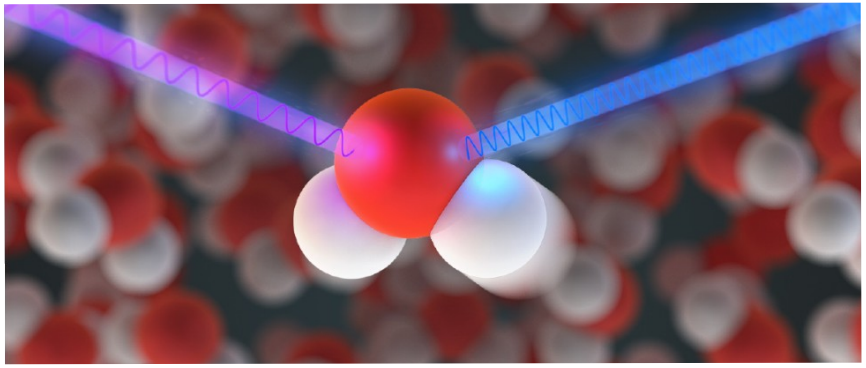
First-principles modeling of RIXS in liquid water:

Core-excited nuclear dynamics and the distribution of local potential energy surfaces



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Acknowledgments

Theory

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Calculations run on resources from The Swedish National Infrastructure for Computing (SNIC)

Experiment

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Alexander Föhlisch

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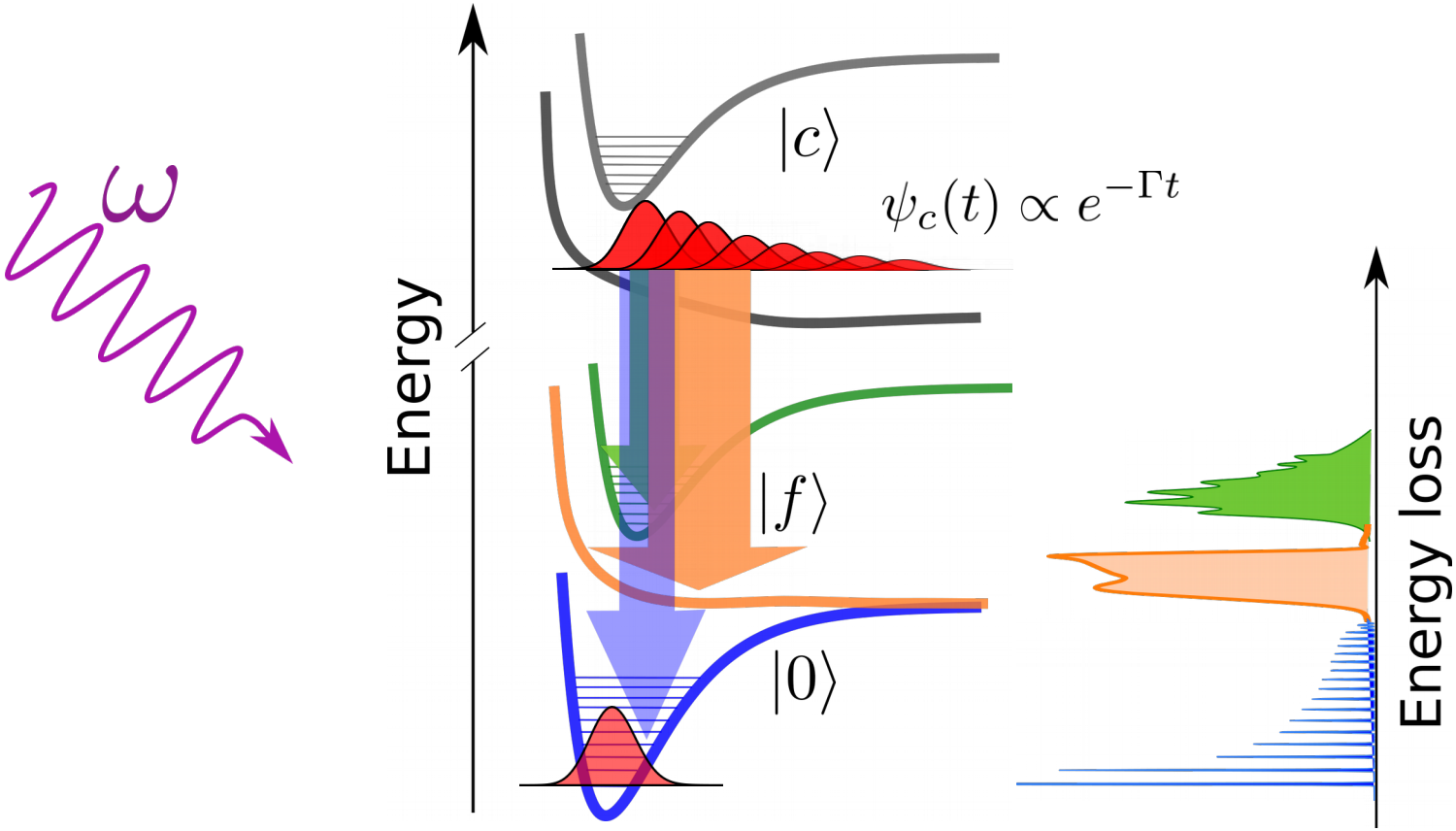
Thorsten Schmitt

Measurements done at the ADDRESS Beamline at PSI

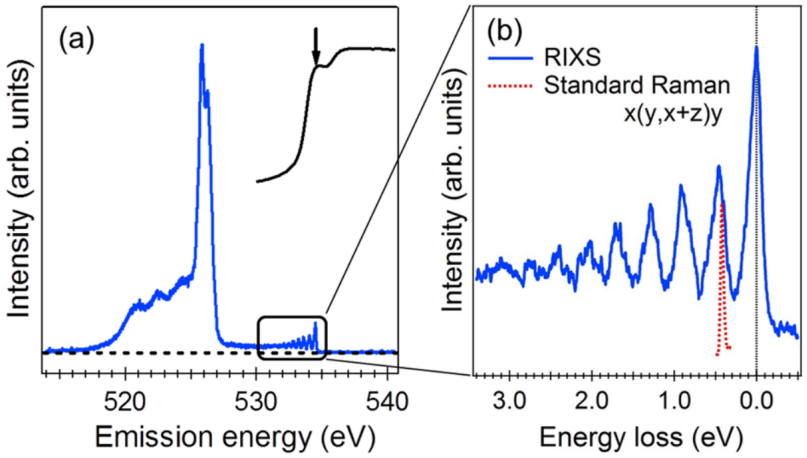
Outline

- Introduction.
- Theoretical Model.
- Core-excited dynamics in liquid water.
- Vibrational RIXS and HB strength in water.
- The splitting of the $1b_1$ resonance.
- Summary.

