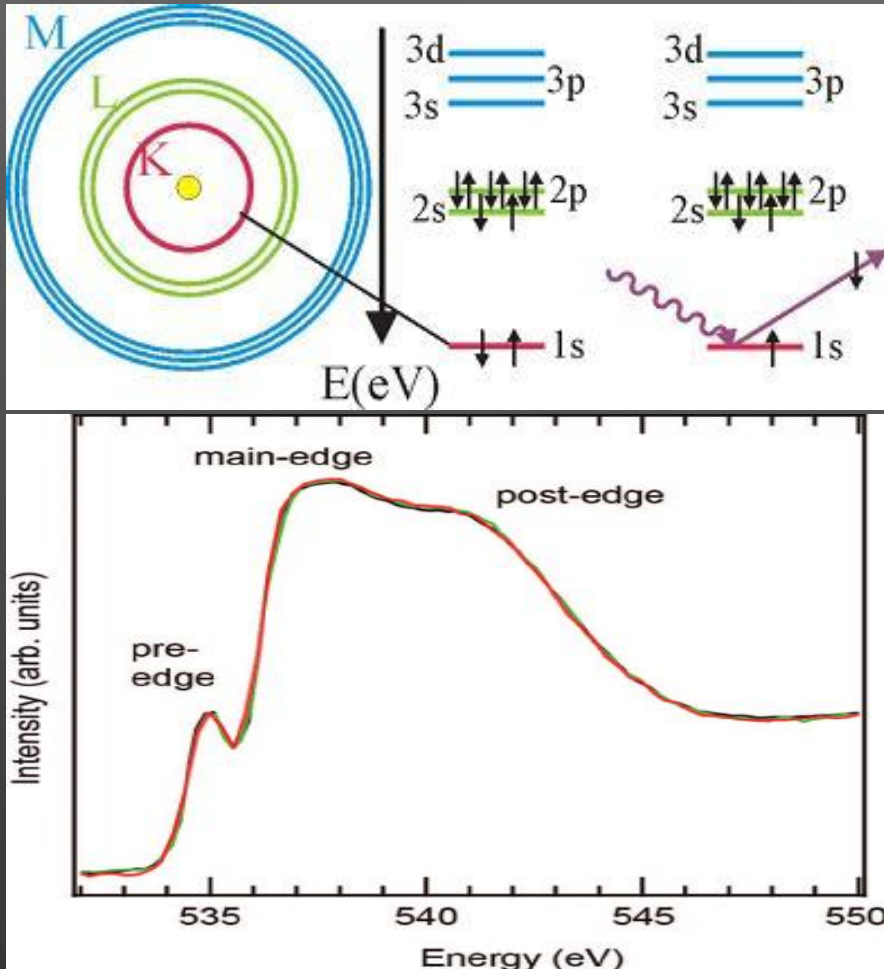


- Infrared Spectroscopy
- X-ray Absorption Spectroscopy
- Neutron diffraction
- X-ray diffraction
- X-ray Raman Scattering

IMG:

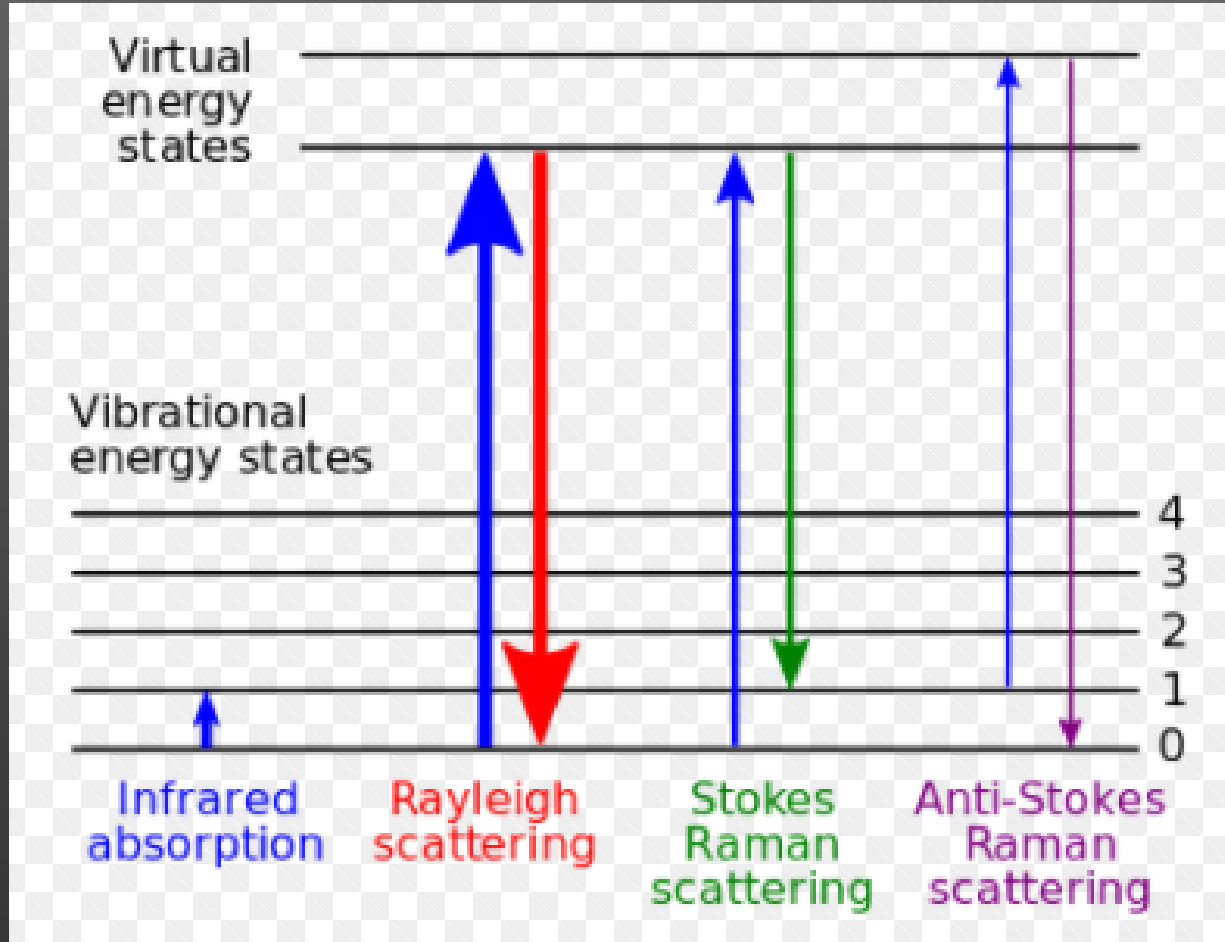
[https://chem.libretexts.org/Textbook_Maps/Introductory_Chemistry_Textbook_Maps/Map%3A_Introductory_Chemistry_\(CK-12\)/15%3A_Water/15.02%3A_Structure_of_Ice](https://chem.libretexts.org/Textbook_Maps/Introductory_Chemistry_Textbook_Maps/Map%3A_Introductory_Chemistry_(CK-12)/15%3A_Water/15.02%3A_Structure_of_Ice)

X-RAY ABSORPTION SPECTROSCOPY



- Excites core e^- in sample atom to a higher energy state.
- $\Delta E \sim 0.1$ to 100 keV.
- The range of absorption is called the edge region (edge of absorption).
- There are three main regions
 - Pre
 - Main
 - Post

