Directional cuts through potential energy surfaces

ANNETTE PIETZSCH
Helmholtz-Zentrum Berlin

IXS conference June 2019

Potential energy surfaces

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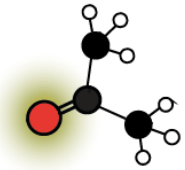
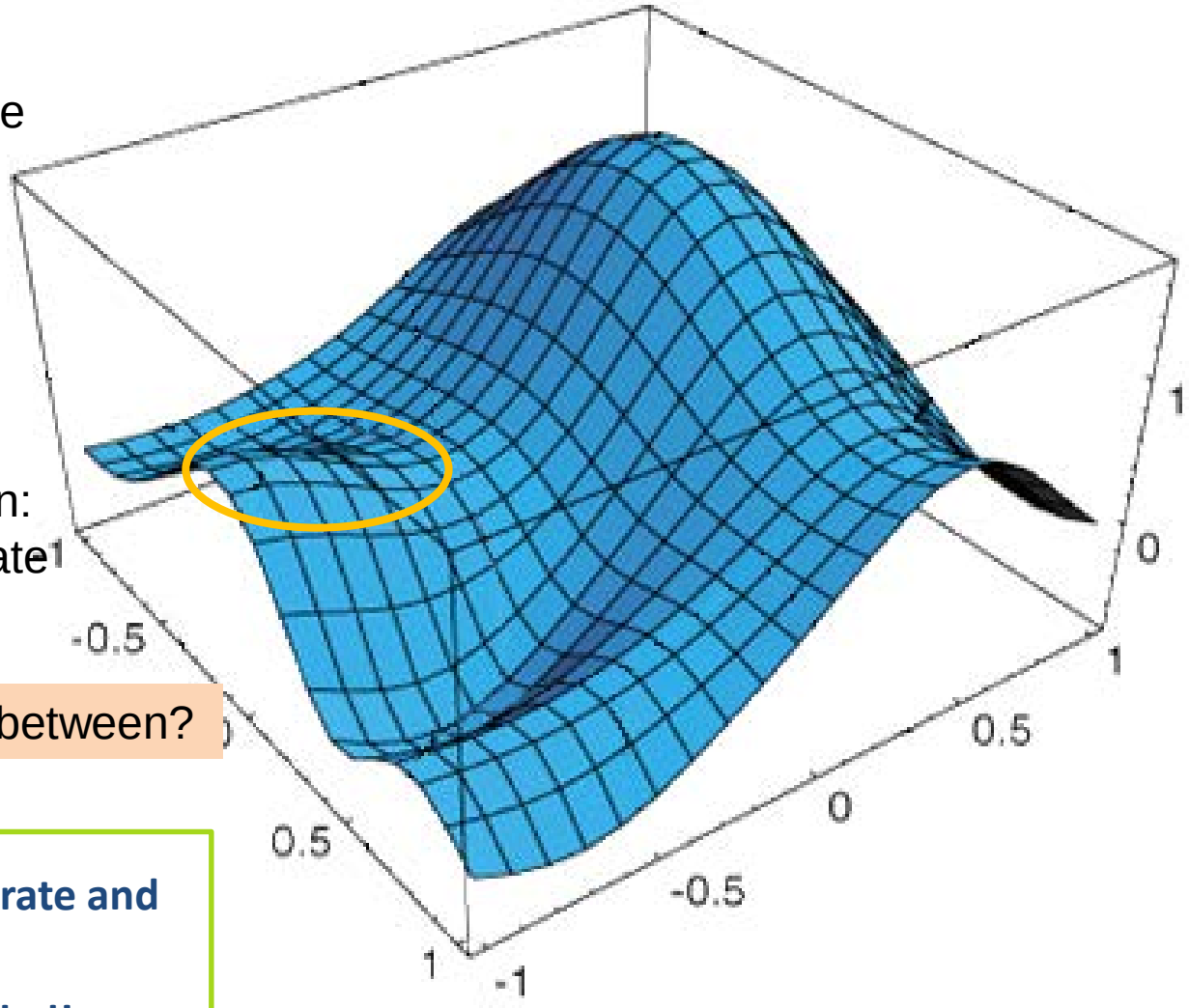
Describes energy of molecule in terms of its structure



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

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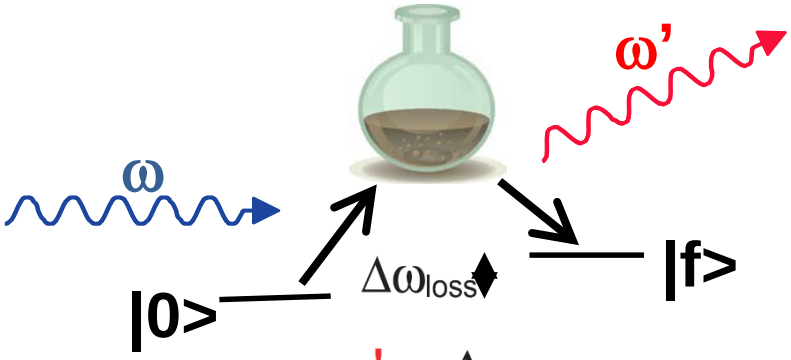
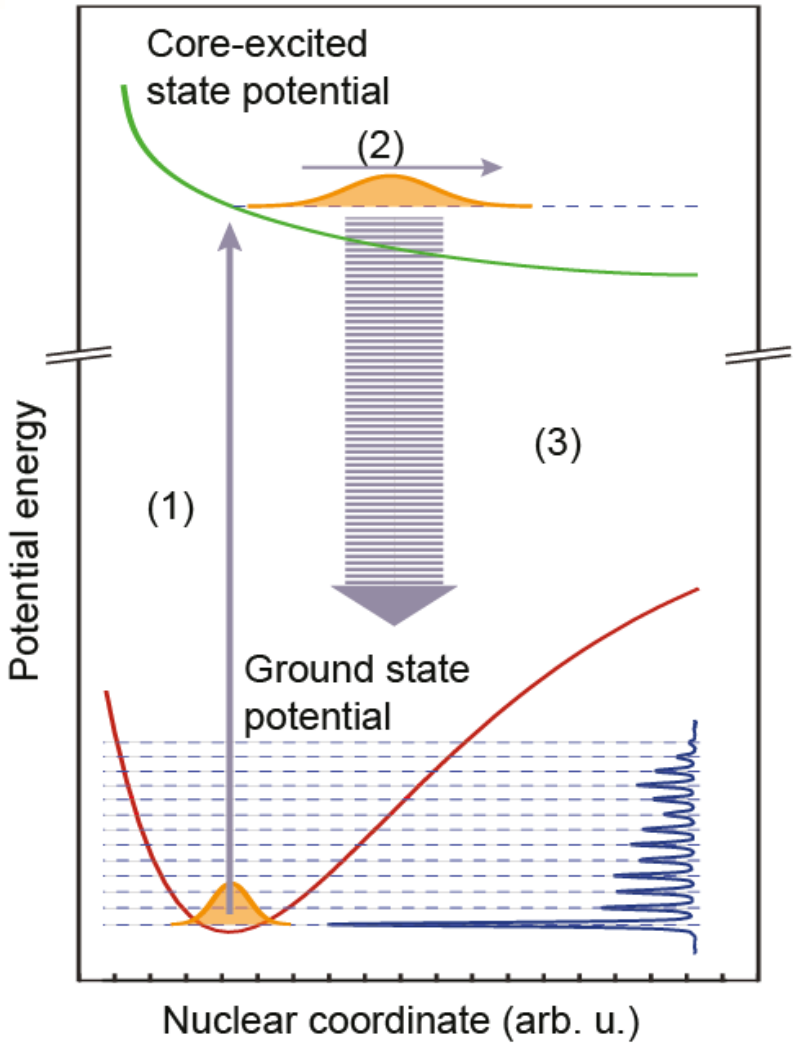
RIXS process



$$\omega - \omega' = \Delta\omega_{loss}$$

$$\Delta\omega_{loss} = \omega_{vib} + \omega_{elec}$$

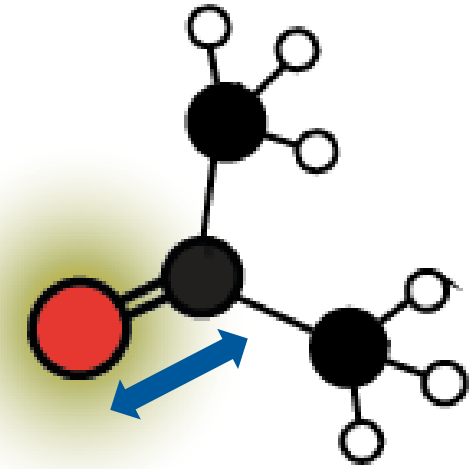


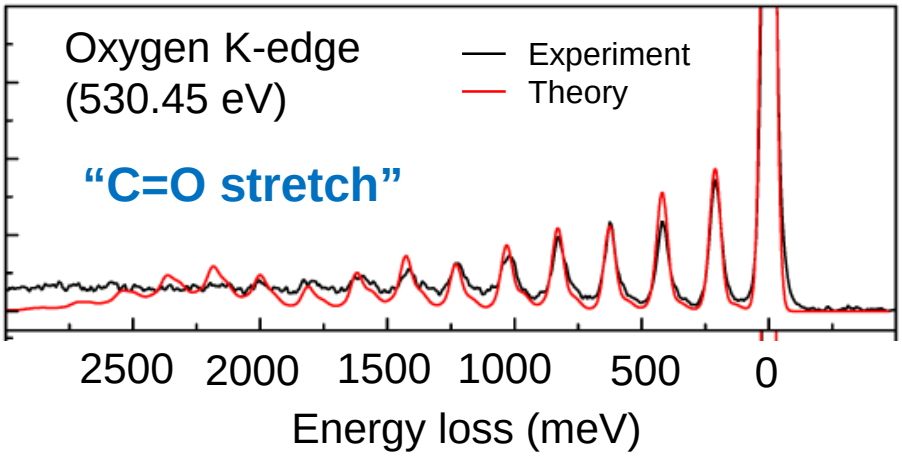
"Sub-natural linewidth Resonant inelastic X-ray scattering (RIXS)"

