Scidac 2015 progress: Advanced Modeling of ions in solutions, on surfaces, and in biological environments

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Temple University: Mike Klein, **Xifan Wu (presenting)**

LBL: Esmond Ng, Chao Yang, Lin Lin

PRINCETON UNIVERSITY

TEMPLE UNIVERSITY

Lawrence Berkeley National Laboratory

Outline

Part I. Projects

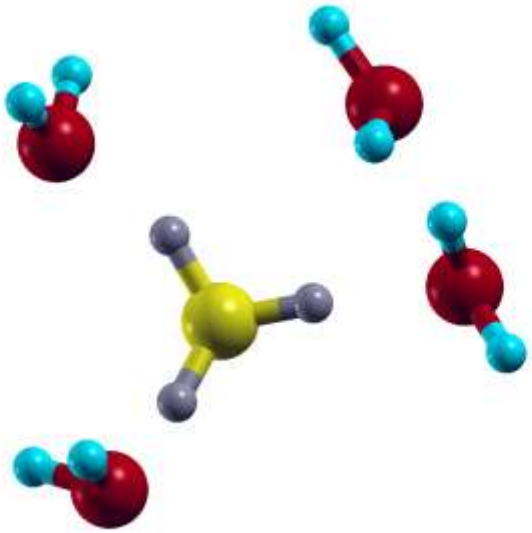
- **Proton transfer of OH- and H3O+ in an accurately modeled H-bond network**
- **X-ray absorption spectra in liquid water by advanced modeling**

Part II. Progress of our team members at LBL

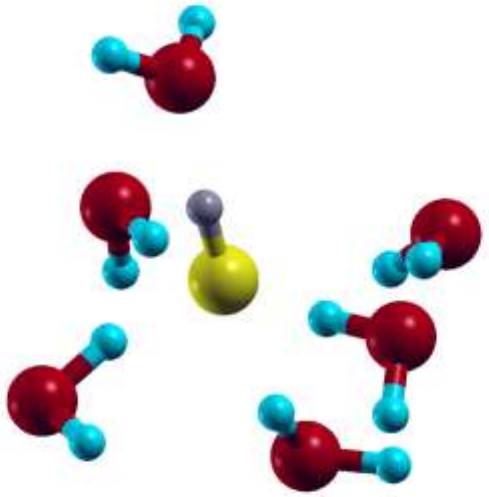
Part III. Other performed projects and introduction of our posters

Proton Transfer through hydronium and hydroxide: Current controversy

PT in H_3O^+ through structural diffusion

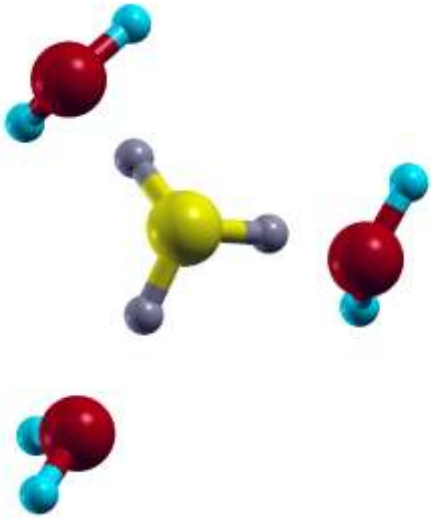


PT in OH^- through structural diffusion

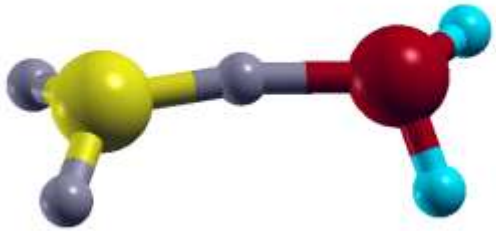


Proton Transfer through hydronium and hydroxide: Current controversy

Proton Transfer mechanism in H_3O^+



Eigen cation

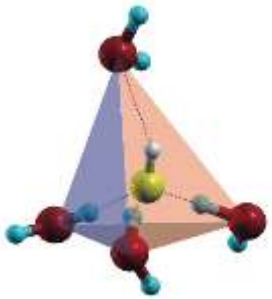


Zundel cation

Proton Transfer through hydronium and hydroxide: Current controversy

Three controversial mechanisms for hydroxide OH-

Mirror image



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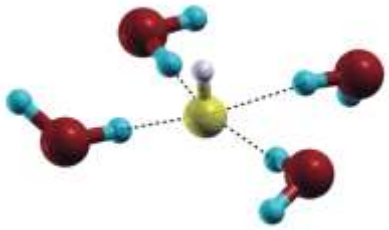
Static hyper-coordination



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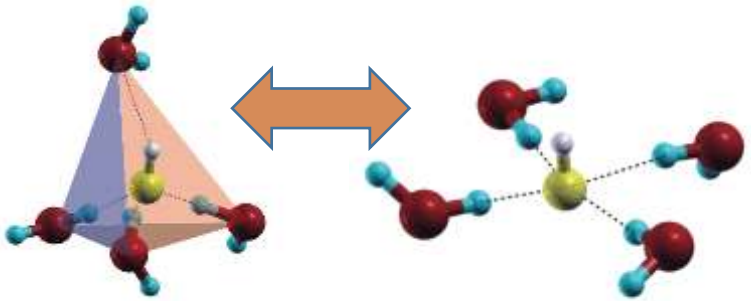
Dynamical hyper-coordination



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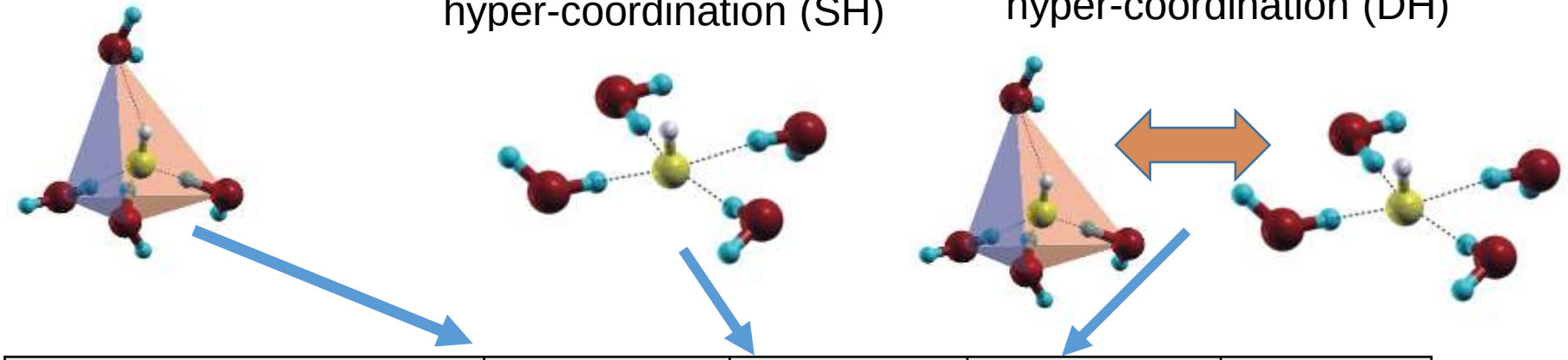
Proton Transfer through hydronium and hydroxide

Three controversial mechanisms for hydroxide OH-

Mirror image (MI)

Static hyper-coordination (SH)

Dynamical hyper-coordination (DH)



Diffusion Coefficient (10^{-9} m^2/s)	MI(PW91)[1]	SH(HCTH)[1]	DH (BLYP)[1]	Exp.[2, 3, 4]
OH^-	18.5	0.44	**1.92**	3.12
H_3O^+	3.24	3.25	**2.83**	6.69
$D(OH^-)/D(H_3O^+)$	5.88	0.14	**0.68**	0.47

Why controversial?

- **All three scenarios can be theoretically obtained by GGA functional**
- **BLYP predicts a qualitatively correct picture, but ions diffuse too slow**
- **The H-bond by BLYP is known to be over-structured**