X-RAY RAMAN SCATTERING



- Scattering experiment using incident photon energy and comparing it scattered photon energy
- There are three cases of scattering events
 - Rayleigh: equal energy photons
 - Stokes: lower energy scattered photon
 - Anti-Stokes: higher energy scattered photon

INTRODUCTION TO MOLECULAR DYNAMICS SIMULATIONS

- Instead of looking at the static picture of a system, we need time evolution and time averaged states of a system!
- MD simulations
 - Take the Hamiltonian from QM for nucleons
 - To solve exactly would be impossible for system of many particles
 - Demote to classical Hamiltonian (i.e. Newtonian mechanics)
 - The potential energy is then calculated either using first principles (ab initio) or a force field (classical)

$$\hat{\mathcal{H}} = \hat{T}_n + \varepsilon_0(\hat{\mathbf{R}}) + V_{mn}(\hat{\mathbf{R}})$$



$$\mathcal{H}(\mathbf{P}, \mathbf{R}) = \sum_{I=1}^N \frac{\mathbf{P}_I^2}{2M_I} + \varepsilon_0(\mathbf{R}) + V_{mn}(\mathbf{R})$$

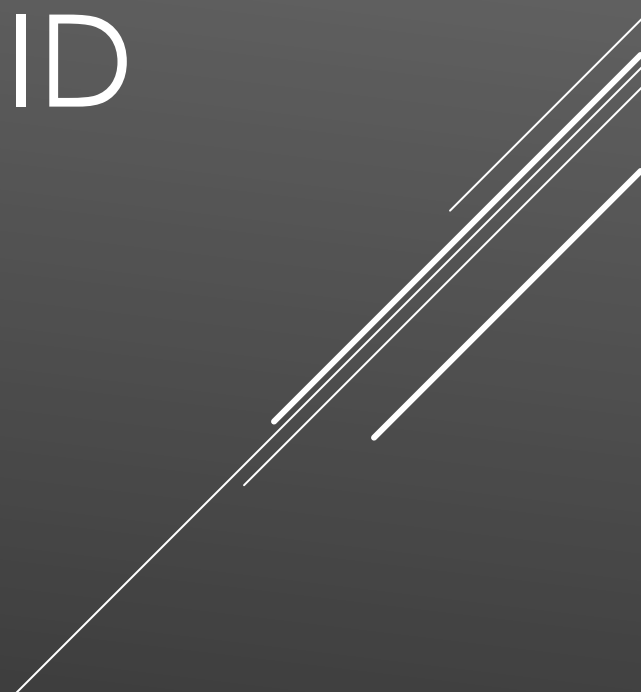
$$\dot{\mathbf{R}}_I = \frac{\partial \mathcal{H}}{\partial \mathbf{P}_I} \quad \dot{\mathbf{P}}_I = -\frac{\partial \mathcal{H}}{\partial \mathbf{R}_I}$$

IMGS:

http://images.slideplayer.com/26/8390106/slides/slide_11.jpg

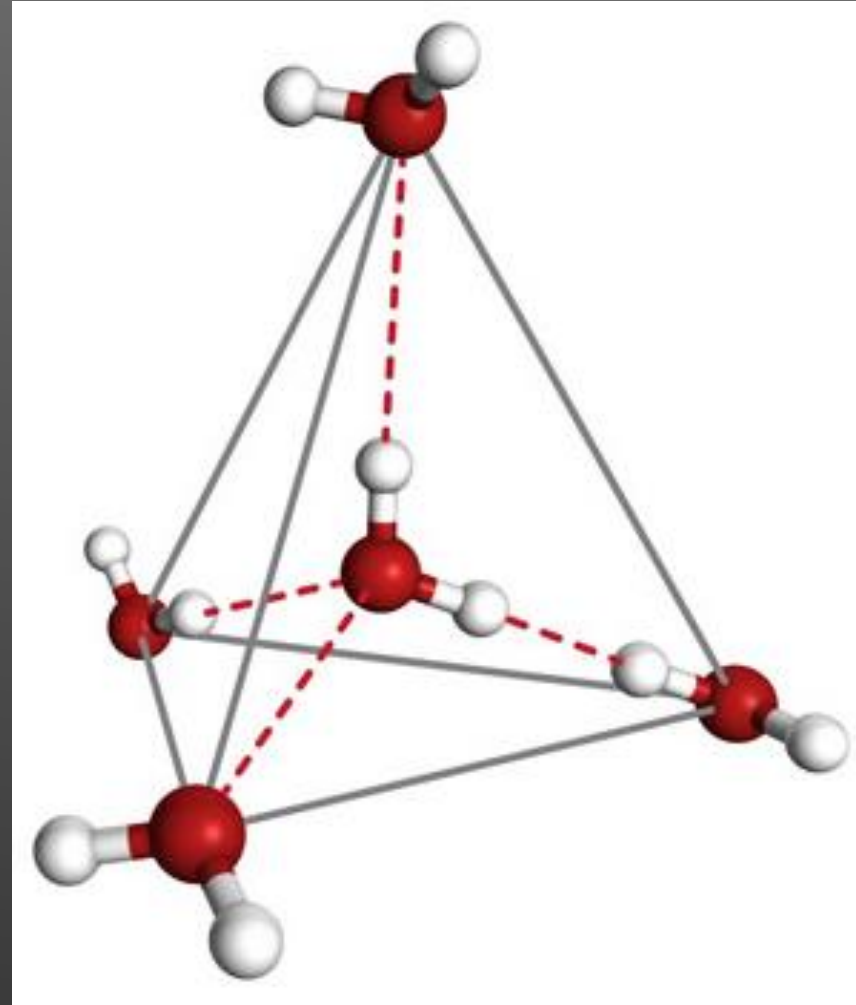
THE STRUCTURE OF THE FIRST COORDINATION SHELL IN LIQUID WATER

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



INTRODUCTION

- Using x-ray absorption & x-ray Raman scattering to suggest tetrahedral structure needs to be reviewed.
- Proposes new structure based on similarities in XAS data between RT water and surface ice