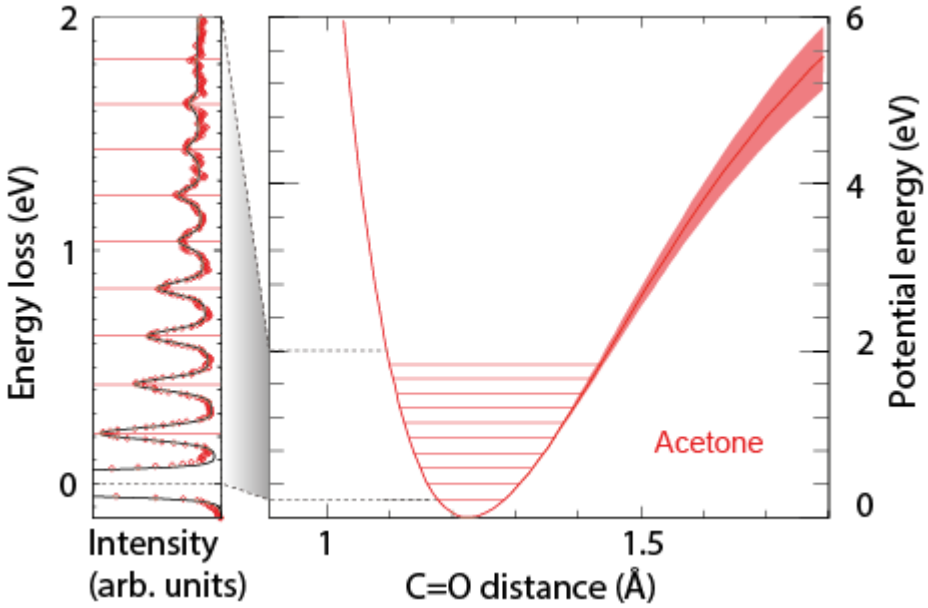
S. Schreck et al., Sci. Rep. ***7,*** *20054 (2016)*
Currently only at ADRESS/SLS

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**

*Y.P.Sun et al., Phys. Rev. B **84,** 132202 (2011)*

Active sites interacting with the fluctuating solvent network

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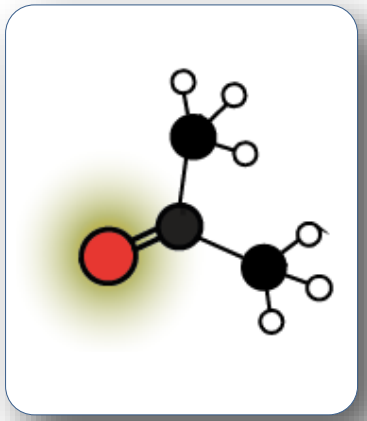
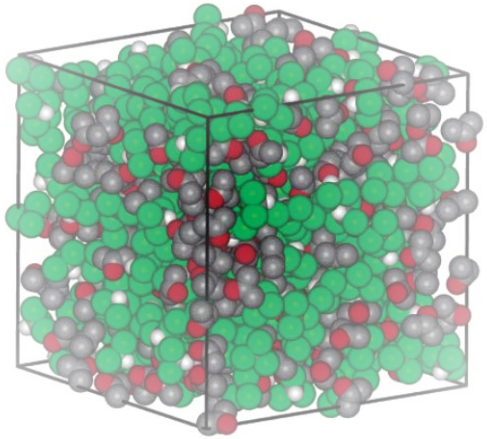
isolated small molecule



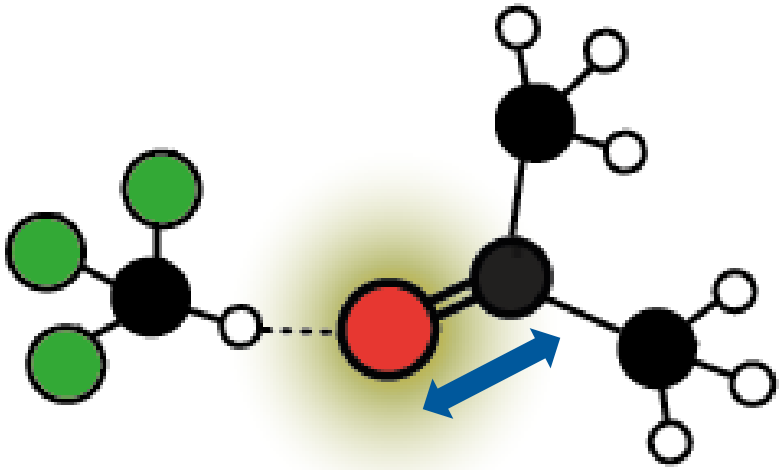
REALITY
(very often)



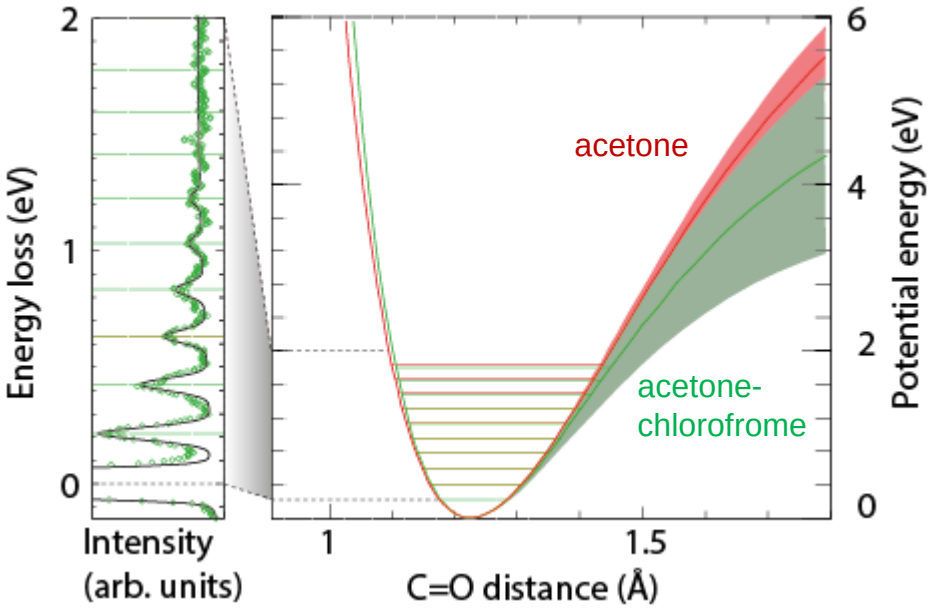
fluctuating bonding networks, solution….

? **Potential energy surface along interaction coordinate**

liquid acetone:
Adding one Hydrogen bond



Azeotrope aceton-chlorofrom mixture



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

S. Schreck et al., Sci. Rep. ***7****, 20054 (2016)*

A fluctuating Hydrogen bonded network: liquid water

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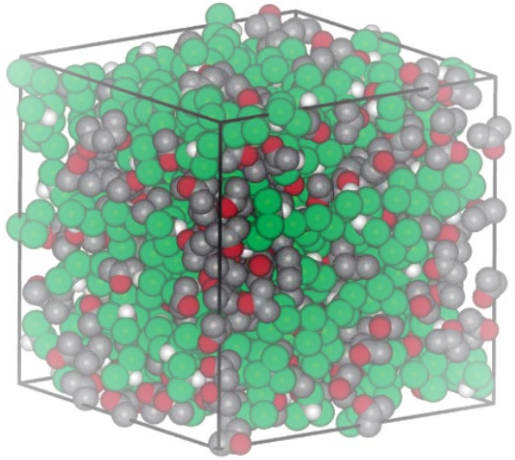
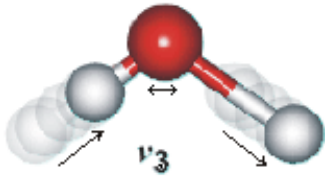
? **Liquid water:**

