Many-body effects in the X-ray absorption spectra of liquid water

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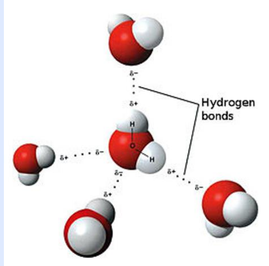

Textbook picture

OR

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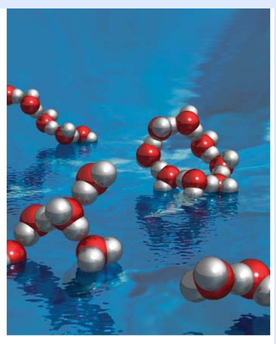


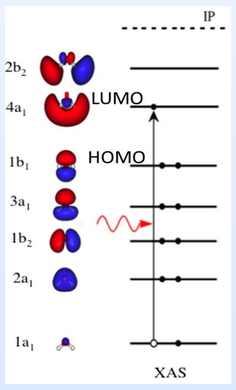
Science **304**, 995-999 (2004)

An intense debate on whether a substantial revision of the standard picture of tetrahedrally bonded water was lasting for 20 years.

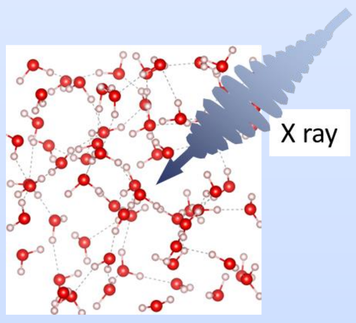
The key to resolve the debate is an accurate ab initio calculation of XAS of water.

The requirement needs accurate modelling of molecular structure and electronic structure.

X-ray Absorption Spectroscopy (XAS)



- XAS: probe the local structure;
- Electrons are excited from core states to the empty states;
- The relative intensity of the features shows a characteristic system dependence;



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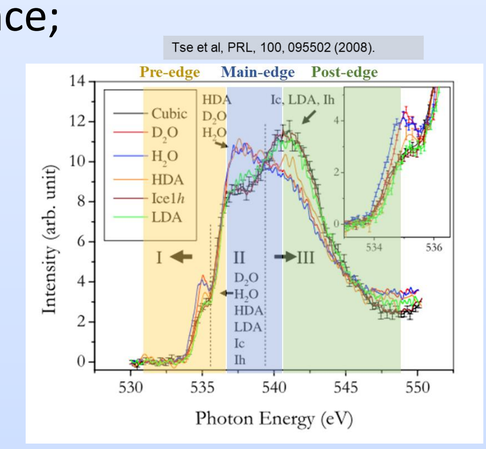
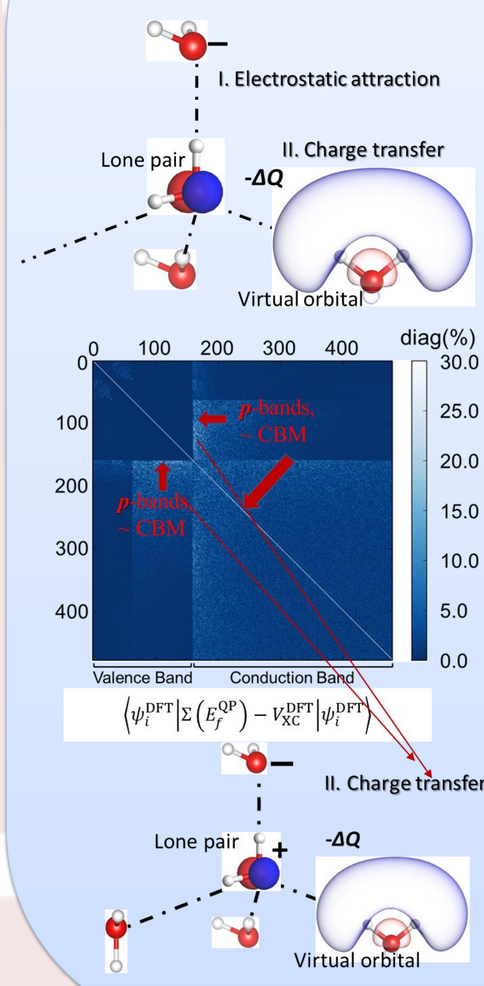