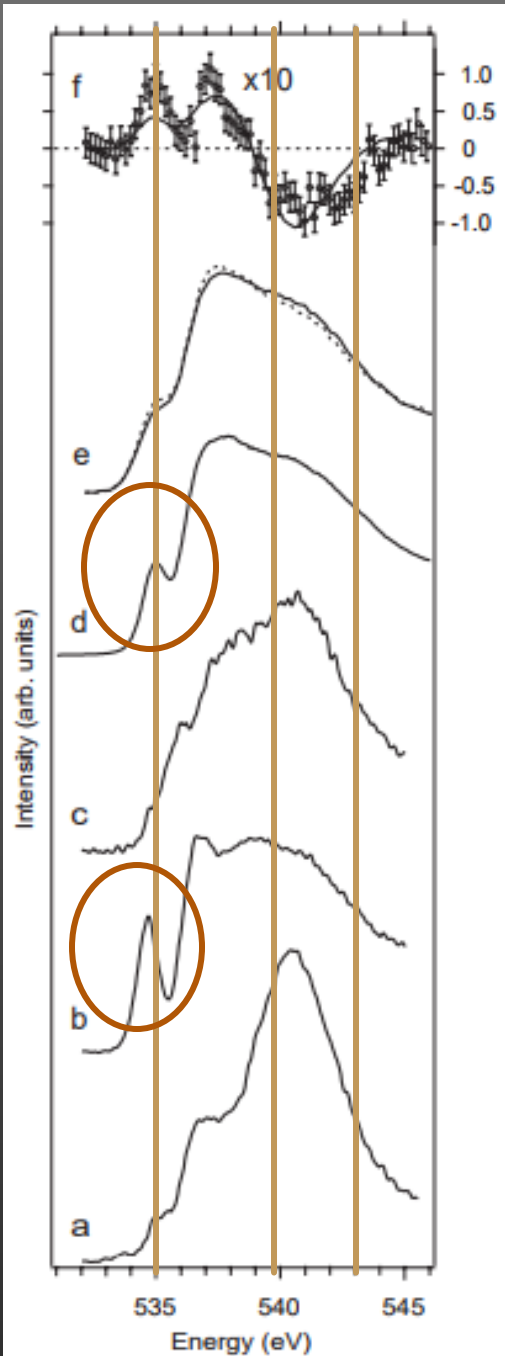


CLUSTER MODEL

- 11 molecule cluster model for MD
 - Central molecule has 4 immediately surrounding water molecules
 - There is a concentric sphere of 6 molecules interacting with the first coordination shell
- Calculated XA Spectra for three cases
 - Bulk Ice
 - Surface Ice
 - NH_3 terminated surface ice

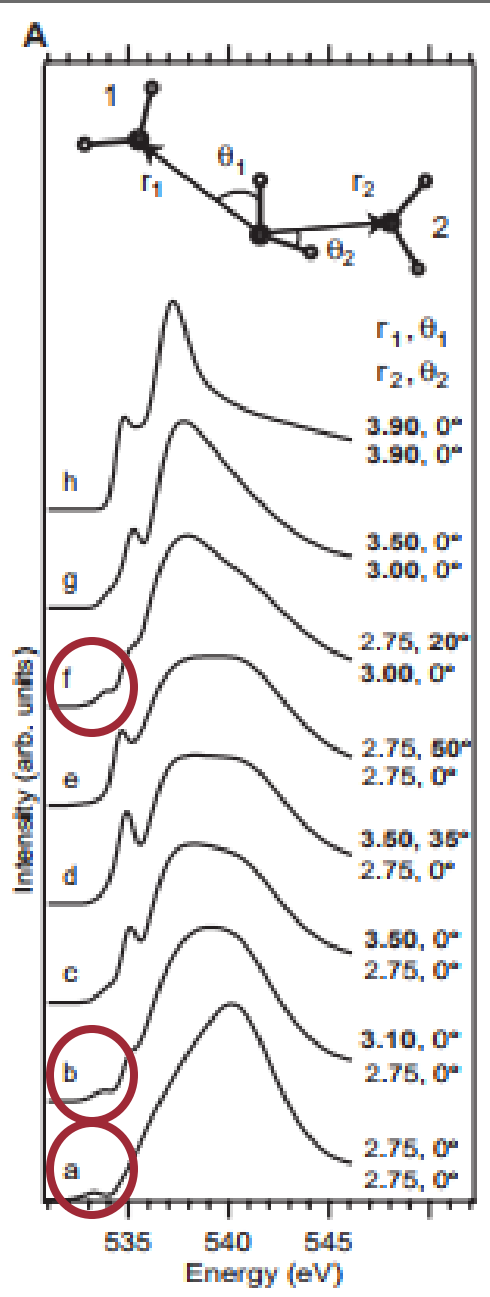
XA SPECTRA EXPERIMENTAL DATA

- A) Tetrahedral bulk ice
 - B) Tetrahedral surface ice
 - C) NH_3 terminated surface ice
 - D) Liquid water at ambient conditions
 - E) Bulk liquid
 - Solid Line: at 25°C
 - Dashed Line : at 90°C
 - F) Difference Spectra
 - Solid Line: Liquid at 25°C minus the bulk ice
 - Circle Curves: Liquid at 90°C minus liquid at 25°C
- Three Sections: Pre Edge, Main Edge, Post Edge
 - Note the similarities between B) and D) in the pre edge section



XA SPECTRAL ANALYSIS

- Figure A): XA spectra
 - shows a systematic approach to change relative positions and angles of two water molecules interacting with a central water molecule.
- Wernet classifies the different spectra into donor configurations of the two nearest neighbors
 - Double Donor (DD- Red circles):
Corresponding to a, b, and f



ANALYSIS

- Figure A): XA spectra

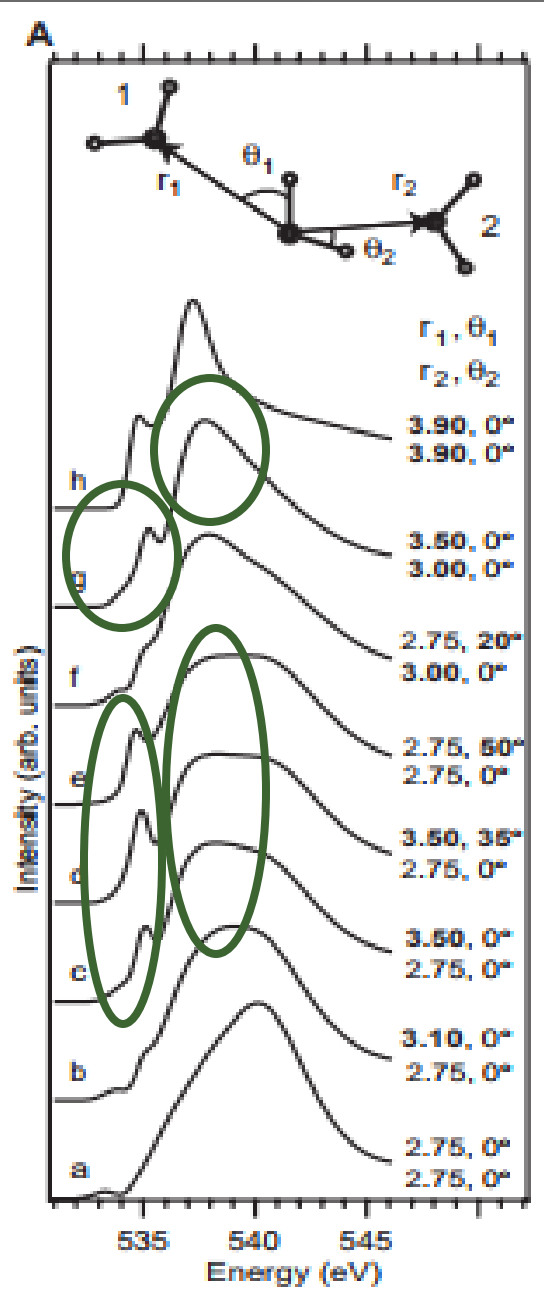
- shows a systematic approach to change relative positions and angles of two water molecules interacting with a central water molecule.