Schematic description of RIXS



Earliest measurements of water

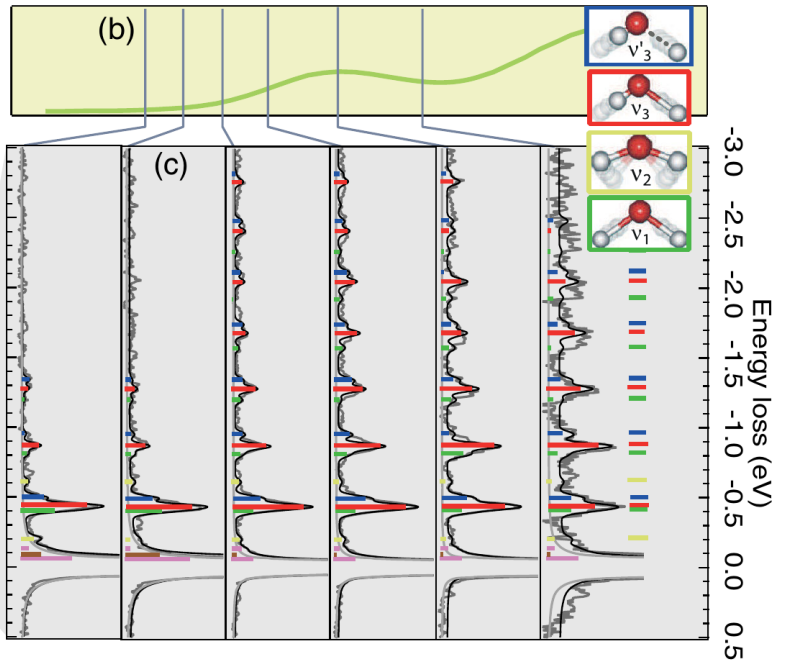


Harada *et al.* Phys. Rev. Lett., 111,193001 (2013).

- *"The monotonic reduction of the energy separation between the various overtones can be explained by assuming a simple Morse function for the ground state potential surface."*
- *"For H2O and D2O* $v_{0\rightarrow 1}$ *coincides closely with the energy of the stretching vibrational mode of gas-phase water rather than that of liquid water, clearly indicating the contribution to the XAS pre-edge peak of molecules with a highly weakened or broken donating H-bond."*

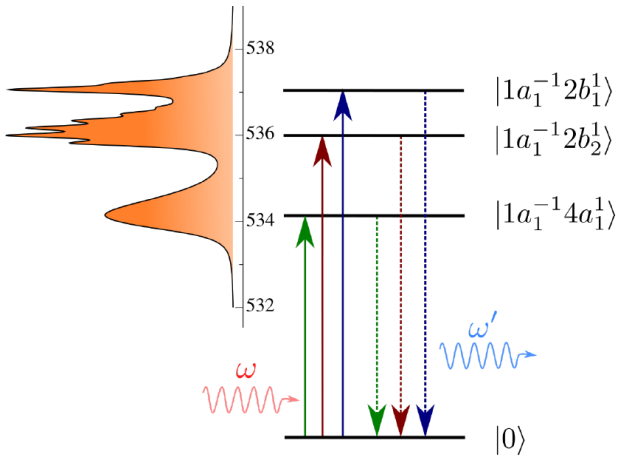
Earliest measurements of water

- *"The profile of the vibrational peaks gets broader with larger energy loss."*
- *"The peak maximum positions, however, correspond to those of the asymmetric stretch mode of liquid water"*
- *"… we observe the presence of an additional mode which we assign to H-O---H molecules where one OH bond has lost its covalency due to bond elongation."*



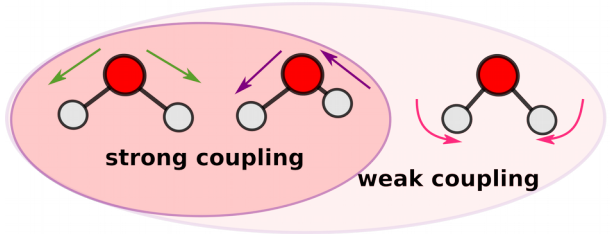
Pietzsch *et al.* Phys. Rev. Lett., 114, 88302 (2015).

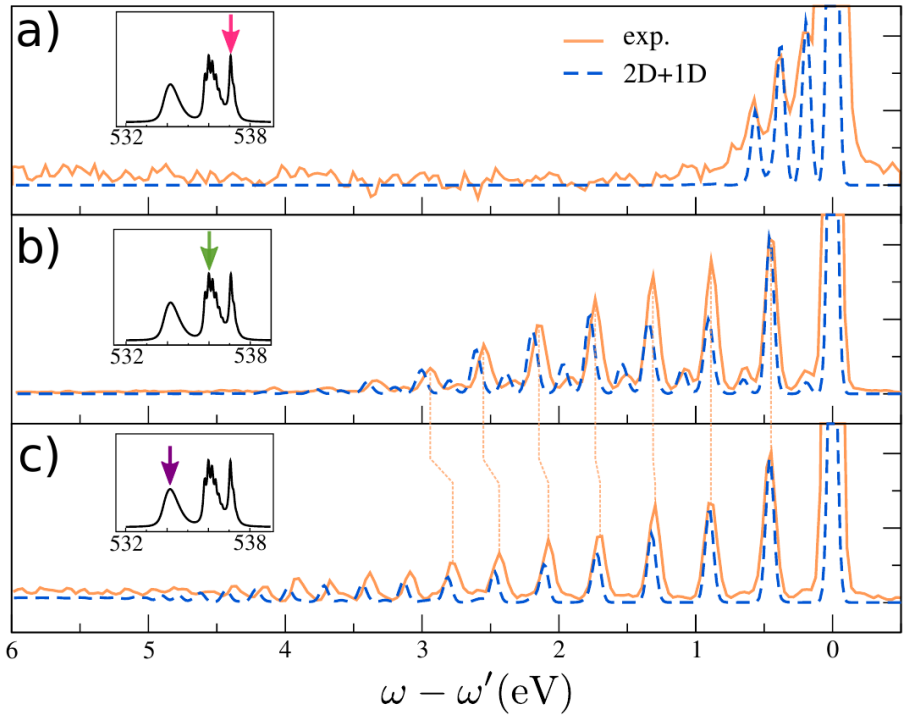
Gas-phase data weighs in!