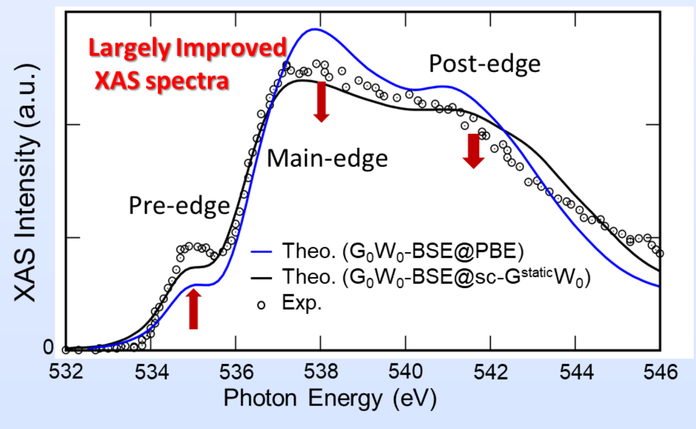
Missing Many-body Effects I: Importance of Self-Consistent QP in Electron-Hole Interaction



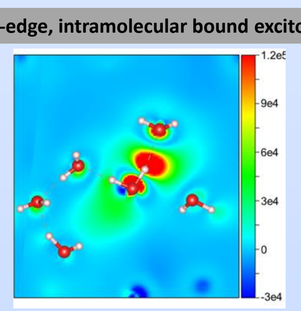
$\left\langle \psi_i^{\mathrm{DFT}} \middle| \Sigma\left(E_f^{\mathrm{QP}}\right) - V_{\mathrm{XC}}^{\mathrm{DFT}} \middle| \psi_i^{\mathrm{DFT}} \right\rangle$

Hydrogen-bond in electronic structure

1. Electrostatic attraction (~80%) (**well described**)
2. Charge transfer (~20%) (**overestimated by delocalized DFT orbitals**)

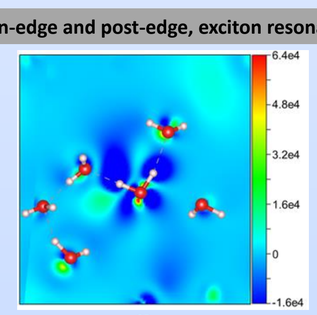


Pre-edge, intramolecular bound exciton



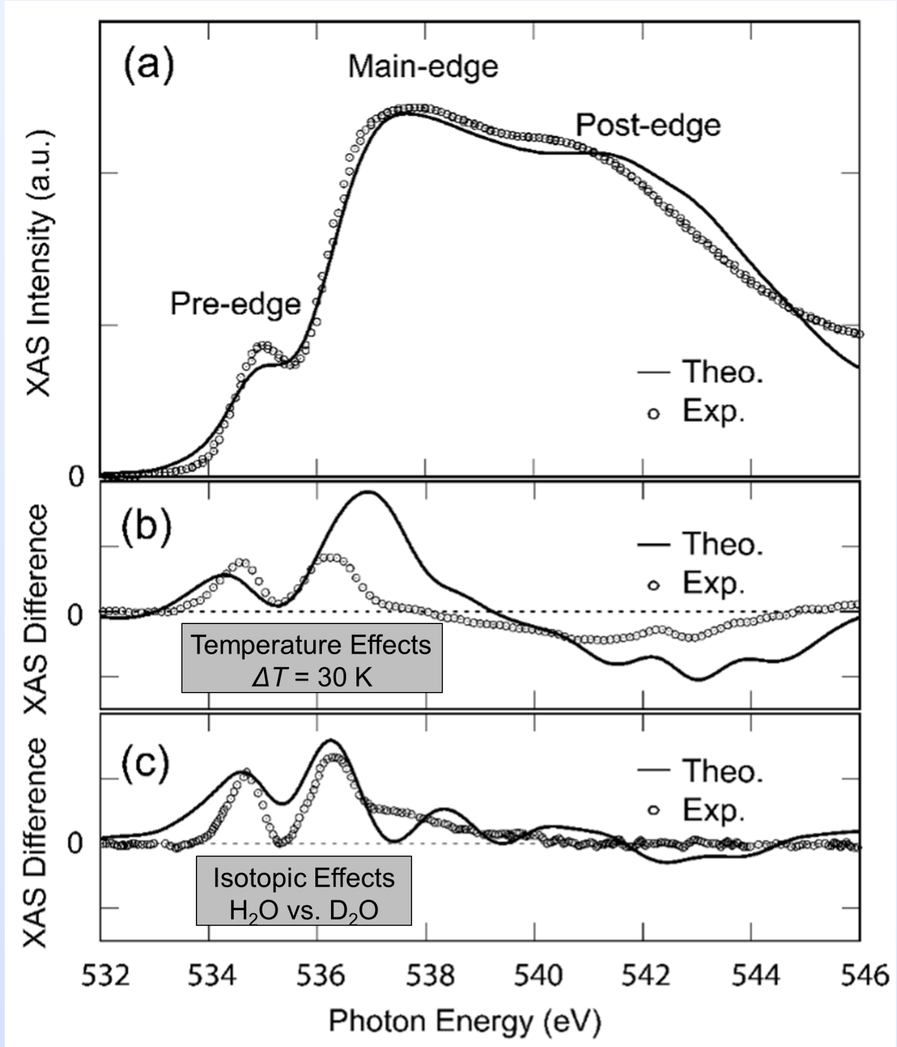
$|\psi_S(r_e,r_h)(\psi_i^{QP})^2 - |\psi_S(r_e,r_h)(\psi_i^{DFT})|^2$