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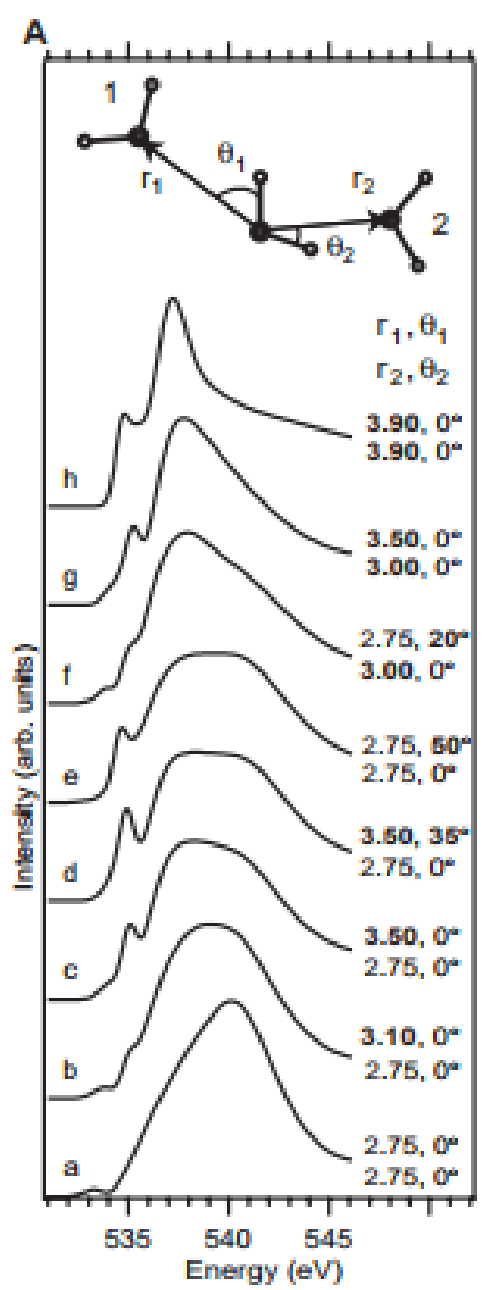
- Single Donor (SD- Green circles): Corresponding to c, d, e, and g

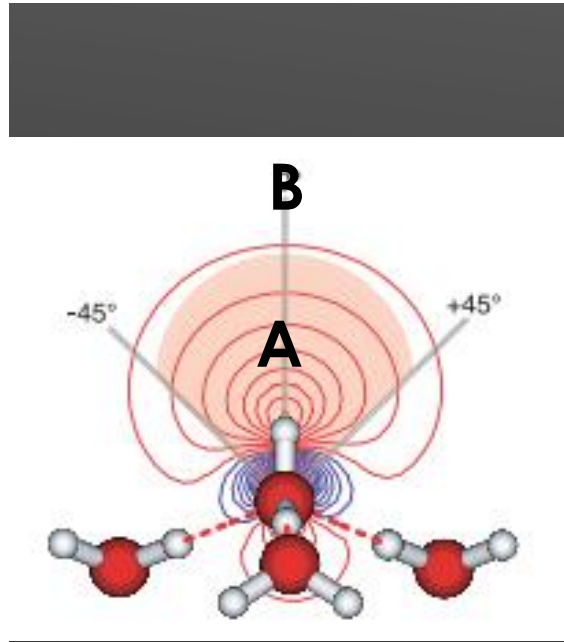
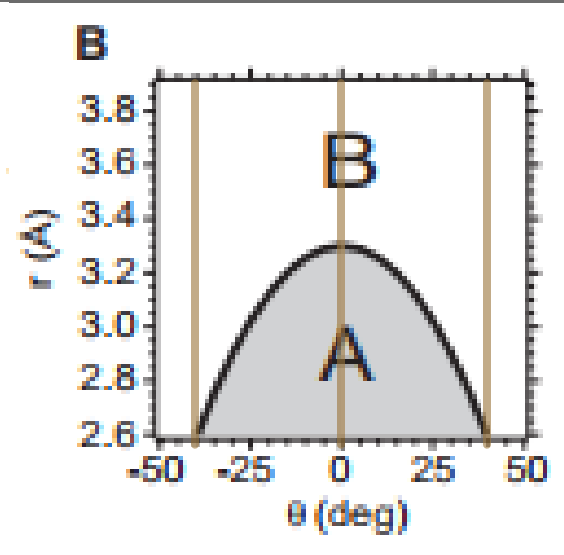
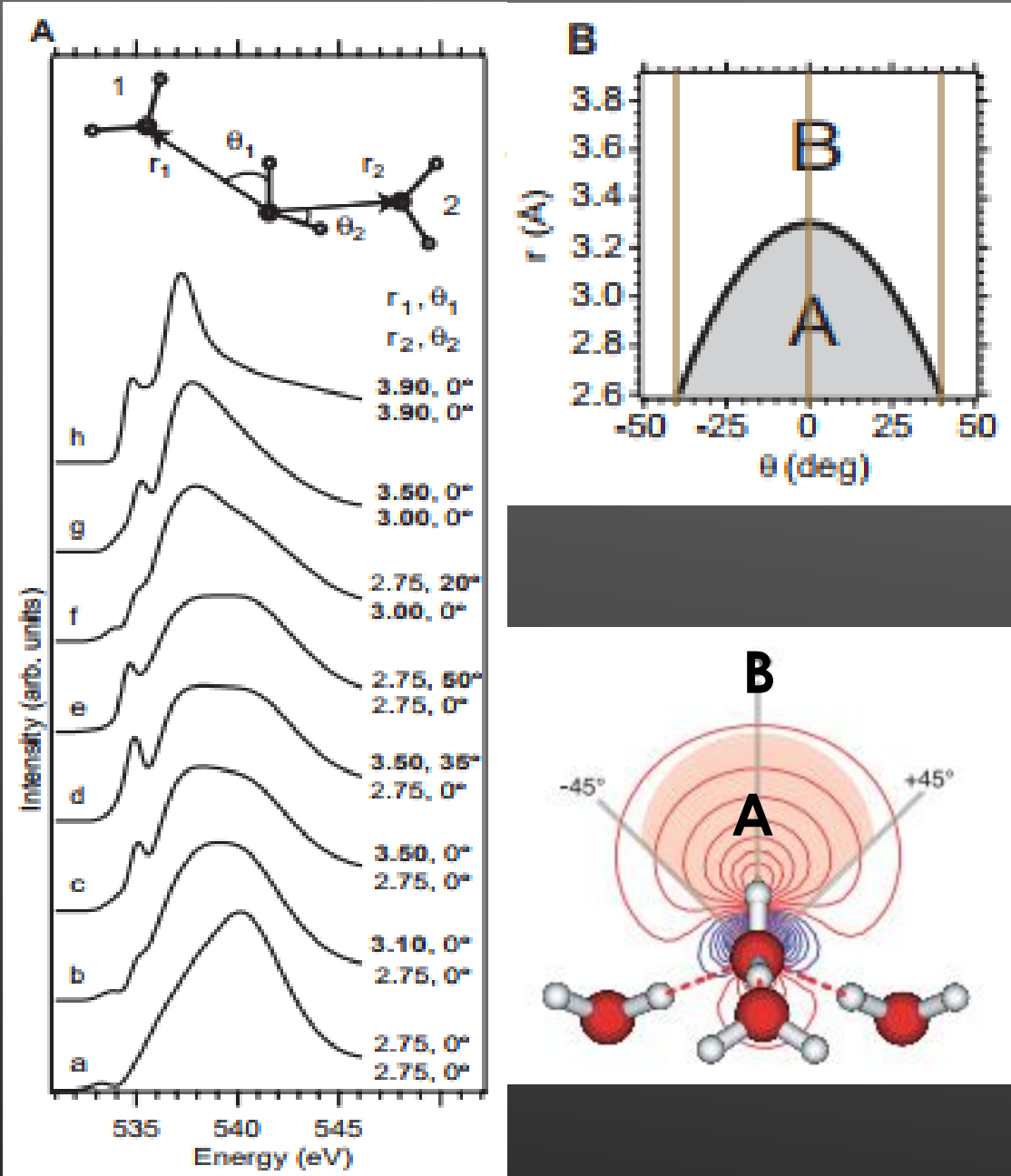
- Distinctive Pre Edge
- Distinctive Main Edge