Nuclear degrees of freedom

$\omega_s = 0.453$ eV $\quad \omega_a = 0.466$ eV $\quad \omega_b = 0.198$ eV





RASPT2 potential energy surfaces
2D+1D Quantum wave packet model

V. Vaz da Cruz *et al* PCCP **19**, 19573 (2017).
R.C. Couto *et al* Nature Communications, **8**, 14165 (2017)

Main questions for the theory

1. Does O1s pre-edge RIXS probe **only** a sub-set of molecules with **weak/broken hydrogen bonds**?

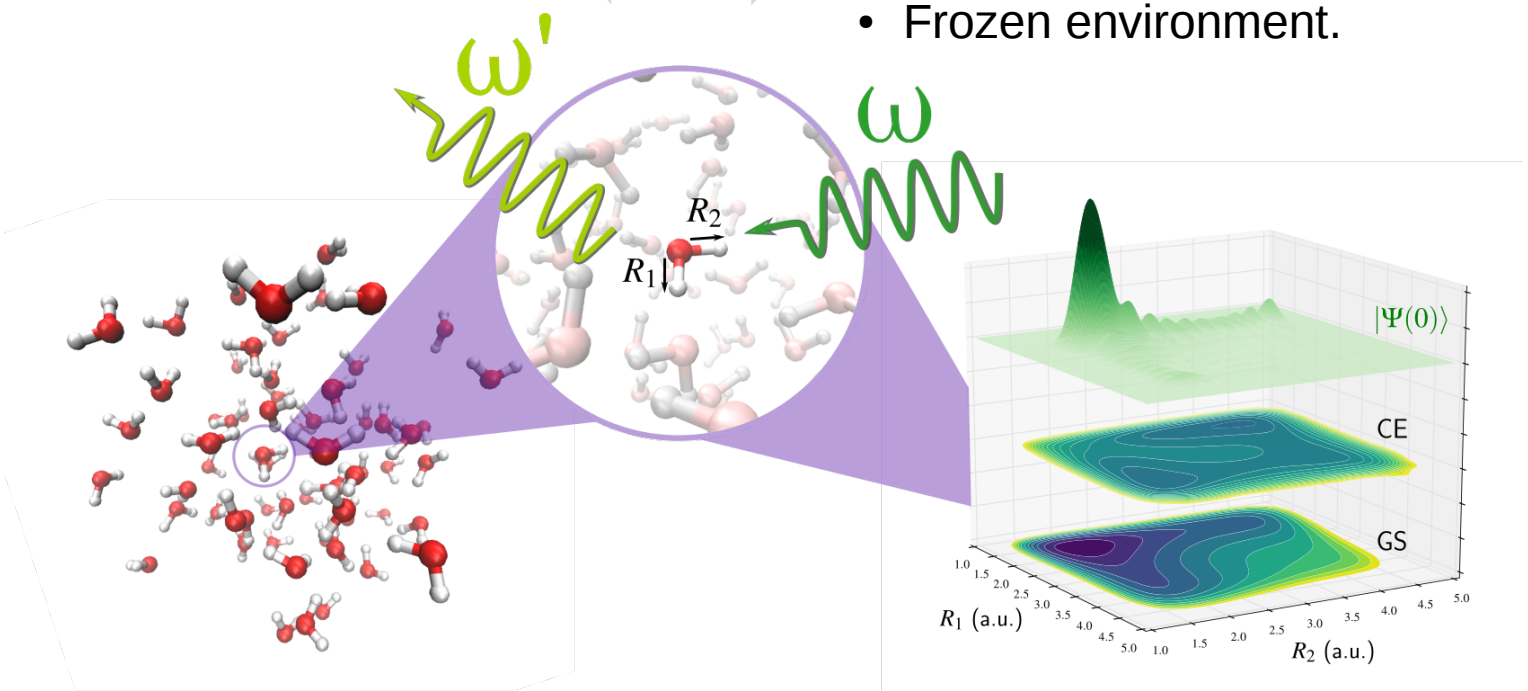
2. Can the vibrational progression in liquid water be explained by a simple **Morse potential,** a **normal-mode** fit, or even a **gas-phase** model?

3. Is the associated channel to the **$1b_1$ electronic state** a reliable probe of **local structure** and **hydrogen bonding**?

Proposed Model of Bulk Liquid Water

- **Ab-initio molecular dynamics.**[a)]
  - CPMD package.
  - DFT/BLYP (plane waves).
  - 64-molecule cluster with PBC.

