Dynamics of resonant X-ray scattering for modern applications

Victor Kimberg

Siberian Federal University, Krasnoyarsk, Russia
Royal Institute of Technology, Stockholm, Sweden

Siberian Federal University, Krasnoyarsk, Russia

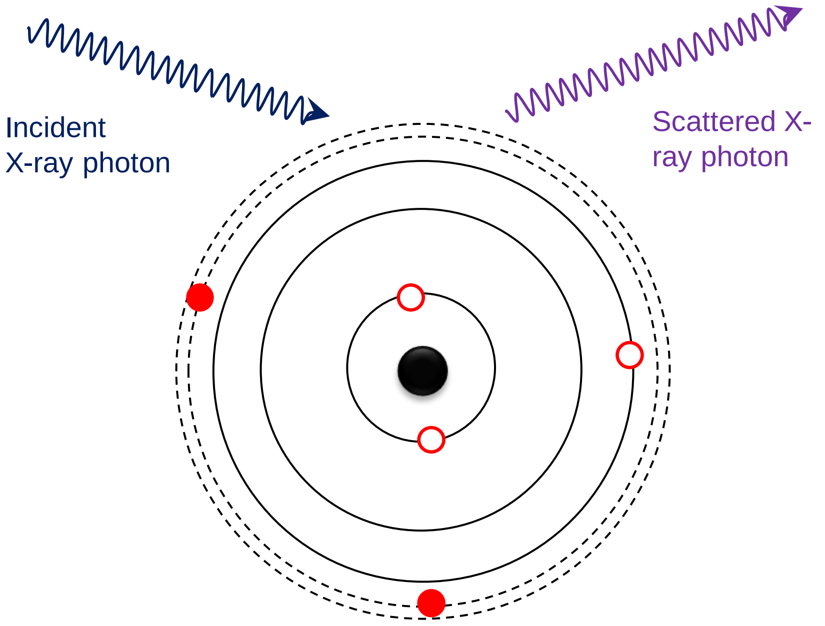
Royal Institute of Technology, Stockholm, Sweden

Outline

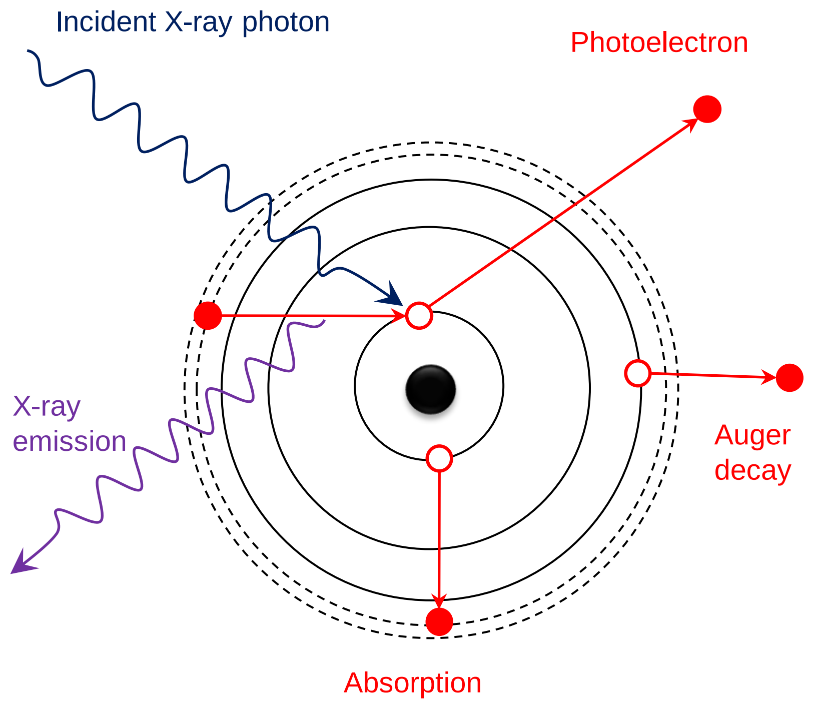
- Introduction. X-ray – matter interaction: resonant vs non-resonant
  - Resonant X-ray spectroscopies
  - History and new development on X-ray radiation facilities
  - Brief theory of vibrational dynamics in RIXS
- Dynamics and structure in resonant X-ray scattering measurements
  - Gating effect in water molecule
  - Study of hydrogen bond network in liquid water
- Summary and conclusions

X-ray matter interaction: elastic and inelastic processes

Elastic scattering



Inelastic (resonant) scattering

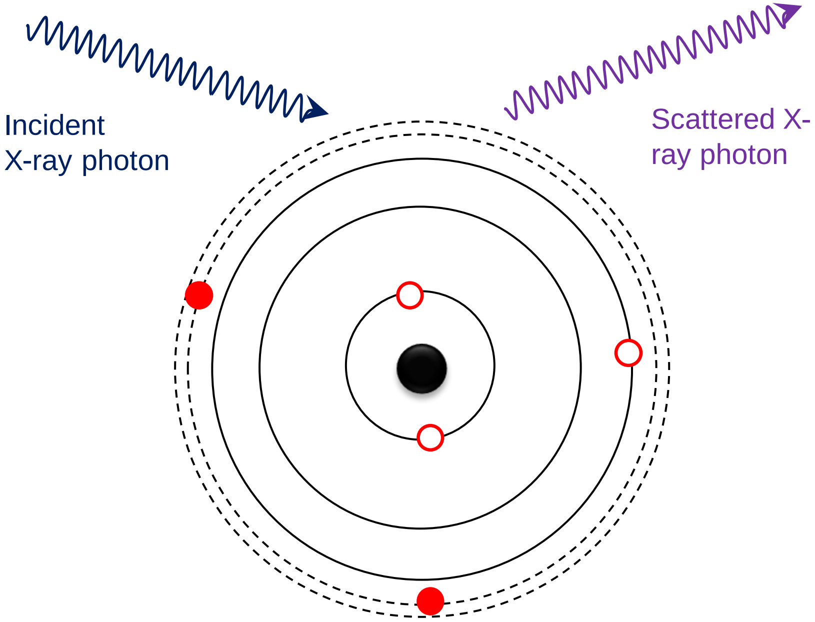


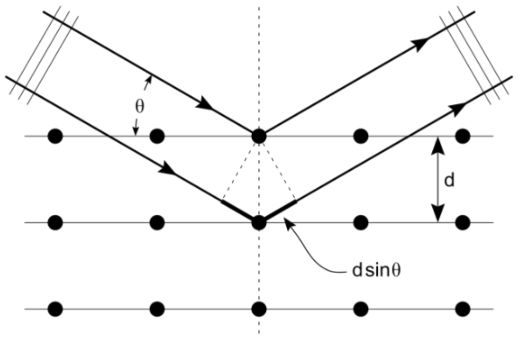
Small angle scattering
X-ray diffraction
X-ray crystallography

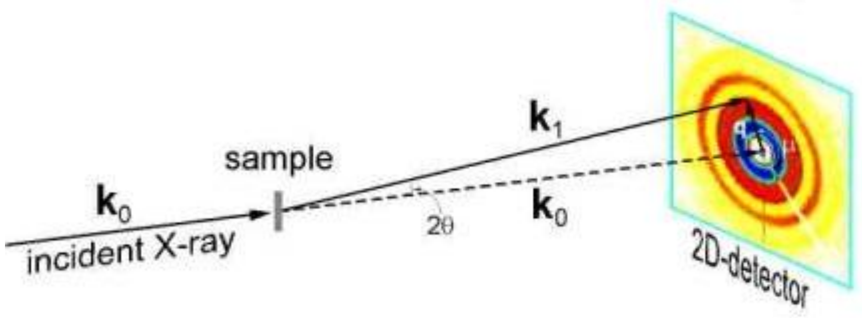
Resonant inelastic x-ray scattering (RIXS)
X-ray photoemission (XPS)
X-ray absorption (XAS)
Auger and resonant Auger (RAS)

X-ray diffraction for structure determination

Scattering of X rays by collection of electrons



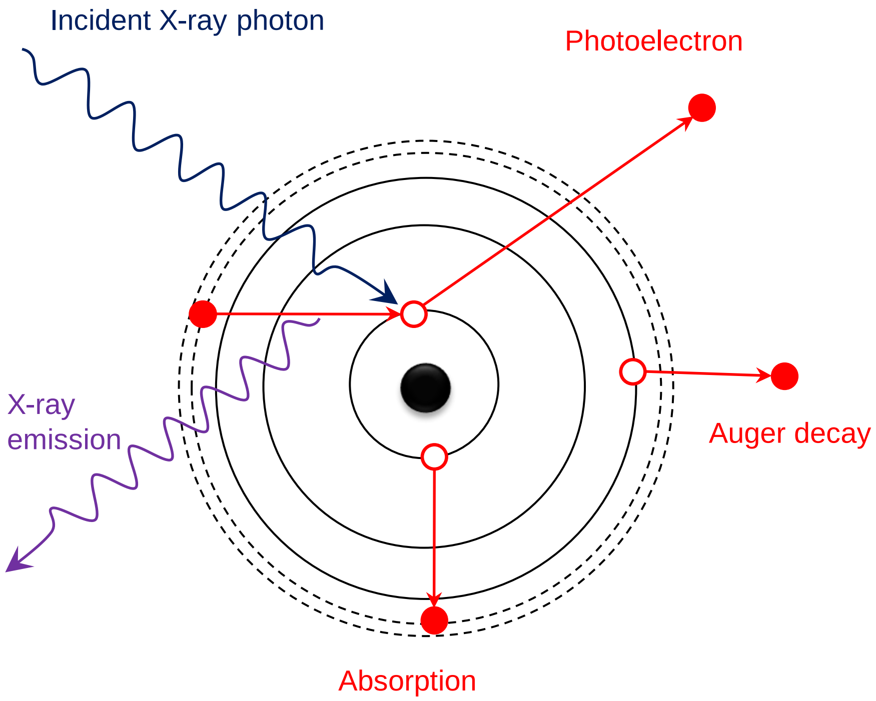




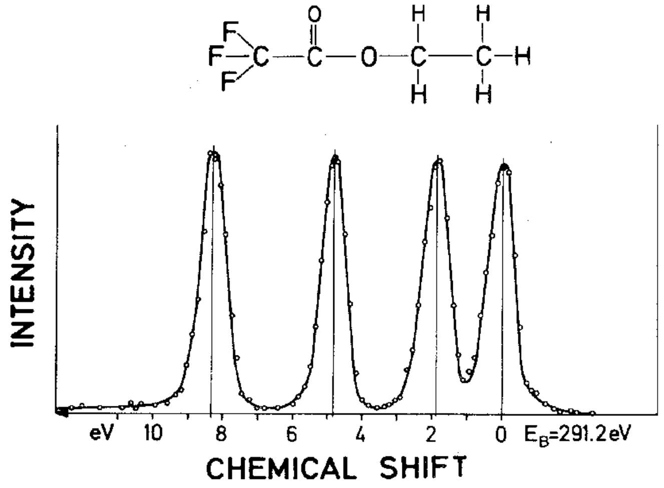
Small angle scattering
X-ray diffraction
X-ray crystallography

Resonant X-ray-matter interaction

X rays interaction induces electronic, vibrational and rotational transitions



- *Soft X-ray* 100~1200 eV (1 ~ 12 nm)
- Core electron photo-absorption edge of many important elements
  - K-edge: **Be** 112 eV, **C** 284 eV, **N** 410 eV, **O** 536 eV, **F** 697 eV...
  - L-edge: **Al** 73 eV; **Si** 99 eV; **S** 163 eV; **Ca** 346 eV; **Fe** 707 eV; **Ni** 853 eV; **Cu** 933 eV…

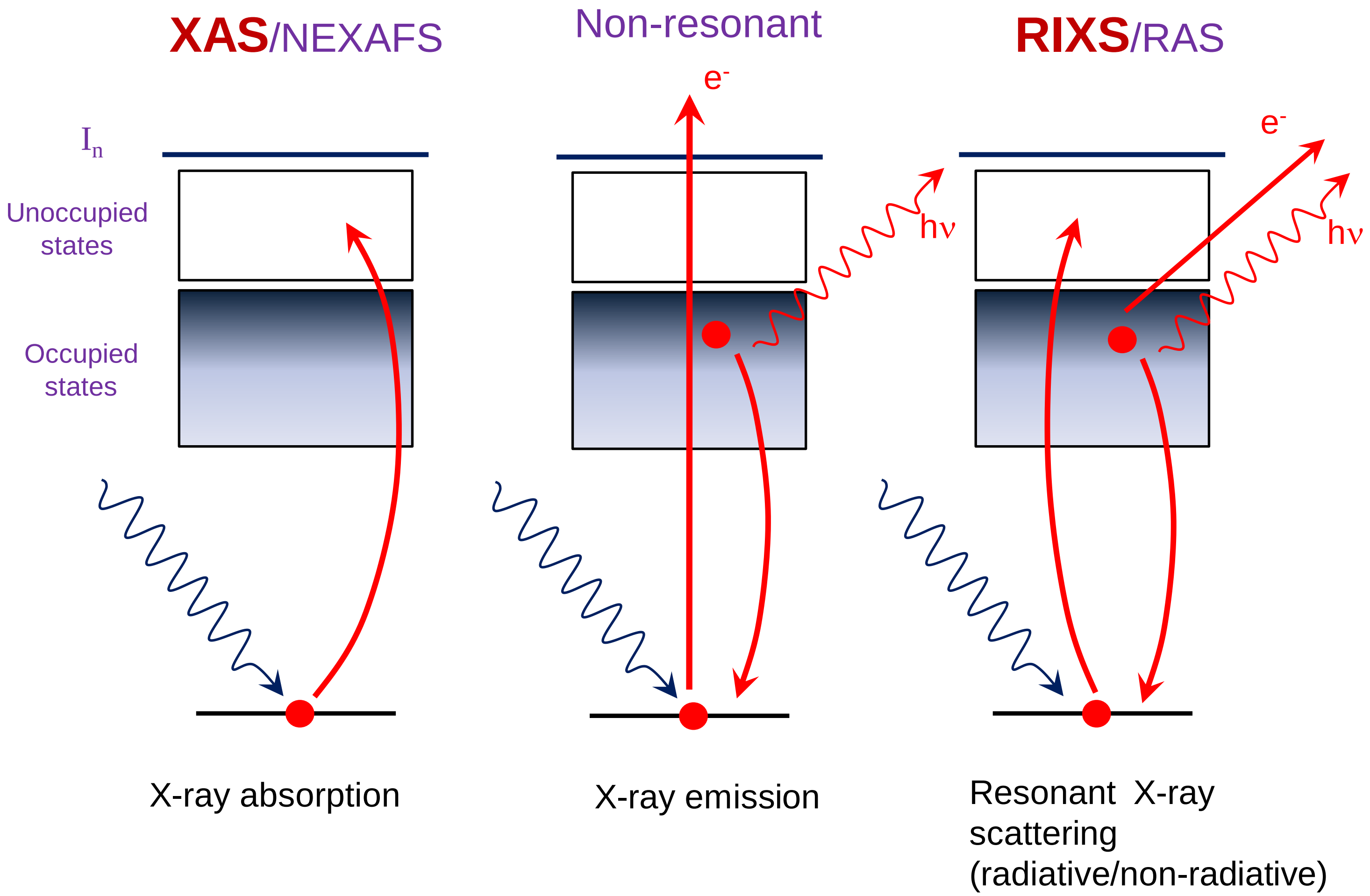


- Unique and sensitive element characterization
- Even site-selective due to chemical shifts

Resonant inelastic x-ray scattering (RIXS)
X-ray photoemission (XPS)
X-ray absorption (XAS)
Auger and resonant Auger (RAS)

C1s photoelectron spectra, K. Siegbahn 1974
Gelius et al., J. Electron Spectrosc. Relat. Phenom. 2, 405.

