First-principles modeling of RIXS in liquid water: Core-excited nuclear dynamics and the distribution of local potential energy surfaces

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Measurements done at the ADDRESS Beamline at PSI

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

\[ \psi_c(t) \propto e^{-\Gamma t} \]
Earliest measurements of water

- “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 $v_{0-1}$ 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.”

Gas-phase data weighs in!

Nuclear degrees of freedom
\[ \omega_s = 0.453 \text{ eV} \quad \omega_a = 0.466 \text{ eV} \quad \omega_b = 0.198 \text{ eV} \]

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.**
  - 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.

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Details of the Quantum Model

**Hamiltonian:**

\[
\hbar \dot k = -\frac{1}{2\mu} \frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu} \frac{\partial^2}{\partial R_2^2} - \frac{\cos \theta_{eq}}{m_0} \frac{\partial^2}{\partial R_1 \partial R_2} + V_k(R_1, R_2, \theta_{eq}),
\]

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

**Individual cross-sections:**

\[
\sigma_k(\omega, \omega') = \frac{1}{\pi} \Re \int_0^\infty dt \ e^{i(\omega - \omega' - \omega_{k0} + \epsilon_0^k + i\Gamma)t} \langle \Psi_k(0) | \Psi_k(t) \rangle,
\]

\[
|\Psi_k(0)\rangle = \int_0^\infty dt \ e^{i(\omega - \omega_{k0} + \epsilon_0^k + i\Gamma)t} |\psi_k(t)\rangle,
\]

\[
|\psi_k(t)\rangle = e^{-i\hbar^k t} |0_k\rangle, \quad |\Psi_k(t)\rangle = e^{-i\hbar^k t} |\Psi_k(0)\rangle
\]

**Liquid phase cross-section**

\[
\sigma_{liq}(\omega', \omega) \approx \sigma(\omega', \omega) = \sum_{k=0}^{64} (d^k_{i,0})^2 (d^k_{f,i})^2 \sigma_k(\omega', \omega)
\]
What happens upon excitation at the O1s pre-edge?
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.
Formation of the smooth background

DFT/BLYP XCH potentials

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

Peak width increases
High energy part is smeared out

Strong overlap between the partial densities of states

Role of inequivalent bonds

Local structures

HB definition

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

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

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

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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!