1. Tuckerman, M. E.; Chandra, A.; Marx, D. *J. Chem. Phys.* 133, 124108 (2010)
2. Tuckerman, M. E.; Chandra, A.; Marx, D. *Chem. Rev.* 2010, 110, 2174
3. Milles, R. *J. Phys. Chem.*, 1973, 77, 685
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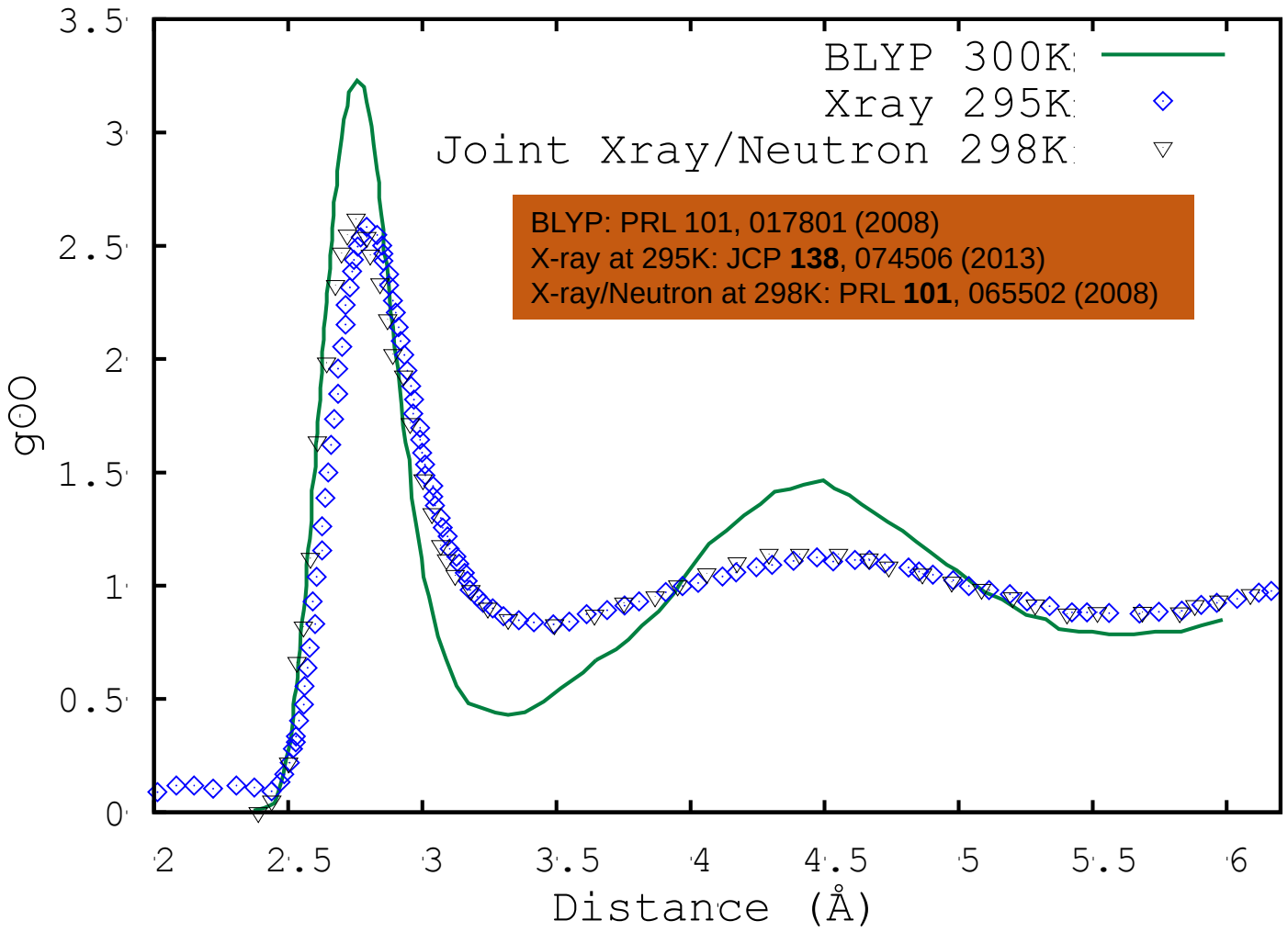
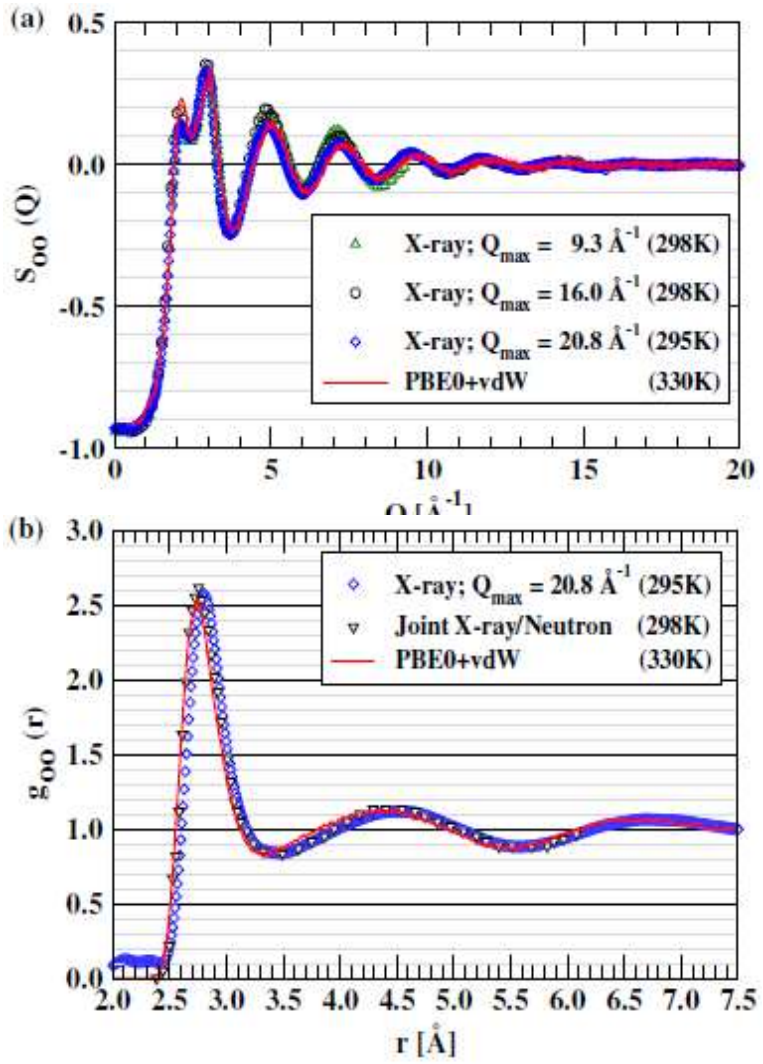
Proton Transfer through hydronium and hydroxide: Current controversy



Proton Transfer with accurately modeled H-bond network



Accurate modeling of H-bond is the key!!

What are missing in GGA-AIMD simulations?

- Inclusion of van der Waals interactions
- Correction of delocalization by hybrid functional
- Treatment of nuclear quantum effects

Our advanced modeling approaches:

- TS-vdW
- PBE0 hybrid functional
- Approximate treatment of nuclear quantum effect by 30K elevated temperature

R. DiStasio et al, J. Chem. Phys. 141, 084502 (2014)

Proton Transfer with accurately modeled H-bond network

Diffusion

Diffusion Coefficient (10^{-9} m^2/s)	BLYP[1]	PBE	PBE vdW	PBE0 vdW	Exp.[2, 3, 4]
OH^-	1.92	16.4	14.0	**3.90**	3.12
H_3O^+	2.83	9.78	11.4	**8.15**	6.69
$D(OH^-)/D(H_3O^+)$	0.68	1.7	1.2	**0.48**	0.47

Proton Transfer rate (per picosecond)

PT rate	PBE	PBE vdW	PBE0 vdW
OH^-	2.92	2.26	0.607
H_3O^+	2.06	2.78	1.90

1. Tuckerman, M. E.; Chandra, A.; Marx, D. *J. Chem. Phys.* 133, 124108 (2010)
2. Tuckerman, M. E.; Chandra, A.; Marx, D. *Chem. Rev.* 2010, 110, 2174
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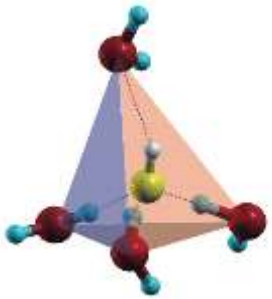
L. Zheng, B. Santra, R. DiStasio Jr., R. Car, M. Klein, X. Wu, manuscript in preparation

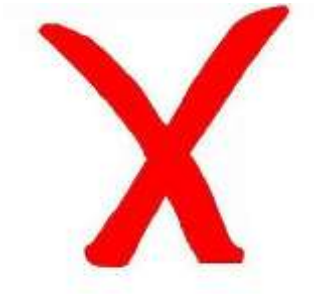
Proton Transfer with accurately modeled H-bond network

OH^-

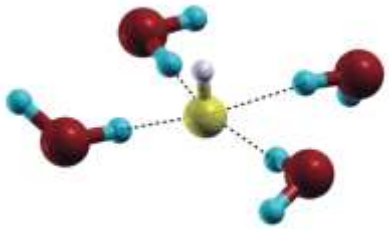
Three controversial mechanisms for hydroxide OH-

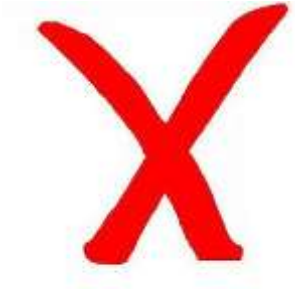
Mirror image



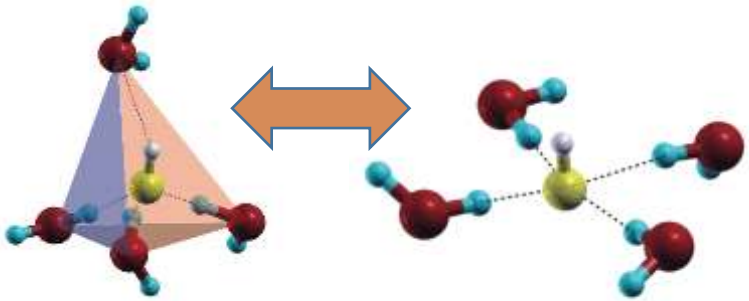


Static hyper-coordination





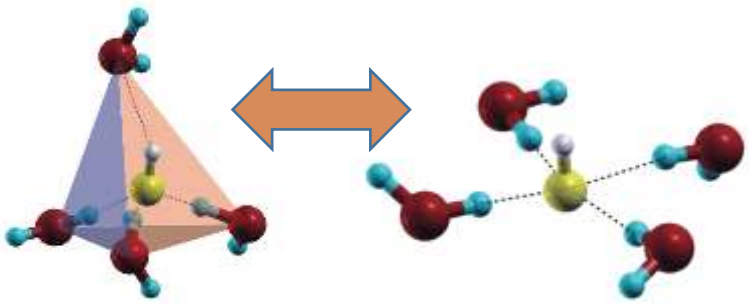
Dynamical hyper-coordination



Proton Transfer with accurately modeled H-bond network

OH^-

Dynamical
hyper-coordination



Ready

Inactive

Presolvation structure of PT in OH-:

- Complex receiving the proton
- Resembling water
- Must change from hypercoordination to tetrahedral like

Diffusion Coefficient (10^{-9} m^2/s)	BLYP[1]	PBE	PBE vdW	PBE0 vdW	Exp.[2, 3, 4]
OH^-	1.92	16.4	14.0	**3.90**	3.12

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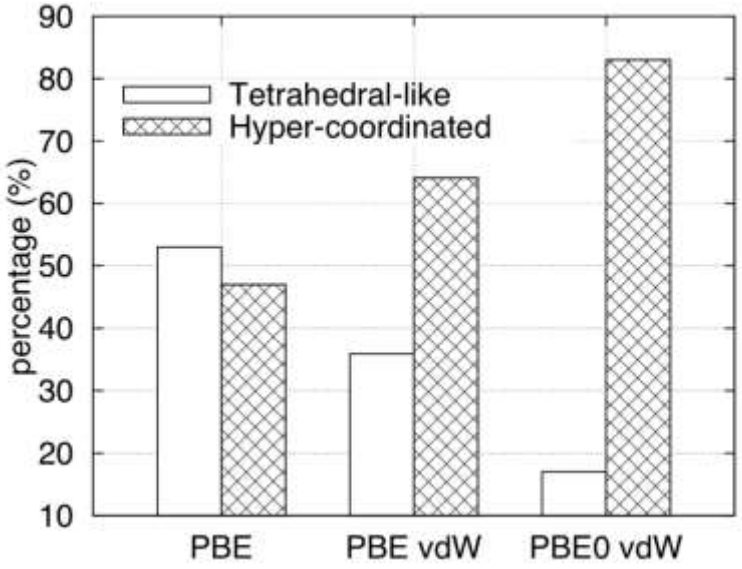
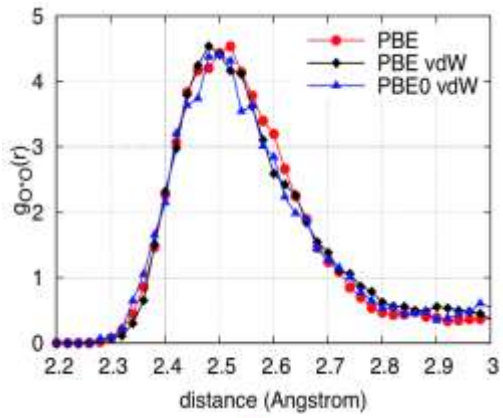
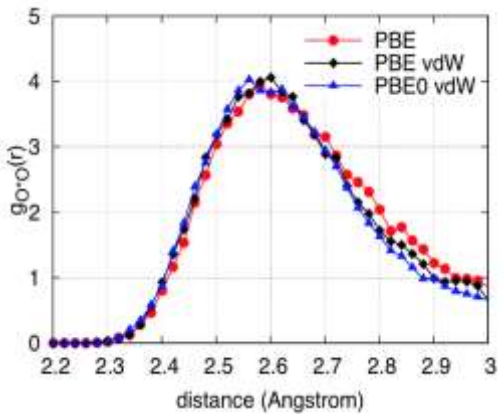
Proton Transfer of OH-: Presolvation structure