Variety of X-ray spectroscopies

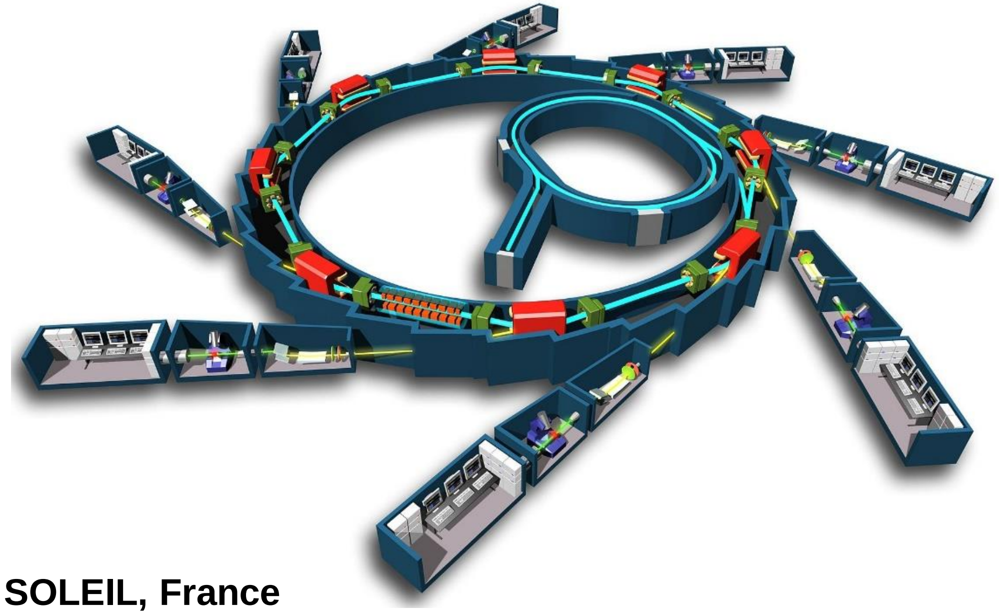


- Gas phase spectroscopy
  +isolated single molecule
  +small broadening
  -chaotic orientation
- Liquids
  +Structure
  +HB networks
  - broadening polarization effects
- Resolution (~500 eV)
  Photon (mono) ~ 0.01 eV
  Spectrum ~ 0.1 eV
  Prospect (MAXIV) ~ 0.01 eV

- Decay of core-excited state (~10 fs) is much faster than molecular rotations
- It is enough for change of molecular geometry, ultrafast dissociation, etc.
- **High-resolution (vibrational resolved) spectroscopy: display nuclear dynamics**

Characteristics of synchrotron radiation

- Broad Spectrum: from microwaves to hard X-rays
- High Brilliance: highly collimated photon beam generated by a small divergence and small size source (spatial coherence)
- High Stability: submicron source stability
- Polarization: both linear and circular
- Pulsed Time Structure: pulsed length down to tens of picoseconds allows the resolution of process on the same time scale



Synchrotron SOLEIL, France

Synchrotron radiation: a bit of history

1st generation: Parasitic operation at the facilities build for high-energy and nuclear physics

- Ivanenko and Pomeranchuk (SU) in 1944 calculated the energy limit obtained due to losses by radiating electrons.
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2nd generation: Dedicated sources 1970s

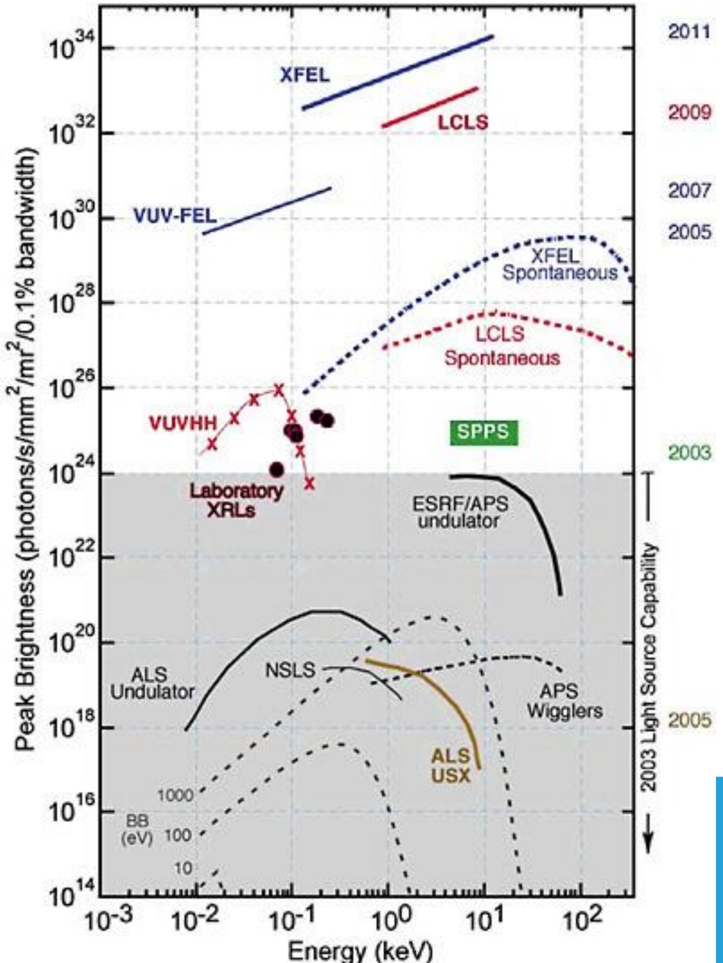
SRS , UK; NSLS, USA; BESSY, DESY, Germany; …

3rd generation: Optimized for brightness 1990s

ESRF in Grenoble; SPring-8, Japan; ALS at Berkeley; MAX-LAB, Sweden; SOLEIL, France;
MAX-IV, Sweden

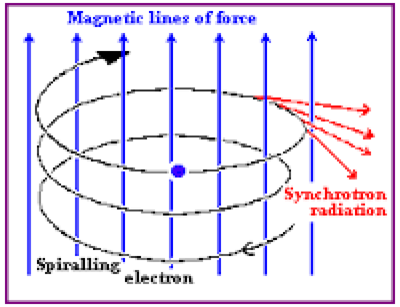
4th generation: Intense short pulses – x-ray free-electron lasers 2000s

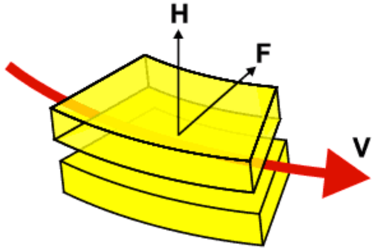
FLASH, Hamburg; LCLS at SLAC, USA; SACLA, Japan
The European XFEL Hamburg; SXL @ MAX-IV, Sweden



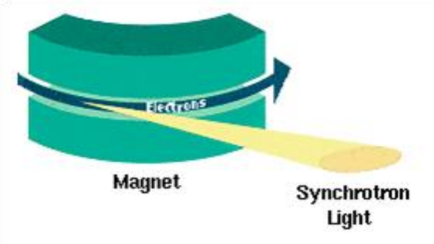
Controlling the Quantum World: The Science of Atoms, Molecules, and Photons. THE NATIONAL ACADEMIES PRESS, Washington, D.C. 2007.

Principles of synchrotron radiation





dipole



- A charged particle moving in a magnetic field radiates energy.
- At non-relativistic velocities - ***cyclotron radiation***
  at relativistic velocities - ***synchrotron radiation***

$$\frac{d}{dt}(\gamma m_e \mathbf{v}) = \frac{e}{c}\mathbf{v}\times\mathbf{B}, \quad \gamma = \frac{1}{\sqrt{1-v^2/c^2}}$$

v is the velocity of electron with charge e and mass m_e, **B** is the magnetic vector, and γ is the Lorentz factor, r is radius of gyration

$$a = \frac{v^2}{r} = \frac{e\beta B}{\gamma m_e}, \quad \beta = v/c, \quad r = \frac{\gamma m_e c^2 \beta}{eB}$$

(Acceleration of electron)

The total emitted power:

$$P_{rel} = \frac{2e^2}{3c^3}\gamma^4 a^2, \quad P_{non-rel} = \frac{2e^2}{3c^3}a^2$$

$$P_{rel} \sim \gamma^4 v^4 / r$$

- Highly relativistic particle: the velocity becomes nearly constant and the term γ^4 determines the loss rate.
- Synchrotron: r is fixed after construction, larger r – smaller losses

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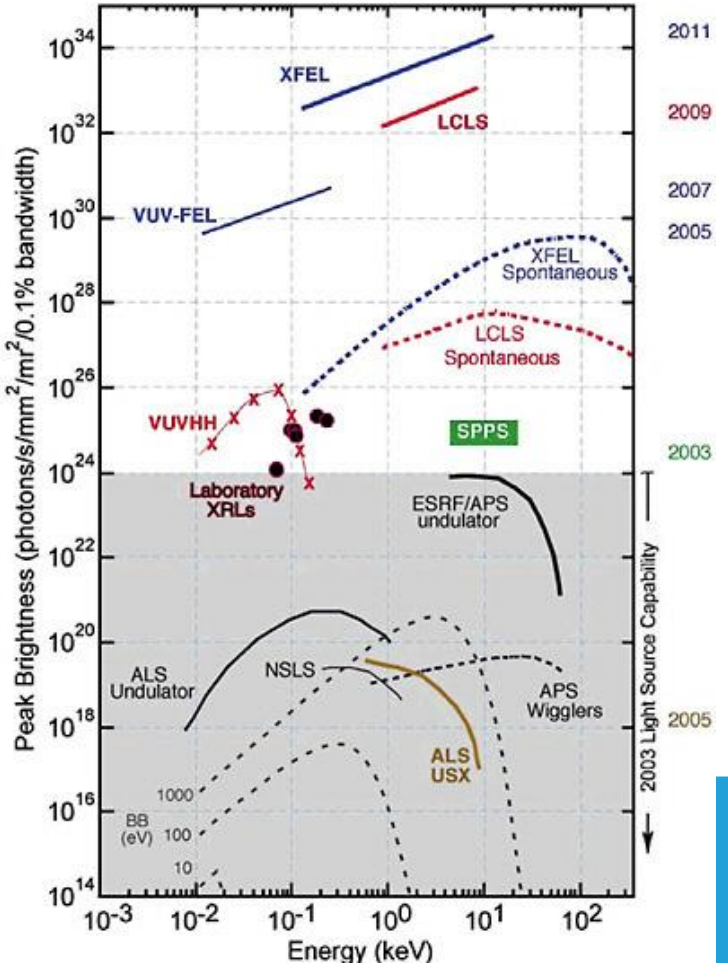

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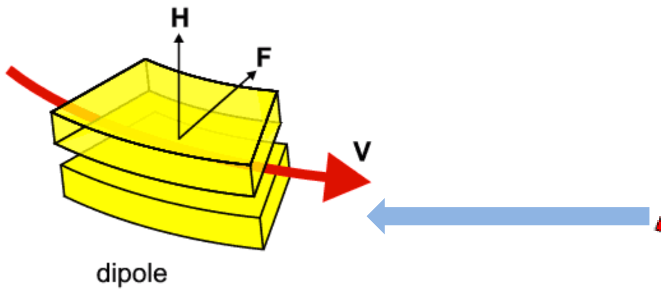
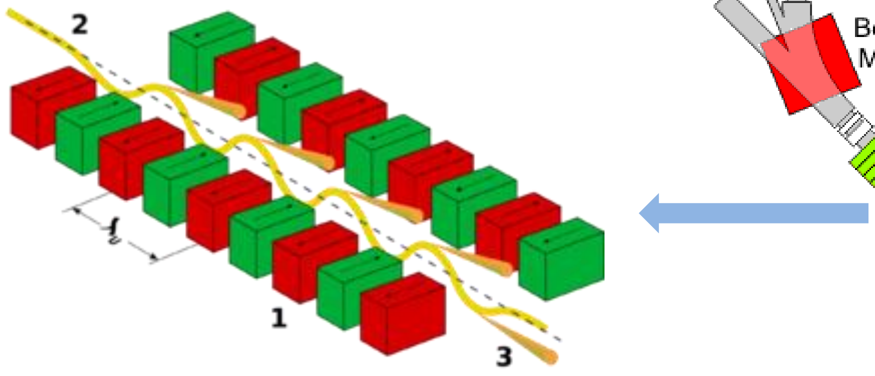
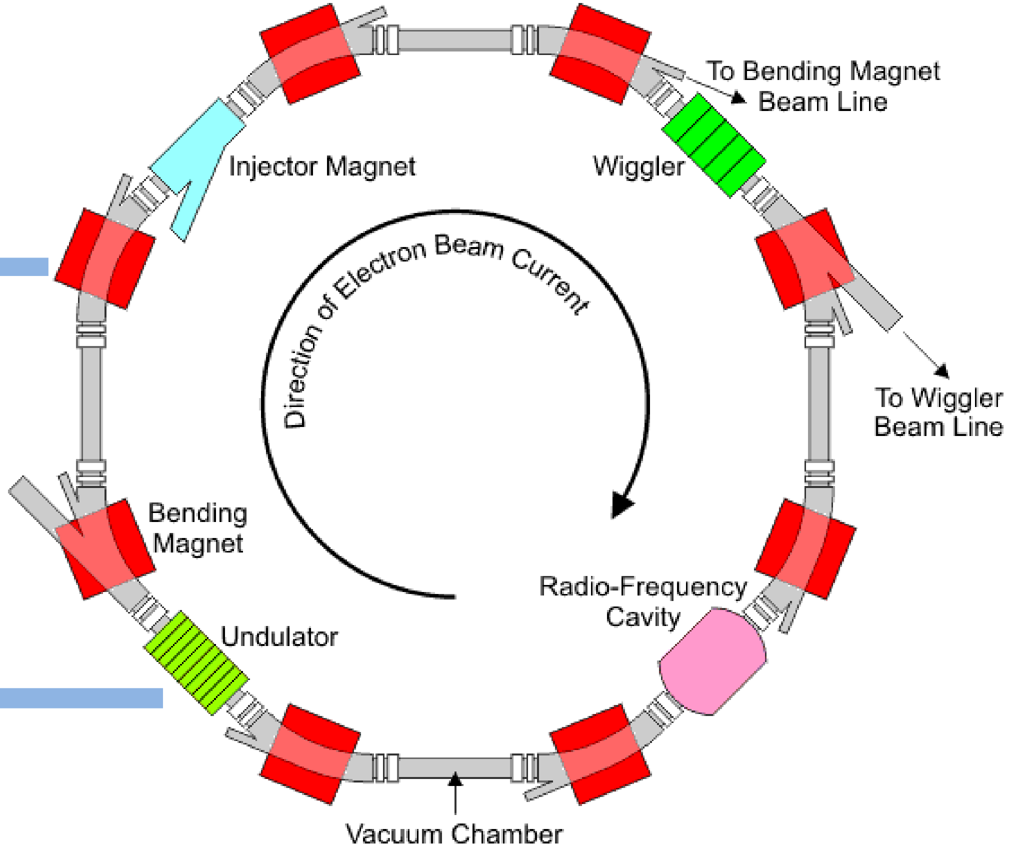
Synchrotron radiation generation







http://pd.chem.ucl.ac.uk/

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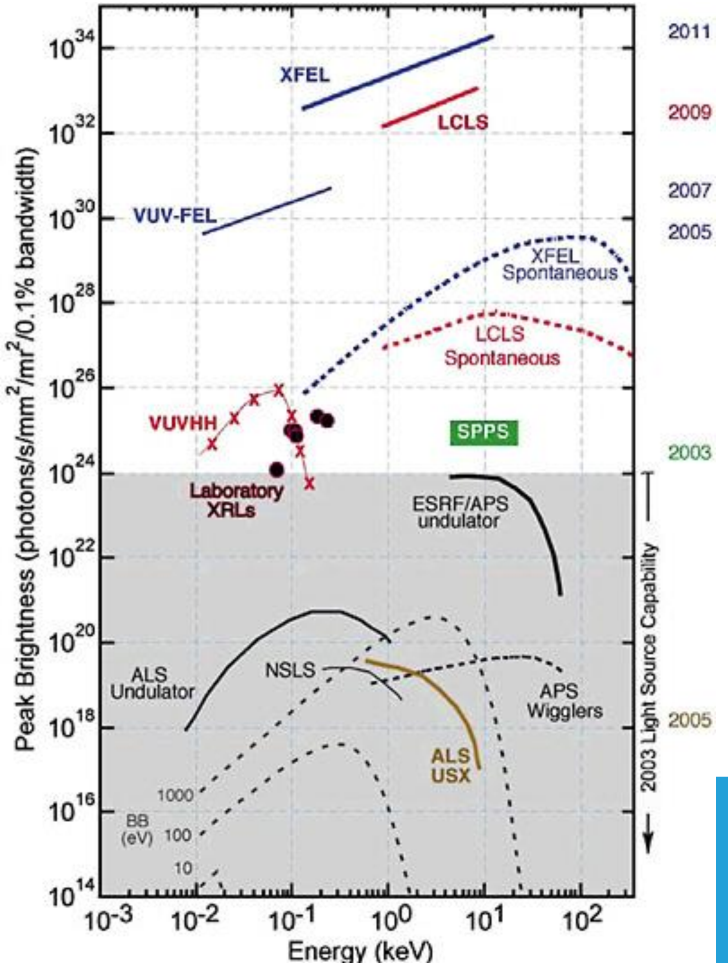

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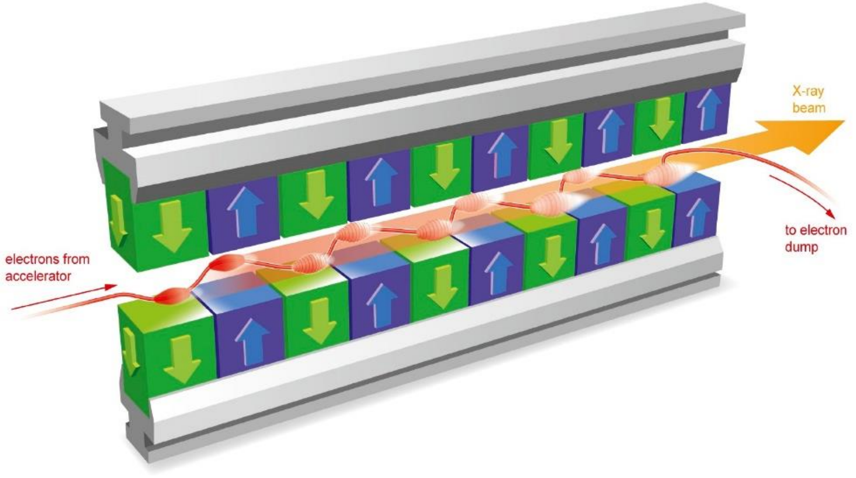
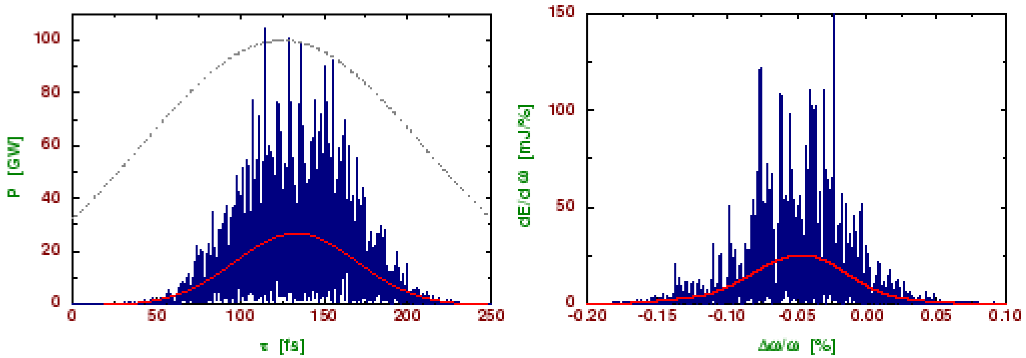
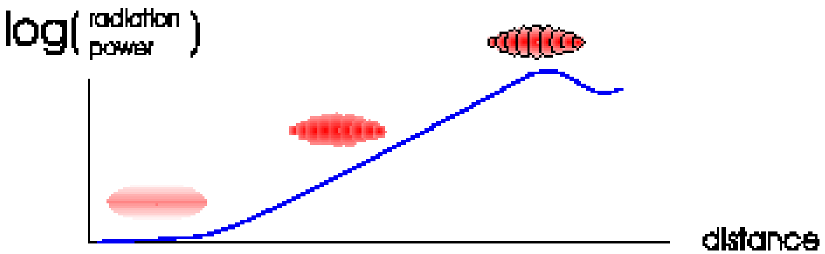
XFEL basics of operation