Bonding network
anomalies
coordination and correlation
structure: controversial

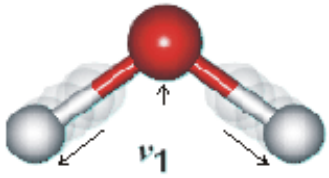


✓ **The water molecule**

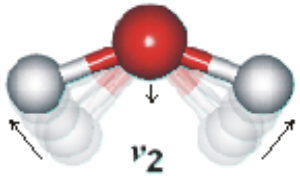
3-atomic molecule
3 normal modes



Asymmetric stretch

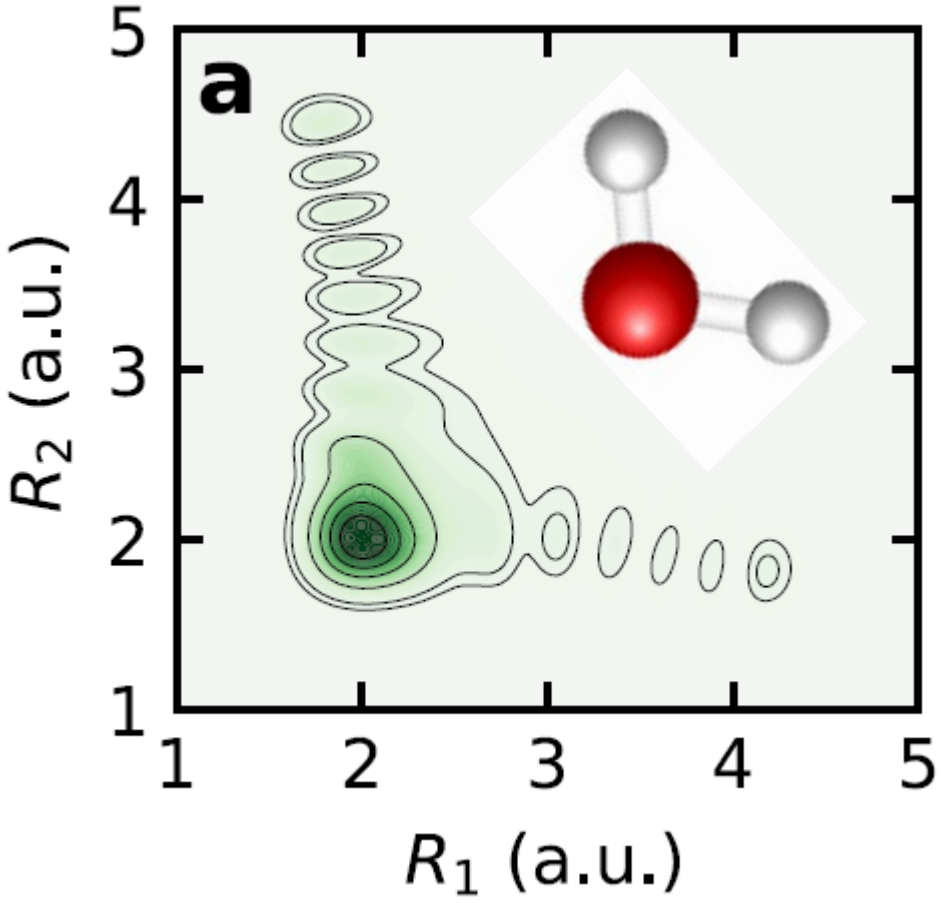


Symmetric stretch



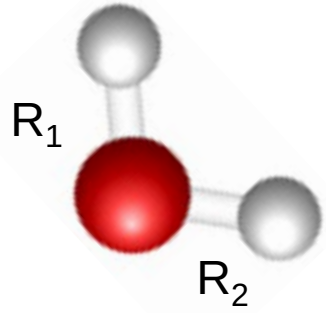
Bend

Core excitation



Coherent excitation of both OH bonds

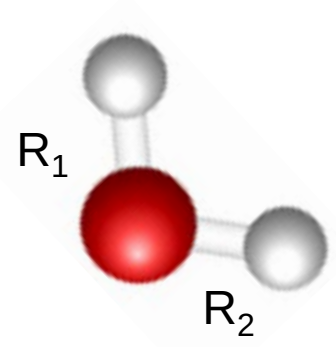
Directional excitation within molecular H_2O



stretch

*R. Couto et al, Nature Commun. **8**, 14165 (2017)*

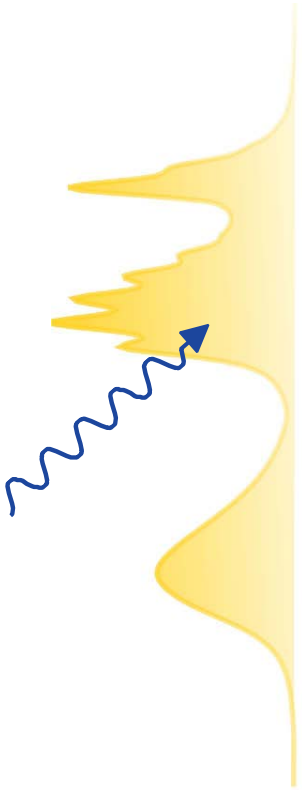
Directional excitation within molecular H_2O

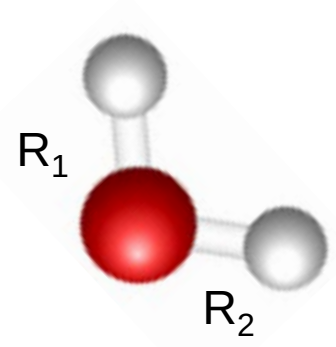


stretch

*R. Couto et al, Nature Commun. **8**, 14165 (2017)*

Directional excitation within molecular H_2O





stretch

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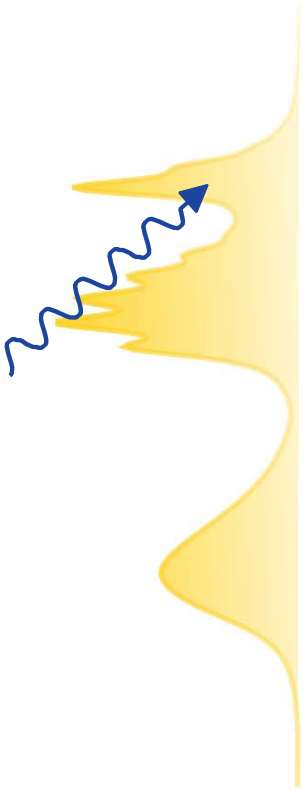
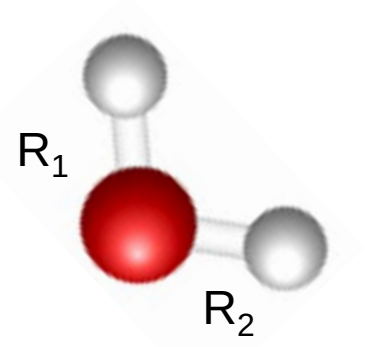
Directional excitation within molecular H_2O

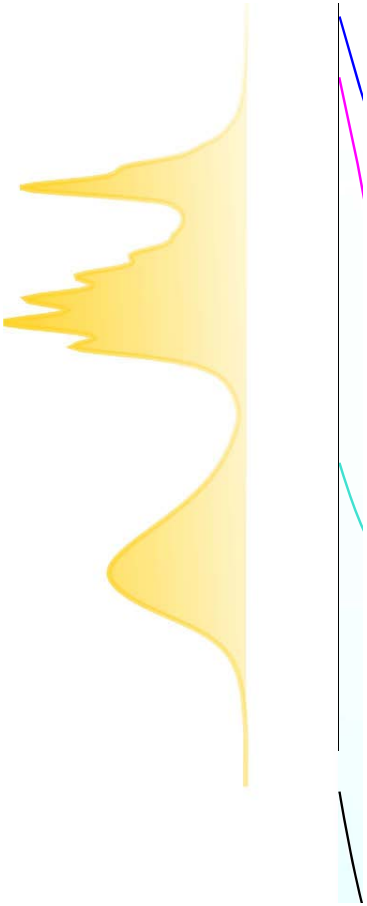


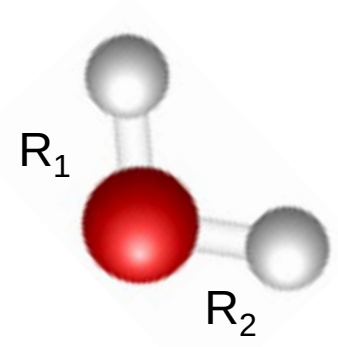


stretch

*R. Couto et al, Nature Commun. **8**, 14165 (2017)*

Directional excitation within molecular H_2O

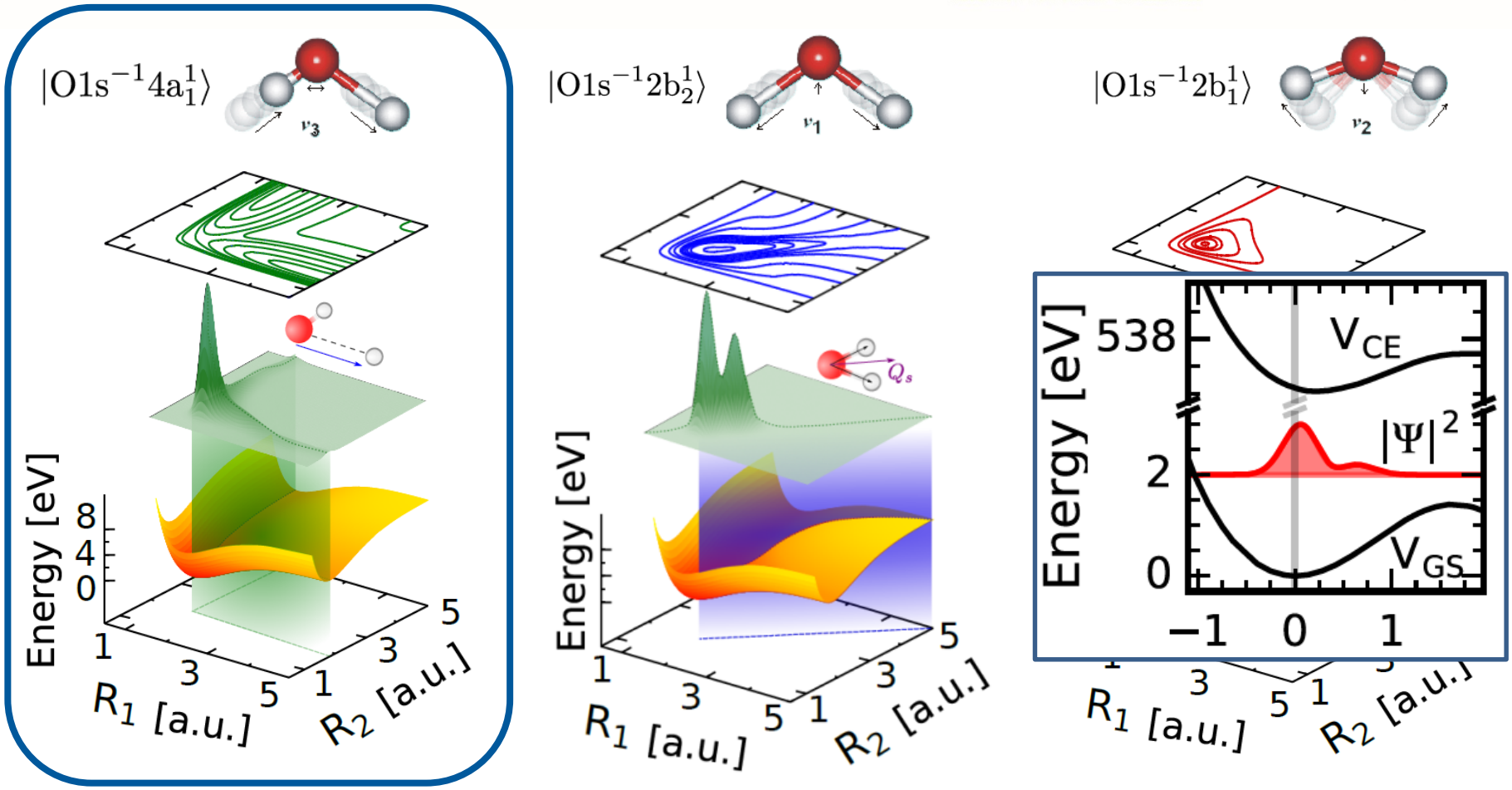




bend stretch

*R. Couto et al, Nature Commun. **8**, 14165 (2017)*

Directional potential cuts in isolated H_2O molecule



*V. V. da Cruz et al, PCCP **30**, 19573 (2017), R. Couto et al, Nature Commun. **8**, 14165 (2017), S. Eckert et al. Phys. Rev. A **97**, 053410 (2018)*

3 different RIXS resonances – 3 directional cuts along the normal coordinates

How does the H2O molecular potential change in the liquid?