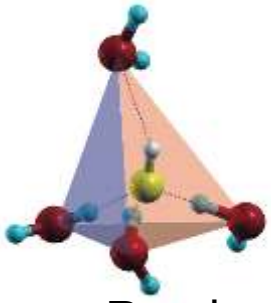
OH^-



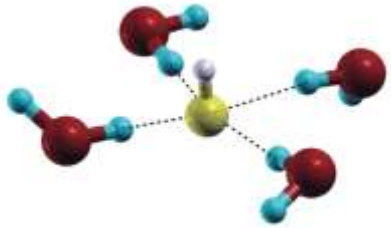




Dynamical hyper-coordination



Ready



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Diffusion Coefficient (10^{-9} m^2/s)	BLYP[1]	PBE	PBE vdW	PBE0 vdW	Exp.[2, 3, 4]
OH^-	1.92	16.4	14.0	**3.90**	3.12

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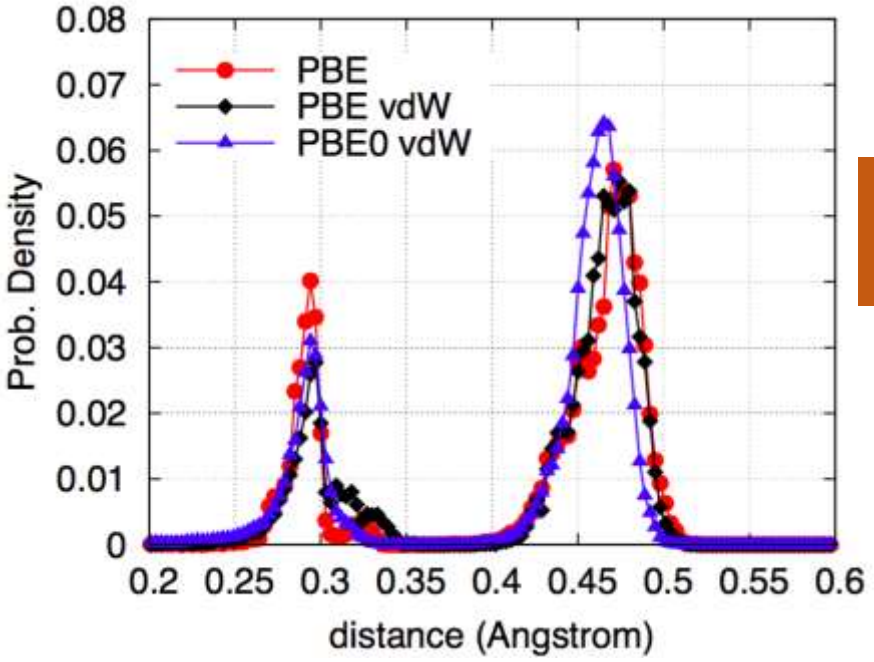
Proton Transfer with accurately modeled H-bond network

OH^-



Weakening of directional H-bond strength !

Diffusion Coefficient (10^{-9} m^2/s)	BLYP[1]	PBE	PBE vdW	PBE0 vdW	Exp.[2, 3, 4]
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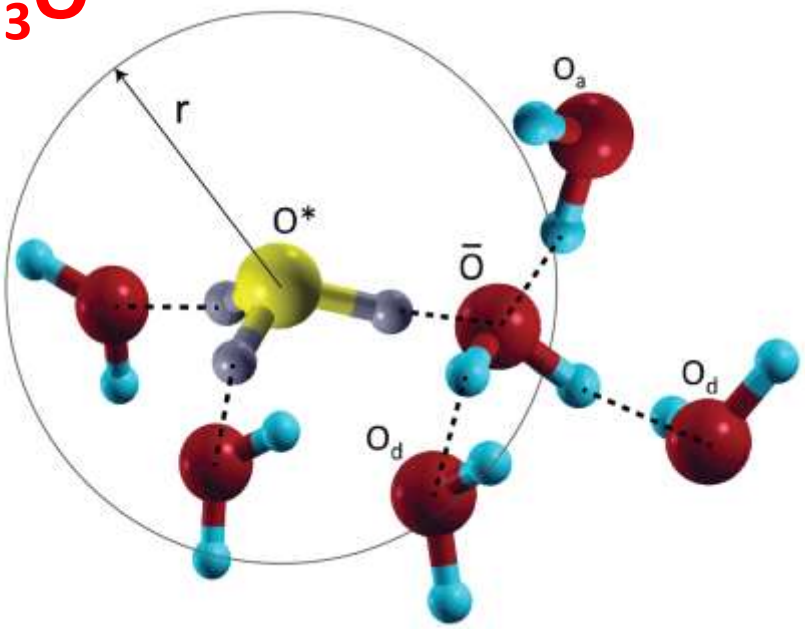
Proton Transfer with accurately modeled H-bond network

H_3O^+



Presolvation structure of PT in H3O+:

- Complex receiving the proton
- Water molecule in first shell
- A2D2 (inactive) to A1D2 (ready)

Diffusion Coefficient (10^{-9} m^2/s)	BLYP[1]	PBE	PBE vdW	PBE0 vdW	Exp.[2, 3, 4]
H_3O^+	2.83	9.78	11.4	**8.15**	6.69

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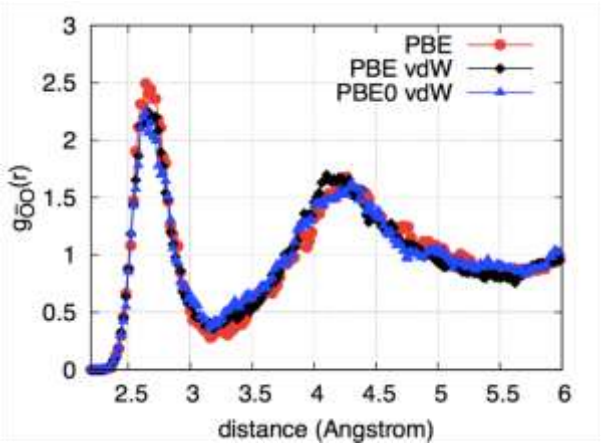
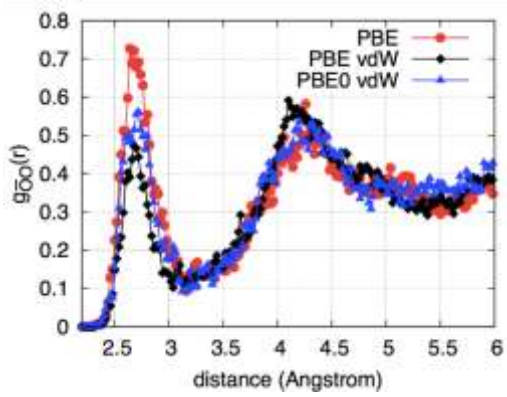
Proton Transfer with accurately modeled H-bond network

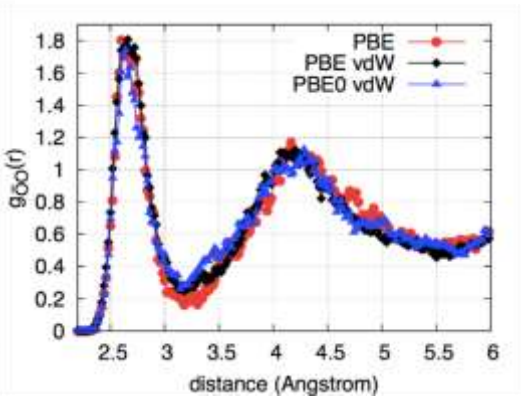
H_3O^+

decompose



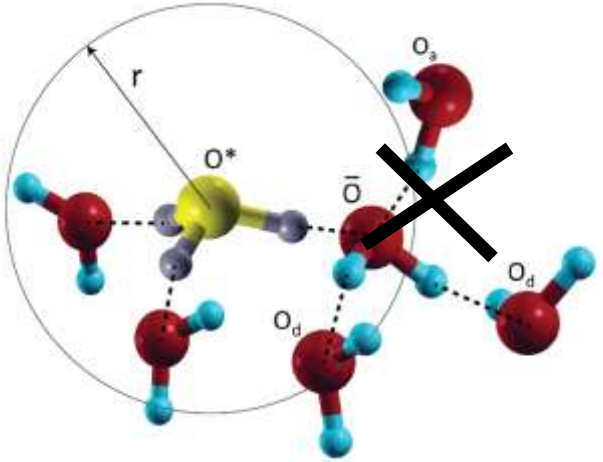


lone pair side



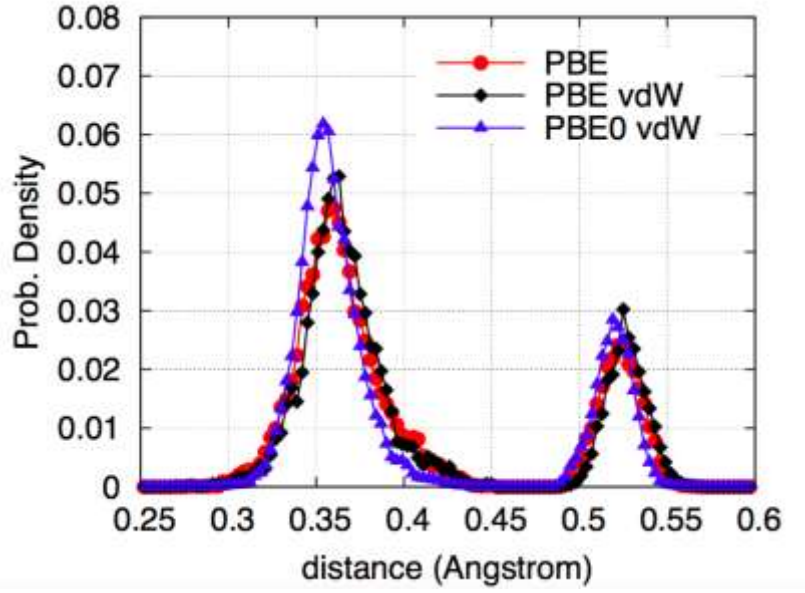
hydrogen side

	Inactive	Ready	
Functional	**A2D2**	**A1D2**	**Others**
PBE	64.35	33.47	2.19
PBE _vdW	58.78	35.22	6.00
PBE0_vdW	51.22	41.94	6.84