ANALYSIS

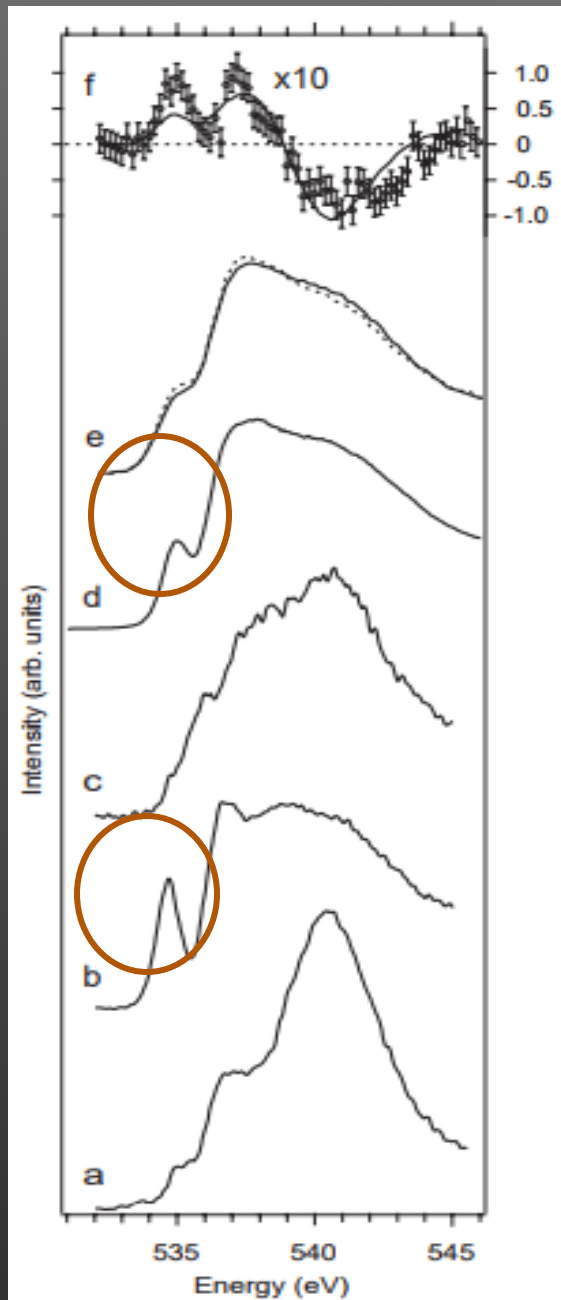
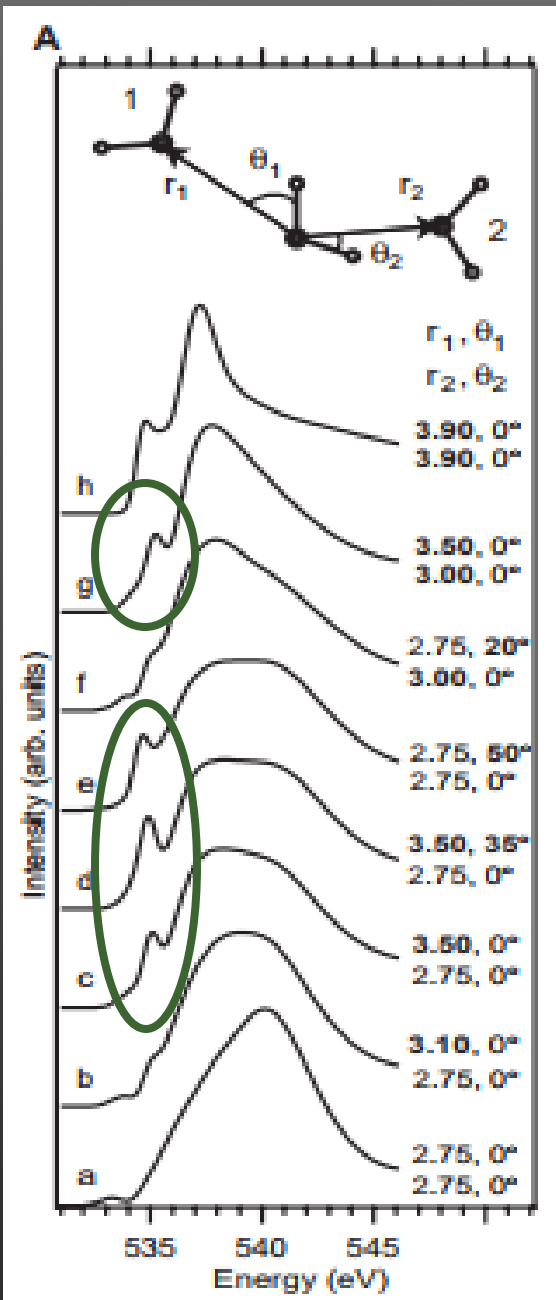
- Figure A): XA spectra
 - shows a systematic approach to change relative positions and angles of two water molecules interacting with a central water molecule.
- Wernet classifies the different spectra into donor configurations of the two nearest neighbors
 - Double Donor (DD- Red circles): Corresponding to a, b, and f
 - Single Donor (SD- Green circles): Corresponding to c, d, e, and g
 - Non-donor (ND): corresponds to h





ANALYSIS

- Figure A) allows Wernet to systematically place each configuration in a two zone scheme: Figure B)
- Classification scheme
 - Bulk Ice (AA configuration): both neighboring water molecules are within Zone A
 - Ice Surface (AB configuration): One neighboring water is within Zone A and another within Zone B
 - To visualize the information that Figure B) has shown, the geometry of the 1st solvation shell has been superimposed with the zones and B



SINGLE DONOR SPECIES

- Where do these Pre Edge intensities come from?
- Excitation of electrons to the antibonding orbital
- H-bond energetics

