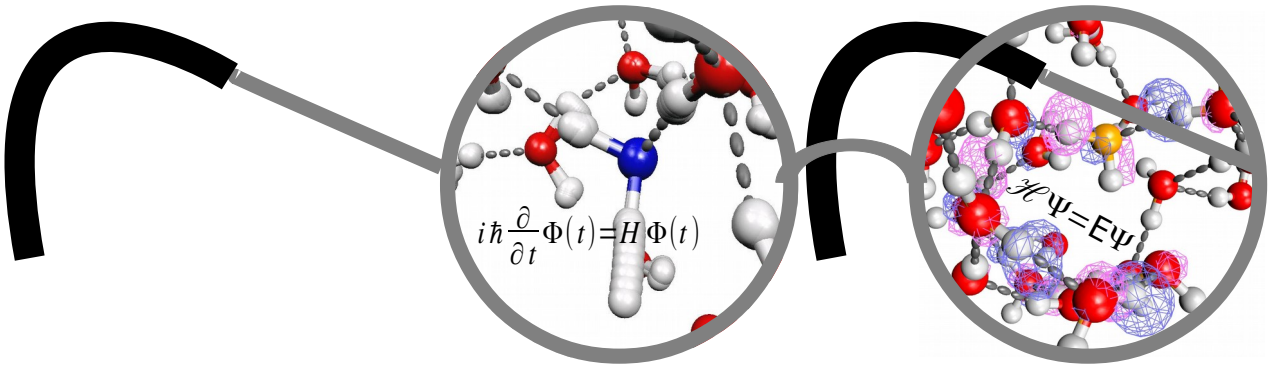


Modeling of X-ray spectroscopies

Michael Odelius
Department of Physics

4FUTURE Intensive course 2019:
Methods for Image and Spectral Data Analysis and Interpretation

Stockholm University

Outline

Spectrum simulations – Part I

Molecular orbital approach

Spectrum simulations – Part II

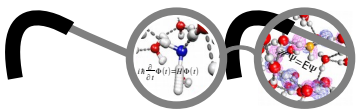
Electronic states approach

Dynamical effects

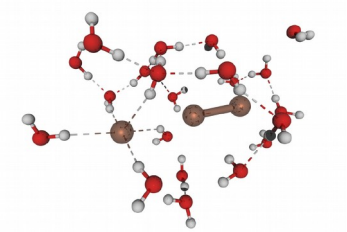
Excited state X-ray spectra

Stockholm University

Outline

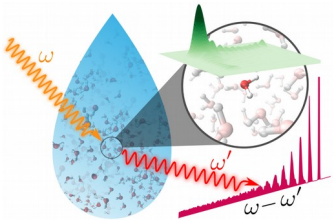


Multi-configurational electronic Ψ



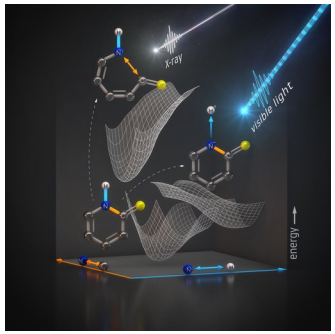
Symmetry breaking
Solvation

I 4d XPS
Relativistic effects



Hydrogen bonding
in liquid water

O 1s RIXS
Dynamics in RIXS



Excited state
proton transfer
in 2-thiopyridone(aq)

N 1s XAS(t)
Excited state XAS

Quantum Chemistry $\mathscr{H}\Psi=E\Psi$

Hartree-Fock

1) Born-Oppenheimer
2) Mean-field approx.