Self-amplified spontaneous emission (SASE)







- Large number of independent "spikes", since started up from chaotic noise.
- Within one spike the radiation is transversely and longitudinally coherent.
- As a result, the radiation produced by such a beam has random amplitudes and phases in time and space: stochastic radiation.

http://photon-science.desy.de/
http://www.xfel.eu/

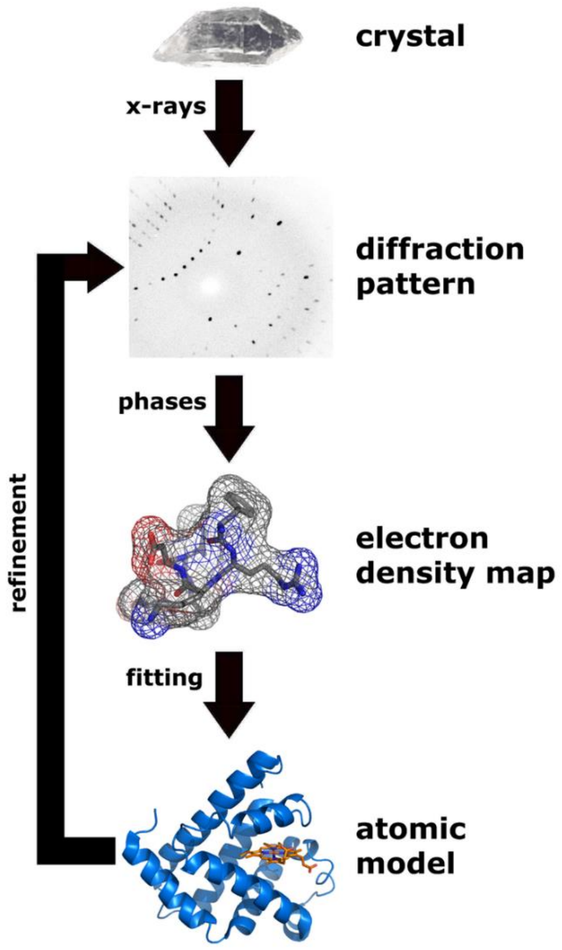
- No effective mirrors in VUV and X-ray range: no resonant cavity as for conventional lasers
- X-ray FEL output beam is produced by a single pass of radiation through the undulator – long size facilities.
- The electron beam must be maintained in a vacuum: numerous vacuum pumps along the beam path.

X-ray radiation sources

Synchrotrons	XFELs	HHG
10^{12}-10^{13} photons/s	10^{12}-10^{13} photons/pulse	10^{12}-10^{13} photons/s
Sub-nanosecond pulse	Femtosecond pulse	Attosecond pulse
Incoherent	Partially coherent	Coherent
Narrow bandwidth	SASE broadband	Fourier transform limited
Soft and hard X rays	Above N1s edge (400 eV)	Below N1s edge (400 eV)
Few 100m / established	Few km / high-cost	Table-top / cheap

New possibilities:
X-ray diffraction imaging of structure and dynamics (BIO)
Controlling of chemical reactions, charge transfer (CHEM)
Nonlinear effects in x-ray range (PHYS)

X-ray study of the structure and dynamics



Biological molecules crystallography first obtained in 1937 for cholesterol (Dorothy Hodgkin, Nobel Prize 1964)

Typically need wavelength ~0.1 nm (scale of covalent bond) and narrow band radiation.

High brilliance 2-3rd generation synchrotrons revolutionized the field, structure determination became a routine procedure, the **milestone of 100 000** structures (Protein Data Bank) will soon be passed.

Record a diffraction pattern of a sample in about one second.

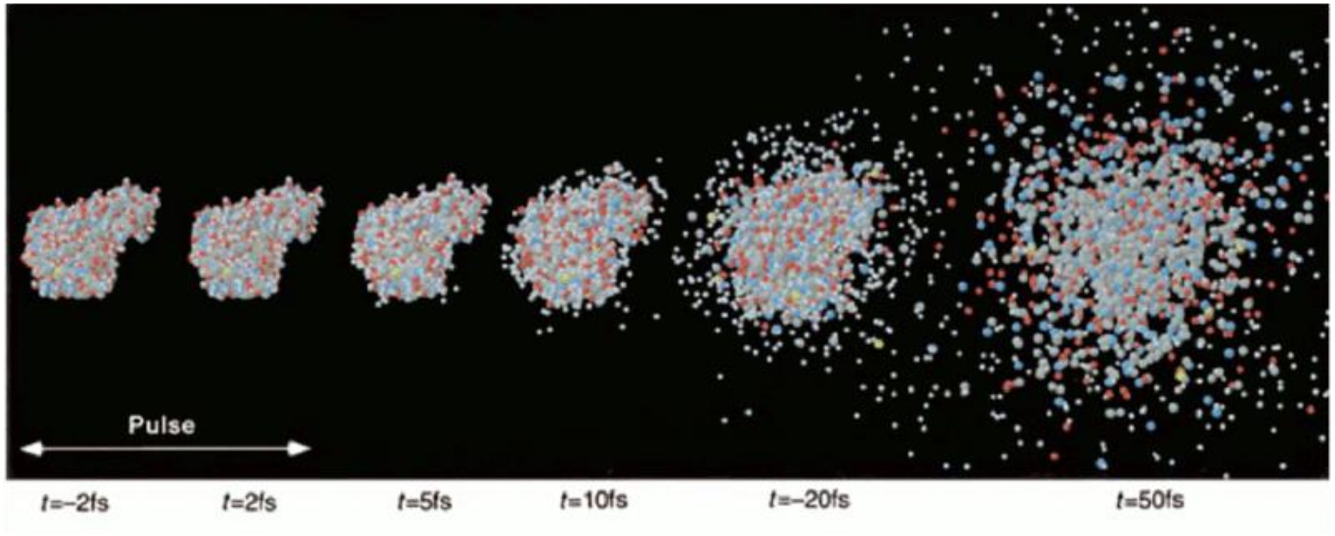
Long recording time shows average positions of atoms.
No dynamical picture is possible.

Crystallization is very difficult techniques and not all biomolecules got crystallized.

Is the structure of molecule in crystal the same as in life tissue?

Diffraction before destruction

- Strong X rays results in strong radiation damage!?
- X-ray exposure shorter than the time-scale of biological sample to explode is needed!
- XFEL pulses of shorter or about a few tens of femtoseconds push back the traditional radiation damage limits of structural biology. The resolution is shown to drop off for pulses longer than 70 fs.



Neutze, et al, *Nature* **406**, 752 (2000)
Barty A, et al. 2012 Nat. Photon. 6, 35–40

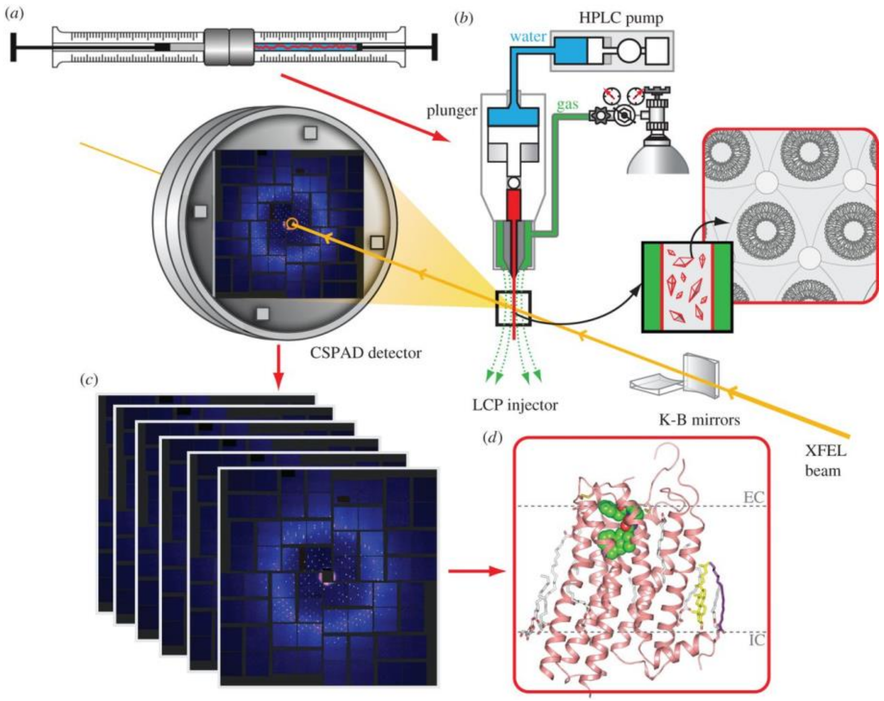
Serial femtosecond crystallography

Nano/microcrystals of photosystem I [1]

Photosystem II to 5.7 Å resolution [2]

Shown that microcrystals of the some photosynthetic reaction centers (e.g. *Blastochloris viridis*) not isomorphous to their larger crystal phase form [3]

Human serotonin receptor GPCR crystal structure to 2.8 Å resolution [4]



Liu W et al., 2014 Phil. Trans. R. Soc. B 369: 20130314.

Chapman HN, et al. 2011 Nature 470, 73–77.
Kern J, et al. 2012 Proc. Natl Acad. Sci. USA **109**
Wohri et al. 2009 Biochemistry **48**,9831–9838
Liu W, et al. 2013 Science **342**,1521–1524

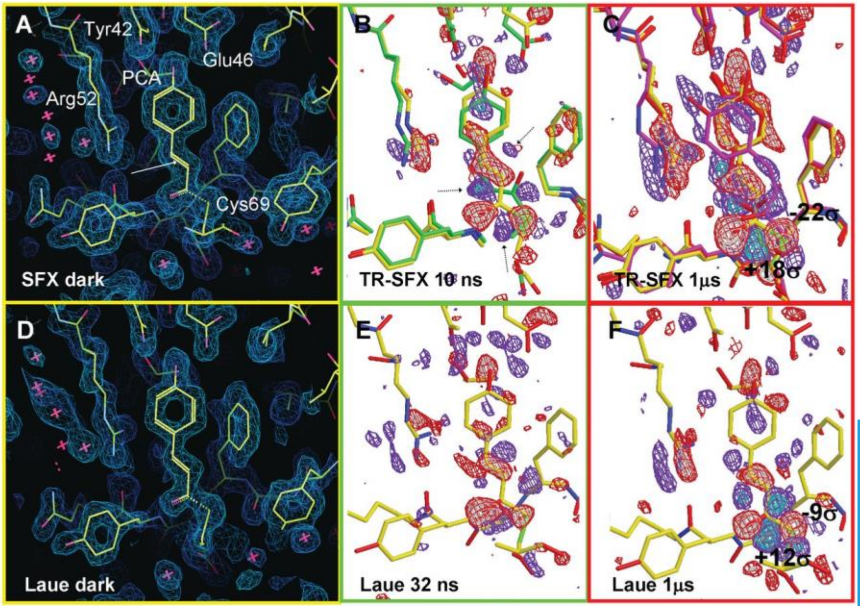
XFEL probes protein dynamics

- Serial femtosecond crystallography (SFX) with XFEL ultrashort pulses for studies of the light-triggered dynamics of biomolecules.
- XFEL-based time-resolved structural studies create opportunities for discoveries in life science that are not accessible using synchrotron radiation.

Advantages as compared to Laue method:

- microcrystals are of lower optical density, thus giving homogeneous molecular excitation
- sample is continuously replaced, the experiment is not sensitive to the accumulated X-ray- and pump laser-induced damage
- the systems are not restricted to probing reactions that return to their resting state (potential for study of chemically driven enzymatic reactions at room temperature to time-resolved diffraction)
- SFX neatly avoids the presence of X-ray damage-induced artefacts in the electron density image

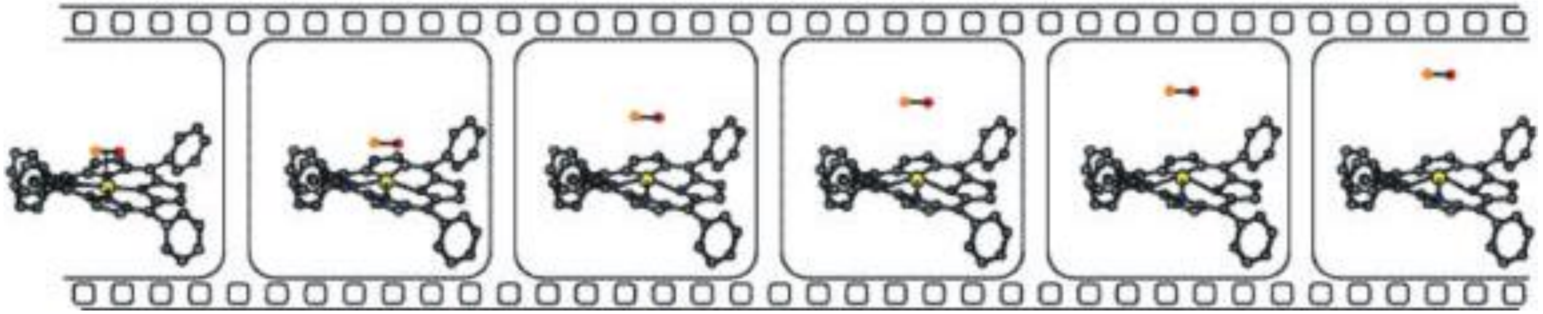
- Microcrystals of photoactive yellow protein (a bacterial blue light photoreceptor)
- High-resolution, time-resolved difference electron density maps obtained
- Structures of reaction intermediates to a resolution of 1.6A



Tenboer, J. *et al*. *Science* **346**, 1242–1246 (2014).
Neutze, Phil.Tr.R.Soc.Lond.B. Biol. Sci., 2014, 369, 20130318.

Ultrafast reaction dynamics with XFELs

"Molecular movies" of ultrafast (fs) reaction dynamics of small systems



One can study nuclear, charge and spin dynamics of ongoing reactions

- Fragmentation, attachment/detachment dynamics
- Solvation dynamics
- Intramolecular charge transfer
- Itermolecular charge transport

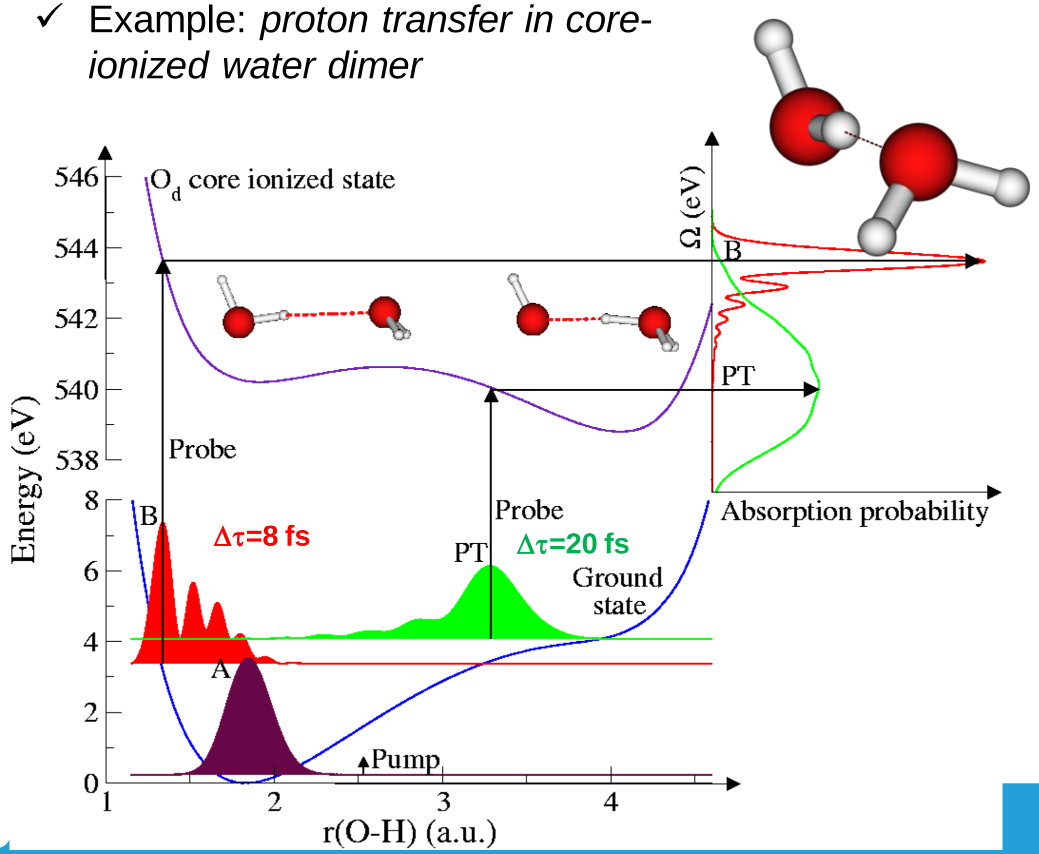
Follow elementary steps of photochemistry in resonant x-ray interaction