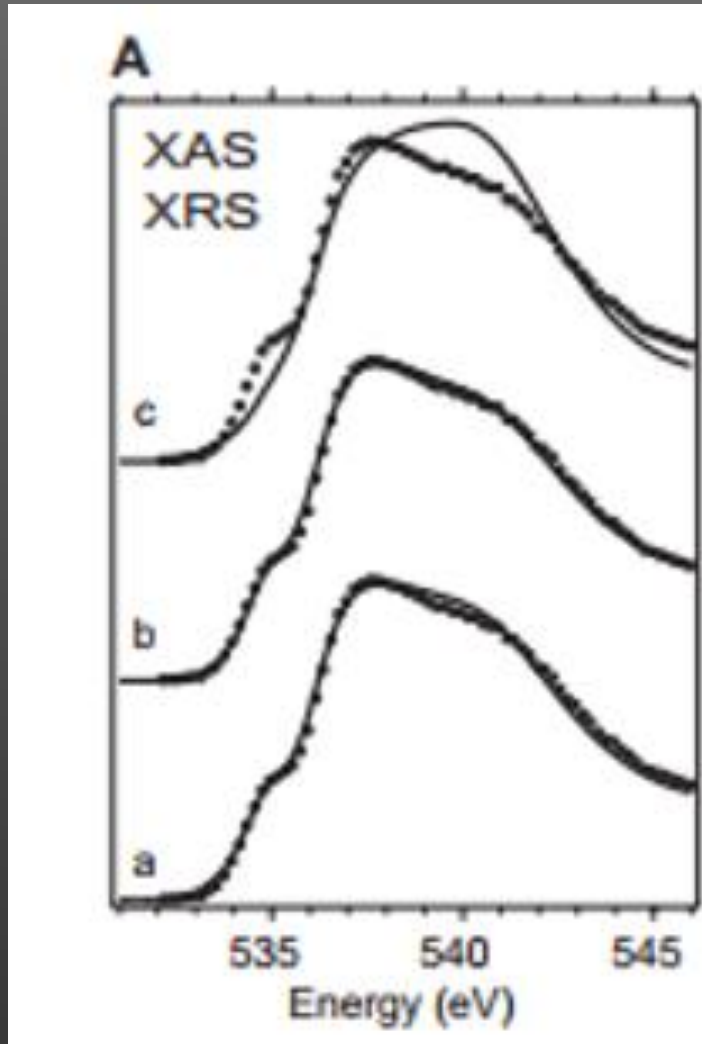
- Left Spectrum: Calculated XA
 - SD species
- Right Spectrum: Experimental XA data
 - B is the surface of ice
 - D is liquid water at RT

COMPUTATIONAL METHODS

Type	Method			
	EXP + FIT	SPC	MCYL	CPMD
		25°C		
DD	15 ⁺²⁵ ₋₁₅	70	50	79
SD	80 ± 20	27	41	20
ND	5 ± 5	3	9	1
		90°C		
DD	10 ⁺²⁵ ₋₁₀	56	39	63
SD	85 ⁺¹⁵ ₋₂₀	37	47	34
ND	5 ± 5	7	14	3

- SPC and MCYL are pair potential energy models
- Car –Parrinello MD (CPMD) is an ab-initio MD package
- MCYL is closest but all disagree heavily from experimentally fitted data
- The simulations from Table 1 cannot reproduce exp. data
- Correspond excellently to the change in ratio of DD:SD with increasing temperature