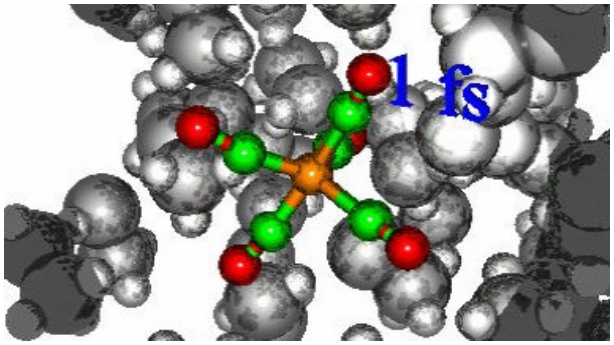
$$\Psi_{HF} = \det | \phi_1, \phi_2, \ldots \phi_N |$$

Momentary
$e^- - e^-$ correlation
missing!

DFT

Singlet determinant

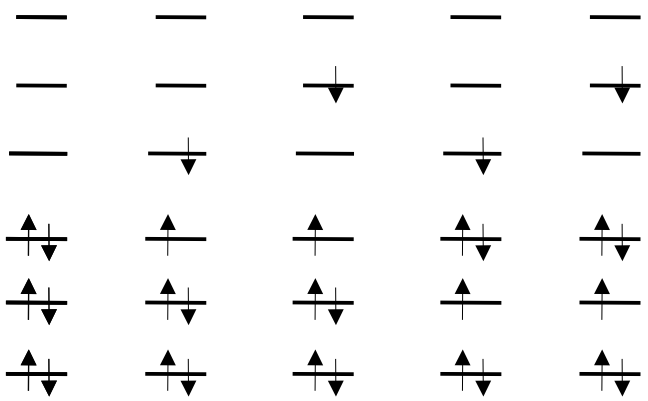
Correlation in $\mathscr{H}$



Post-HF

Multi-determinant

Wave function correlated



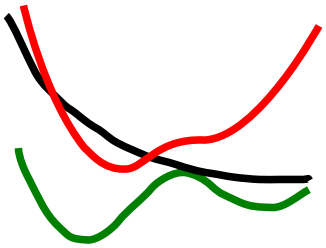
Ab initio Molecular dynamics

F=ma

$$\boldsymbol{F}_I = -\nabla_I \langle H_e \rangle \approx -\langle \Psi_0 | \nabla_I H_e | \Psi_0 \rangle$$

Quantum dynamics

$$i\hbar \frac{\partial}{\partial t} \Phi(\{\boldsymbol{r}_i\}, \{\boldsymbol{R}_I\}; t) = H \Phi(\{\boldsymbol{r}_i\}, \{\boldsymbol{R}_I\}; t)$$



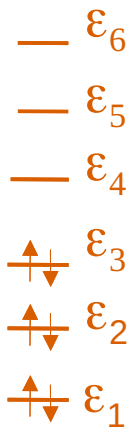
Stockholm University

The Quantum chemistry Nightmare $\mathscr{H}\Psi=E\Psi$

Hartree-Fock

Singlet determinant
Independent particle or
Mean-field approximation

$$\Psi_{HF} = \det|\phi_1,\phi_2,..\phi_N|$$

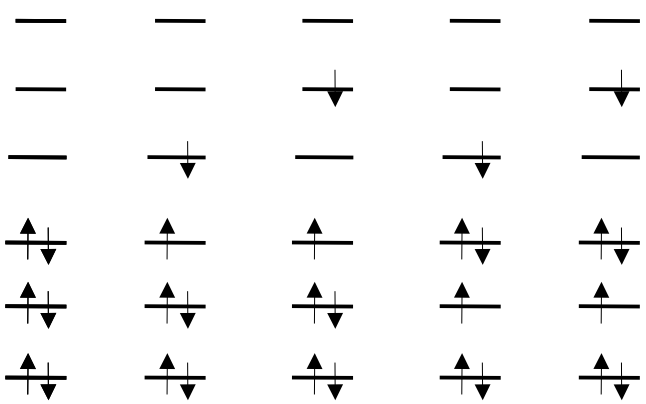


Momentary
e^- - e^- correlation
missing!