Figure: Pellegrini, UCLA, Stöhr , SSRL

IR pump x-ray probe: spectroscopy of light-induced nuclear dynamics

- ❑ Short brilliant IR pulse creates a vibrational wave packet in the ground state
- ❑ The wave packet dynamics is tested with site-selective and time resolved XFEL's ***x-ray absorption/photoelectron spectroscopy***

✓ Example: *proton transfer in core-ionized water dimer*



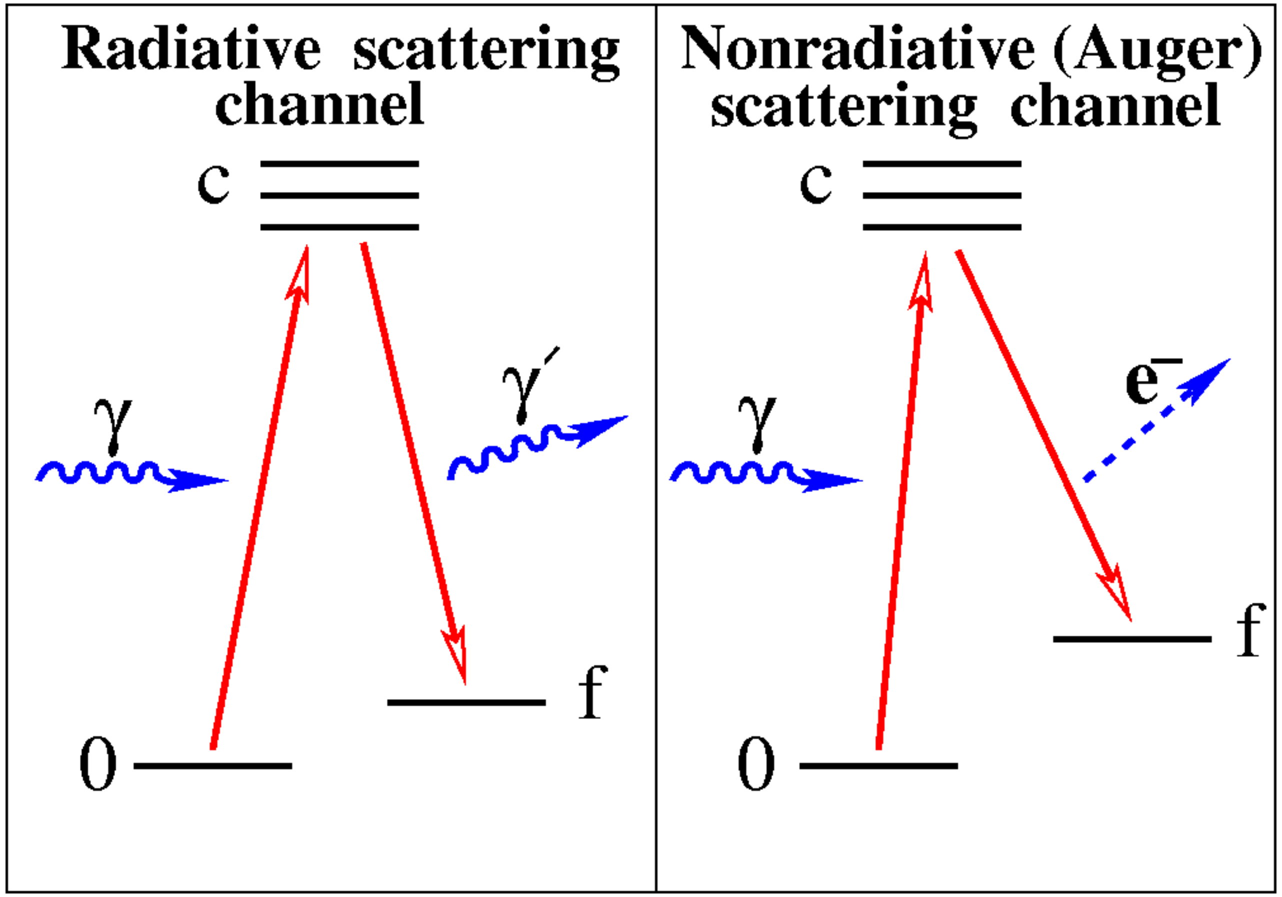
• Using femtosecond x-ray pulses:
-Measure the continuous time evolution of nuclear motion
-*Femtochemistry*
-Synchronization of x-ray pulse to comb of IR pulse

• Theory (KTH)
Guimarães, VK, Gelmukhanov, Ågren, *PRA* **70**, 062504 (2004);
Guimarães et al, *PRA* ***71***, 043407; *PRA* **72**, 012714 (2005)

• ***eSPec*** program: Guimaraes et al.

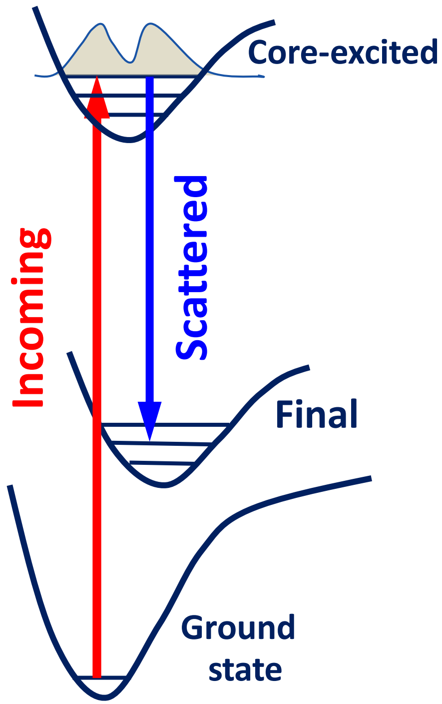
Felicíssimo et al, *J Chem Phys, 122*, 094319 (2005).

Resonant X-ray scattering: pump-probe with synchrotrons



In the resonant X-ray scattering (RXS) the molecule is core excited by X-ray photon.
The core excited state decays to final states emitting X-ray photons or electrons.

Theory of vibrationally resolved RIXS



Theoretical Description

<u>Energy domain</u>

$$\sigma(\omega',\omega) = \sum_{\nu_f} |F_{\nu_f}|^2 \Delta\left(\omega - \omega' - \omega_{f0} - \epsilon_{\nu_f} + \epsilon_{\nu_0}, \Gamma_f\right),$$

$$F_{\nu_f} = \sum_{\nu_c} \frac{\langle \nu_f | D_{fc} | \nu_c \rangle \langle \nu_c | D_{c0} | \nu_0 \rangle}{\omega - \omega_{c0} + \epsilon_{\nu_0} - \epsilon_{\nu_c} + \imath\Gamma} \qquad \Delta(x,y) = \frac{y}{\pi(x^2+y^2)}$$

<u>Time domain</u>

$$\sigma(\omega',\omega) = \frac{1}{\pi}\mathrm{Re}\int_0^\infty e^{\imath(\omega-\omega'-\omega_{f0}+\epsilon_{\nu_0}+\imath\Gamma_f)t}\sigma(t)dt,$$

$$\sigma(t) = \langle \Psi(0) | \Psi(t) \rangle$$

$$|\psi_c(t)\rangle = e^{-\imath h_c t} D_{c0} |\nu_0\rangle, \qquad |\Psi(t)\rangle = e^{-\imath h_f t} |\Psi(0)\rangle.$$

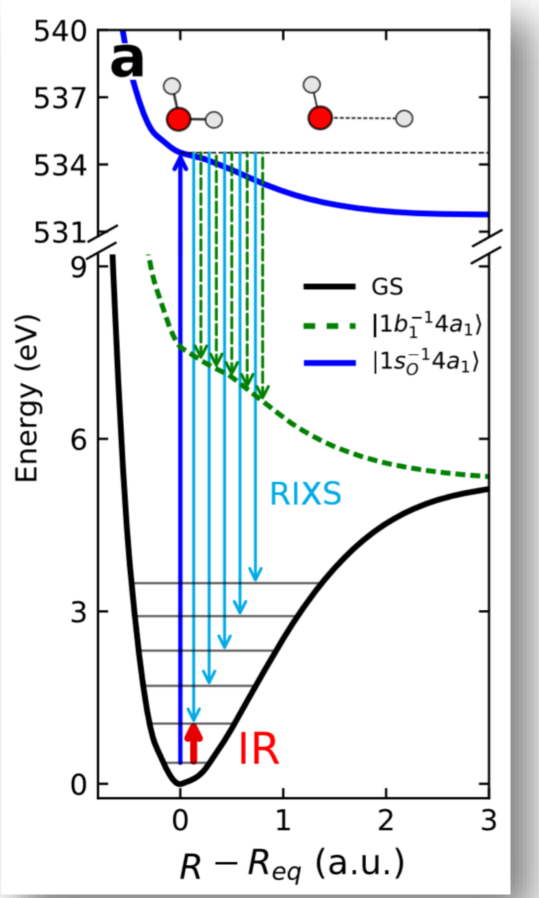
$$|Y(0)\rangle = D_{fc} \int_0^\infty e^{\imath(\omega-\omega_{c0}+\epsilon_{\nu_0}+\imath\Gamma)t} |\psi_c(t)\rangle dt,$$

RIXS = Resonant Inelastic X-ray Scattering

F. Gel’mukhanov and H. Ågren, Physics Reports, 312, 87 (1999)

RIXS via dissociative core excited state

Mixed approach: mD time dependent + nD stationary model



Purpose: Treat systems which dissociate fast along at least one coordinate

We partition the nuclear Hamiltonian at the electronic state as

$$h_i = h_i^{(m)} + h_i^{(n)}, \quad i = 0, c, f$$

where m is the TD partition and n is the TI partition. The total wavefunction is then

$$|\psi_i^{(m)}(t)\rangle|\nu_i\rangle, \qquad \imath\frac{\partial}{\partial t}|\psi_i^{(m)}\rangle = h_i^{(m)}|\psi_i^{(m)}\rangle, \quad h_i^{(n)}|\nu_i\rangle = \epsilon_{\nu_i}|\nu_i\rangle.$$

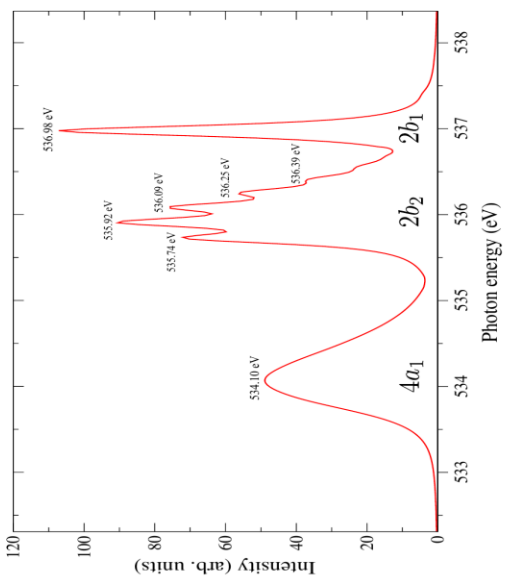
And the TD core-excited wave-packet is written as

$$|\psi_c(t)\rangle = e^{-\imath h_c^{(n)}t}|\nu_0\rangle e^{-\imath h_c^{(m)}t}D_{c0}|\mu_0\rangle = \sum_{\nu_c} e^{-\imath\epsilon_{\nu_c}t}|\nu_c\rangle\langle\nu_c|\nu_0\rangle|\psi_c^{(m)}(t)\rangle,$$

$$|\psi_c^{(m)}(t)\rangle = e^{-\imath h_c^{(m)}t}D_{c0}|\mu_0\rangle.$$

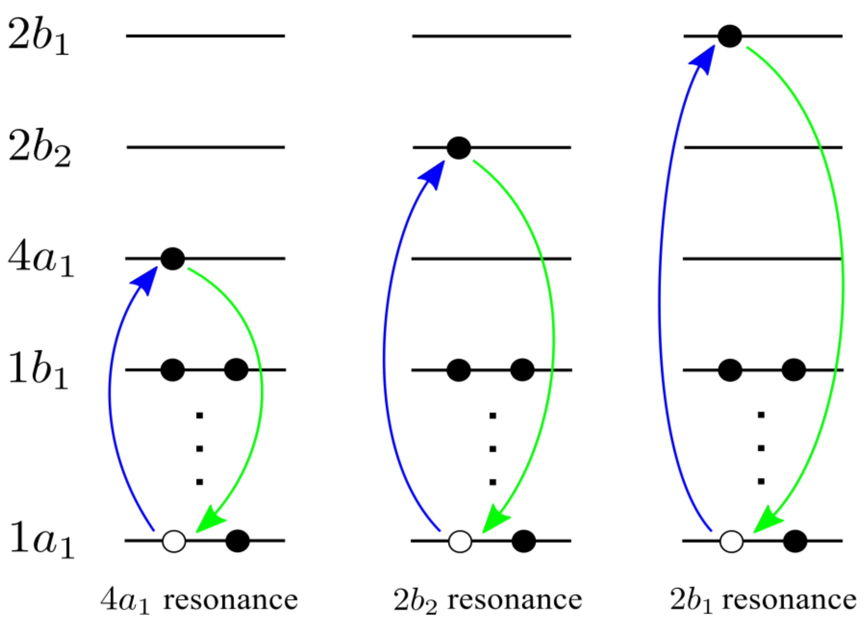
R. Couto et al., Nature Comm. 8, 14165 (2017)
V. Vaz da Cruz et al., PCCP 19, 195 (2017)

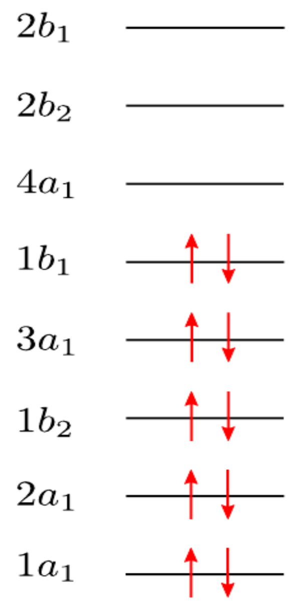
Quasi-elastic RIXS in water via 3 lowest core-excited states



XAS

Electronic

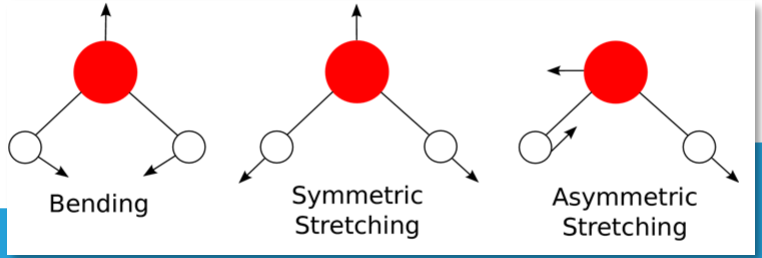




RASPT2 calculations for all electronic structure

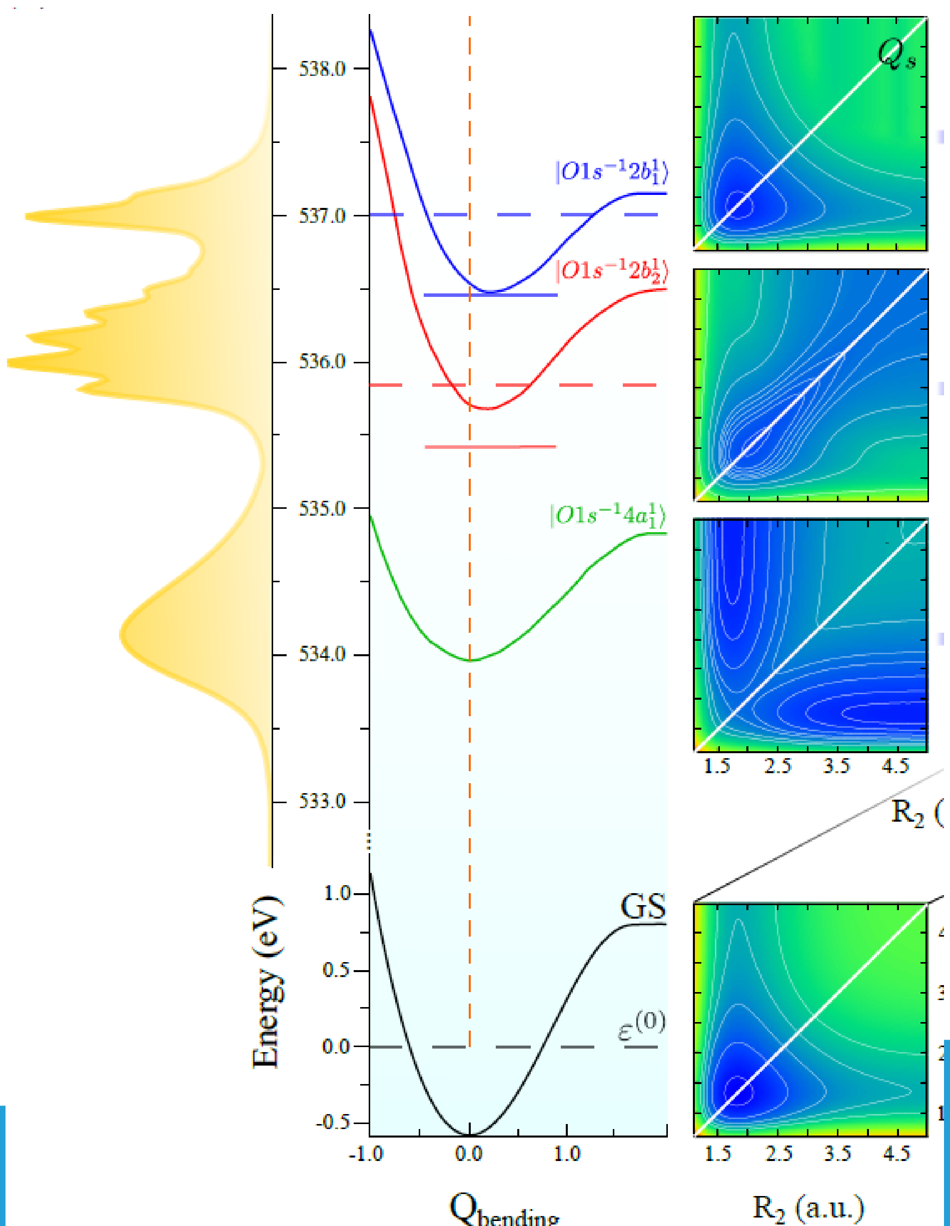
Quantum dynamics for all vibrational motion