L. Zheng, B. Santra, R. DiStasio Jr., R. Car, M. Klein, X. Wu, manuscript in preparation

Proton Transfer with accurately modeled H-bond network



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Proton Transfer with accurately modeled H-bond network

1. Settle down the controversy on the proton transfer mechanism in OH-
2. Delocalization correction by hybrid functional
3. van der Waals interaction
4. Slow down PT in OH- towards experimental direction
5. The PT of H3O+ is much less affected due to error cancelation

L. Zheng, B. Santra, R. DiStasio Jr., R. Car, M. Klein, X. Wu, manuscript in preparation

Outline

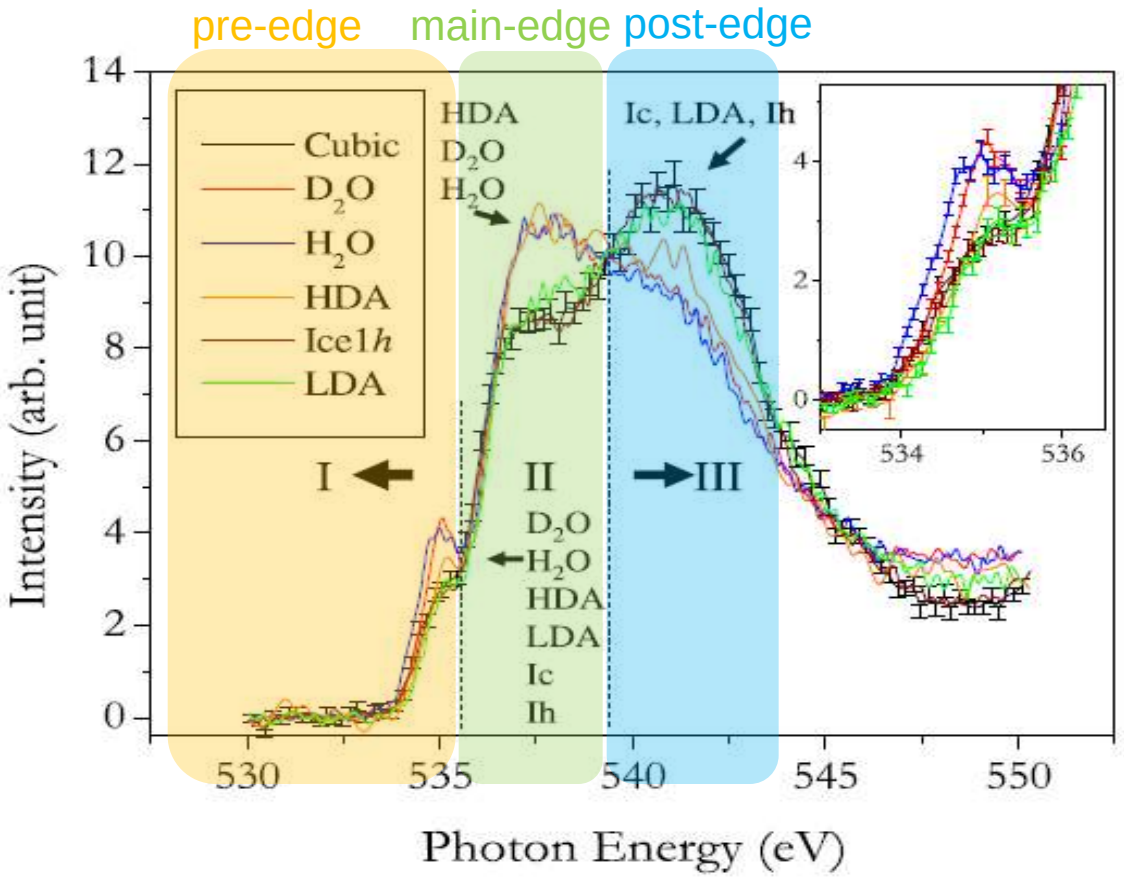
Part I. Projects

- **Proton transfer of OH- and H3O+ in an accurately modeled H-bond network**
- **X-ray absorption spectra in liquid water by advanced modeling**

Part II. Progress of our team members at LBL

Part III. Other performed projects and introduction of our posters

X-ray absorption of liquid water and ice

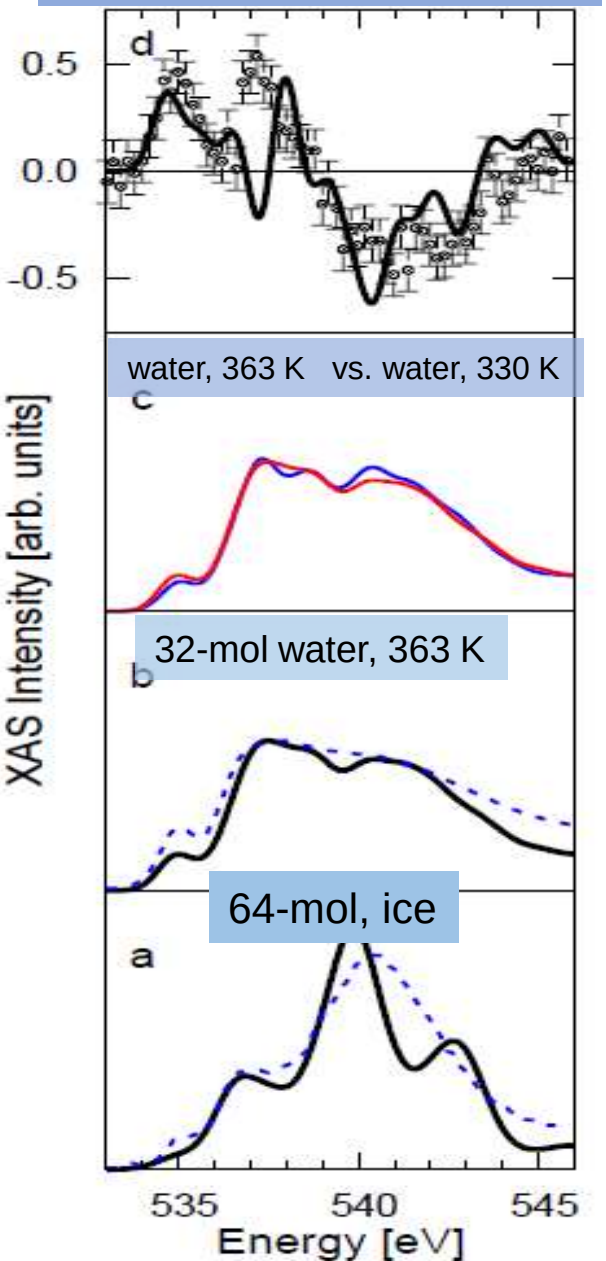


J. Tse *et. al.* Phys. Rev. Lett. 100,095502(2008)

- The spectral width (~ 11 eV) is the same in all spectra
- Three features (pre-edge, main-edge, post-edge) are present in the same energy range in all spectra
- The relative intensity of the features shows a characteristic system dependence