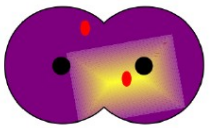
Post-HF

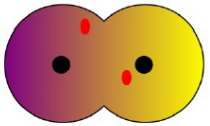
Multi-determinant

Wave function correlated



Dynamical correlation







Static correlation



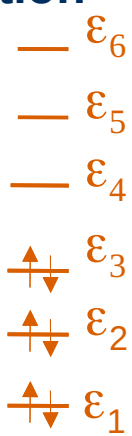
Stockholm University

The Quantum chemistry Nightmare $\mathcal{H}\Psi=E\Psi$

Hartree-Fock

Singlet determinant
Independent particle or
Mean-field approximation

$\Psi_{HF}= \det|\phi_1,\phi_2,..\phi_N|$

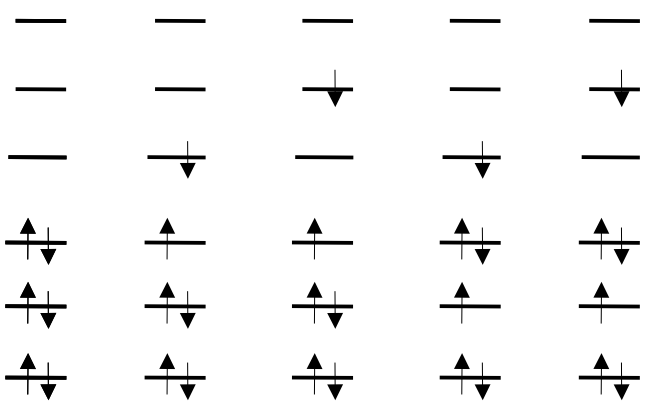


Momentary
e^- - e^- correlation
missing!

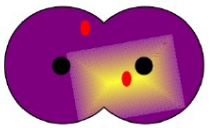
Post-HF

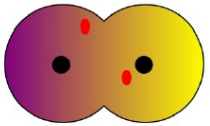
Multi-determinant

Wave function correlated



Dynamical correlation







Static correlation

HF → CIS…….CISD……. FULLCI
HF → CCS…….CCSD……. FULLCC
HF → CASSCF….RASSCF... FULLCI
HF → MP2….MP3…..MP4…. MP∞
CASSCF → CASPT2, MRCI,…..MRCC
RASSCF → RASPT2 RAS-MRCI

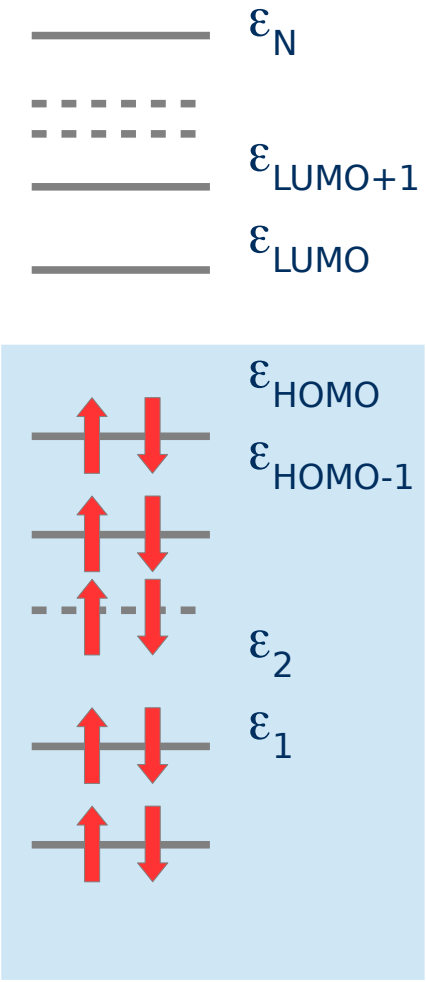
Stockholm University

The many-body Ψ in Hartree-Fock (and Kohn-Sham DFT)