- **Quantum wave packet dynamics**
  - eSPec code (developed by us).
  - 1D potential scans along each bond.
  - DFT potentials.
  - XCH transition dipole moments.
  - Frozen environment.



a) Similar to: M. Odelius J. Phys. Chem. A, **113**, 8176-8181 (2009)

Details of the Quantum Model

Hamiltonian:

$$h^k = -\frac{1}{2\mu}\frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu}\frac{\partial^2}{\partial R_2^2} - \frac{\cos\theta_{eq}}{m_O}\frac{\partial^2}{\partial R_1 R_2} + V_k(R_1, R_2, \theta_{eq}),$$

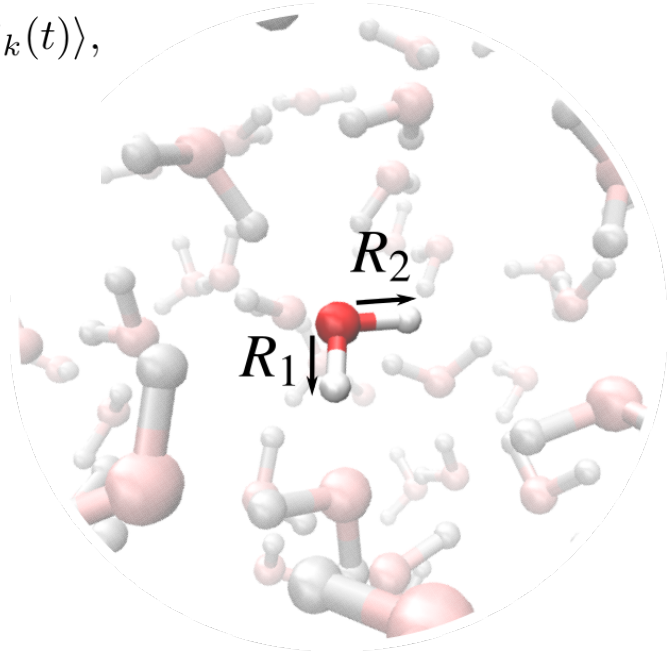
$$V_k(R_1, R_2, \theta_{eq}) = V_k(R_1, R_{eq}, \theta_{eq}) + V_k(R_{eq}, R_2, \theta_{eq}) - V_k(R_{eq}, R_{eq}, \theta_{eq}),$$

Individual cross-sections:

$$\sigma_k(\omega, \omega') = \frac{1}{\pi}\mathrm{Re}\int_0^\infty dt\ e^{\imath(\omega-\omega'-\omega_{f0}^k+\epsilon_0^k+\imath\Gamma)t}\langle\Psi_k(0)|\Psi_k(t)\rangle,$$

$$|\Psi_k(0)\rangle = \int_0^\infty dt\ e^{\imath(\omega-\omega_{i0}^k+\epsilon_0^k+\imath\Gamma)t}|\psi_k(t)\rangle\ ,$$

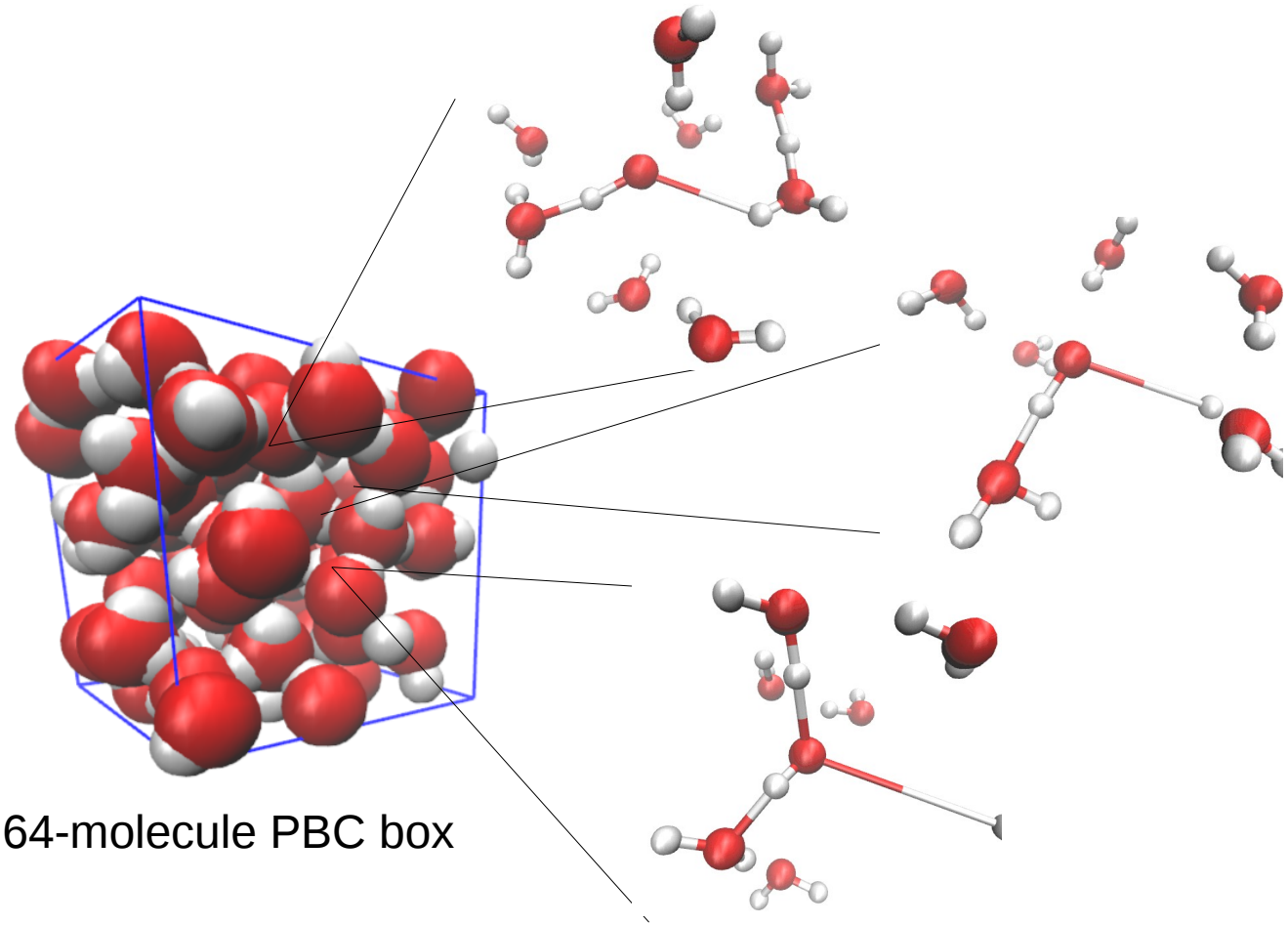
$$|\psi_k(t)\rangle = e^{-\imath h_i^k t}|0_k\rangle, \quad |\Psi_k(t)\rangle = e^{-ih_f^k t}|\Psi_k(0)\rangle$$