X-ray absorption of liquid water and ice

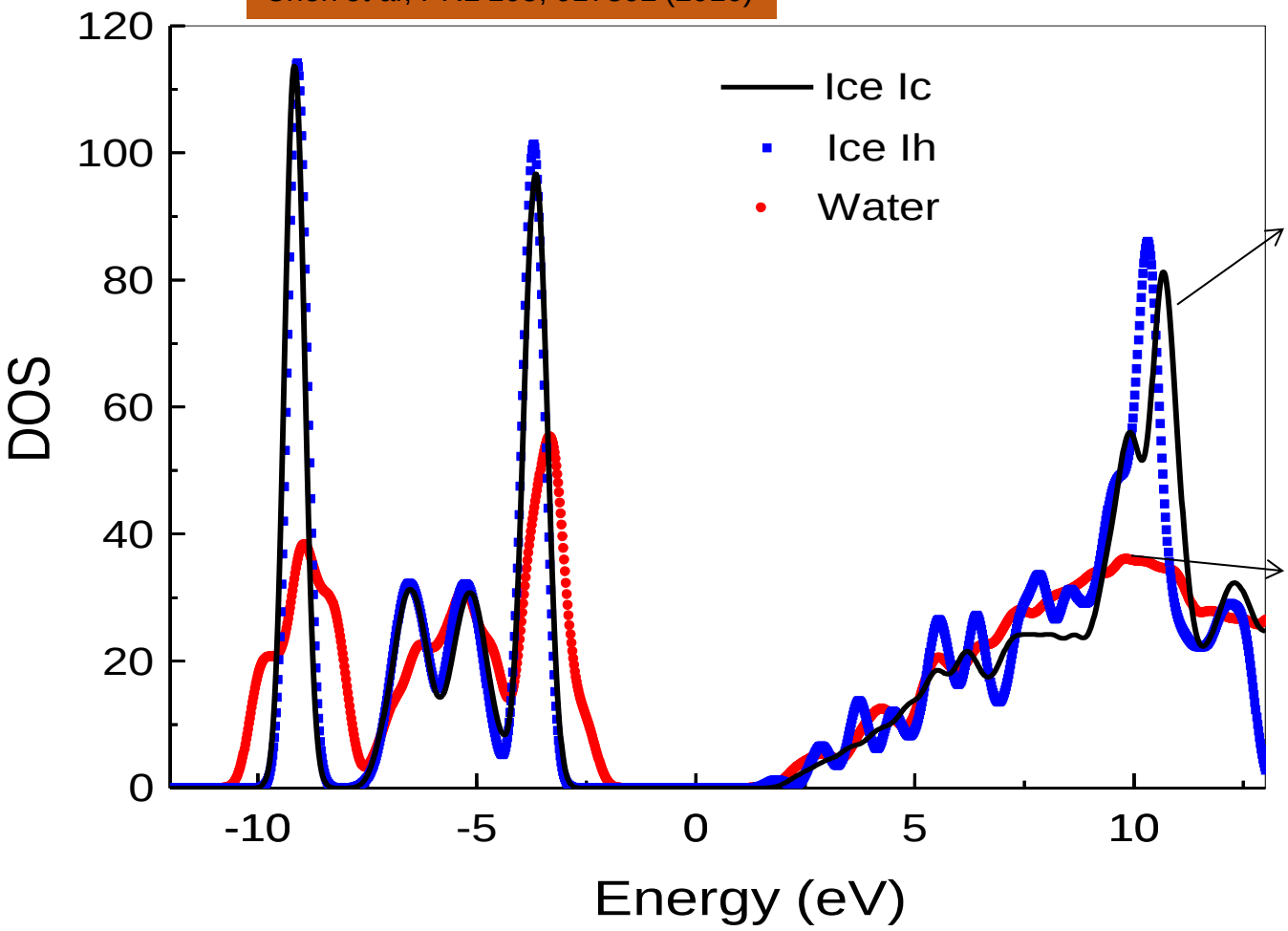
Variation of the spectrum with T

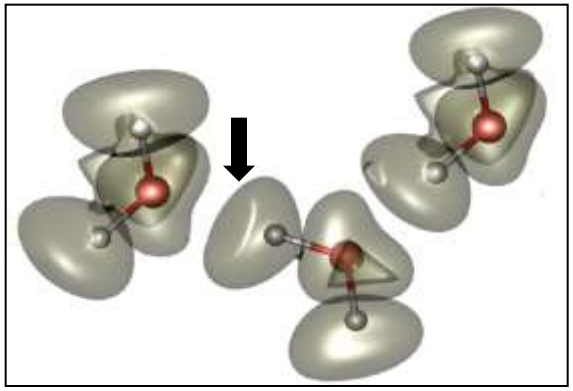


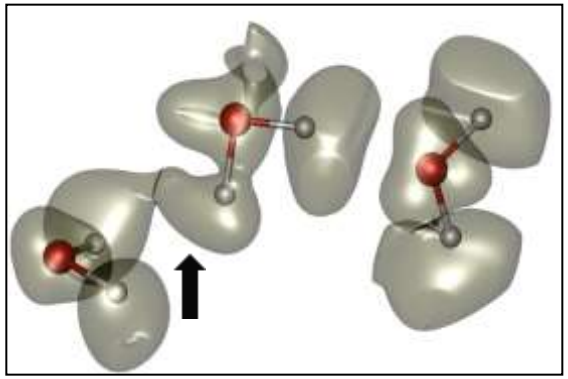
- Quasiparticle treatment based on GW approximation is crucial in obtaining the XAS spectra
- Difference in XAS between water and ice

X-ray absorption of liquid water and ice: the difference in main peak

Chen *et al*, PRL 105, 017802 (2010)







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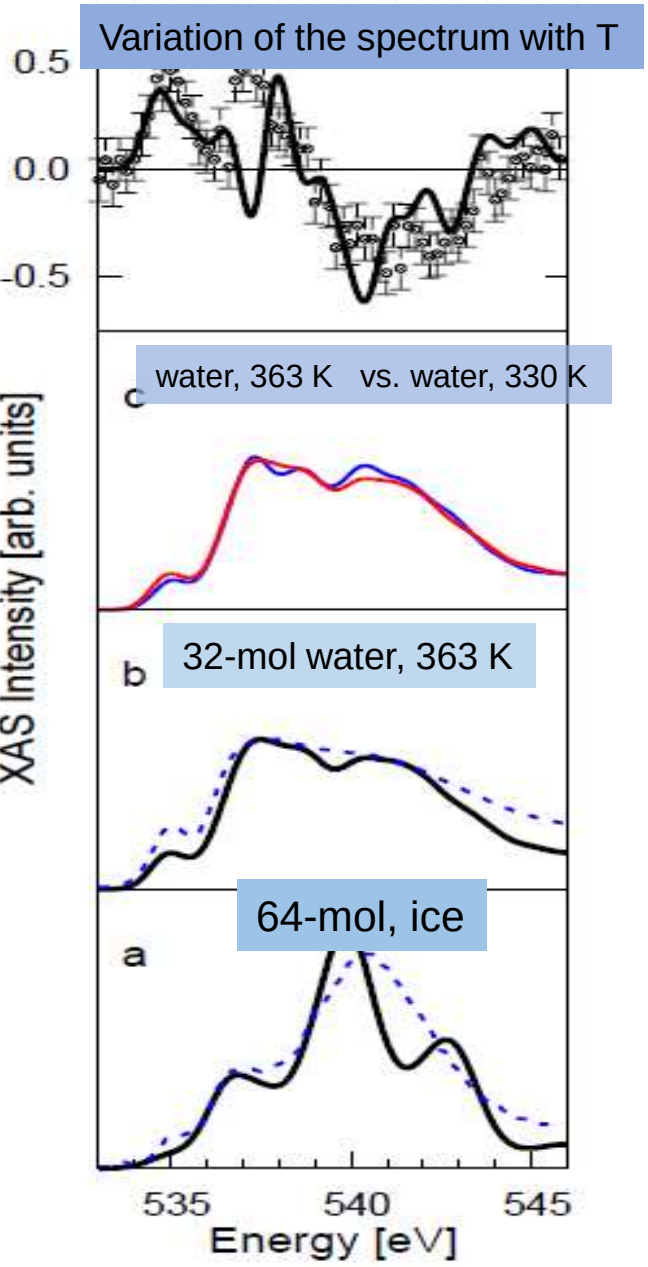
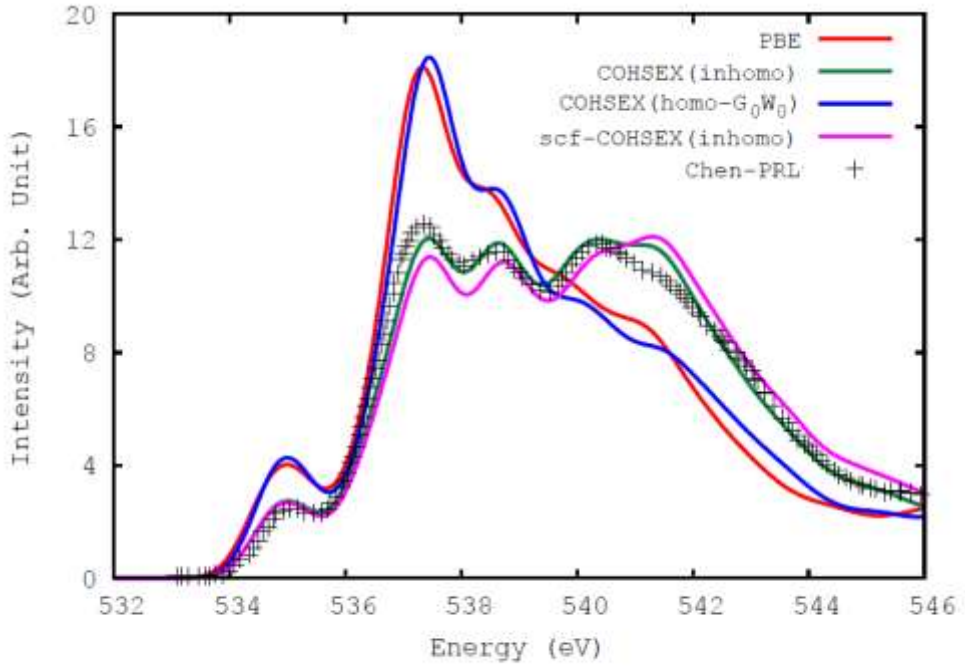


AIMD: ab initio molecular dynamics

- **Importance of of electron excitation calculations?**
  - GW vs. DFT method
  - G0W0 vs self-consistent GW
- **The importance of molecular modeling of water by AIMD?**
  - vdW and hybrid functional
  - nuclear quantum effect
  - *ab initio* vs. classical MD
  - size effect in water model

X-ray absorption of liquid water



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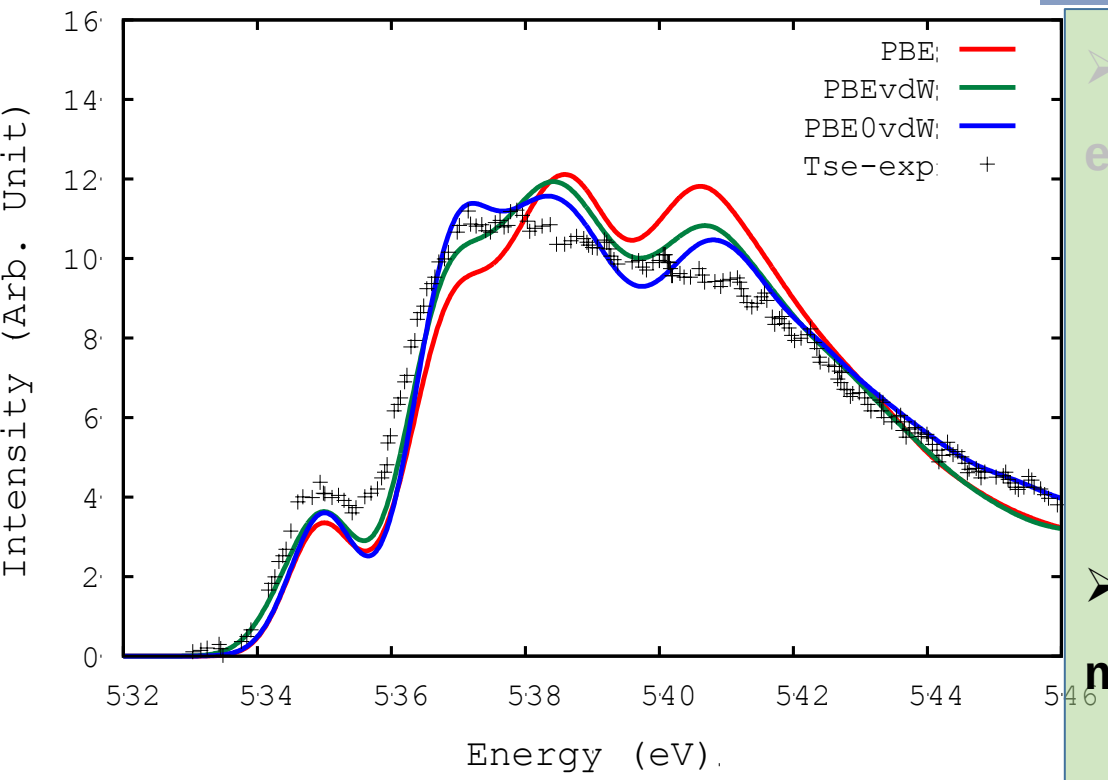
  - size effect in water model

X-ray absorption of liquid water : recent advanced modeling

Z. Sun, et. al. in preparation



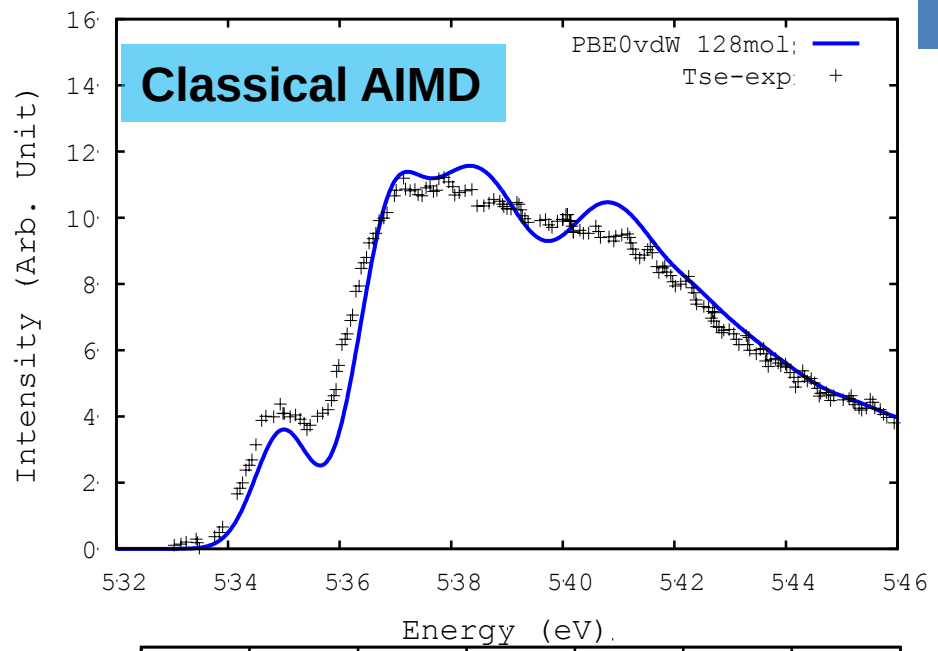
Liquid water modeled in a cubic box of 128-mol