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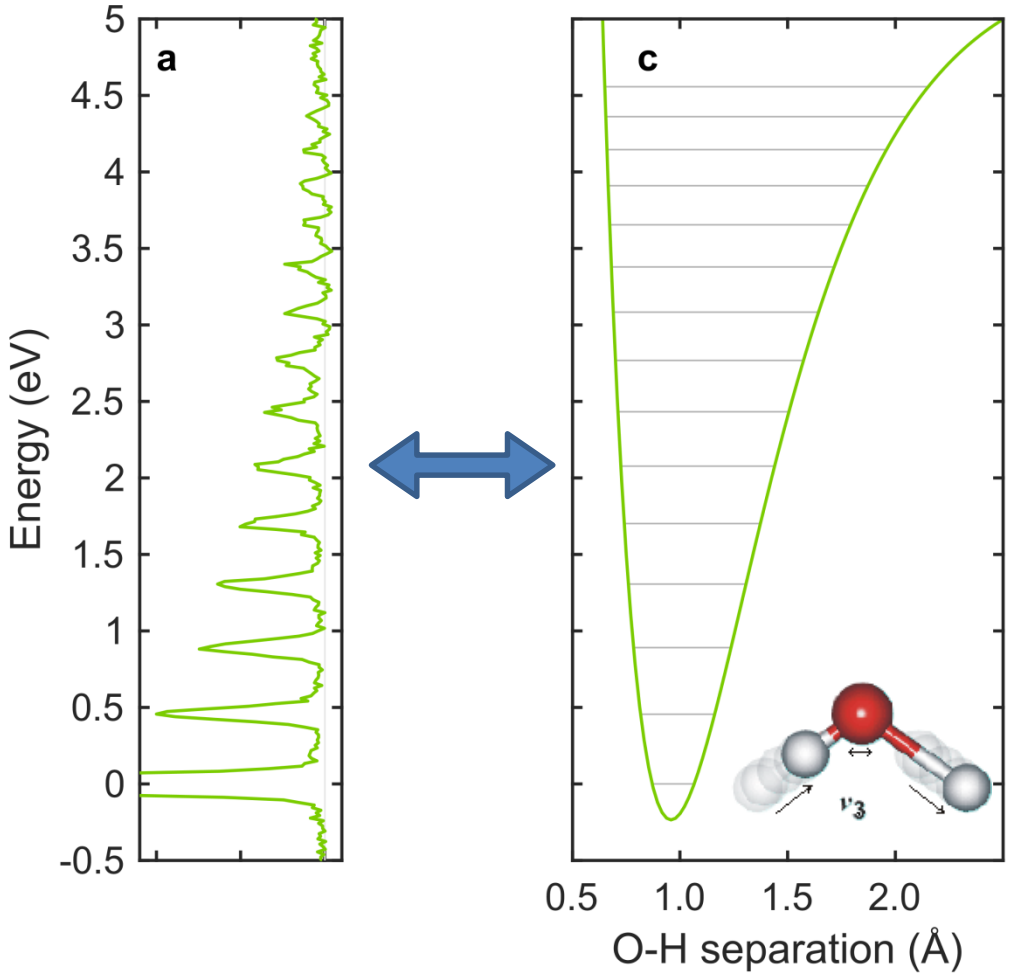
Gas

Liquid



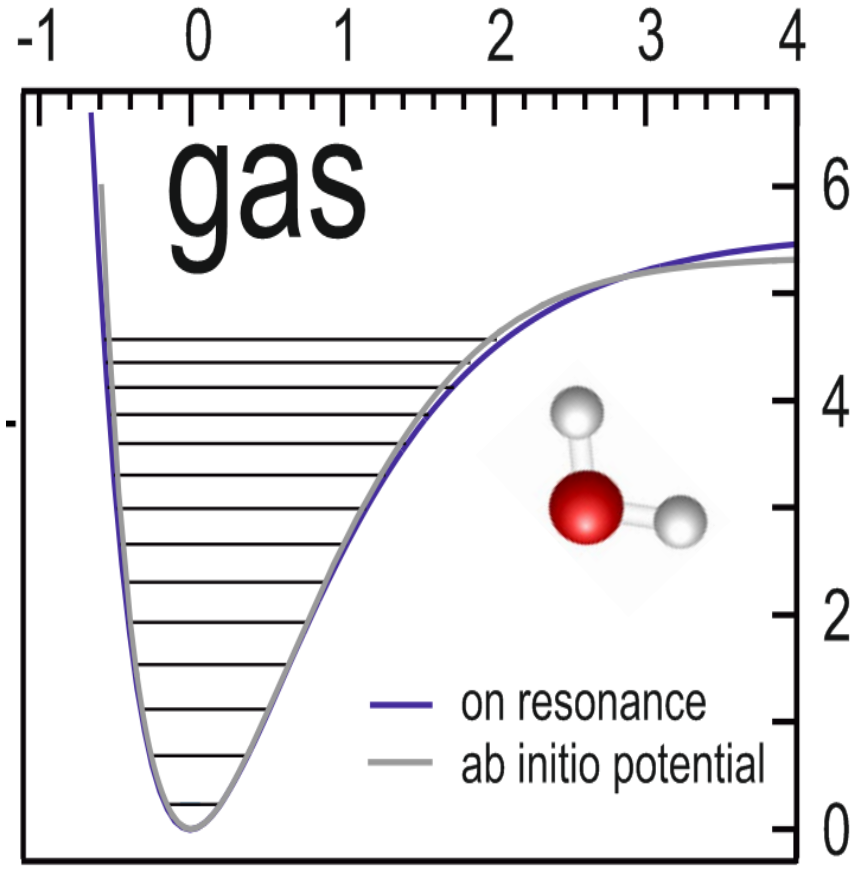
single molecular potential

??

J. Niskanen et al.,submitted to PNAS

Excitation on pre peak

Compare to calculations



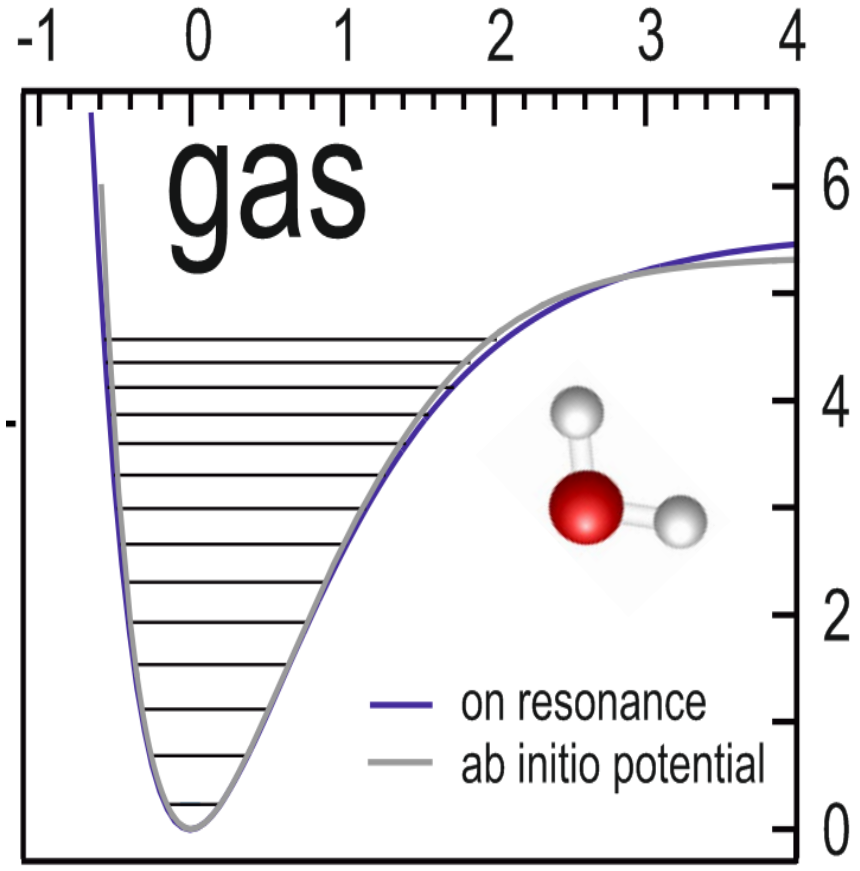
Reconstruct with Morse potential

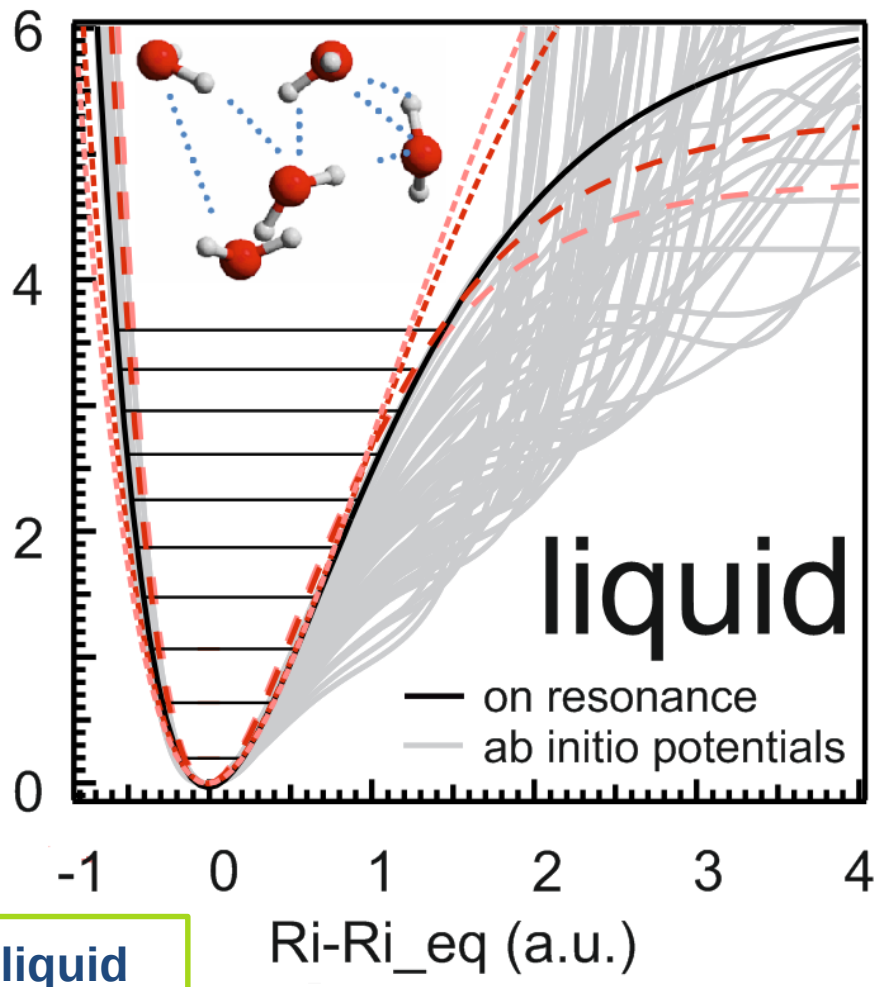
- ✓ **Matches well**
- ✓ **Fits well to calculations**