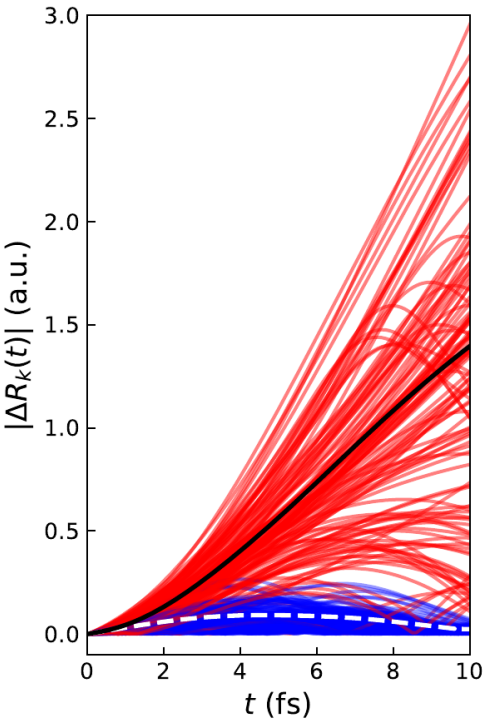
Liquid phase cross-section

$$\sigma_{liq}(\omega', \omega) \approx \overline{\sigma}(\omega', \omega) = \sum_{k=0}^{64}(\mathrm{d}_{i,0}^k)^2(\mathrm{d}_{f,i}^k)^2\sigma_k(\omega', \omega)$$

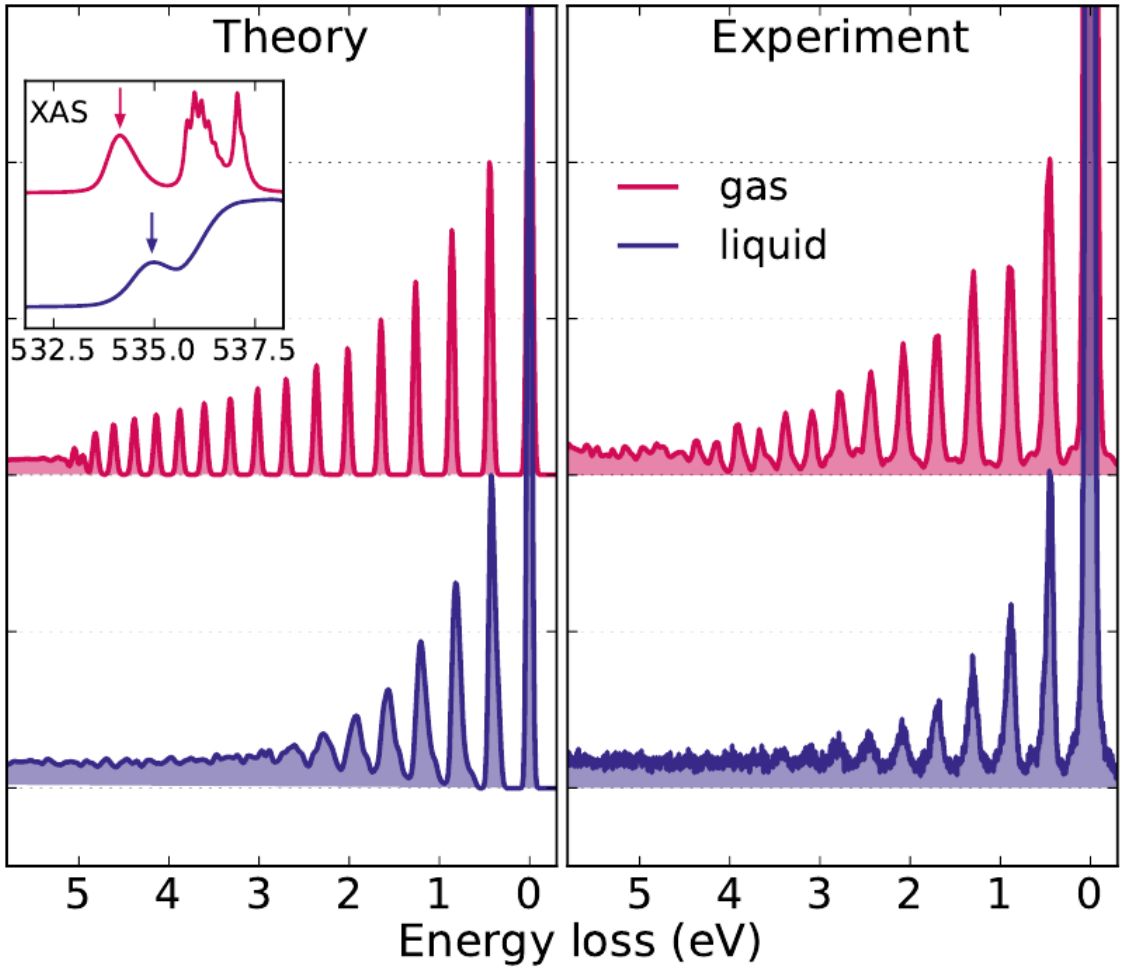
What happens upon excitation at the O1s pre-edge?