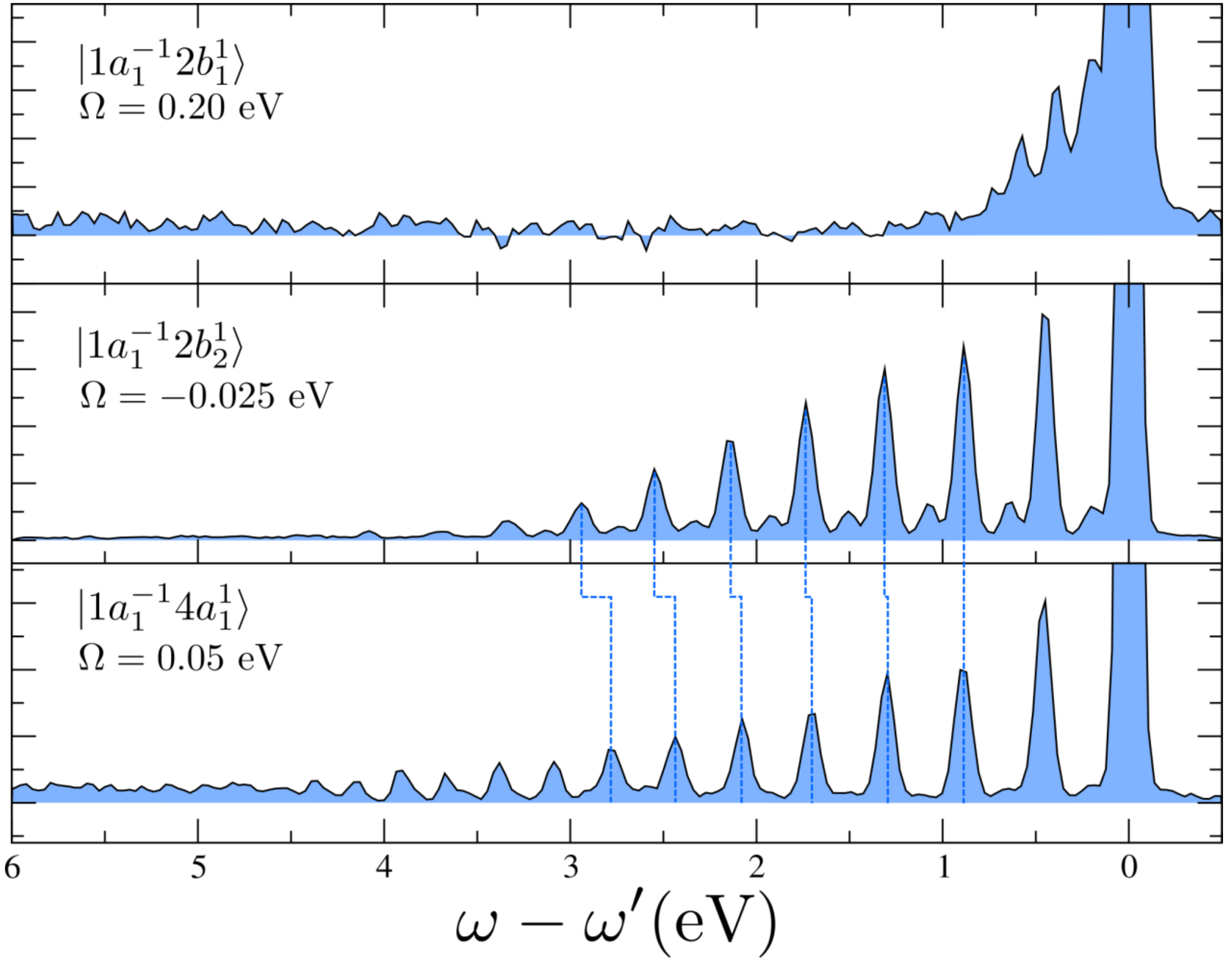
Nuclear



- Darling-Dennison coupling of stretching modes (strong)
- Fermi coupling – symmetric stretching and bending (weak)
- We treat the bending mode (1D) separately from the two coupled stretching modes (2D)

Quasi-elastic RIXS of gas-phase H2O





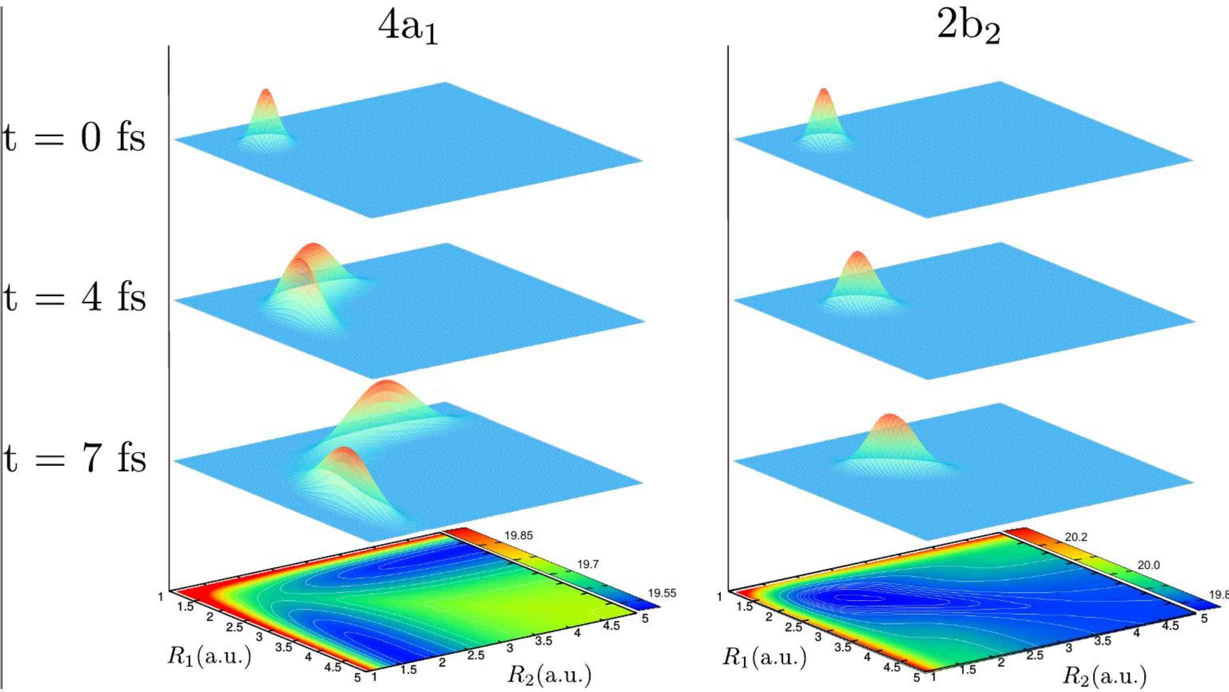
R. Couto, et al., Nature commun 8, 14165 (2017)
Vaz da Cruz, et al., PCCP 19, 195 (2017)

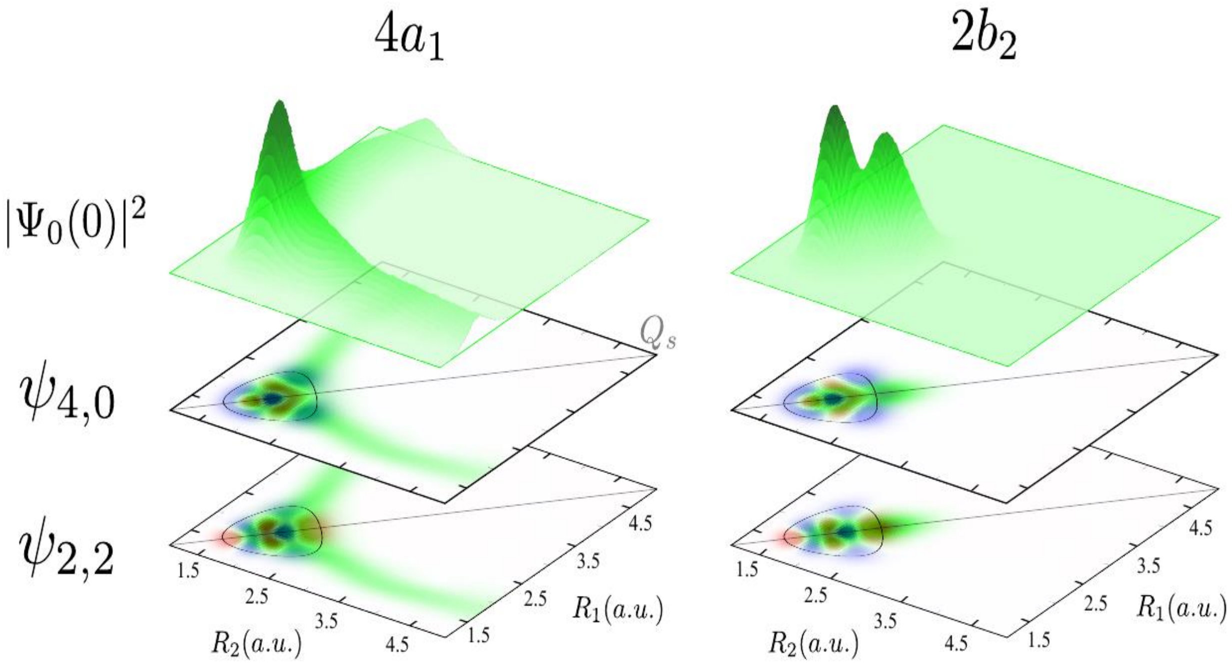
Propensity rules and selective gating

Overlap of core-excited wave packet and ground state wave functions

Multi-mode wave packet motion $|y_c|^2, \quad y_c = e^{-ih_c t}|0\rangle$

$$|\Psi_{\nu_i}(0)\rangle = \int_0^\infty e^{\imath(\omega-\omega_{i0}+\varepsilon_0-\epsilon_{\nu_i}+\imath\Gamma)t}|\psi_i(t)\rangle dt$$



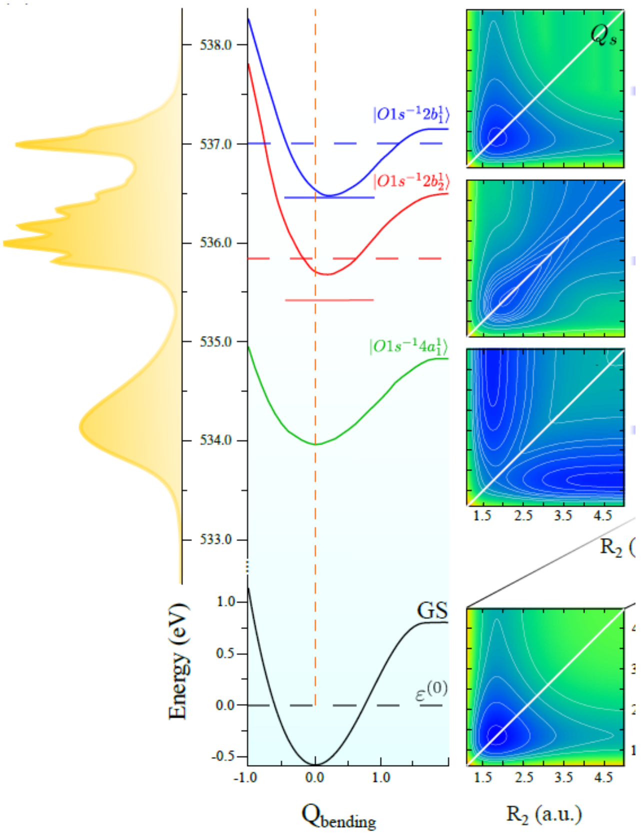


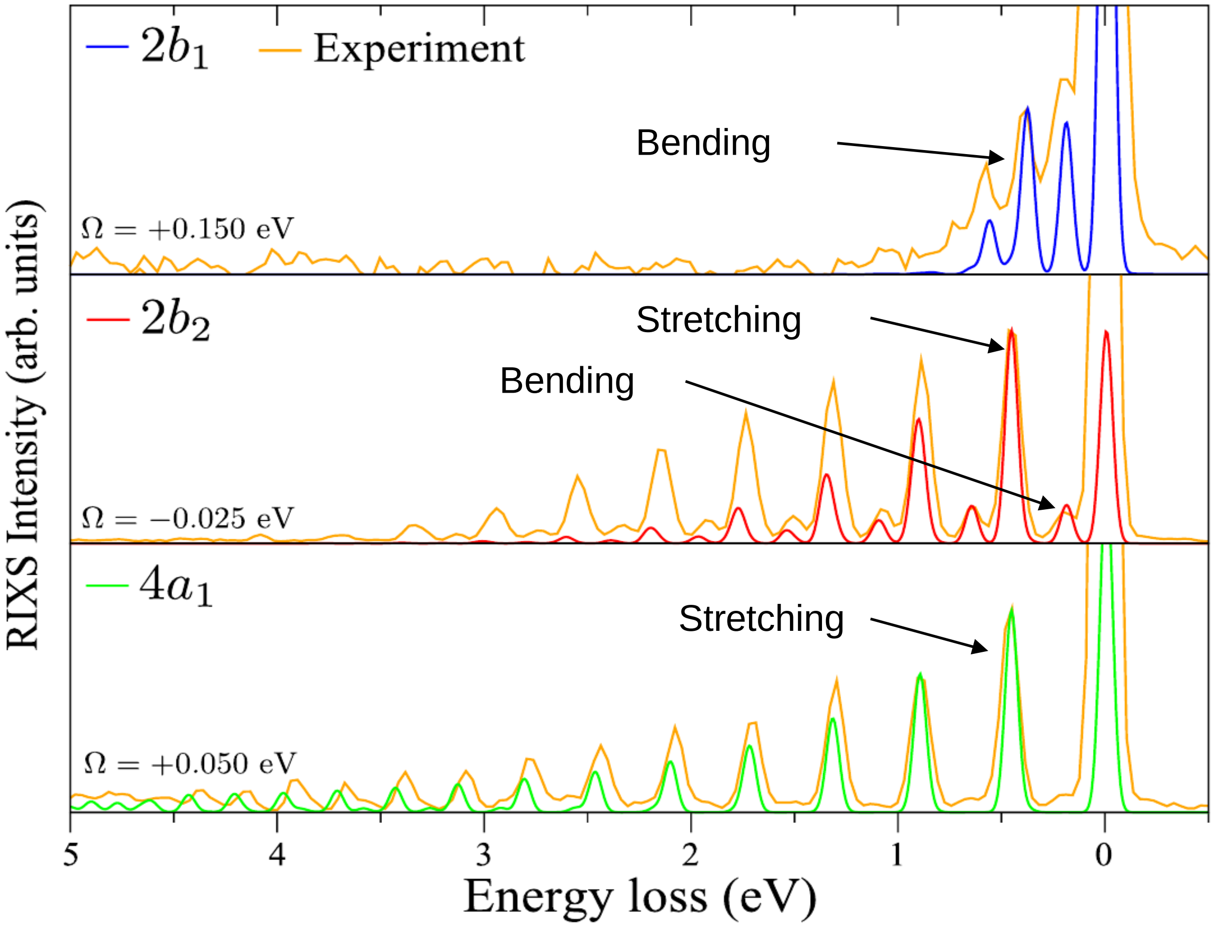
Schrödinger's cat dissociation

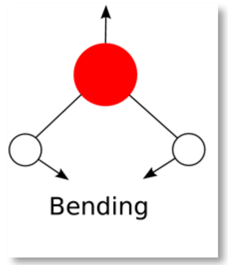
Nature communication 8, 14165 (2017)
PCCP 19, 195 (2017)
Scientific Reports 7, 43891 (2017)

$$F = -\imath\langle\psi_{n_s,n_a}|\Psi_0(0)\rangle$$

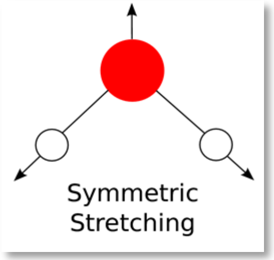
Selective gating to vibrational modes via RIXS