Occupied and virtual **HF (Kohn-Sham) orbitals**

Spin orbitals: $\psi_\iota = \phi_\iota(1)\sigma_\iota(1)$

$\psi_1\ \psi_2\ \psi_3\ \psi_4\ \cdots\cdots\ \psi_{HOMO-1}\ \psi_{HOMO} \;\vdots\; \psi_{LUMO}\ \psi_{LUMO}\ \psi_{LUMO+2}\ \cdots$



Slater determinant:

$$\Psi_{HF\ or\ DFT}(1,2) = \sqrt{½}\ |\phi_1(1)\alpha(1)\phi_1(2)\beta(2)|$$
$$= \sqrt{½}\ [\phi_1(1)\alpha(1)\phi_1(2)\beta(2) - \phi_1(1)\beta(1)\phi_1(2)\alpha(2)]$$

$$\Psi_{HF\ or\ DFT} = \sqrt{1/n!}\ |\psi_1\ \psi_2 \ldots \psi_n|$$

Electronic states - single/multi-configurational wavefunctions

Closed shell states

$$\Psi_{\text{Singlet}} = \sqrt{½}\,|\phi_a(1)\alpha(1)\phi_a(2)\beta(2)|$$

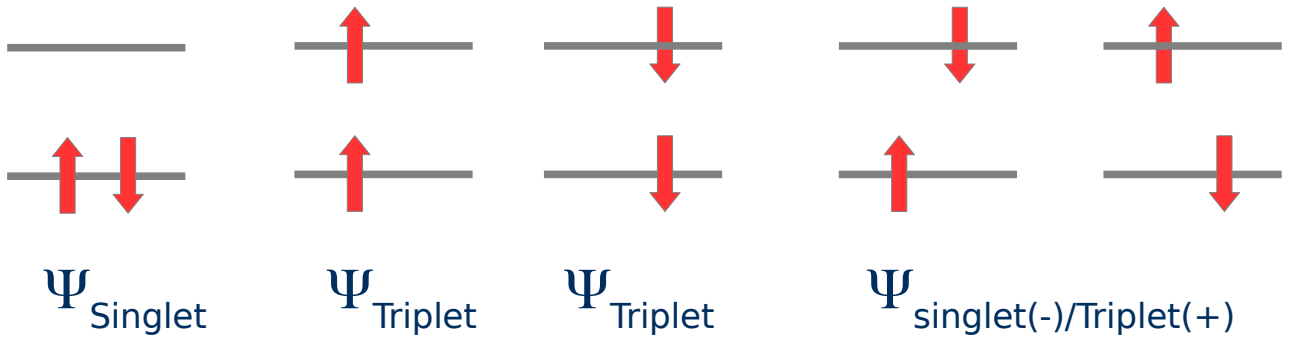
Open-shell states

$$\Psi_{\text{Doublet}} = |\phi_a(1)\alpha(1)|$$

$$\Psi_{\text{Triplet}} = \sqrt{½}\,|\phi_a(1)\alpha(1)\phi_b(2)\alpha(2)|$$

may require multi-configurational wave functions!

$$\Psi_{\text{Open-shell singlet}} = ½\,|\phi_a(1)\alpha(1)\phi_b(2)\beta(2)| - ½\,|\phi_a(1)\beta(1)\phi_b(2)\alpha(2)|$$



Multi-configurational Quantum Chemistry

Variational degrees of freedom in the wavefunction

HF, DFT - Self-consitent field (SCF)