64-molecule PBC box



Calculated RIXS spectra for gas and liquid

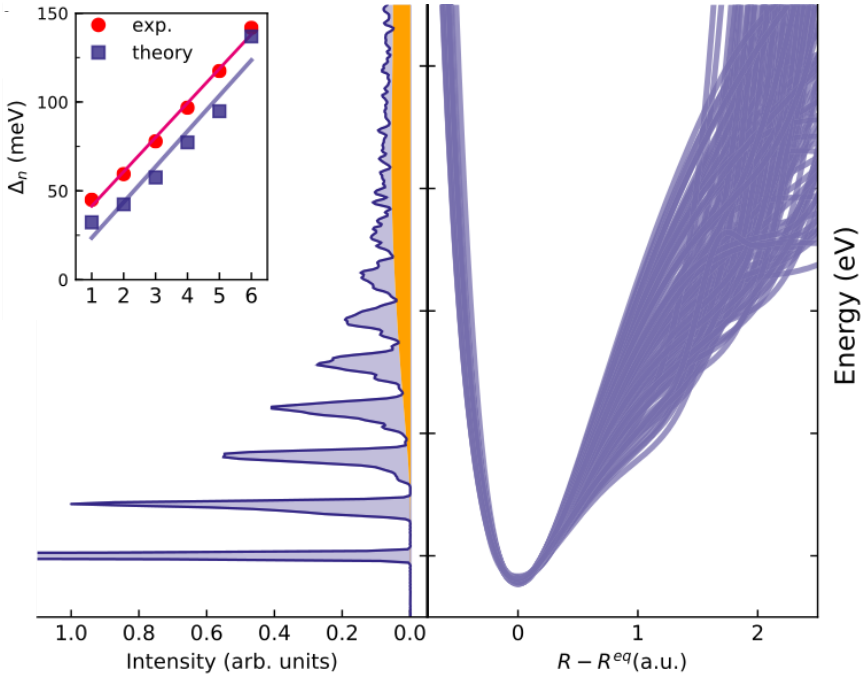


- Gas and Liquid phase have similar peak positions.
- Shortening of the vibrational progression in the liquid and formation of a background in the > 3 eV region.

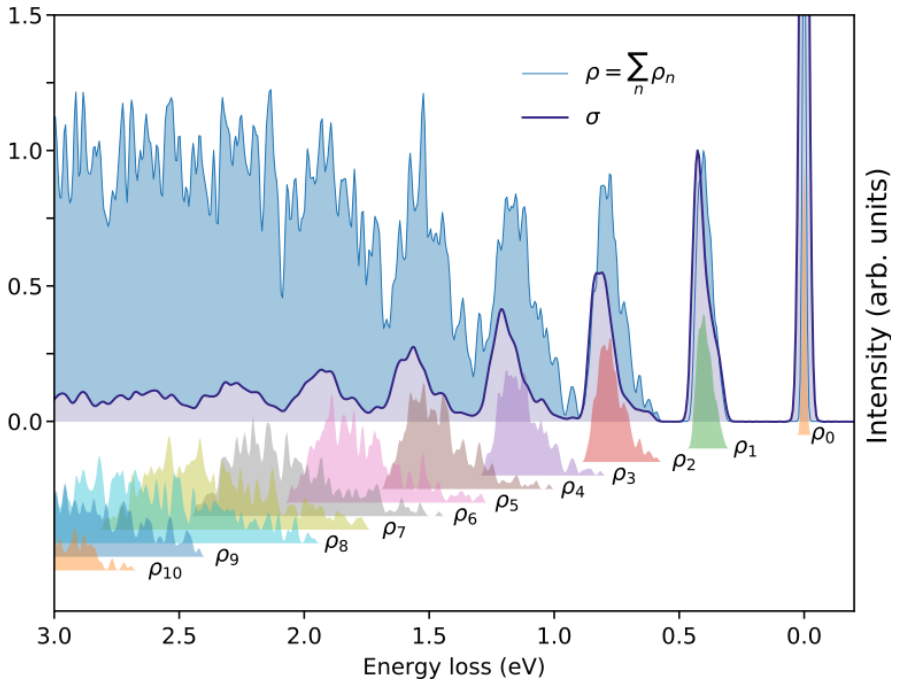
Vaz da Cruz *et al.* Nat. Commun., **10**, 1013 (March. 2019).

Formation of the smooth background

DFT/BLYP
XCH potentials



$$\rho_m(\epsilon) = \sum_{k=1}^{64} \sum_{n_1+n_2=m} \Phi(\epsilon - \epsilon^k_{n_1,n_2} + \epsilon^k_{0,0})$$



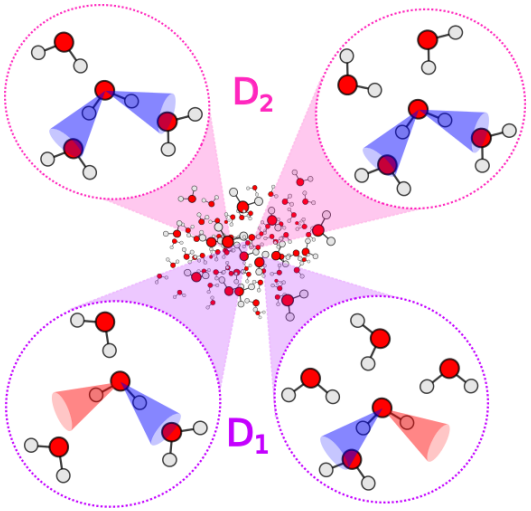
Peak width increases
High energy part is smeared out

Strong overlap between the partial densities of states

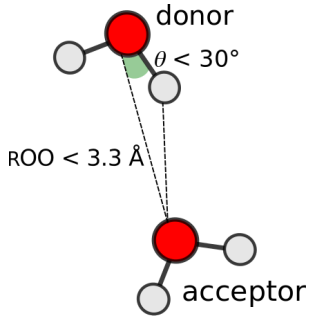
Vaz da Cruz *et al.* Nat. Commun., **10**, 1013 (March. 2019).