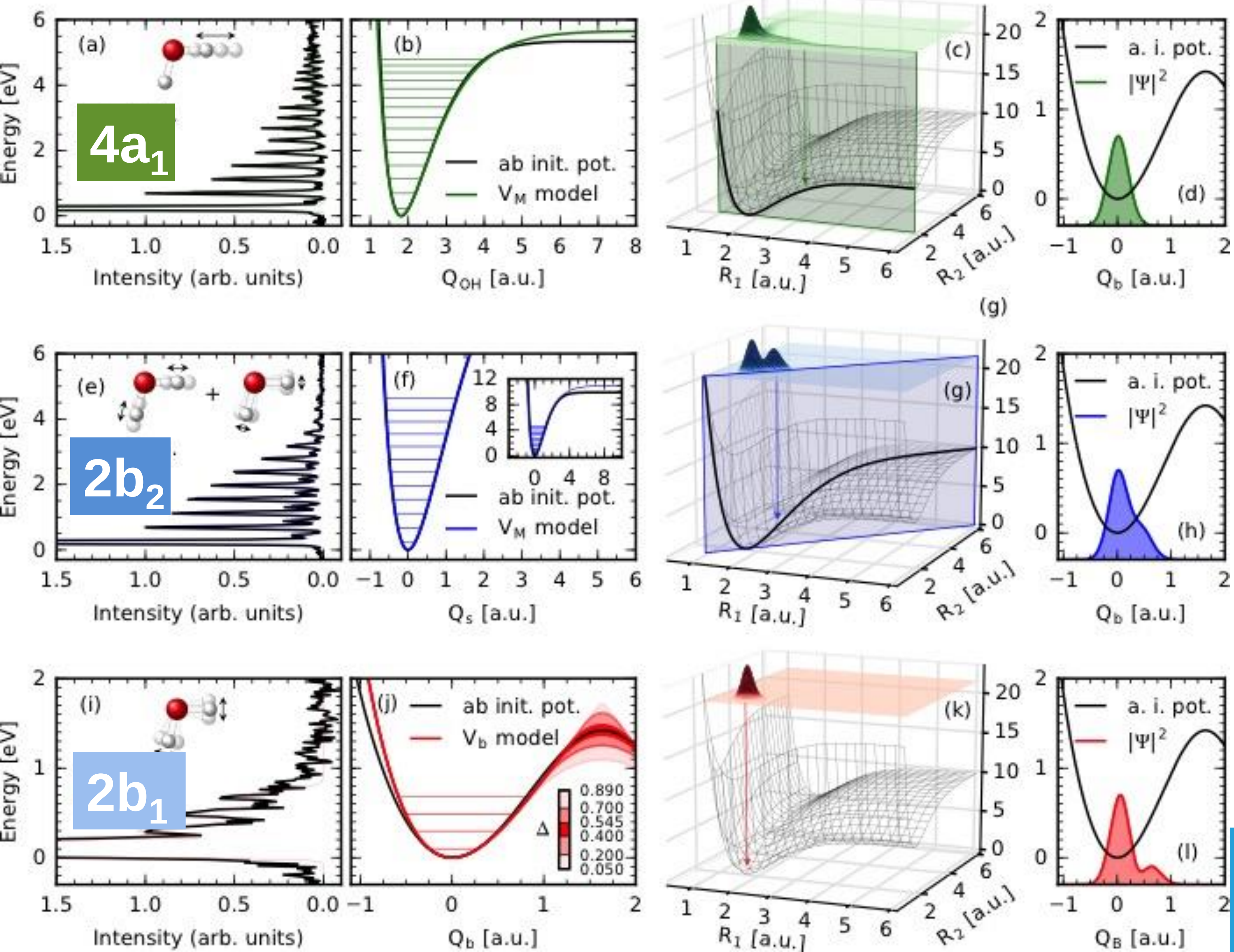


Pure symmetric stretching mode is suppressed



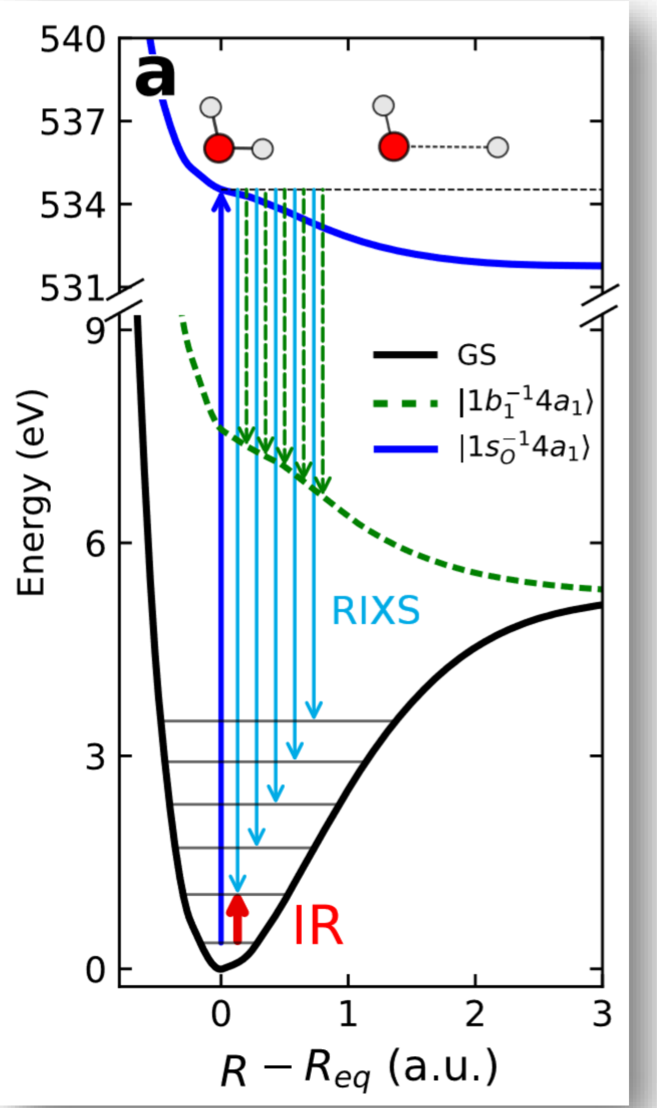
R. Couto, et al., Nature commun 8, 14165 (2017)

- ✓ Selective vibrational gating is general effect: core-excited potential and since that spatial core-excited wave packet dynamics dependent on the electronic excitation.
- ✓ Selecting vibration along reaction coordinate – control chemical reactions.

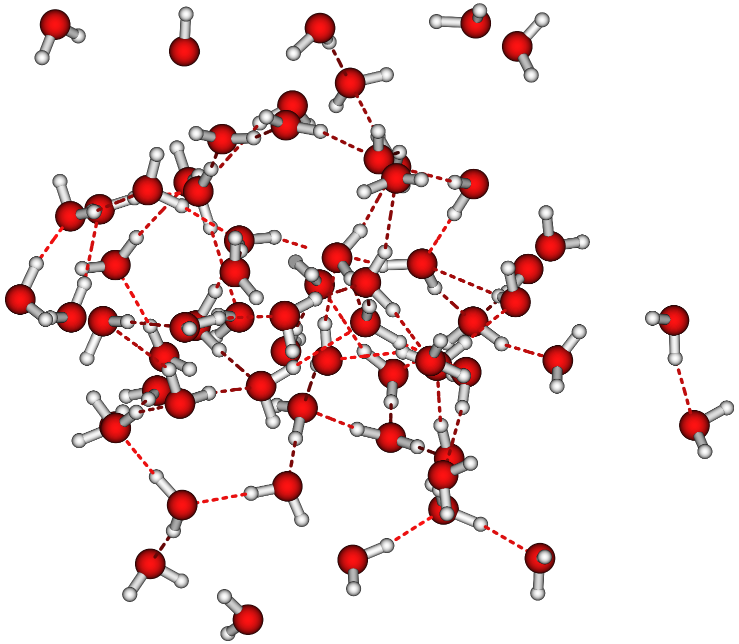


1D cut of potential along valley of potential energy surface

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



Structure and dynamics in RIXS of liquid water

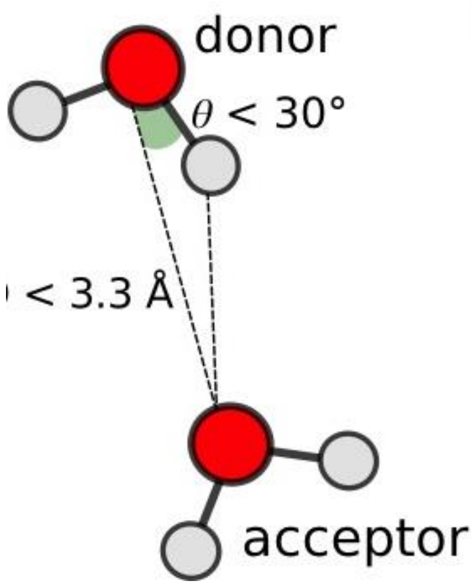


- 1st inelastic scattering channel
- Quasi-elastic scattering channel (final=ground)

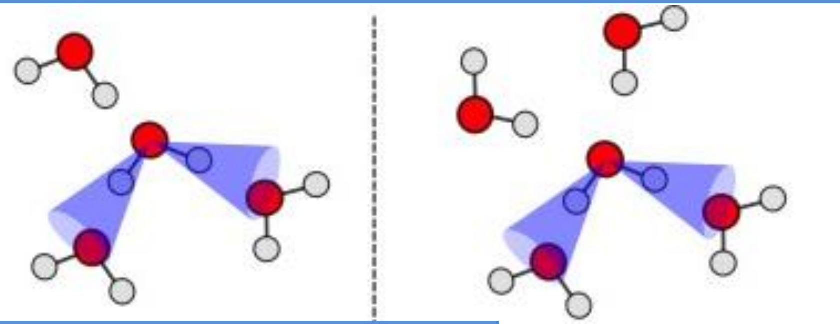
J. Niskanen et al., PNAS 116, 4058 (2019)
V. Vaz da Cruz, et al, Nat Commun. 10, 1013 (2019)

Classification of hydrogen bonds (HB)

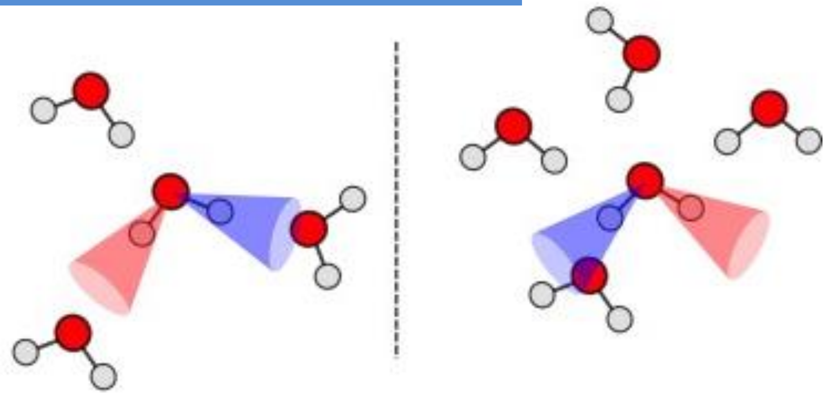
Definition of HB formation (geometrical criteria)[1,2)]



D2-double donor ("low density?", ice-like, tetrahedral)



D1-single donor ("high density?")



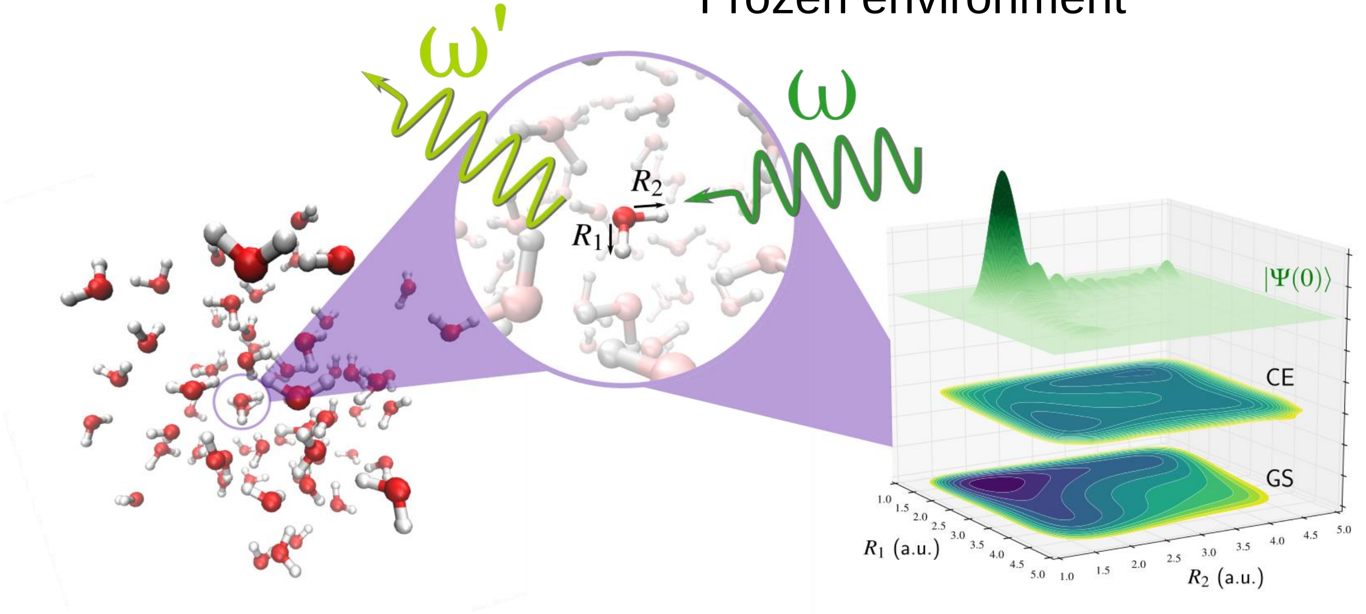
1) P. Wernet et al, Science 304, 995 (2004)
2) R. Kumar, J.R. Schmidt, J.L. Skinner, J Chem Phys 104, 7671 (2007)

Model of bulk liquid water for RIXS

Ab-initio molecular dynamics[1)]
- CPMD package
- DFT/BLYP (plane waves)
- 64 molecules in PBC

Quantum wave packet dynamics
- eSPec code (developed by us)
- 1D potential scans along each bond
- DFT potentials
- XCH, FCH and HCH dipoles
- Frozen environment

$$\sigma(\omega',\omega)=\sum_{k=1}^{64}\sigma_k(\omega',\omega)$$



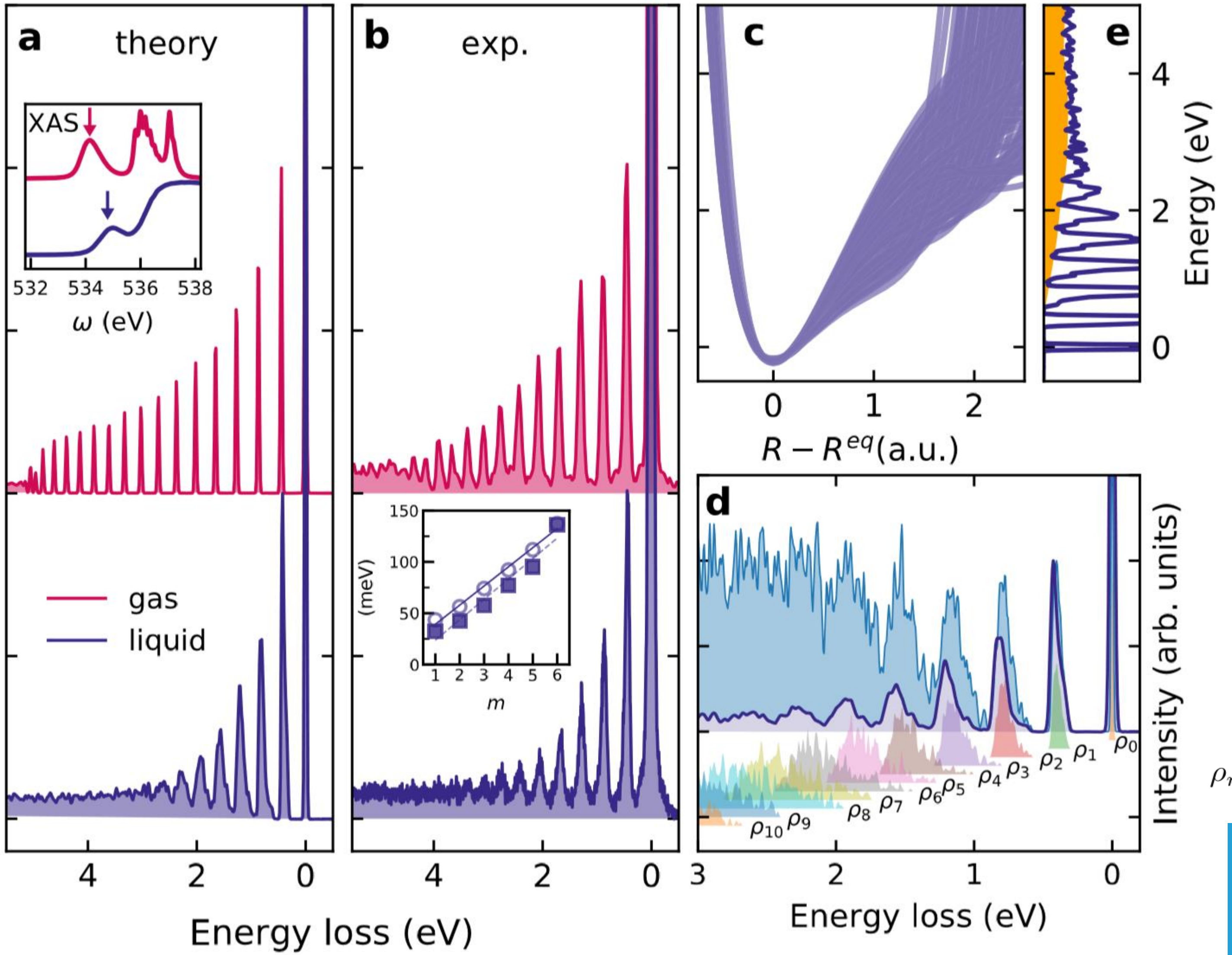
1) Similar to ref: M. Odelius J. Phys. Chem. A, **113**, 8176-8181 (2009)
2) V. Vaz da Cruz, et al, Nat Commun. 10, 1013 (2019)