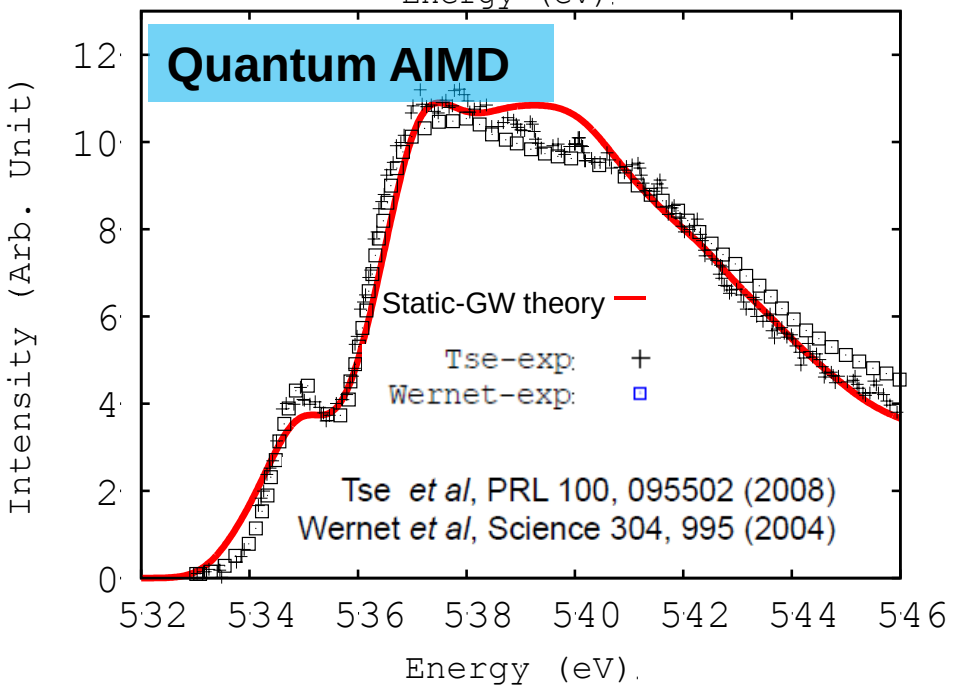
AIMD: ab initio molecular dynamics

- Importance of of electron excitation calculations?
  - GW vs. DFT method
  - G0W0 vs self-consistent GW
- **The importance of molecular modeling of water by AIMD?**
  - **vdW and hybrid DFT**
  - nuclear quantum effect
  - *ab initio* vs. classical
  - size effect in water model

Tse *et al.*, PRL 100, 095502 (2008)

X-ray absorption of liquid water : nuclear quantum effect





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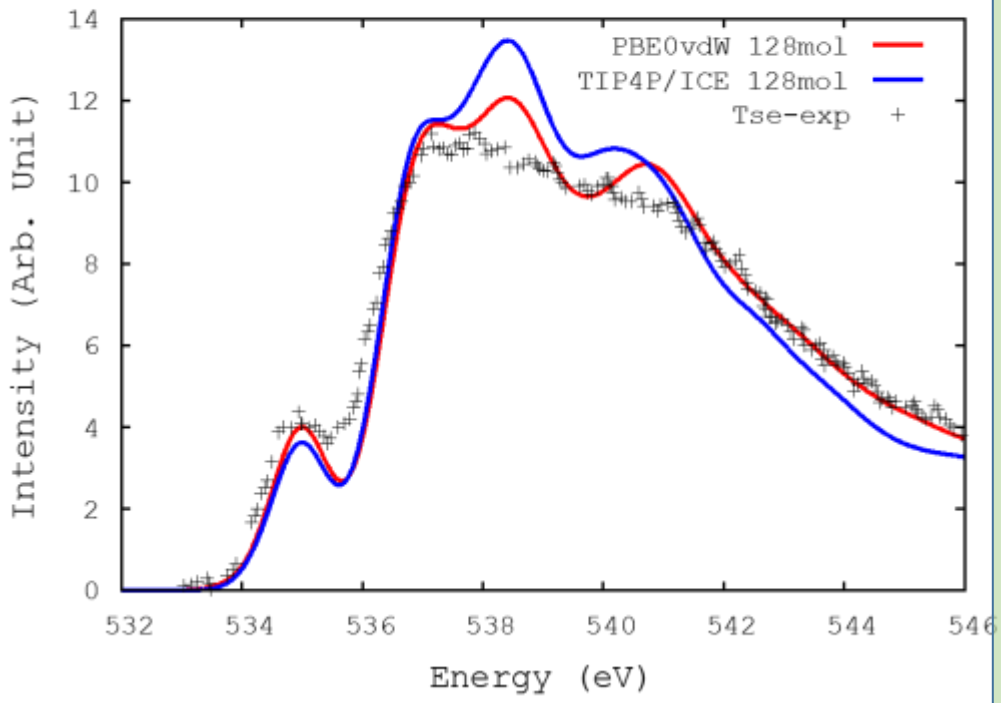
XAS of 128mol TIP4P/ICE water



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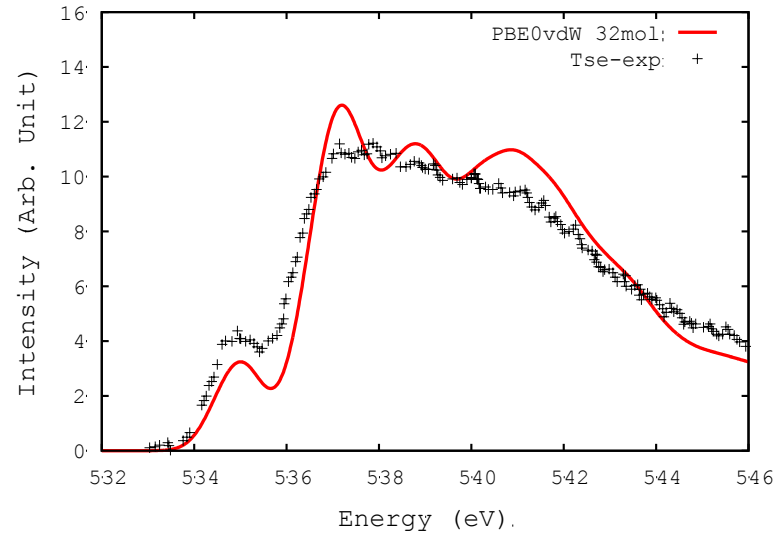