*S. Eckert et al. Phys. Rev. A **97**, 053410 (2018)*

Excitation on pre peak

Compare to calculations

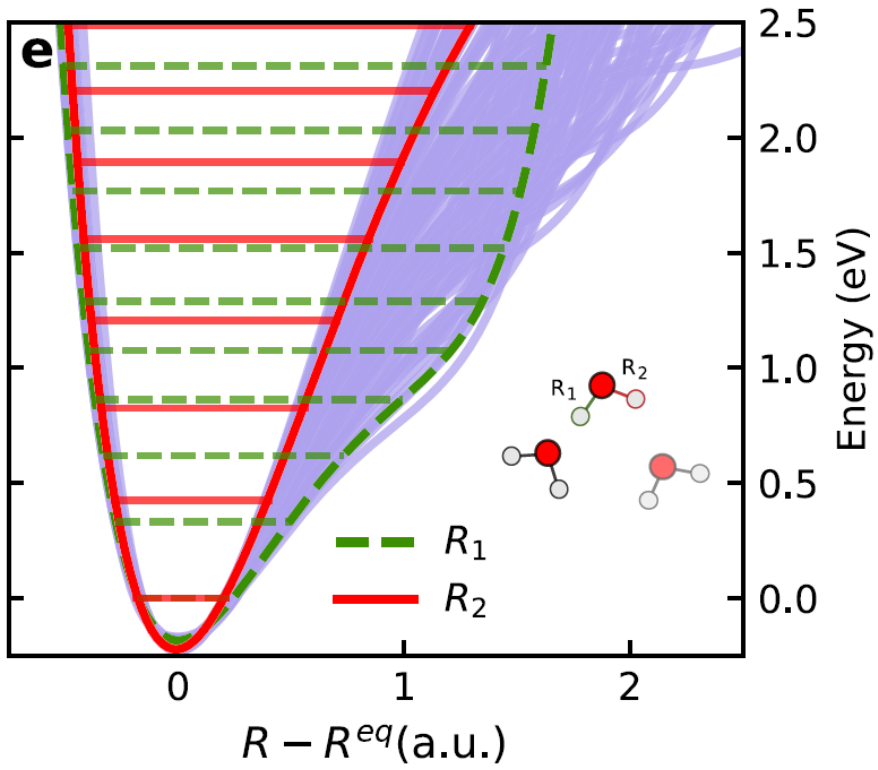


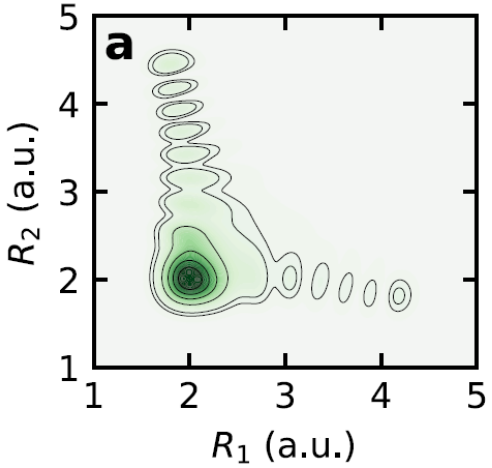


Morse reconstruction not working for liquid

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

Excite both (different) OH bonds



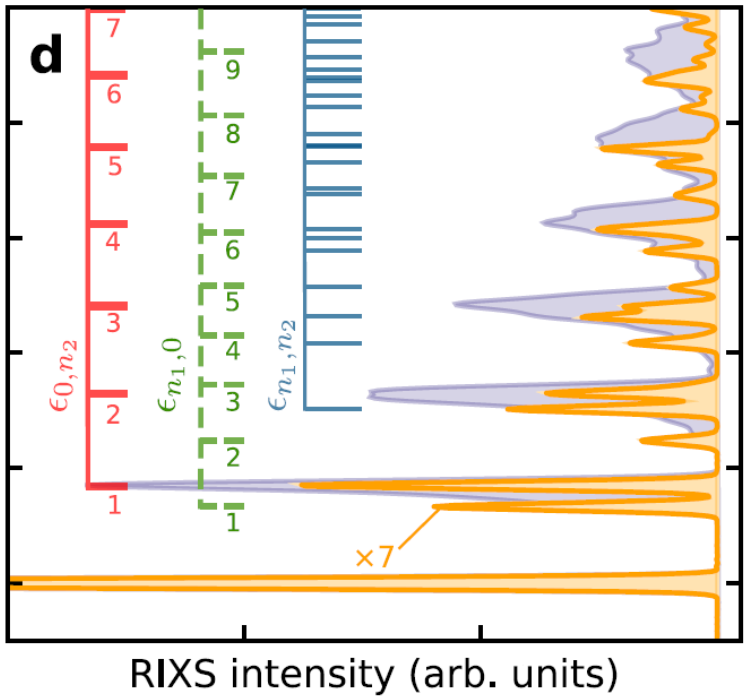


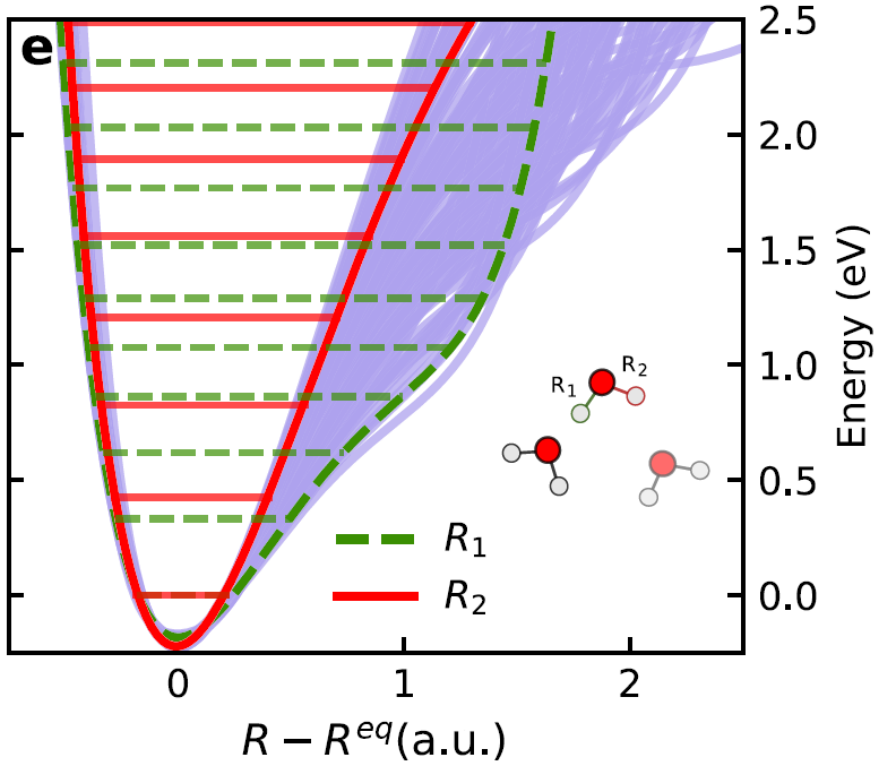
Coherent excitation of both OH bonds

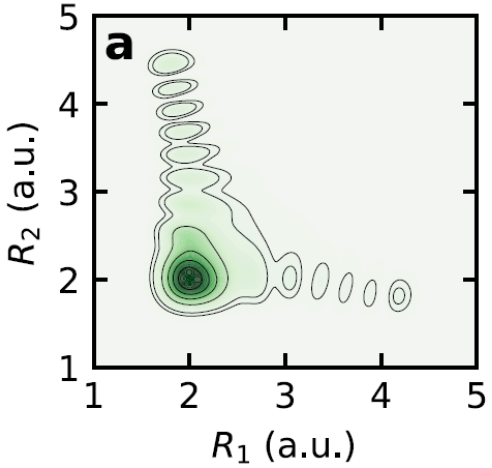
→ In liquid often very different bonds!