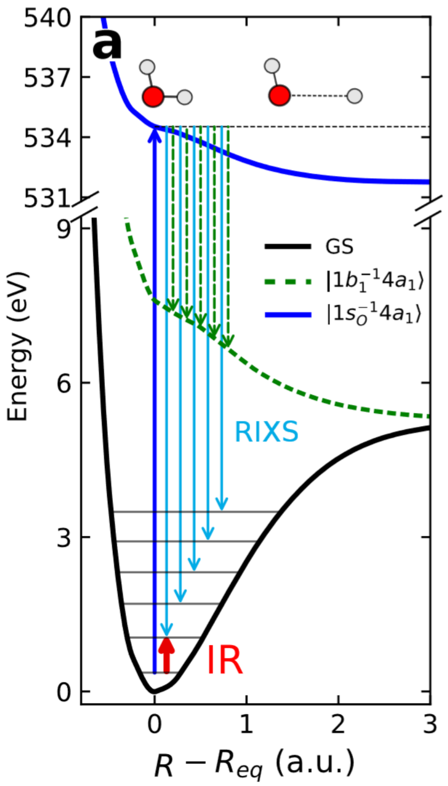
Quasi-elastic RIXS channel: gas phase vs liquid

Shortening of vibrational progression and formation of smooth background

Gas phase

Liquid phase

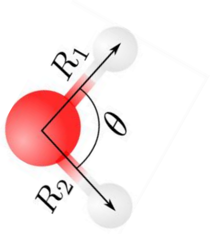




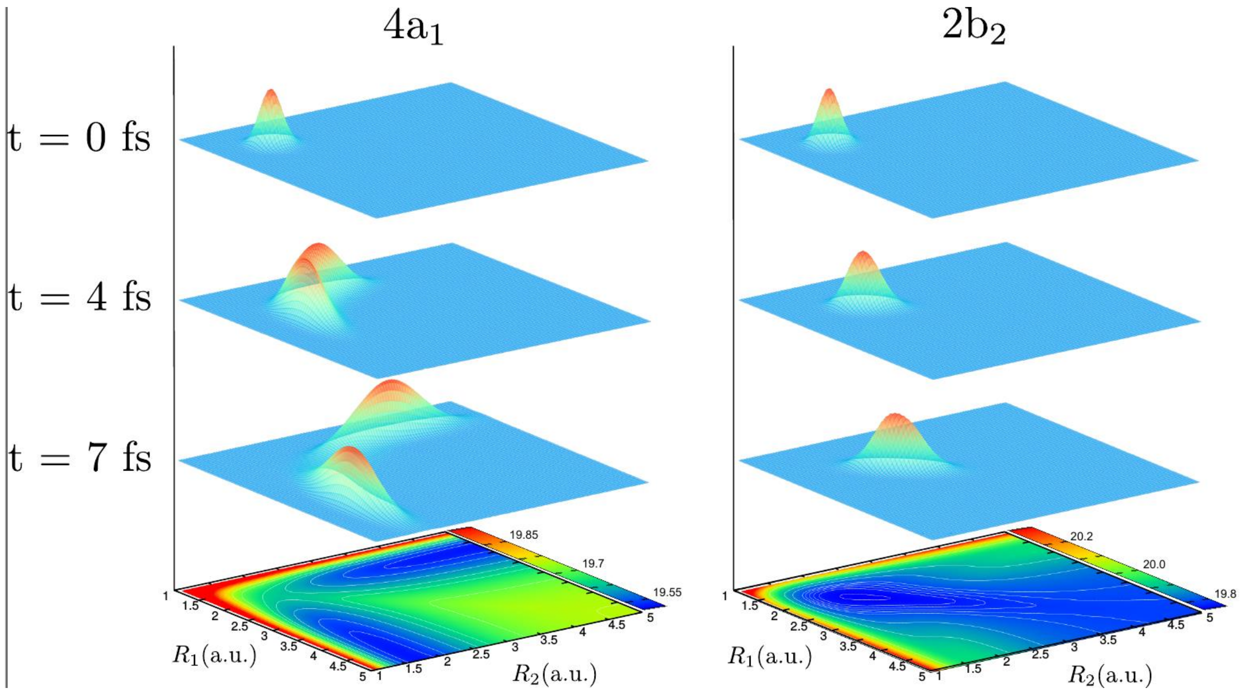
$$\rho_m(\epsilon) = \sum_{k=1}^{64} \sum_{n_1+n_2=m} \Phi(\epsilon - \epsilon^k_{n_1,n_2} + \epsilon^k_{0,0})$$

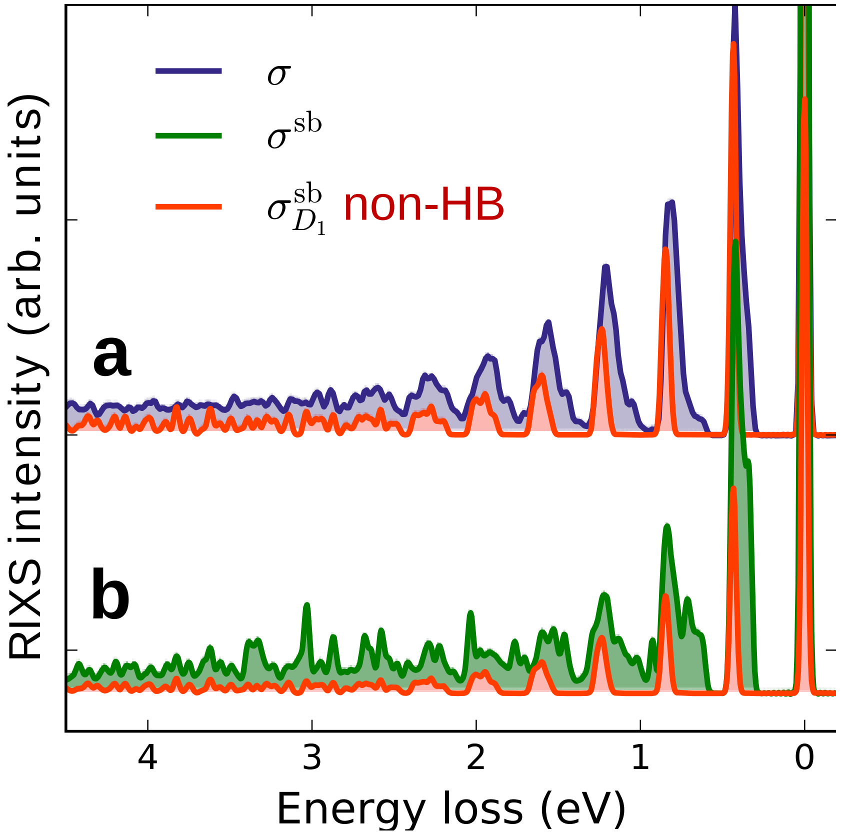
V. Vaz da Cruz, et al,
Nat Commun. 10, 1013 (2019)

Breakdown of single bond-approximation widely used in theory



Multi-mode wave packet motion $\left|y_c\right|^2, \quad y_c = e^{-ih_c t}\left|0\right\rangle$



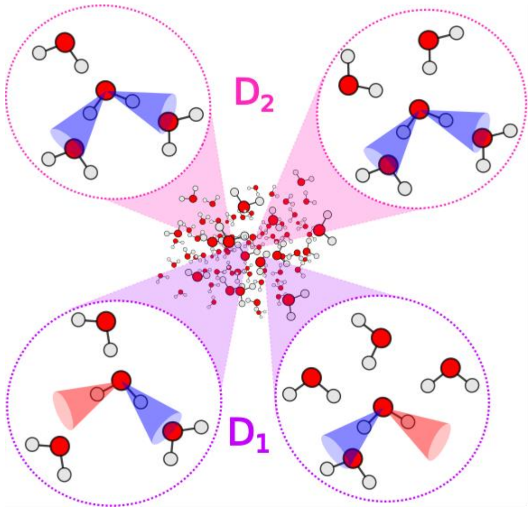


Schrödinger's cat dissociation: gas phase

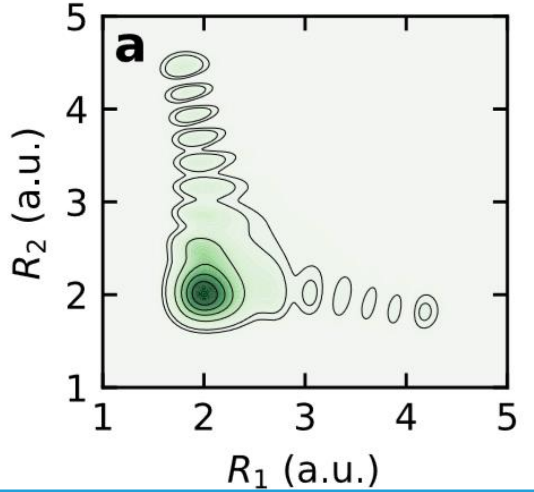
Nature communication, 8, 14165 (2017)
Scientific Reports, 7, 43891 (2017)

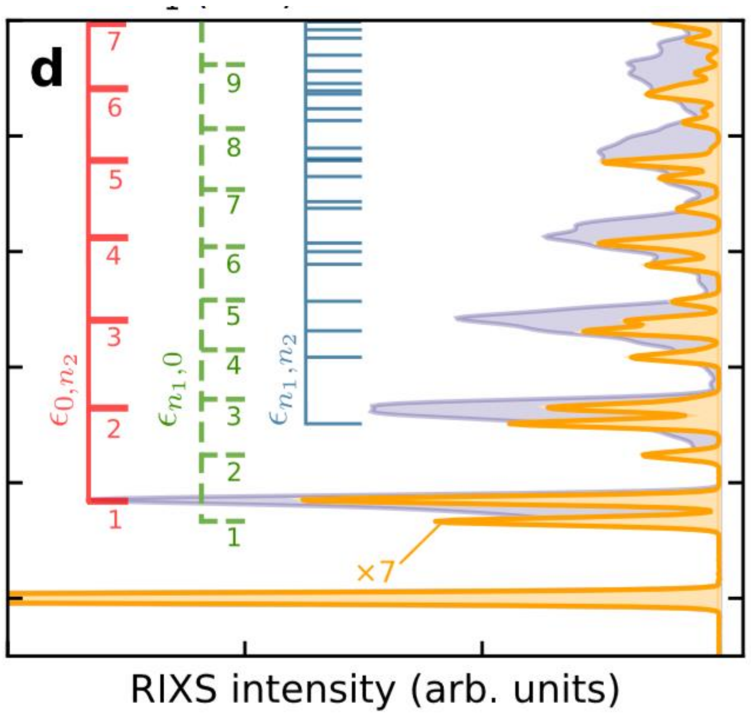
Role of inequivalent bonds in liquid

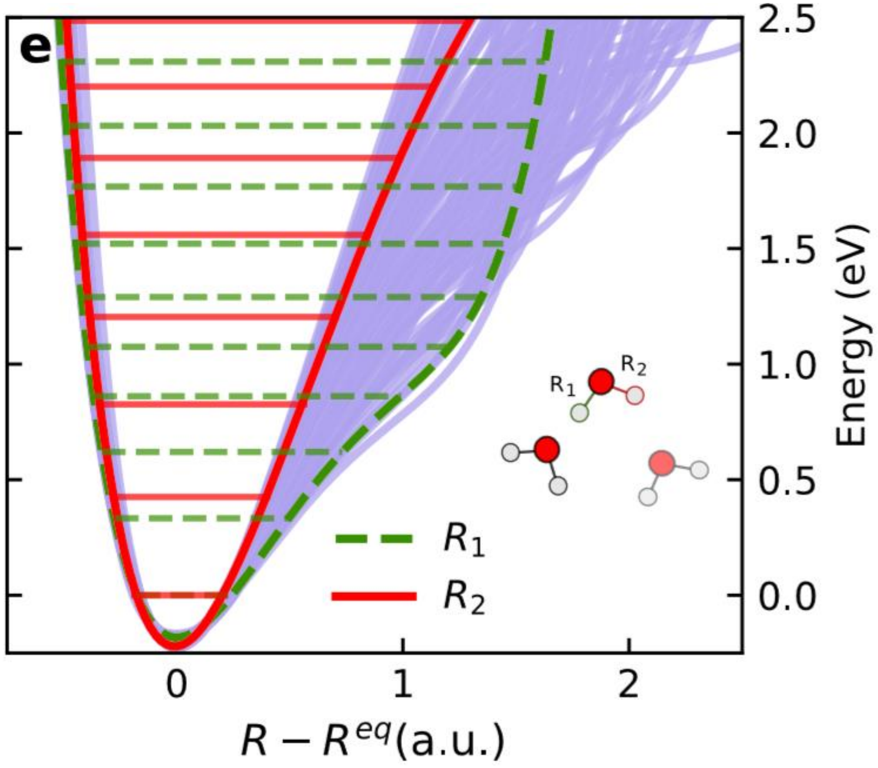
Local structure



Both OH bonds are excited coherently







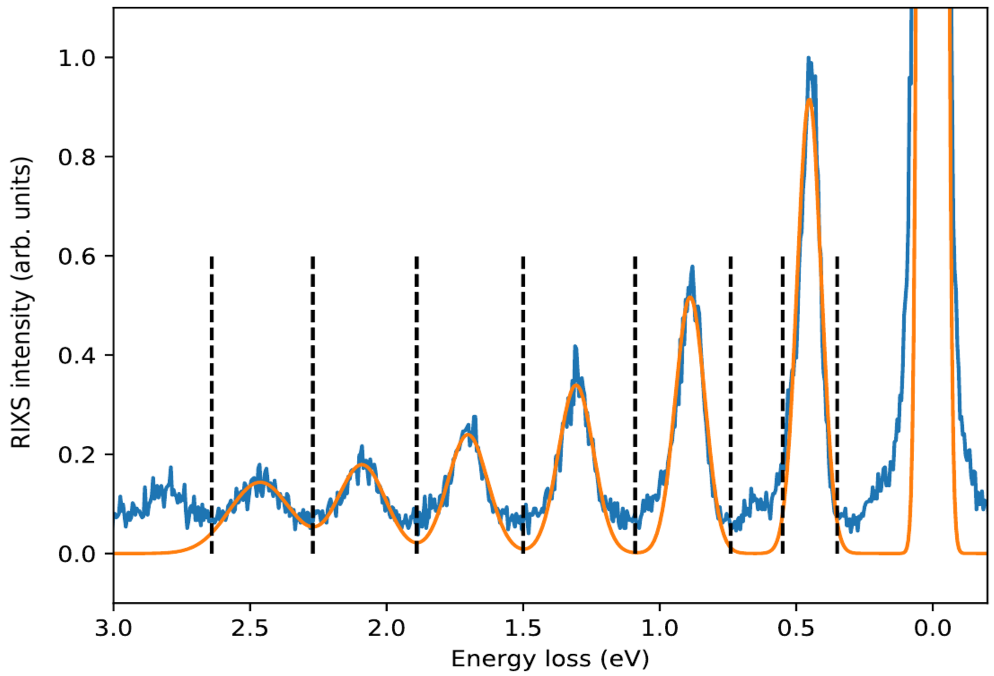
Steep potential (broken HB):
Peak number = Quantum number

Shallow potential (strong HB) :
Peak number ≠ Quantum number!

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

Confidence intervals for the OH potentials from experimental RIXS data using genetic algorithm

Peak intervals



- **The fitness criterion of our GA** is based on the concept of a "vibrational eigenvalue distribution"
- We consider whether a given eigenvalue lies within the width of a given peak $\Delta\varepsilon_m$ in the RIXS spectrum
- We consider the first six peaks (m= 1, …, 6) of the experimental RIXS spectrum (which are the most relevant according to our analysis).