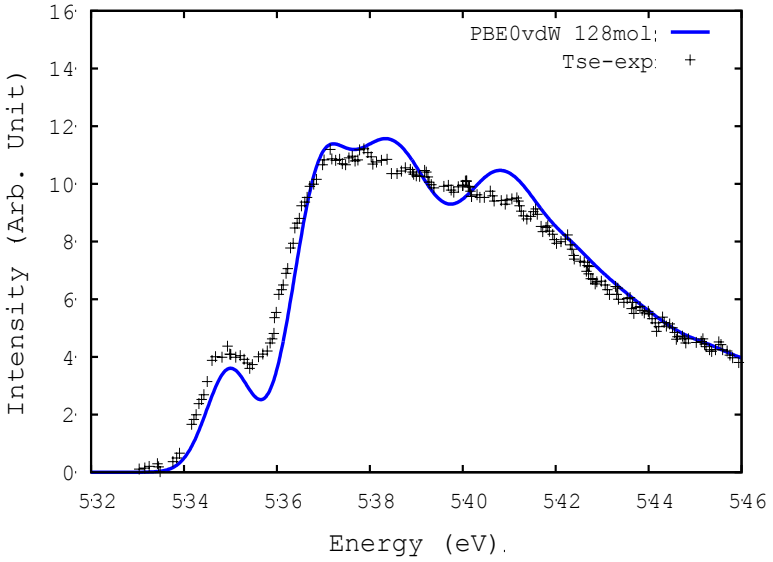

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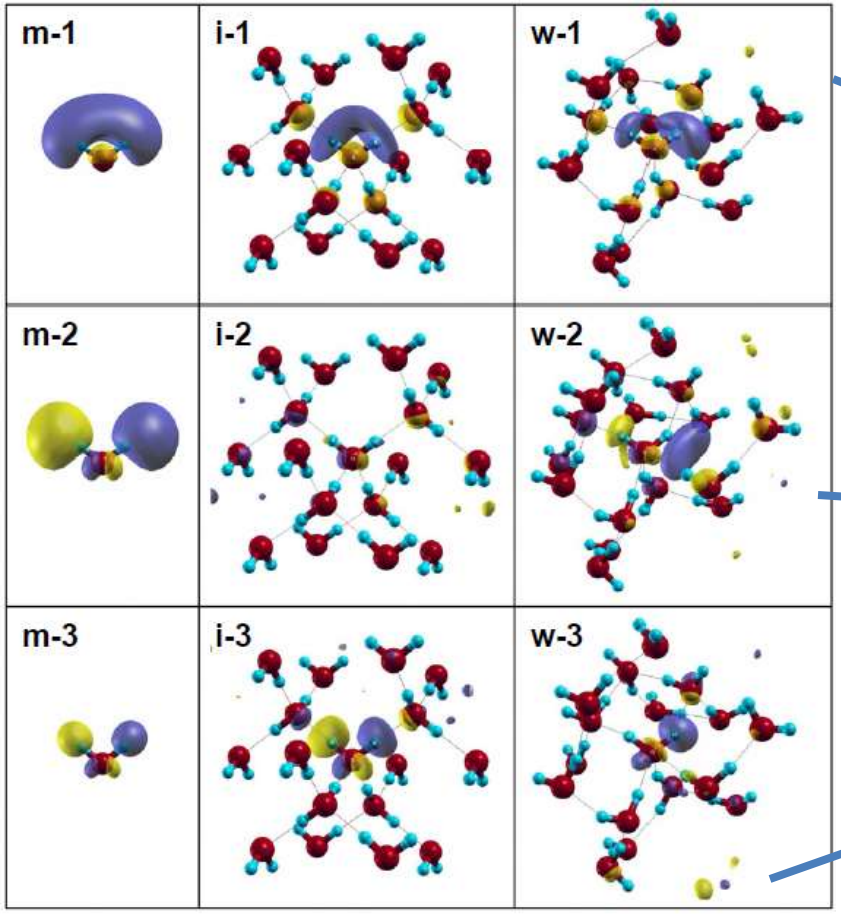
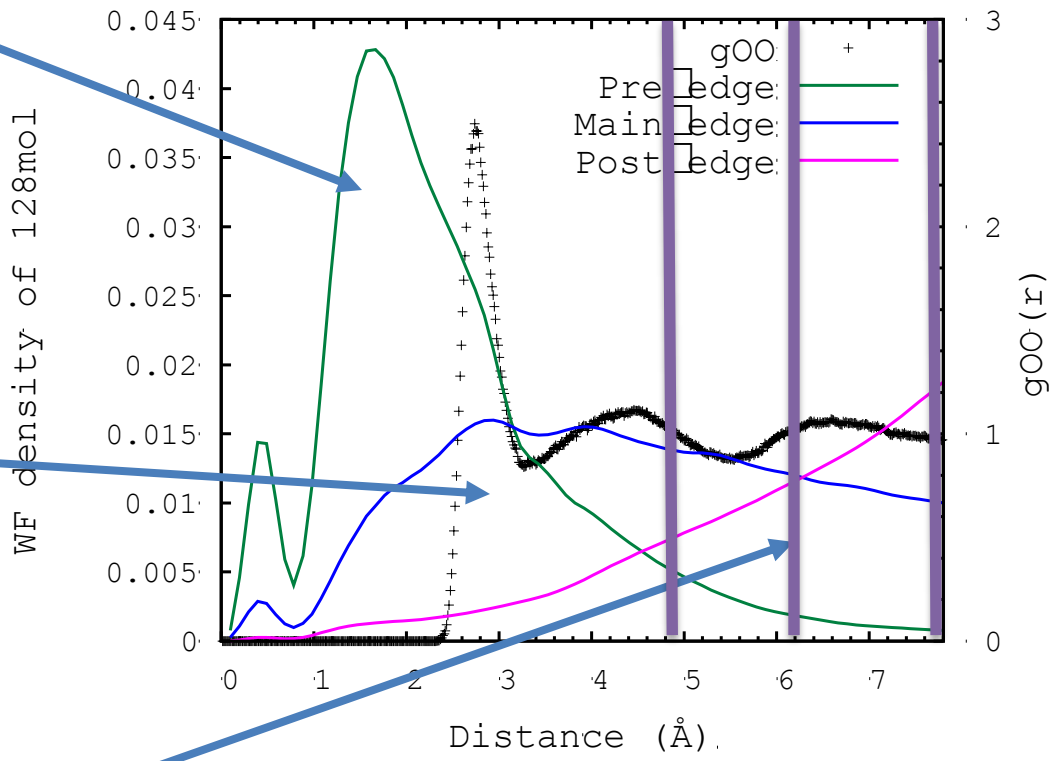
X-ray absorption of liquid water : advanced modeling



32-mol box | 64-mol box | 128-mol box

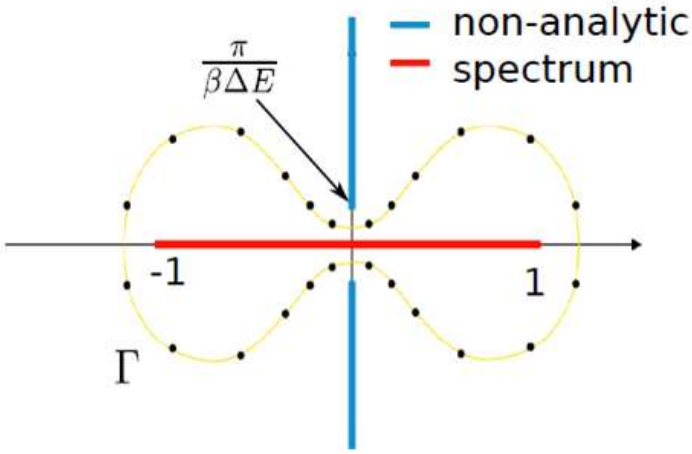


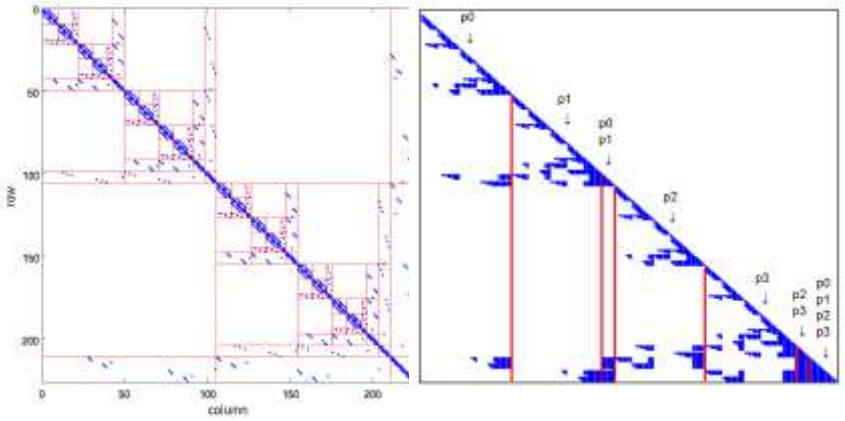
X-ray absorption of liquid water : Summary

- Solve the XAS theoretical modeling in water
- Electron excitation theory is crucial to go beyond the DFT approach
- Self-consistent GW is important to obtain the correct transition matrix
- van der Waals interaction, correction of delocalization error by PBE0, nuclear quantum effect are all important
- Size of modeling the water is also important

PEXSI (Pole Expansion and Selected Inversion)

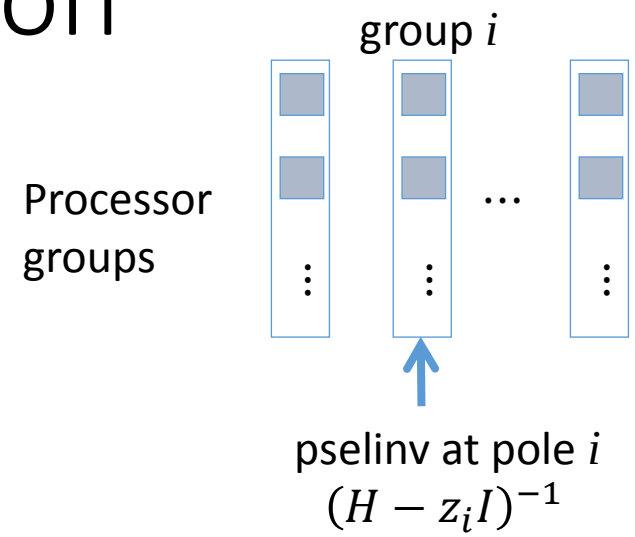
- An efficient way to evaluate electron density $\rho = \mathrm{diag}(XX^*)$, energies and forces without diagonalizing Kohn-Sham Hamiltonian (L. Lin, R. Car, C. Yang, J. Lu, L. Ying, W. E) in ab initio MD simulation
- Pole expansion $XX^* \approx Im\left[\sum_i^M \omega_i (H - z_i I)^{-1}\right]$
- Selected Inversion: compute selected entries of $(H - z_i I)^{-1}$ using sparse matrix techniques.
- Complexity: $O(n_e)$ for 1D, $O\left(n_e^{3/2}\right)$ for 2D, $O(n_e^2)$ for 3D
- Work for both insulators and metals

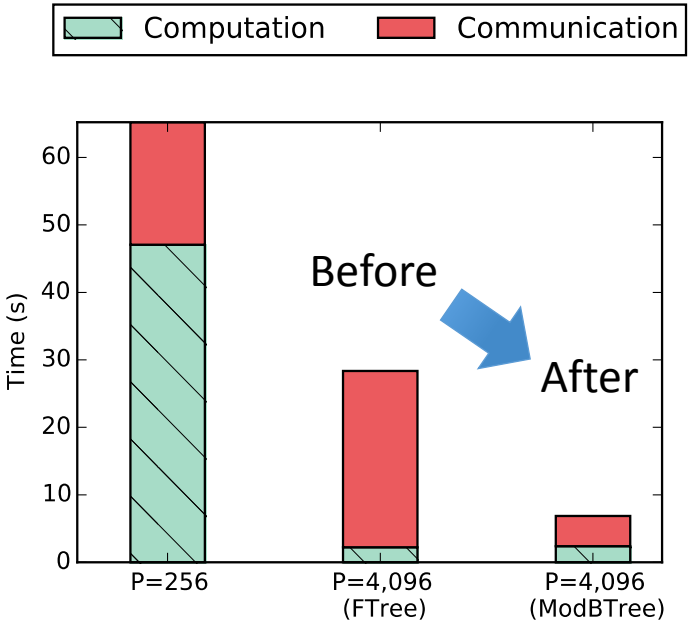




PEXSI Parallelization

- Multi-level parallelism for high performance parallel computation
  - Embarrassing parallelization at the pole level.
  - Elimination tree level parallelism
  - Asynchronous communication
  - Overlap communication with computation
  - Tree-based restricted collective communication

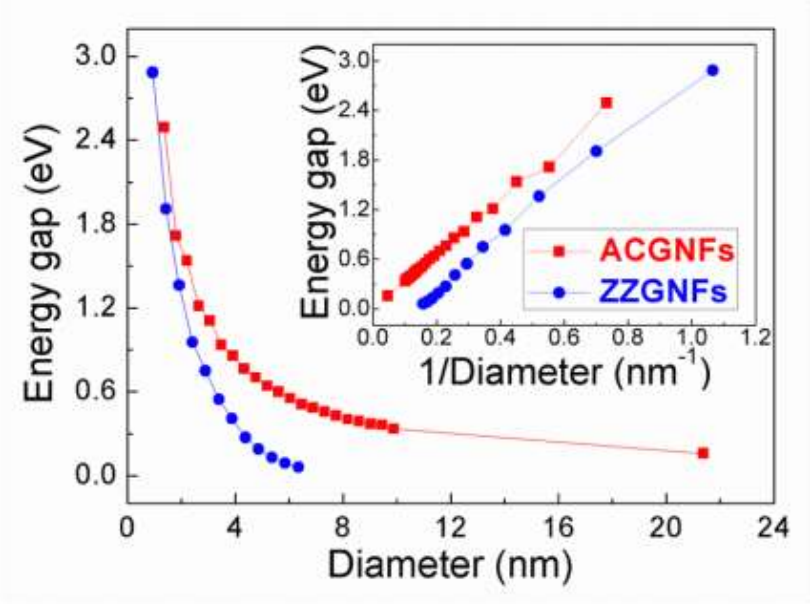




[Jacquelin-Lin-Yang, ACM TOMS, 2015]