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

Excite both (different) OH bonds







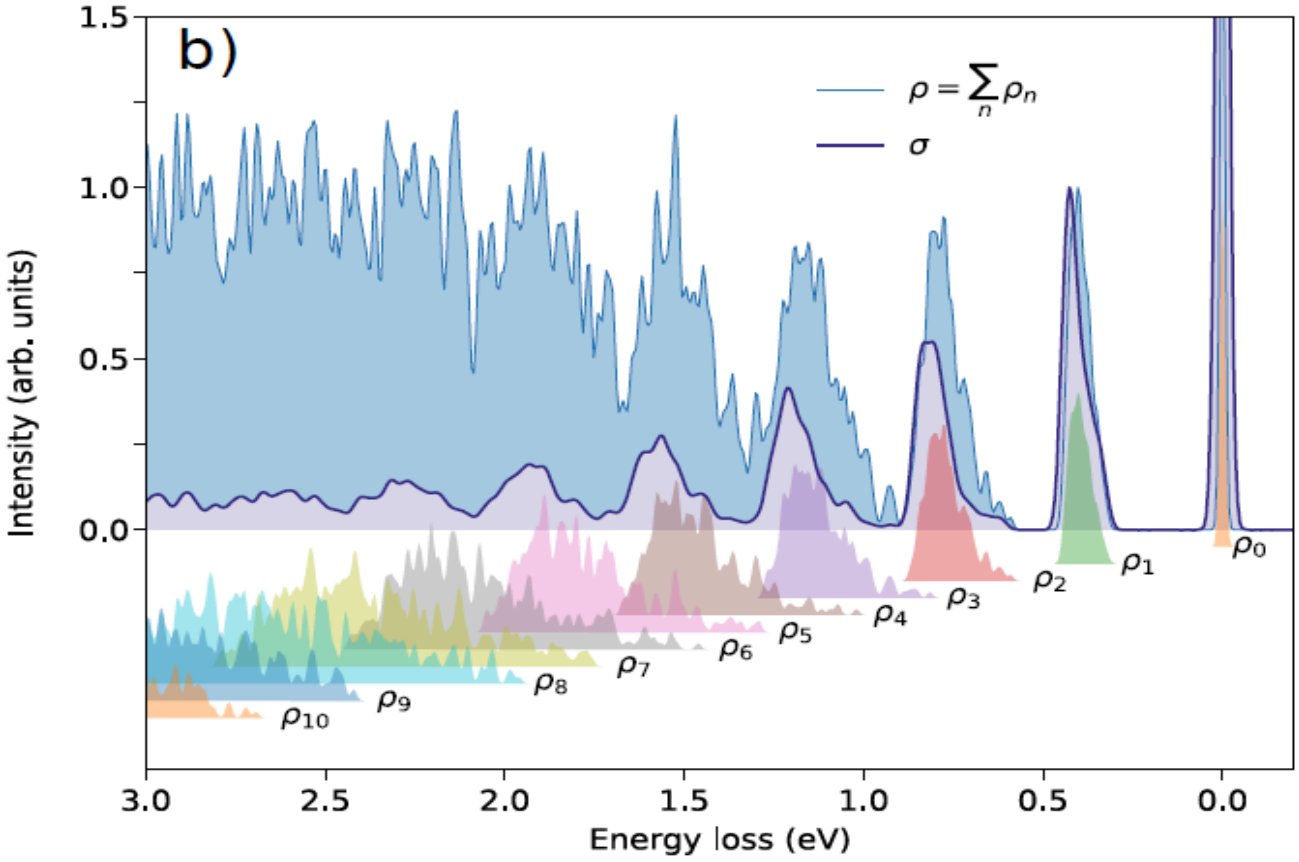
Single molecule spectrum!

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

Excite many molecules

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

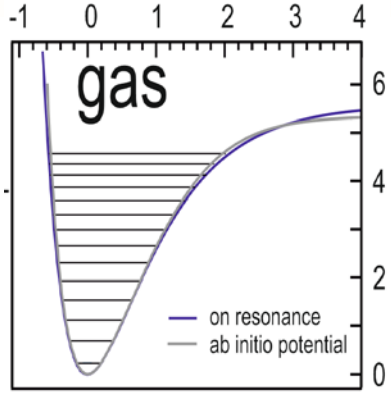
Overlap of partial density of states ρ

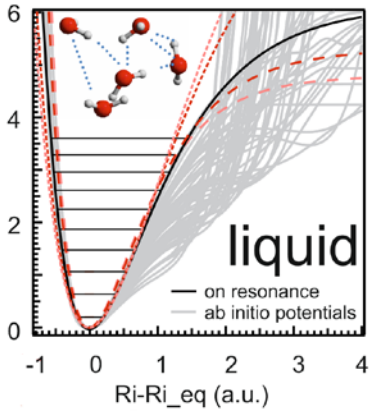


→ **Breakdown 1-to-1 correspondence of eigenvalue to vibrational peak!**

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

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)

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

Summary

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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!

Acknowledgements

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Dynamic Pathways in Multidimensional Landscapes

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16 – 20 September 2019, Magnus Haus, Berlin-Mitte

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Prof. Dr. Alexander Föhlisch
Prof. Dr. Svante Svensson
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Am Kupfergraben 7
Berlin-Mitte, Germany

CONTACT

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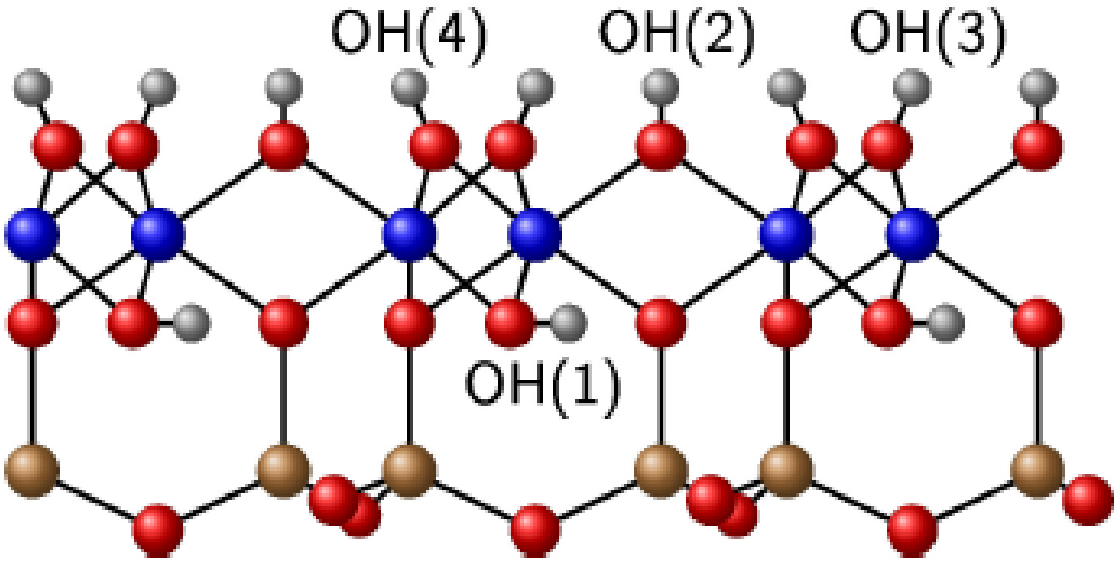
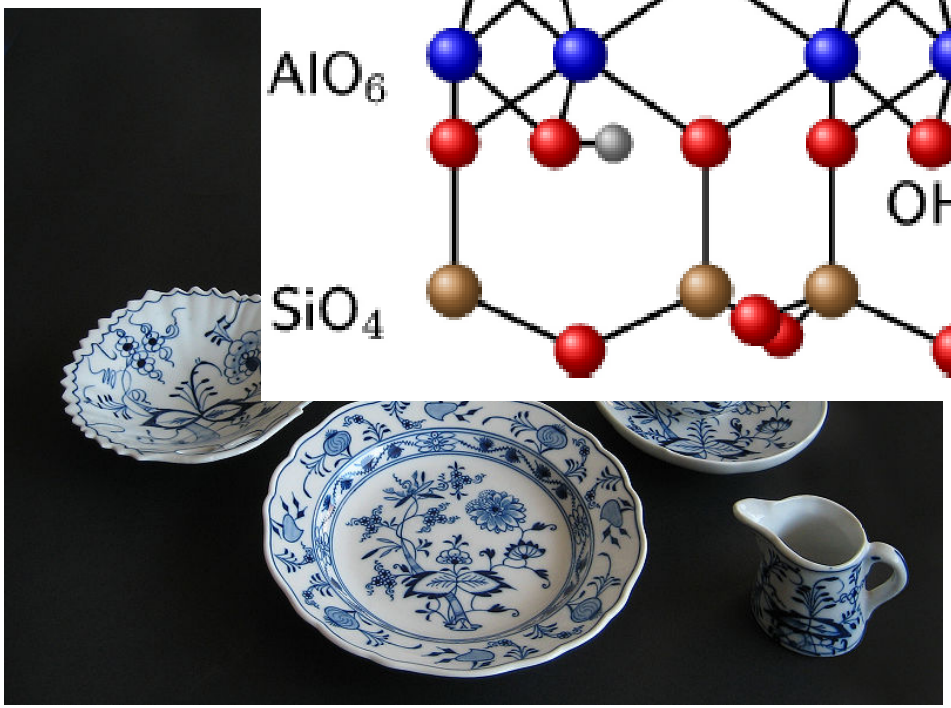
hz-b.de/SXR2019

One center in a complex material?