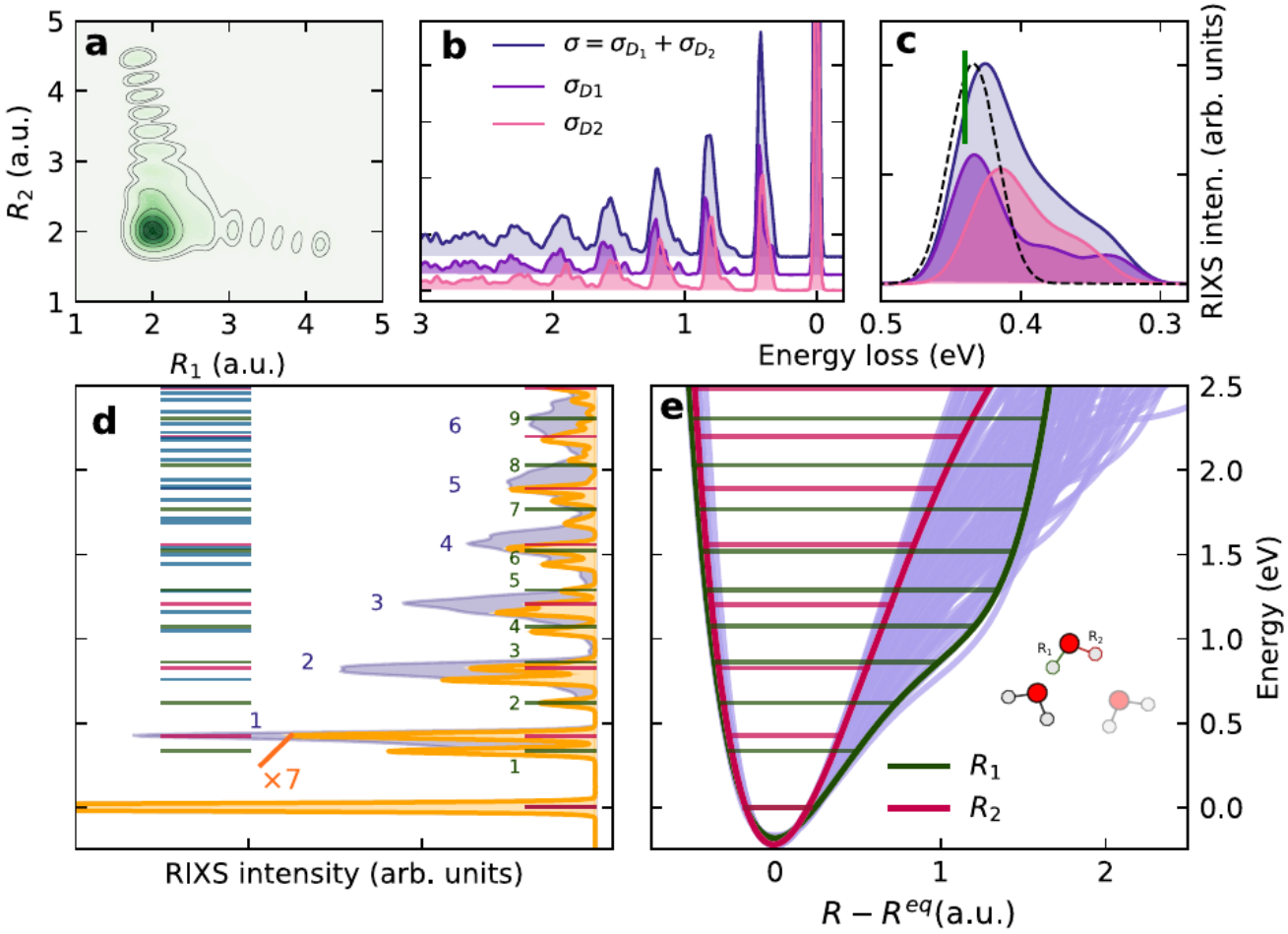
Role of inequivalent bonds

Local structures



HB definition



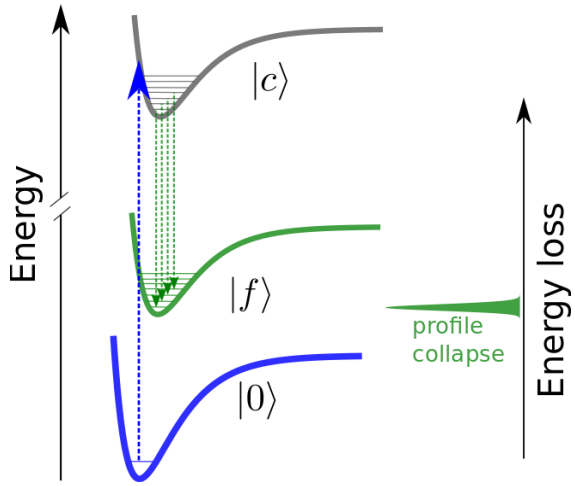


Vaz da Cruz *et al.* Nat. Commun., **10**, 1013 (March. 2019).