Eigenvalue distribution arrays

Weak/no - HB	$(111111),$	$(111112),$
Strong HB	$(112212),$	$(112222), \cdots$

To extract potential information in liquid, we allow for more than one vibrational eigenvalue to be located within the energy range around a given vibrational in RIXS

Reconstruction of the potentials from experimental RIXS through the genetic algorithm

- **Individuals:** set of potential parameter (*B, β, α, D*)

$$V(R) = V_M(R) + Be^{\beta R}, \quad V_M(R) = D\left(1 - e^{\alpha R}\right)^2$$

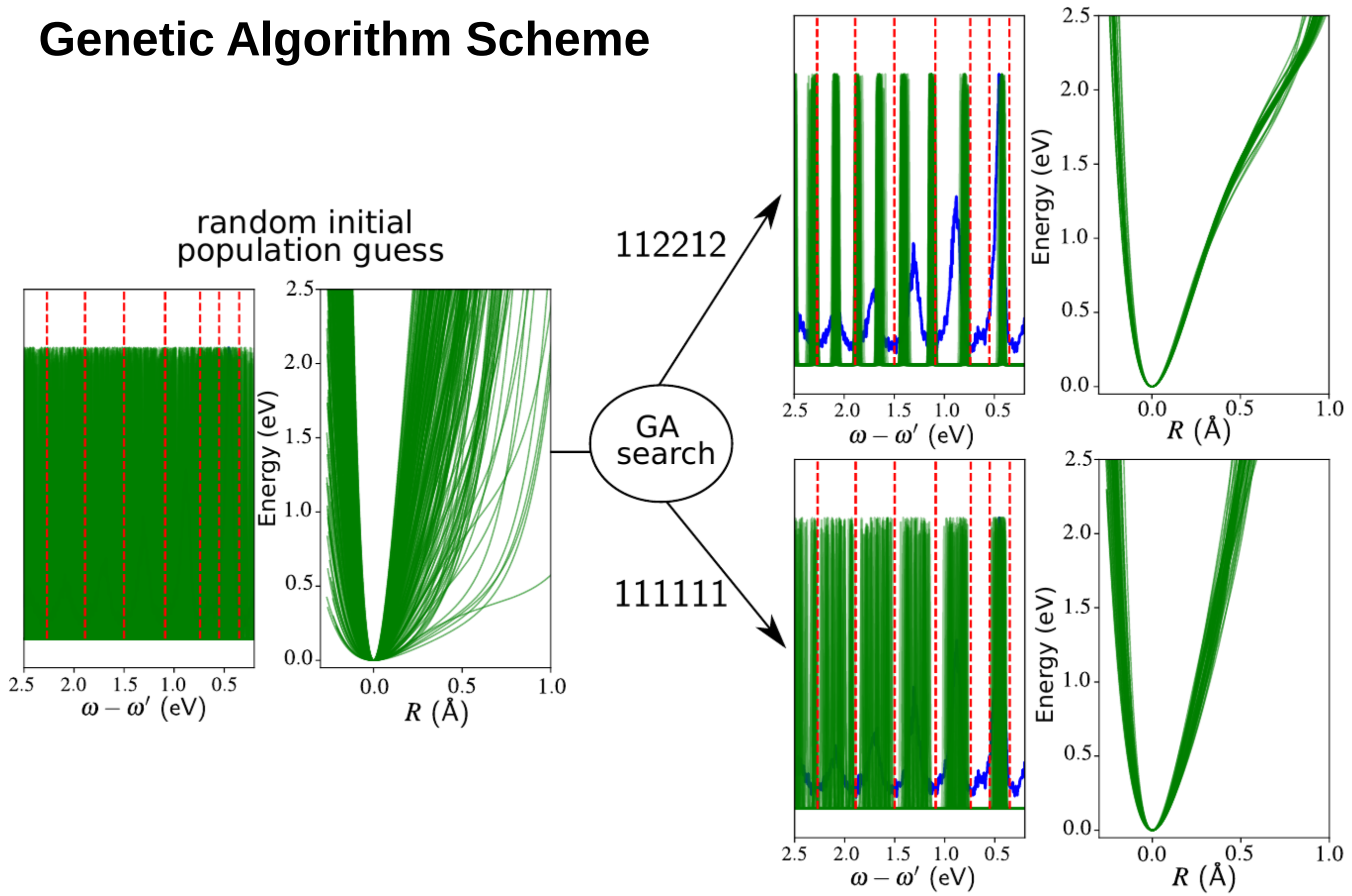
- **Initial population:** randomly generated distribution of the potentials (quasicontinuum spectrum)

- **Fitness criterium:** “vibrational distribution”.

Weak/no - HB	(111111),	(111112),
Strong HB	(112212),	$(112222), \cdots$

- Example of the distribution of the OH potentials selected by GA for two individual constraints: (111111) and (112212)

Genetic Algorithm Scheme



Fortin, F.-A., et al, DEAP: Evolutionary algorithms made easy. J. Mach. Learn. Res. 13, 2171–2175 (2012).

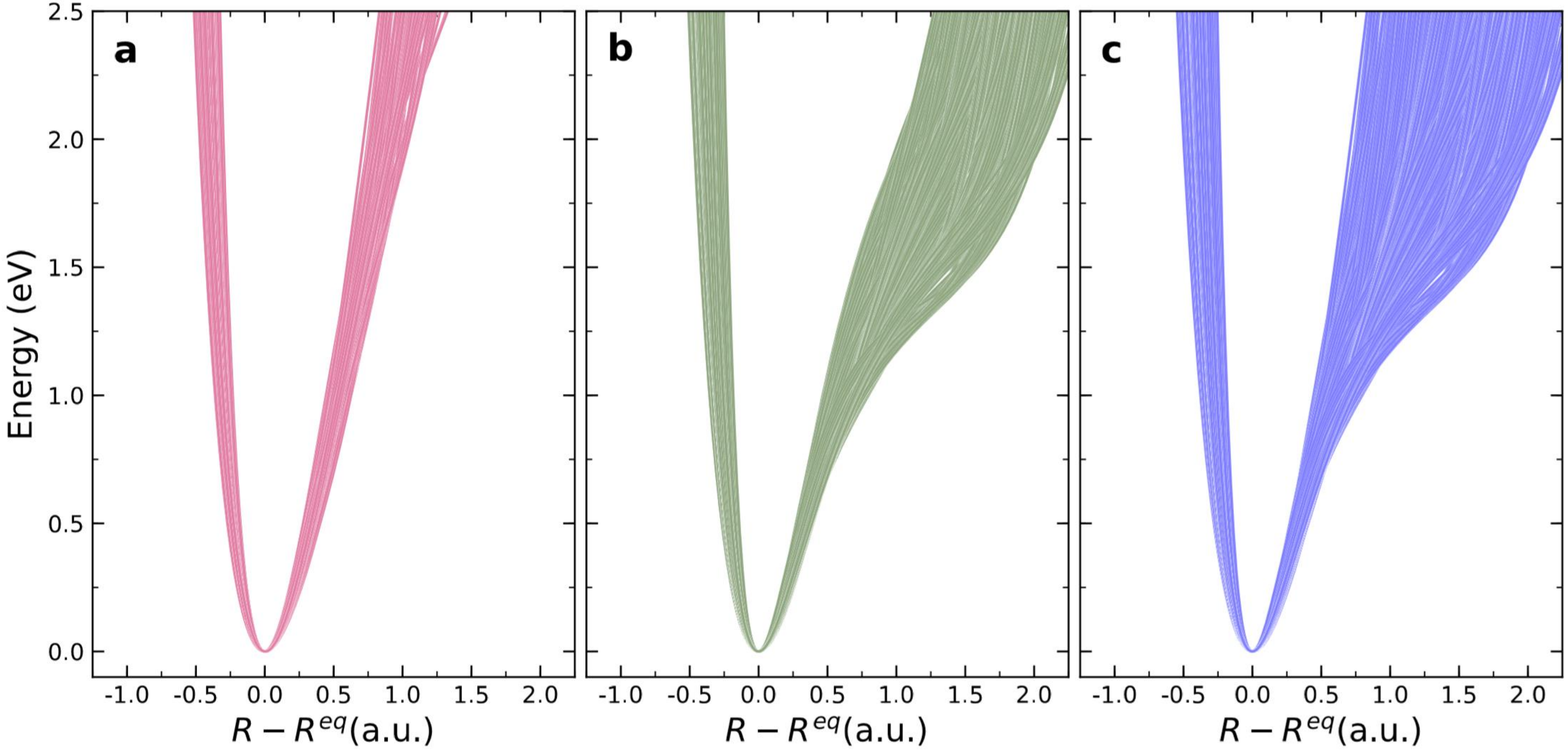
V. Vaz da Cruz, et al, Nat Commun. 10, 1013 (2019)

Distribution of OH potentials extracted from experiment RIXS

(111111)

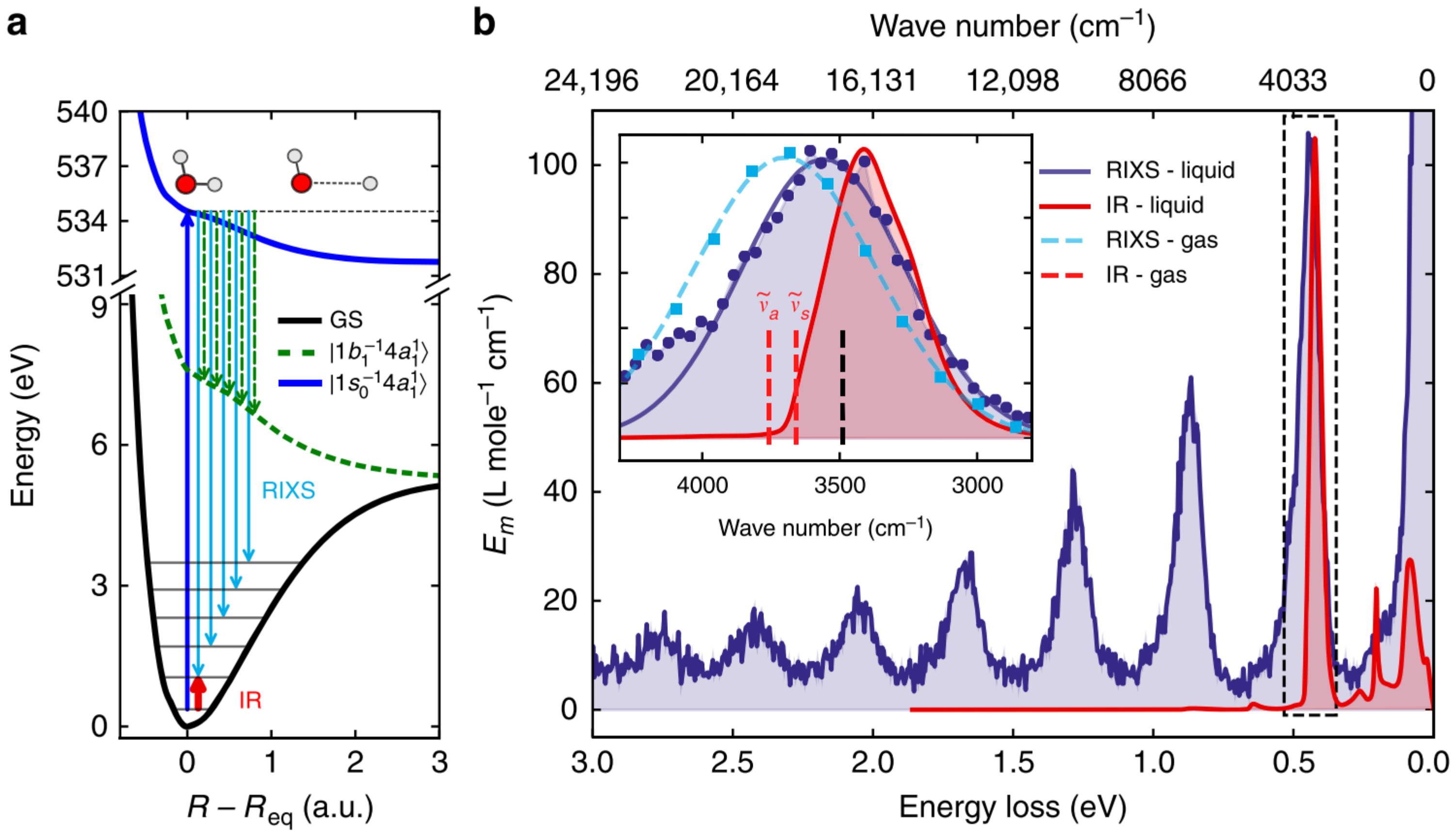
(112121)
(112222) …

Weak/no HB **Strong HB** **Full set**



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

RIXS vs IR spectroscopy for potential reconstruction



IR: main contribution in IR absorption is 0 → 1 dipole allowed OH transition (higher lying dipole forbidden IR transitions are more than two orders of magnitude smaller)[1].

Transition dipoles OH stretch:

IR absorption: OH with broken HB (high-frequency) much smaller than HB OH modes (low-frequency)

RIXS[3]: reversed! – molecules with a weak/broken hydrogen bond are excited preferentially.

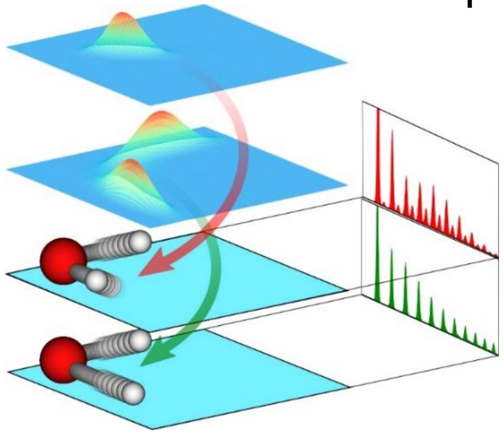
Theoretical density of states[2] (black dashed bar)

1) Bertie, J. E. & Lan, Z. Appl. Spectrosc. 50, 1047–1057 (1996)
2) Auer, B. M. & Skinner, J. L. J. Chem. Phys. 128, 224511 (2008)
3) V. Vaz da Cruz, et al., Nat Commun. 10, 1013 (1019)

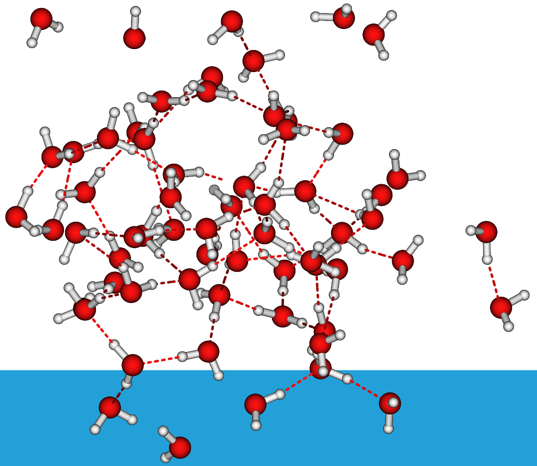
Summary

- New sources of X-ray radiation and the modern applications allows to study the nature with unprecedented details.

- Resonant X-ray scattering can serve as pump-probe technique opens up the new approzhes for quantum systems study.



- High-resolution experiments accompanied by *ab initio* simulations shows advantages of RIXS in studying molecular structure and potentials via nuclear dynamics control
  - Vibrational gating effect: pathways control with frequency detuning
  - Ultrafast dissociation as a key for potentials probing



- Liquid phase
  - Average number of HB per molecule
  - Reconstruction of the confidence interval for the potentials using the experimental spectra with advanced numerical algorithms

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THEORY

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Faris Gelmukhanov
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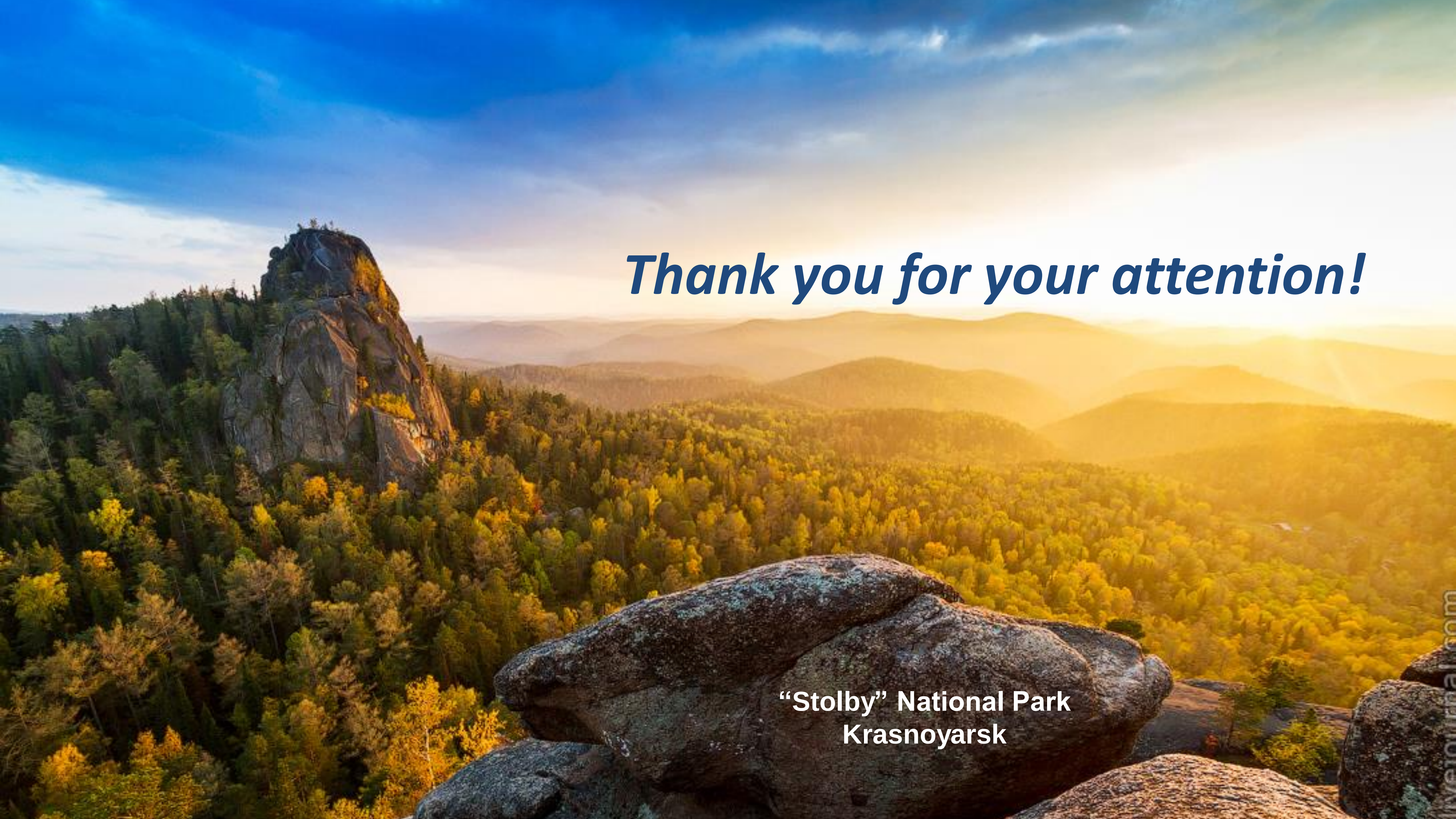
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Krasnoyarsk