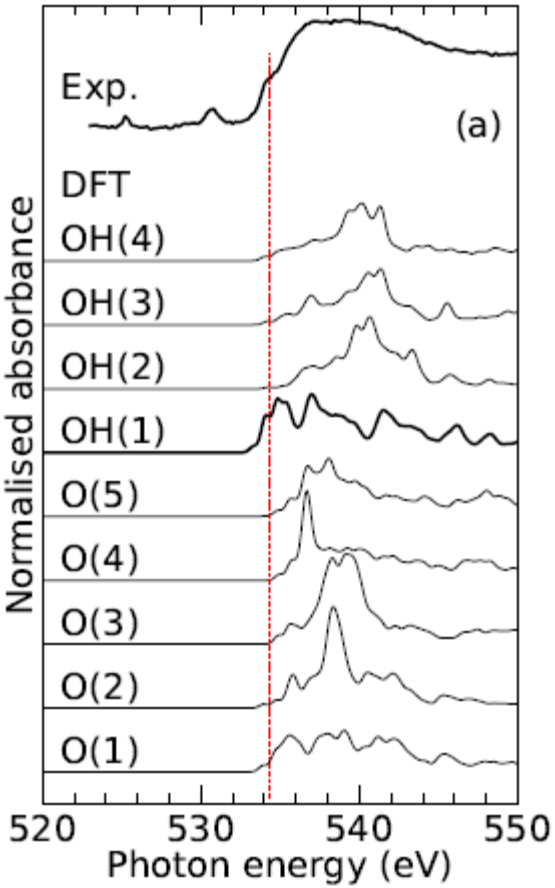
Kaolinite clay

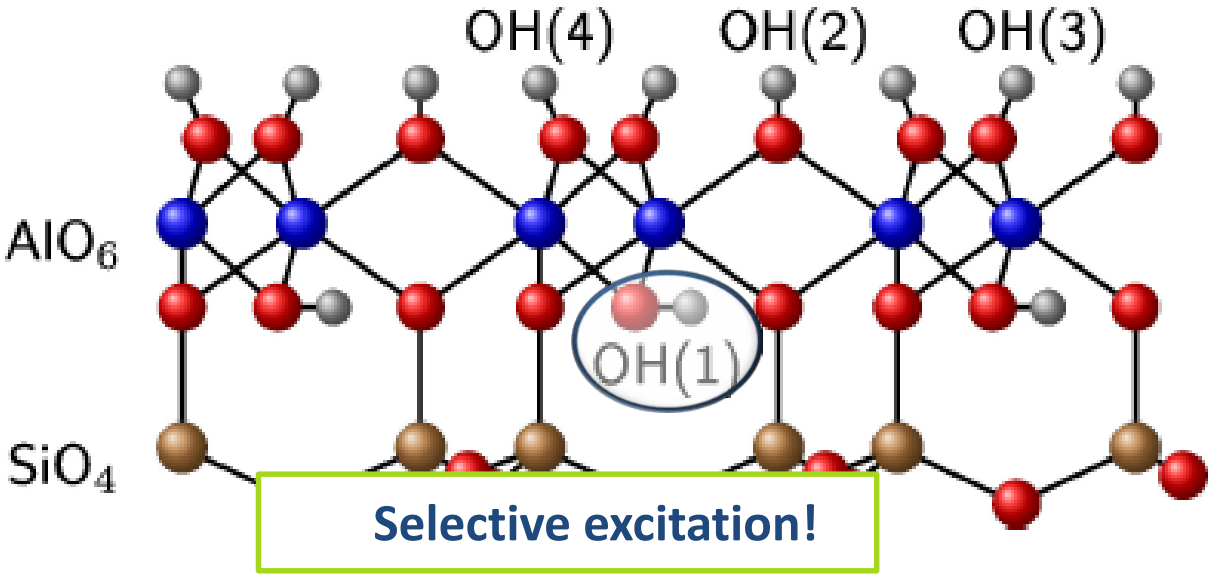
$Al_2Si_2O_5(OH)_4$



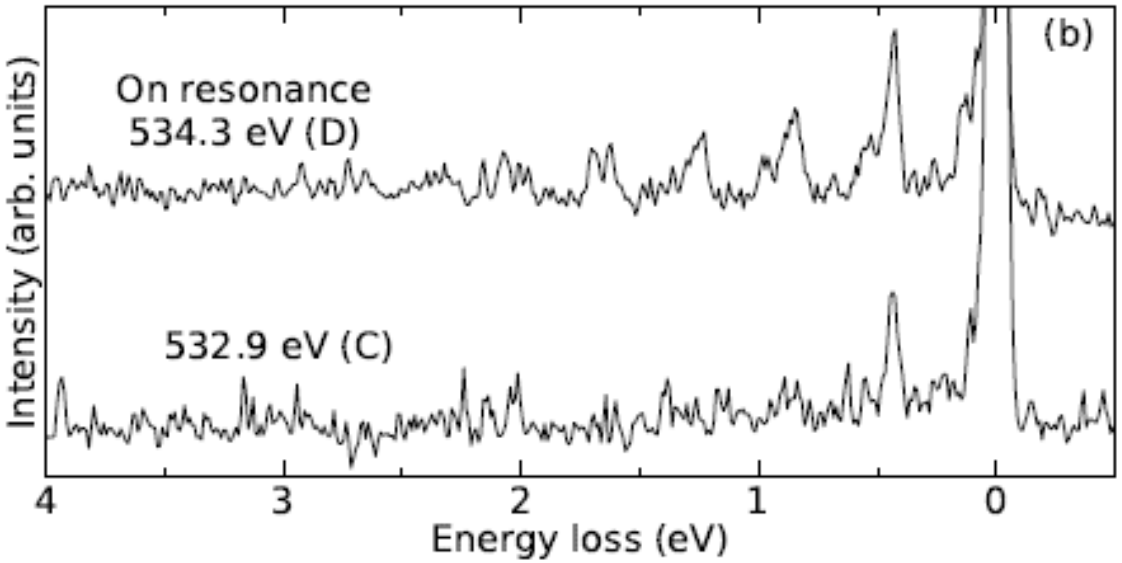


Complex systems: O-H in Kaolinite



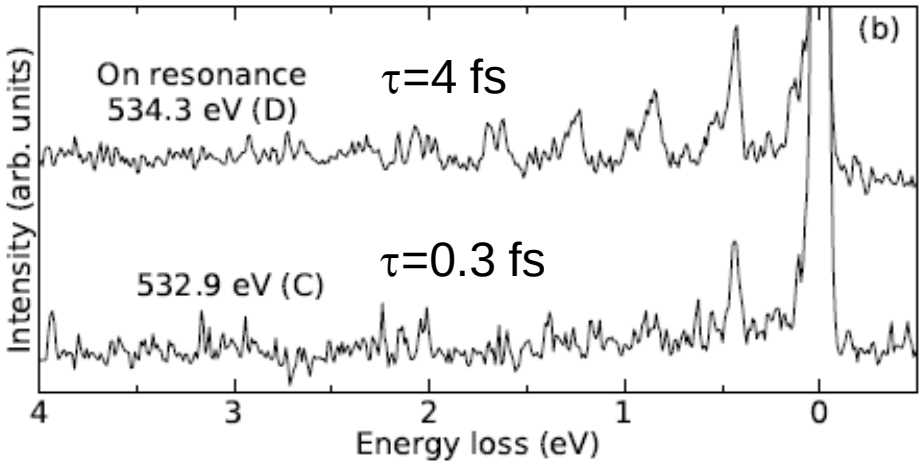


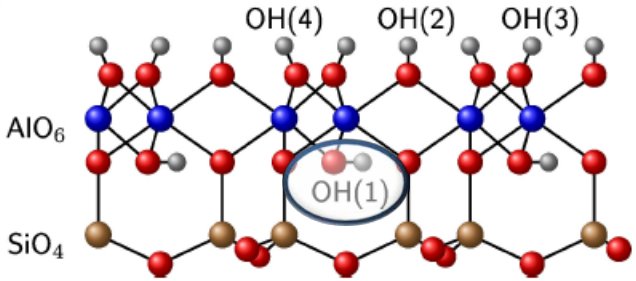
Selective excitation!

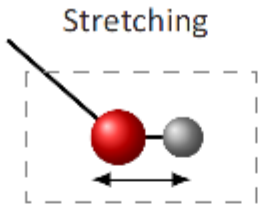


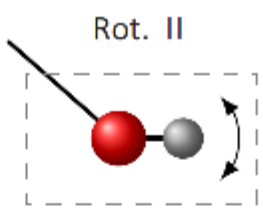
E. Ertan et al., PRB 95, 144301 (2017)