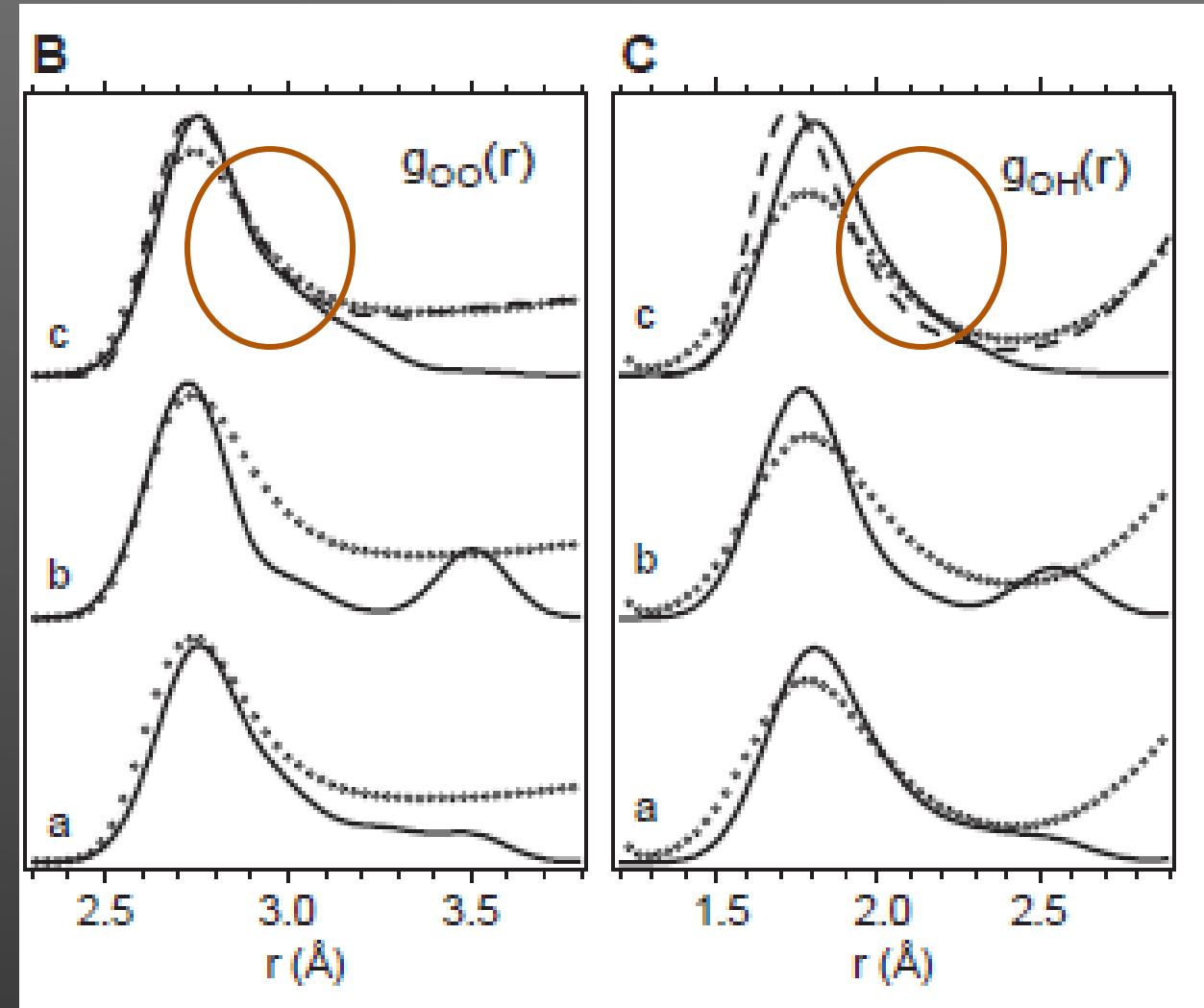
COMPUTATIONAL SPECTRA

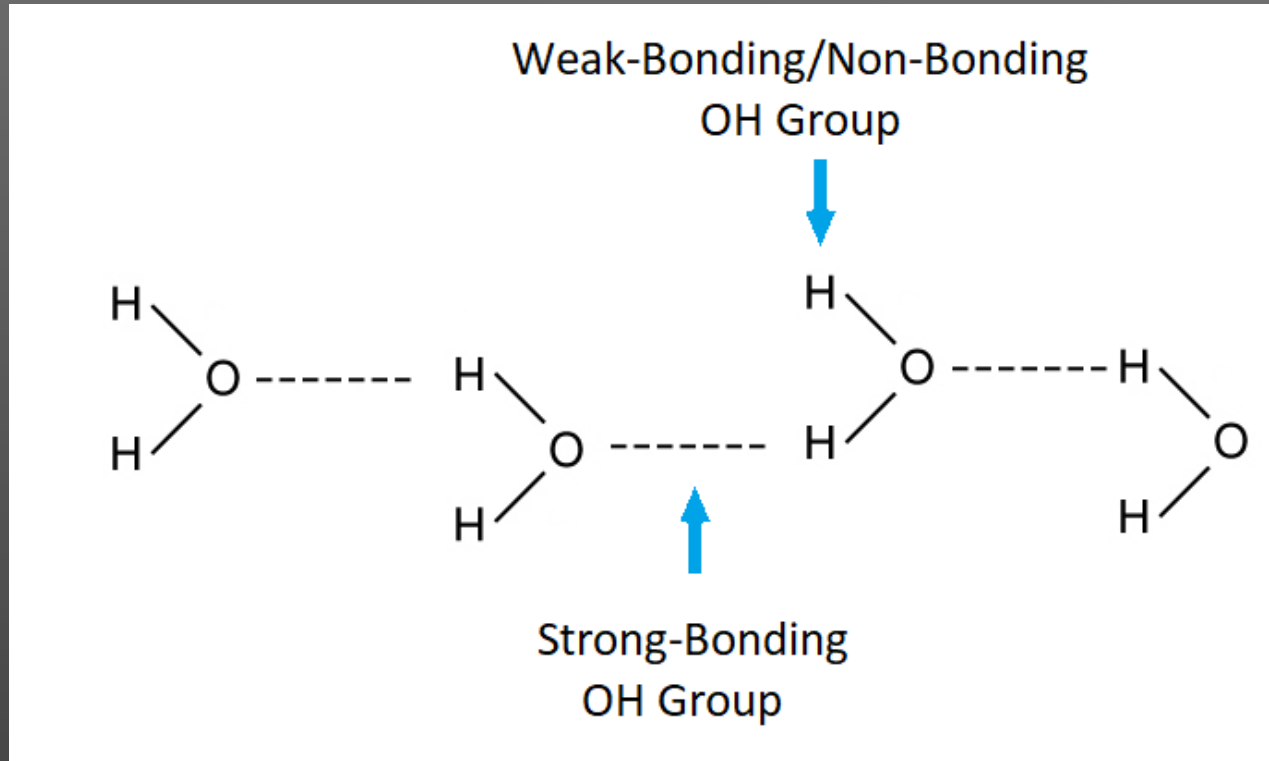


- Figure A is comparing calculated (Solid) vs. Experimental (Dashed) XA spectra
- DD:SD:ND ratios are the differences between models a), b), and c)
 - Models a) and b) use a ratio of 10:85:5 (differ only bond lengths and angles)
 - Model c) uses a ratio of 70:27:3

COMPUTATIONAL ANALYSIS

- Curve c) in Figures B and C- the dashed lines are representative of a computation using a potential energy force field SPC
- However at the ranges of $2.9\text{\AA} - 3.3\text{\AA}$ for Figure B) shows similarity
- This stands as well for the ranges of $1.9\text{\AA} - 2.3\text{\AA}$ for Figure C)
- Thus Wernet concludes that the deviations from experimental XA spectra is attributed to too few species with SD character in the SPC simulation





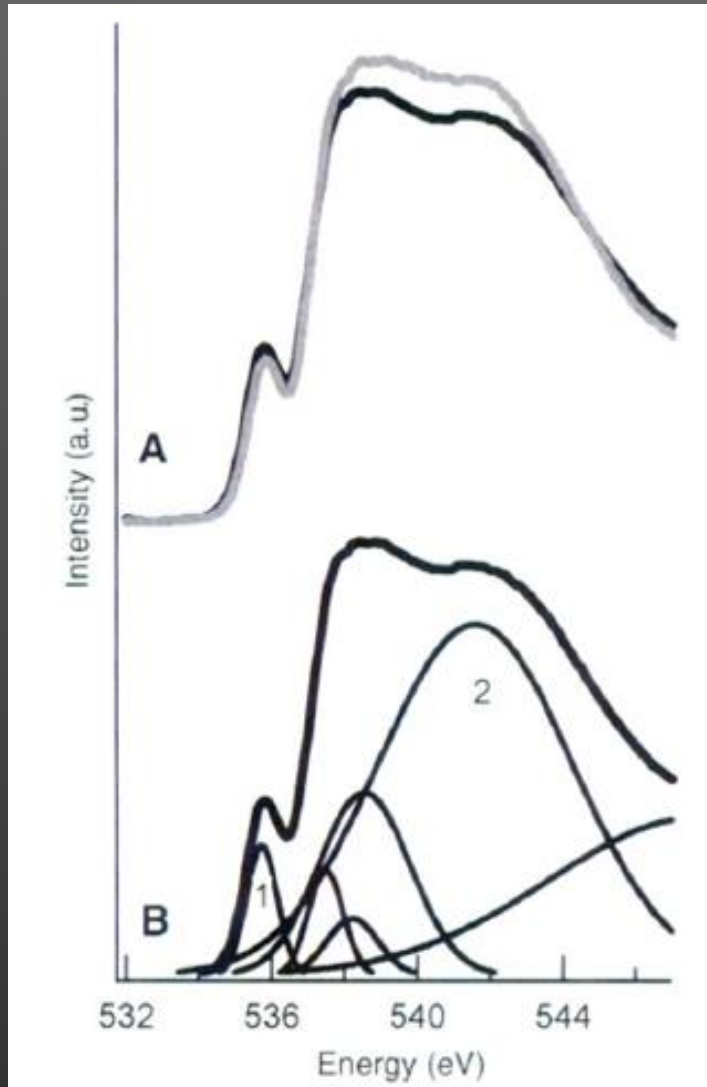
TWO H-BOND STRUCTURE PROPOSED

ENERGETICS OF HYDROGEN BOND NETWORK REARRANGEMENTS IN LIQUID WATER

J.D Smith et al. , *Science* **306**, 851 (2004)

