Directional cuts through potential energy surfaces

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Describes energy of molecule in terms of its structure

Equilibrium points well known: Static molecule in ground state (ball and stick model)

Excitation: what happens in-between?

- Dynamics on PES control rate and selectivity
- Detailed info on PES needed!
Sub natural linewidth RIXS

RIXS process

\[ \omega - \omega' = \Delta \omega_{\text{loss}} \]
\[ \Delta \omega_{\text{loss}} = \omega_{\text{vib}} + \omega_{\text{elec}} \]

"Sub-natural linewidth Resonant inelastic X-ray scattering (RIXS)"

Currently only at ADRESS/SLS

Vibrational progression – cut through potential energy surface!
liquid acetone: the potential along the C-O bond

Morse fit: potential along C=O bond
- Shows behavior further away from equilibrium
- 1D cut

Active sites interacting with the fluctuating solvent network

isolated small molecule

REALITY (very often)

fluctuating bonding networks, solution....

? Potential energy surface along interaction coordinate
Azeotrope aceton-chloroform mixture

- Hydrogen bond weakens the C-O potential
- Quantitative plot

A fluctuating Hydrogen bonded network: liquid water

Liquid water:
Bonding network anomalies
coordination and correlation
structure: controversial

The water molecule
3-atomic molecule
3 normal modes

- Asymmetric stretch
- Symmetric stretch
- Bend
Core excitation

Coherent excitation of both OH bonds
Directional excitation within molecular H$_2$O

Directional excitation within molecular H$_2$O

Directional excitation within molecular H$_2$O

Directional excitation within molecular H₂O

Directional excitation within molecular H$_2$O


bend     stretch
Directional potential cuts in isolated H$_2$O molecule


3 different RIXS resonances – 3 directional cuts along the normal coordinates
How does the H2O molecular potential change in the liquid?

Single molecular potential

J. Niskanen et al., submitted to PNAS
Excitation on pre peak

Compare to calculations

Reconstruct with Morse potential
✓ Matches well
✓ Fits well to calculations

Excitation on pre peak

Compare to calculations

Morse reconstruction not working for liquid
Excite both (different) OH bonds

Coherent excitation of **both** OH bonds

→ In liquid often very different bonds!

V. Vaz da Cruz et al., Nat. Commun. 10, 1013 (2019)
Excite both (different) OH bonds

Single molecule spectrum!

V. Vaz da Cruz et al., Nat. Commun. 10, 1013 (2019)
Excite many molecules

Many different molecules due to local environment (H-bond network)

Overlap of partial density of states $\rho$

$\rightarrow$ Breakdown 1-to-1 correspondence of eigenvalue to vibrational peak!
Liquid water is not straightforward!

**Gas**
- Isolated molecule
- Symmetric structure
- 3 normal vib modes
→ 1 PES
- Morse reconstruction works

**Liquid**
- Surrounded by other molecules
- Assymetry due to local environment
- Coherent excitation of 2 very different OH bonds
→ Set of PES
- Morse reconstruction gives steep limit
- Steep potential: weak H bond
- Shallow potential: strong H bond
→ Breakdown 1-to-1 correspondence for eigenvalue to vib peak (width)

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V. Vaz da Cruz et al., Nat. Commun. 10, 1013 (2019)
Summary

Sub natural linewidth RIXS

✓ Maps potential energy surfaces
✓ Cuts along interaction coordinates

In liquid water

✓ Coherent excitation into 2 different OH bonds
✓ Calculations give set of PES
✓ Morse reconstruction: limit of weak H-bond
✓ Startpoint for PES reconstruction where calculations too expensive

✓ Soon possible even at METRIXS@BESSY!
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CALL FOR APPLICATIONS:
Beating the Complexity of Matter through the Selectivity of X-rays
16 – 20 September 2019, Magnus Haus, Berlin-Mitte

DYNAMIC PATHWAYS IN MULTIDIMENSIONAL LANDSCAPES

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One center in a complex material?

Kaolinite clay

$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
Complex systems: O-H in Kaolinite

E. Ertan et al., PRB 95, 144301 (2017)
Elongated bond induces rotation
→ Effect of environment

E. Ertan et al., PRB 95, 144301 (2017)
Excitation on pre peak

Liquid water PES
Steeper than gas
Core excited state dynamics?

**RIXS Inherent temporal component**

Scattering duration time:

$$\tau^2 = \frac{1}{(\Omega^2 + \Gamma^2)}$$

- **Detuning**
  $$\Omega = \omega - \omega_{\text{res}}$$

→ Shortens scattering duration time

Liquid acetone O K-edge

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*Pietzsch et al., PRL 106, 153004 (2011)*

Where does it lead to?

? resolution

Interaction with surrounding
→ additional dipolar broadening $\gamma_s$:

$$\gamma_s \propto \Delta \mu_f \cdot \mu_s$$

*(dipole moments of solute and solvent)*

$$\Delta \mu_f = \mu_{final} - \mu_0$$

In sub natural linewidth RIXS:
Final state = ground state
$\Delta \mu_f = 0 \rightarrow \gamma_s = 0$

Set by
✓ x-ray optics
✓ Source properties