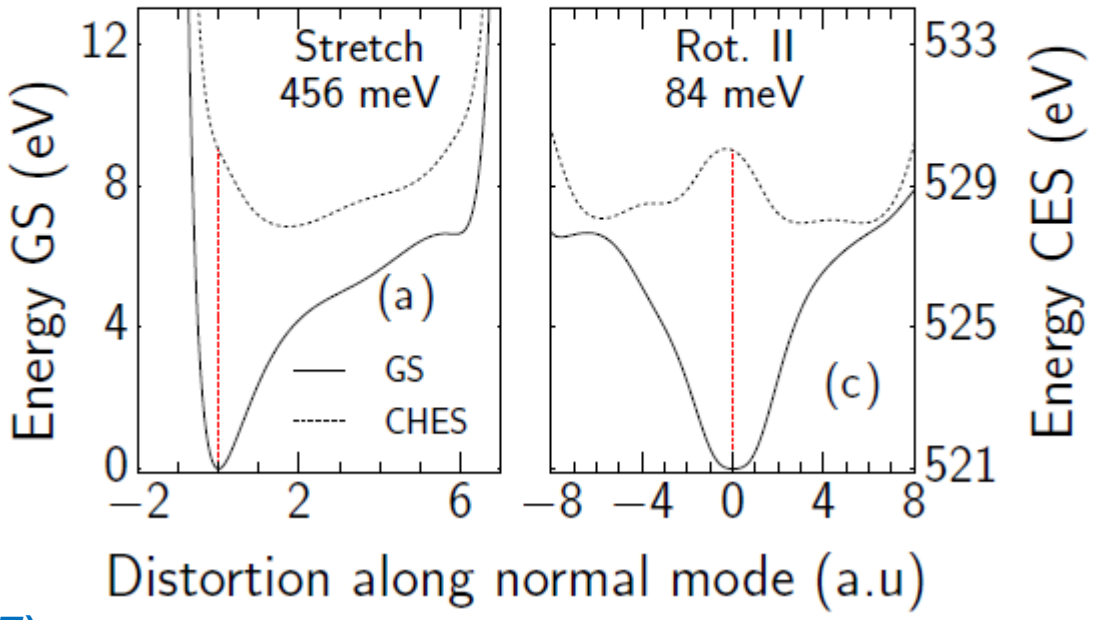
Complex systems: O-H in Kaolinite









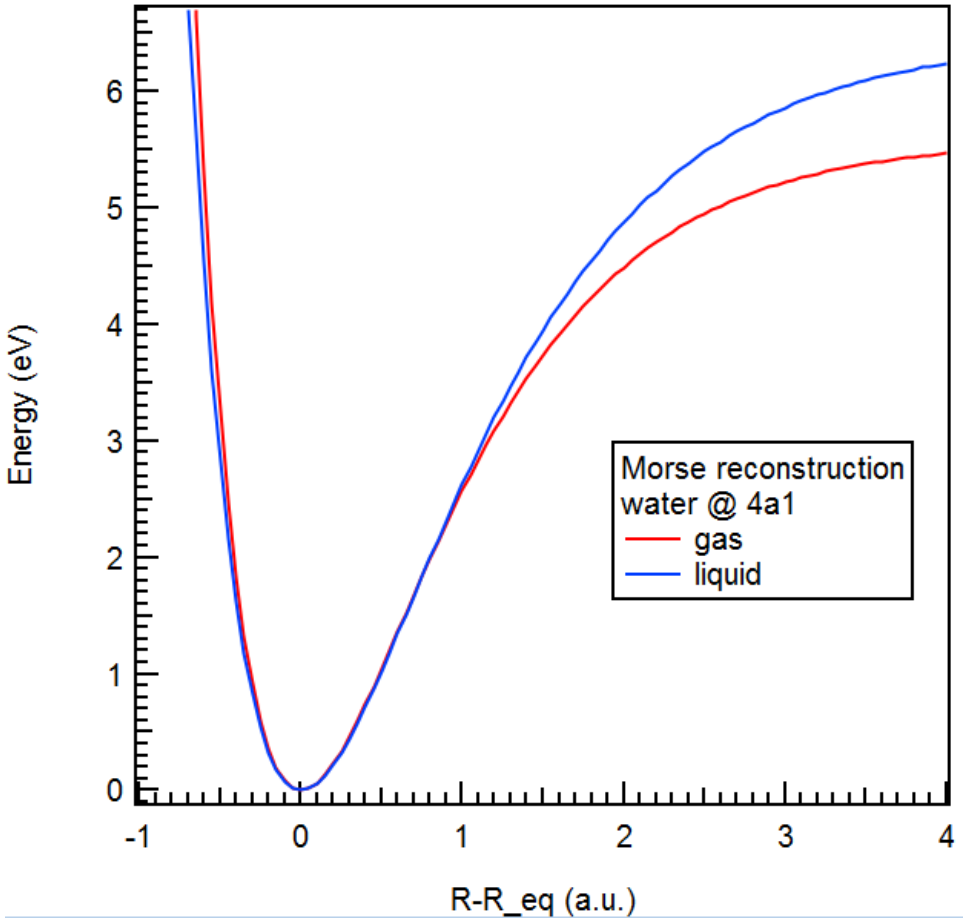


Elongated bond induces rotation

→ Effect of environment

E. Ertan et al., PRB 95, 144301 (2017)

Excitation on pre peak

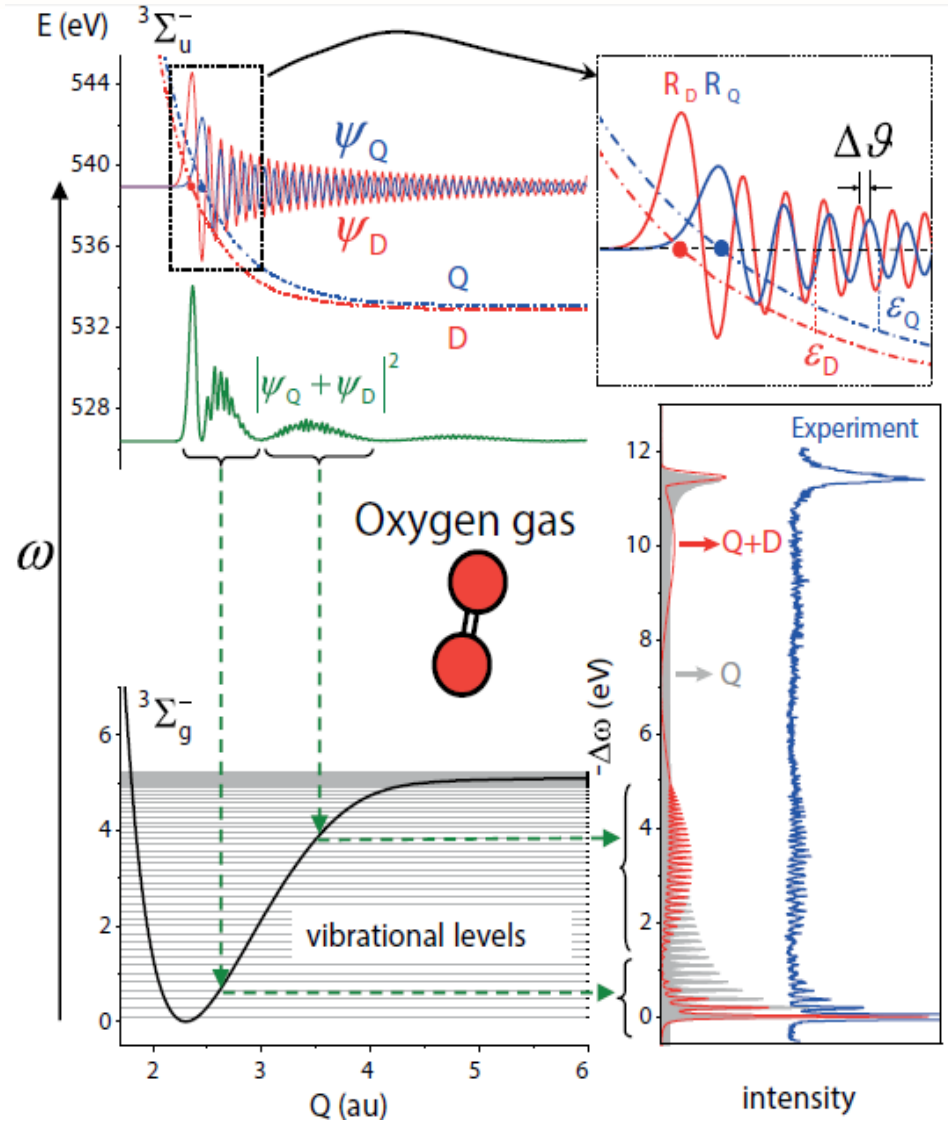


Liquid water PES
Steeper than gas

Core excited state dynamics ?

HELMHOLTZ
RESEARCH FOR GRAND CHALLENG

HZB Helmholtz Zentrum Berlin



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

RIXS Inherent temporal component

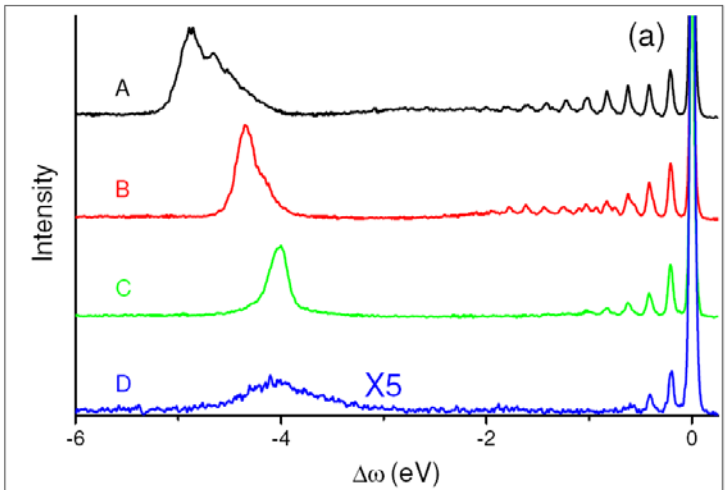
Scattering duration time:

$$\tau^2 = 1 / (\Omega^2 + \Gamma^2)$$

- **Detuning**

$$\Omega = \omega - \omega_{res}$$

→ **Shortens scattering duration time**



Liquid acetone O K-edge

Y.P.Sun et al., Phys. Rev. B **84,** 132202 (2011)

Where does it lead to?

? resolution

Interaction with surrounding
→ additional dipolar broadening γ_s:

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

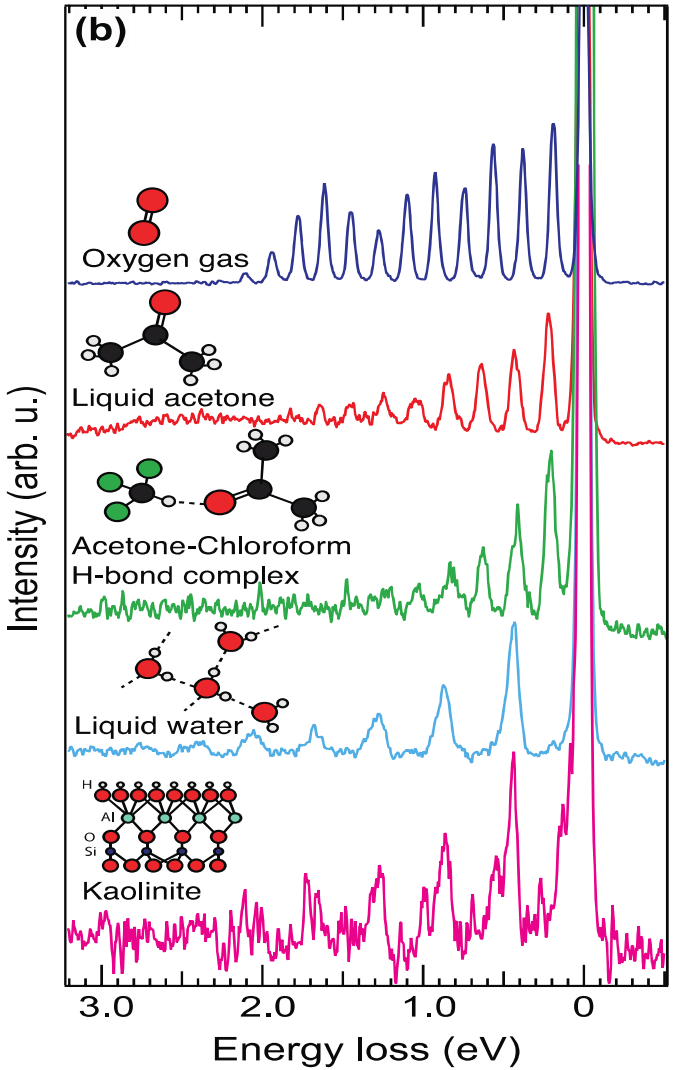
(dipole moments of solute and solvent)

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

In sub natural linewidth RIXS:
Final state = ground state
$\Delta\mu_f$=0 → γ_s=0

Set by

- ✓ **x-ray optics**
- ✓ **Source properties**



*Y.P.Sun et al., Phys. Rev. B **84,** 132202 (2011)*

*S. Schreck et al., Sci. Rep. **7,** 20054 (2016)*