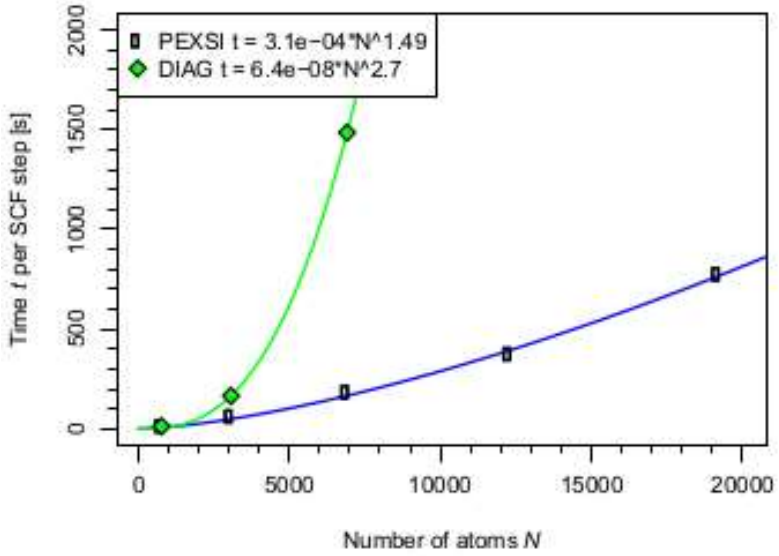
Application

- Electronic structure of large-scale graphene nanoflakes of different edges.
- SIESTA-PEXSI for large system size: 11700 atoms



[Hu-Lin-Yang-Yang, JCP, 2014]

- Integrated with SIESTA, CP2K
- On-going SciDAC collaboration for electronic structure of WTe2 layered systems.



Monolayer graphene
6400 cores used, 256 cores per pole, 50 poles

(http://manual.cp2k.org/trunk/CP2K_INPUT/FORCE_EVAL/DFT/LS_SCF/PEXSI.html)

Poster by Fausto Martelli from Princeton University

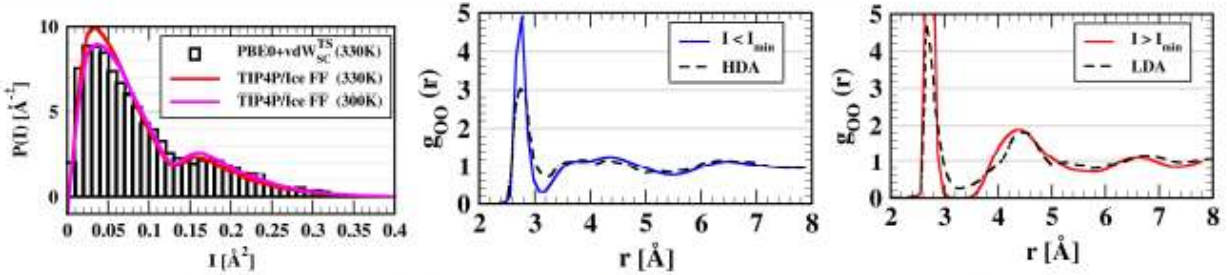


Figure 1 : Left panel: I distribution in the IPES from *ab initio* and model potentials. Middle panel: $g_{OO}(r)$ for low I sites compared to experimental $g_{OO}(r)$ of high density amorphous (HDA) ice. Right panel: $g_{OO}(r)$ for high I sites compared to the experimental $g_{OO}(r)$ of low density amorphous (LDA) ice.

3. Santra, B., DiStasio R. A. Jr., Martelli, F., and Car, R.. *Mol. Phys.*, doi:10.1080/00268976.2015.1058432

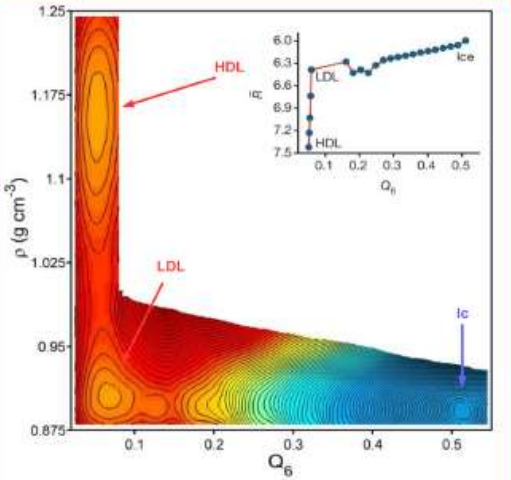


Figure 2 : Free energy plotted vs density and global order parameter Q_6. Simulations used 192 molecules at $T = 228.6$ K and $p = 2.2$ kbar. Q_6 measures angular order. Inset: the average ring length $\bar{R}$ as a function of Q_6.

- Monte Carlo simulations with enhanced sampling techniques show the existence of three basins in the free energy lendscape of deeply supercooled ST2 water: a high density liquid (HDL) basin, a low density liquid (LDL) basin, and a stable cubic ice (Ic) basin[4]. The H-bond network shows a distinct topology, measured by the ring distribution, in each of these three basins.

4. Palmer, J. C., Martelli, F. Liu, Y. Car, R. Panagiotopoulos, A. Z. and Debenedetti, P. G., *Nature*, **510**, 385-388 (2014)

Poster by Hsin-Yu Ho from Princeton University

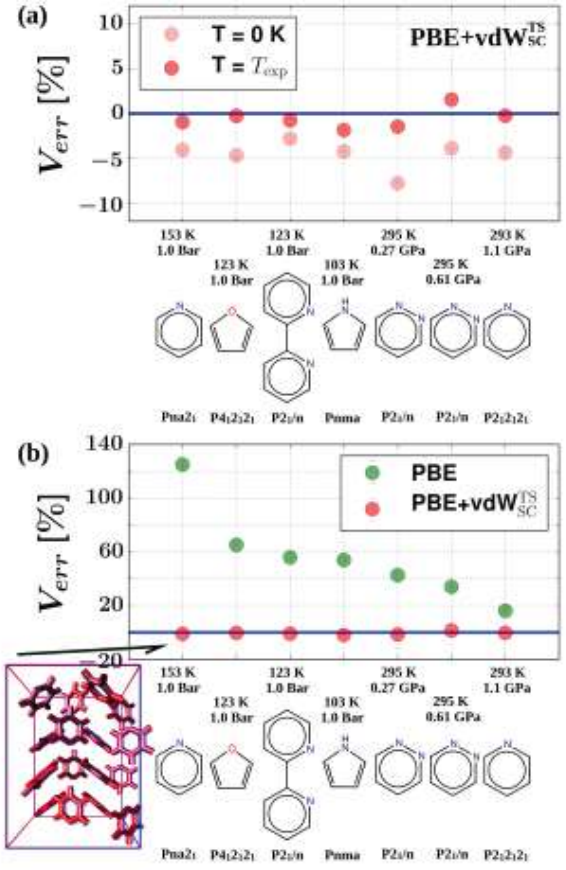


Figure 3: (a) PLMC structures from AIMD at p_{exp} and both $T = 0$ K and $T = T_{exp}$. (b) PLMC structures from AIMD at p_{exp} and T_{exp} with and without vdW. The inset shows an overlay of the calculated equilibrium structure with the experimental X-ray structure.

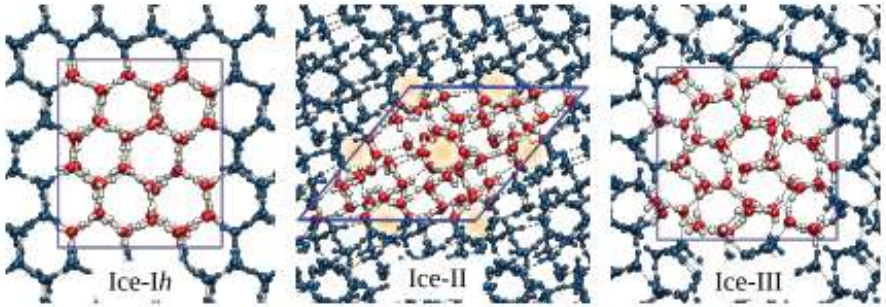


Figure 4: Snapshots of ice I*h*, II, and III at the experimental triple point (0.21 GPa and 238 K).

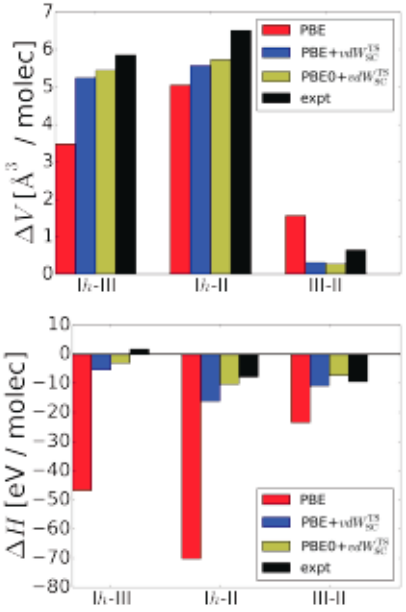


Figure 5: Volume (ΔV) and enthalpy (ΔH) differences between the ice phases at the triple point.

Most recent work

The Phase Diagram of High-Pressure Superionic Ice

Jiming Sun,[1] Bryan K. Clark,[2] Salvatore Torquato,[1,3,4] and Roberto Car*[1,3,4]

[1] *Department of Physics, Princeton University*

[2] *Department of Physics, University of Illinois at Urbana-Champaign*

[3] *Department of Chemistry, Princeton University*

[4] *Princeton Institute for the Science and Technology of Materials*

July 16, 2015

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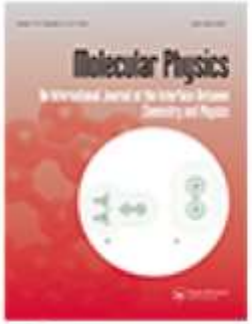

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A systematic study of chloride ion solvation in water using van der Waals inclusive hybrid density functional theory

Arindam Bankura[a], Biswajit Santra[b], Robert A. DiStasio Jr.[b], Charles W. Swartz[a], Michael L. Klein[a] & Xifan Wu[c]

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[b] Department of Chemistry, Princeton University, Princeton, NJ, USA

[c] Department of Physics, Temple University, Philadelphia, PA, USA

Published online: 06 Jul 2015.

Future work

- Nuclear quantum effects on important ions solutions
- Highly parallelized RPA-GW
- OH radical in water
- Thermodynamics of water
- Interfaces of water and functional materials

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- Jimin Sun (Princeton)
- Hsin-Yu Ho (Princeton, Chemistry)

- Esmond Ng (LBL)
- Chao Yang (LBL)
- Lin Lin (UC Berkeley)

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