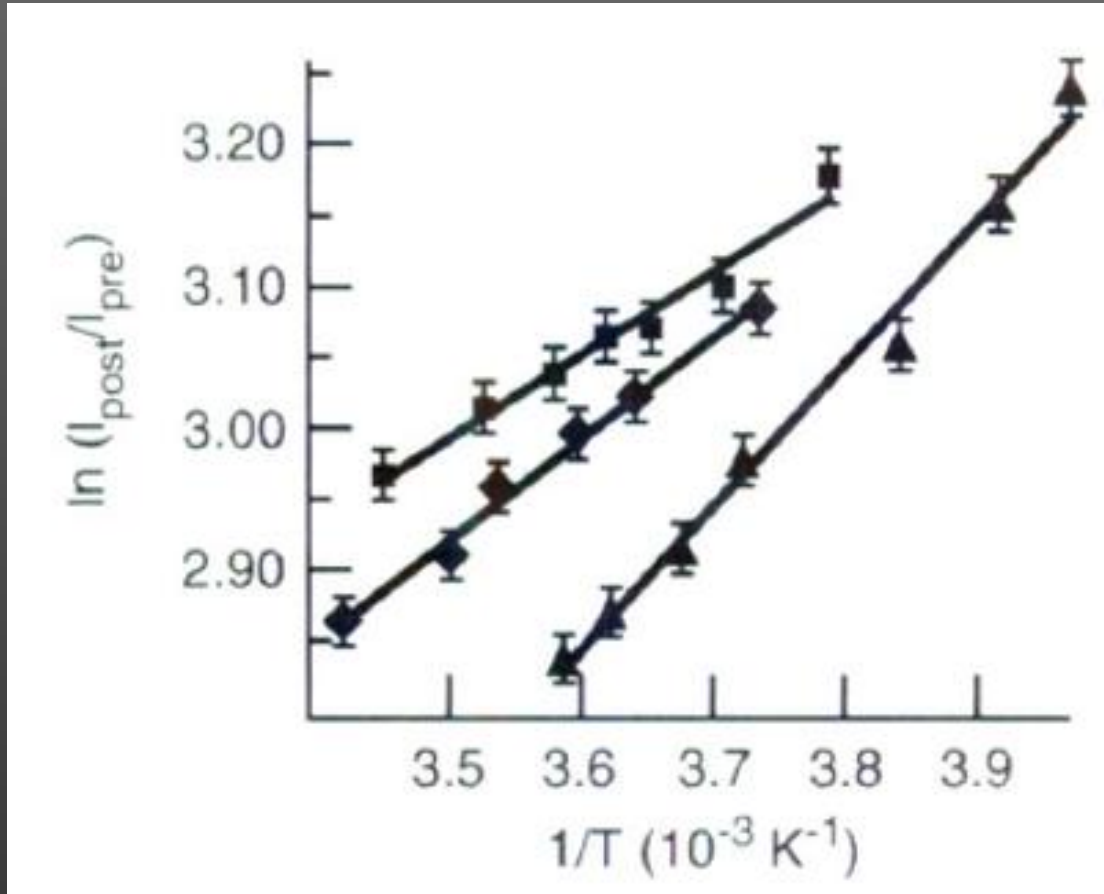
A decorative graphic consisting of several parallel white lines of varying lengths, slanted diagonally from the bottom right towards the top right, located in the lower right quadrant of the slide.

INTRODUCTION TO SMITH'S POINTS




- Refutes Wernet's claims that liquid water is not four-coordinated.
- Recorded Total Electron Yield-Near Edge X-Ray Absorption Fine Structure (TEY-NEXAFS) spectra for supercooled and normal water.
- In A, over a 37K (251K - 288 K) Temp range
 - I_{pre} increased by 20-25%
 - I_{post} decreased by 12-18%
- In B, spectra decomposed into 6 Gaussian sub bands
 - 1 and 2 most significant

ANALYSIS OF PRE/POST INTENSITY EDGE REGIONS



- Pre & Post represent the two H-bonding configurations.
- Plotted post/pre intensities vs $1/T$ to generate a straight-line slope.
- Slope - ΔE , 1.5 ± 0.5 kcal/mol.
- Calculated a $27\% \pm 0.9\%$ H-Bond energy loss.
- Experimentally derived, not based on model.

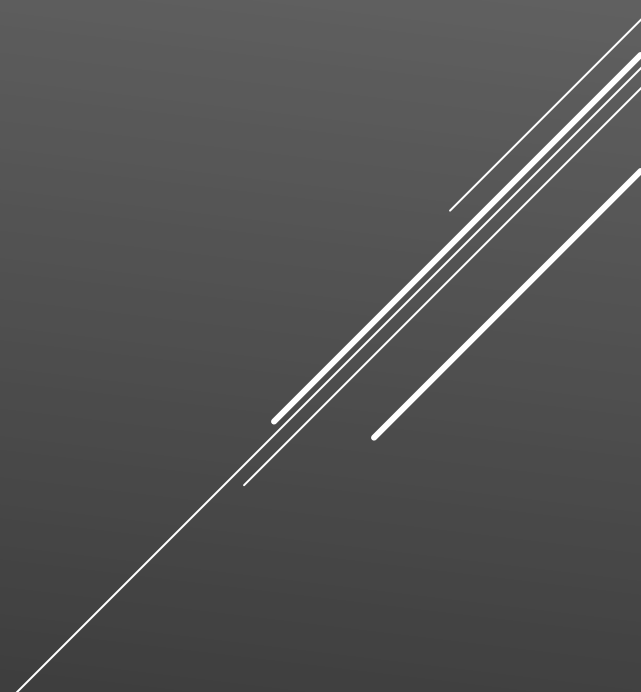
COMPARISON TO ST2 MODEL

- Used Blumberg ST2 MD Simulation for other energetic criteria.
 - Blumberg et al. used lower limit of -4 kcal/mol to calculate average of 2.2 bond per mol.
 - Underscores XAS sensitivity to H-Bond distortion with respect to exact definition used to compute it.
 - Difference in Blumberg's lower limit and average bond energy of -5.5 kcal/mol for ST2 model is consistent with Smith's ΔE .
- 

SMITH'S ARGUMENT AGAINST WERNET

- Wernet deduced pre-edge peak corresponds to a loss of $55\% \pm 15\%$ of H-bonding energy (vs. $27\% \pm 0.9\%$ loss for Smith)
- Smith's ΔE reflects energy required to distort/break H-Bond in XAS, which when used in Wernet's XA computation, agrees with tetrahedral structure (~ 3.3 bonds/mol)
- Wernet's 11 molecule cluster model does not accurately reflect liquid water.
- Wernet's permissive criteria for that energy accounts for the discrepancy. (critical differences in H bond structure criterion)

SUMMARY



WERNET

- Claimed diffraction data from non-crystalline materials provide poor radial distribution functions to assign local geometries
- Derived a new model for liquid water using cluster model in MD simulation.
- Compared MD model to experimental data and found agreement.
- States liquid water is not predominantly tetrahedral geometry, but rather a two-bond configuration.

SMITH

- Recorded TEY-NEXAFS spectra for supercooled and normal water.
- Calculated the difference in energy of the two H-Bond configurations as 1.5 ± 0.5 kcal/mol.
- Refuted Wernet and states this energy coincides with the distribution of H-Bond strength in overstructured water model.
- Wernet misinterpreted results because intensities in XA spectra are not as simply connected to structure as Wernet's model suggests. (Schwartz)

WAS IT DIFFERENT DATA OR INTERPRETATION?

- Example of SD/DD population at 25 Celsius and 90 Celsius
- If Wernet's relative populations of SD/DD at 298 and 363 K are used to calculate Smith's H-Bond Energy (ΔE) using Boltzmann Distribution, returns 0.99 and 1.54 kcal/mol.

- Take $\frac{SD}{DD} \rightarrow \frac{P_1}{P_0}$, $\frac{P_1}{P_0} = e^{-\frac{\Delta E}{RT}}$, $\Delta E = -RT \ln\left(\frac{SD}{DD}\right)$

- $\frac{SD}{DD} = \frac{80}{15}$ at 25°C, $\frac{85}{10}$ at 90°C

- Smith retained error tolerance of 1.5 ± 0.5 kcal/mol
- The information was the same, the interpretation was different!

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- Ph. Wernet et al., *Science* **304**, 995 (2004).
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 - C. Schwartz, R. Saykally, D. Predergast, *J. Chem. Phys.* **113**, 044507 (2010).
 - R. L. Blumberg et al., *J. Chem. Phys.*, **80**, 5230 (1984)
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