Main-edge and post-edge, exciton resonance state



$|\psi_S(r_e,r_h)(\psi_i^{QP})^2 - |\psi_S(r_e,r_h)(\psi_i^{DFT})|^2$

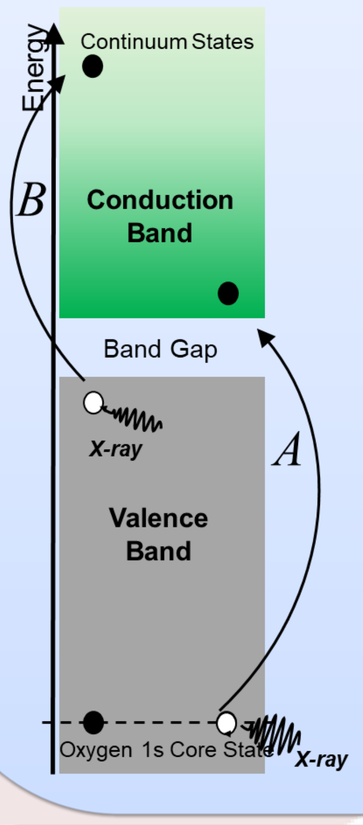
Calculated and Experimental XAS Spectra of Liquid Water



- Good agreement between Exp. and Theo.;
- Delicate effects: Temperature and Isotopic
- The calculation based on PI-DPMD water structure; Less than 10% of HBs is broken

Missing Many-body Effects II: Coupling of Core-Level and Valence-Level Transition in XAS

Soft X-ray: 535 eV – 550 eV



Optical transition in subspace *A*:

- Strong core-hole potential
- Large excitonic effects
- Dominant optical transitions

Optical transition in subspace *B*:

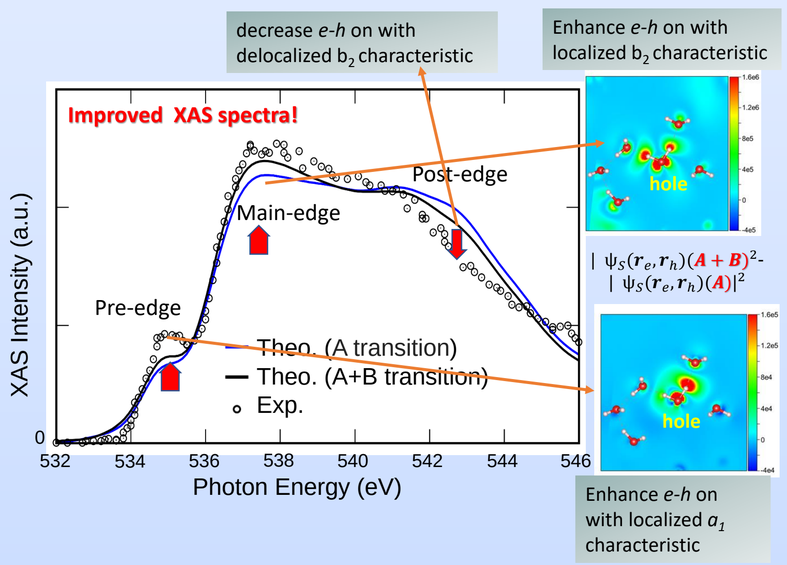
- Valence => lying continuum
- Small excitonic effects
- Neglected previously

Complete Hilbert Space:

$H = A \oplus B$ **Effect need to be checked !**

decrease *e-h* on with delocalized b_2 characteristic

Enhance *e-h* on with localized b_2 characteristic



$|\psi_S(r_e,r_h)(A+B)^2 - |\psi_S(r_e,r_h)(A)|^2$

Enhance *e-h* on with localized a_1 characteristic

Conclusion

Molecular Structure

1. Large cell size
2. Water structure from DeePMD based on PI-AIMD on SCAN0 XC functional
3. Include nuclear quantum effects

Electron-hole Interaction Treatment

1. Quasielectron & quasihole $\psi_i^{\mathrm{QP}} \neq \psi_i^{\mathrm{DFT}}$

Solution: self-consistent ψ_i^{QP}

2. Complete Hilbert Space: $\mathcal{H} = \mathcal{A} \oplus \mathcal{B}$

Solution: S-approximation by downfolding method

The emerging picture of the water structure is fully consistent with the conventional tetrahedral model.

References

1. F. Tang et al. *Proc. Natl. Acad. Sci.*, **2022**, 119, e2201258119.
2. P. Wernet et al., *Science* **2004**, 304, 995–999.