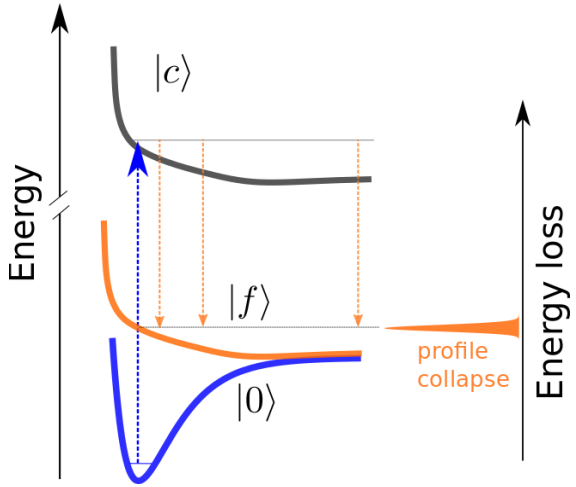
The $1b_1$ splitting at the pre-edge

Atomic peaks revisited

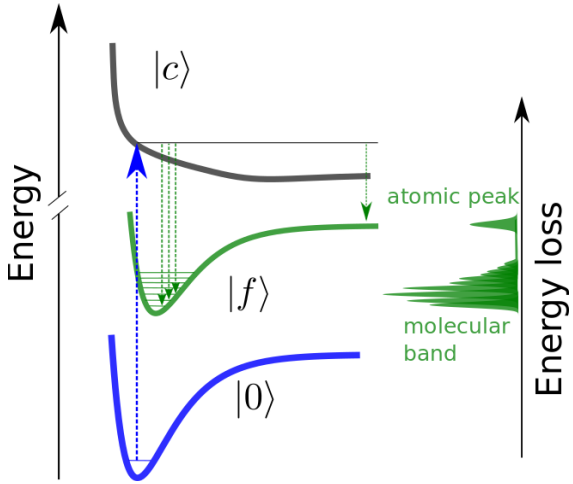
Case 1



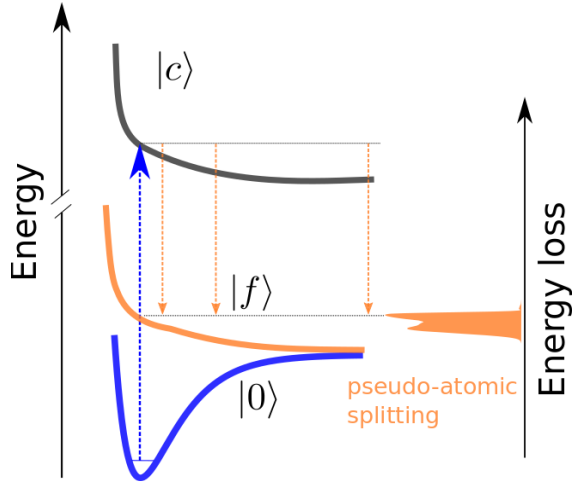
Case 2



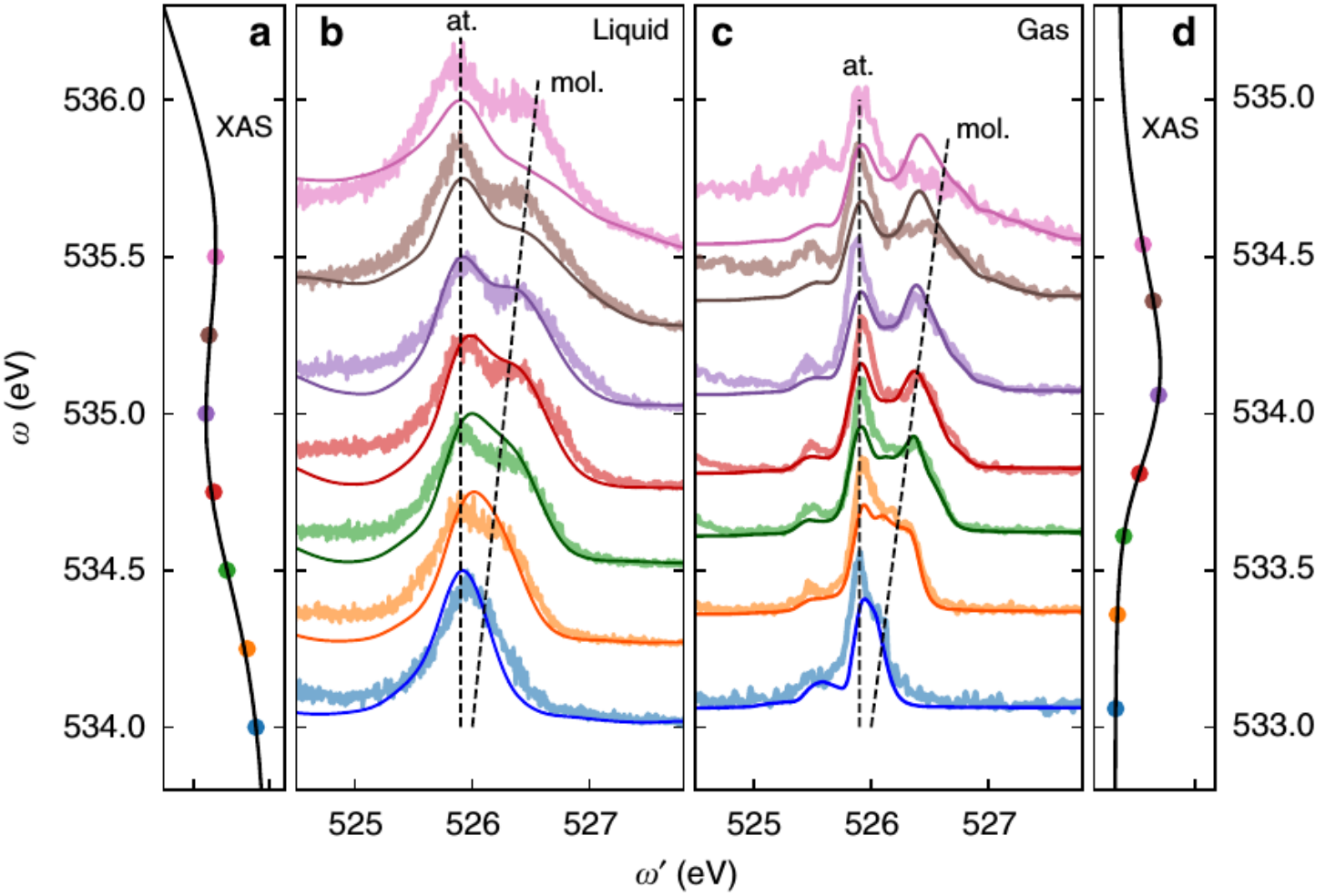
Case 3



Case 4



The emergence of the $1b_1$ split-peak



Vaz da Cruz *et al.* Nat. Commun., **10**, 1013 (March. 2019).

For more details on the split peak and the structure of water...

PNAS

Compatibility of quantitative X-ray spectroscopy with continuous distribution models of water at ambient conditions

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Niskanen *et al.* PNAS, **116**, 4058 (March. 2019).

Summary

- We have found that a broad distribution of local structures is probed at the O1s pre-edge of liquid water.
- The differences between the progression in gas-phase and liquid reflect the variations in local HB environment.
- The core-excited ultra-fast dynamics is an effective probe of hydrogen-bonds strength of in liquid water via the distribution of potential energy surfaces accessed.
- The $1b_1$ split-peak is caused by nuclear dynamics, however it is formed by transitions close to the equilibrium geometry being much less sensitive to hydrogen bonding.

Thank you!