$\Psi_{HF\ or\ DFT} = \sqrt{1/n!}\ |\psi_1\ \psi_2 \dots \psi_n|$

$\phi_i(r) = \sum_{b=1,2\dots N} c_{ib}\ \chi_b(r)$

Multi-configurational CI

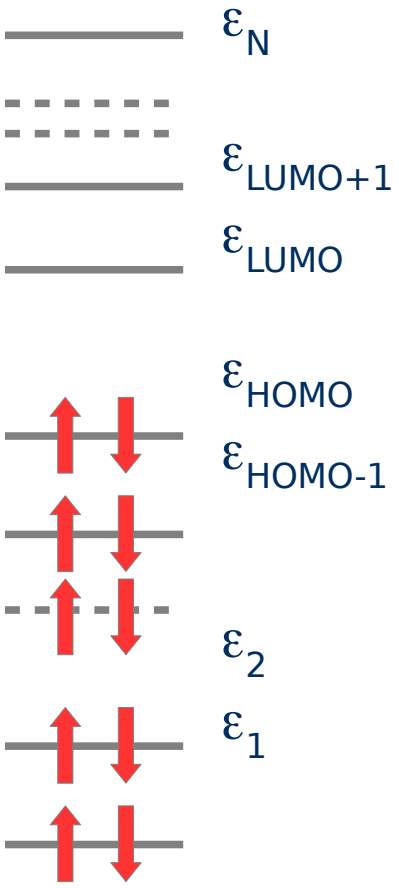
$\Psi_{MC} = \sum_{i1,i2\dots,in} C_{i1,i2\dots,in.}\ |\psi_{i1}\ \psi_{i2} \dots \psi_{in}|$

$\phi_i(r)$ from reference calculation (HF)

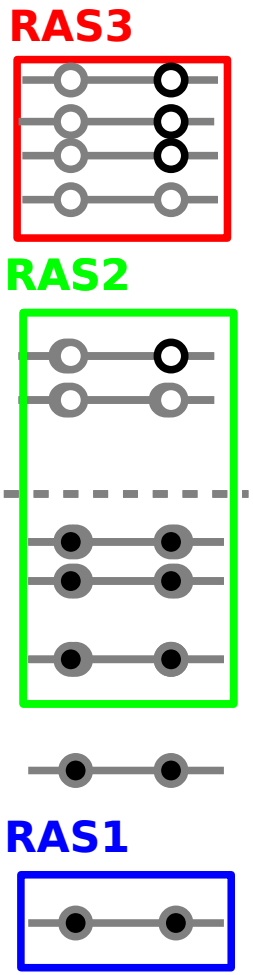
Multi-configurational SCF CASSCF, RASSCF…

$\Psi_{MC} = \sum_{i1,i2\dots,in} C_{i1,i2\dots,in.}\ |\psi_{i1}\ \psi_{i2} \dots \psi_{in}|$

$\phi_i(r) = \sum_{b=1,2\dots N} c_{ib}\ \chi_b(r)$



Multi-configurational quantum chemistry



RASSCF (Restricted Active Space SCF)

Accurate and efficient description of

Valence- and core-excited states

Scalar Relativistic

Multiplet effects

Spin-orbit coupling

RASPT2 Both static and dynamical correlation

Chemical bonding
Open-shell configurations
Dissociation

K- L- M- N-edge core-level spectra

Modelling X-ray absorption spectroscopy

Ground state of Methanol:

$$\Psi_{GS} = |\psi_{O1s}^{2}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{0}\rangle$$

Lowest valence-excited state:

$$\Psi_{VE} = |\psi_{O1s}^{2}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{1}\, \psi_{LUMO}^{1}\rangle$$

C and O K-edge lowest core-excited states:

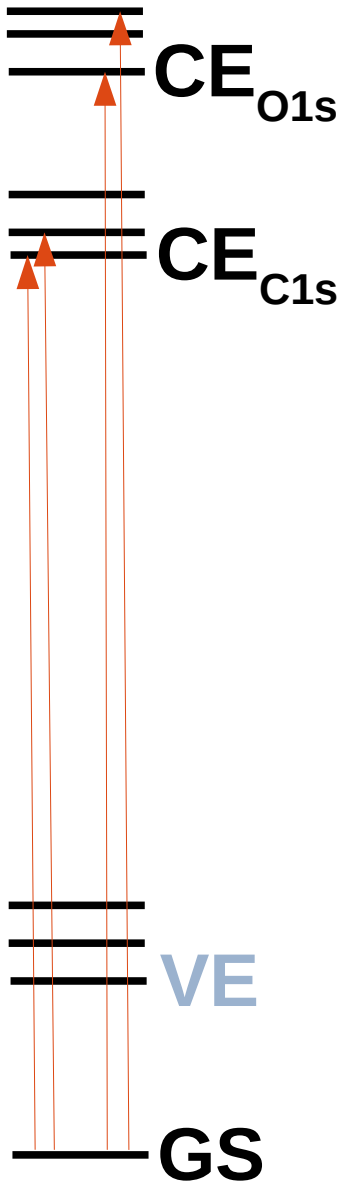
$$\Psi_{C1s\ CE} = |\psi_{O1s}^{2}\, \psi_{C1s}^{1} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{1}\rangle$$

$$\Psi_{O1s\ CE} = |\psi_{O1s}^{1}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{1}\rangle$$

Shake-up core-excited states:

$$\Psi_{O1s\ CE} = |\psi_{O1s}^{1}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{1}\, \psi_{LUMO}^{2}\rangle$$

Notice that orbital notation is just a shorthand for the dominant determinant in the multi-configurational wave function!!



Modelling time-resolved X-ray absorption spectroscopy

Ground state of Methanol:

$$\Psi_{GS} = |\psi_{O1s}^{2}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{0}\rangle$$

Lowest valence-excited state:

$$\Psi_{VE} = |\psi_{O1s}^{2}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{1}\, \psi_{LUMO}^{1}\rangle$$

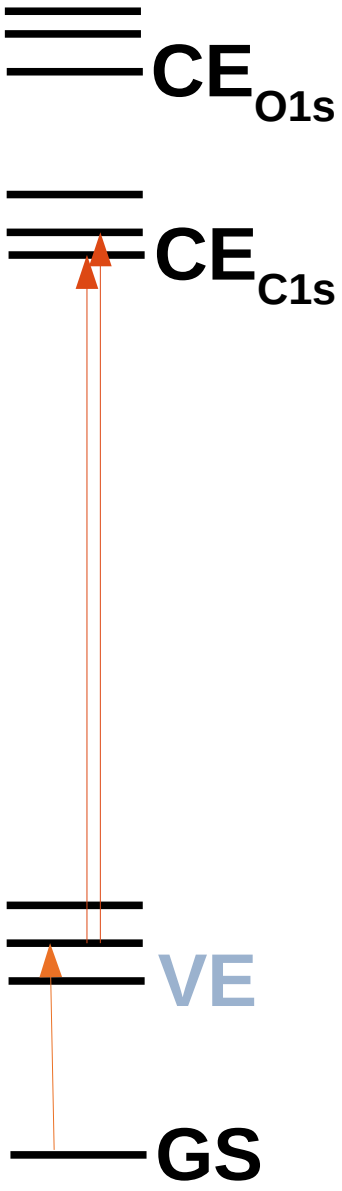
C and O K-edge lowest core-excited states:

$$\Psi_{C1s\ CE} = |\psi_{O1s}^{2}\, \psi_{C1s}^{1} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{1}\rangle$$

$$\Psi_{O1s\ CE} = |\psi_{O1s}^{1}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{1}\rangle$$

Shake-up core-excited states:

$$\Psi_{O1s\ CE} = |\psi_{O1s}^{1}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{1}\, \psi_{LUMO}^{2}\rangle$$



Modelling Resonant Inelastic X-ray Scattering (RIXS)

Ground state of Methanol:

$$\Psi_{GS} = |\psi_{O1s}^{2}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{0}>$$

Lowest valence-excited state:

$$\Psi_{VE} = |\psi_{O1s}^{2}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{1}\, \psi_{LUMO}^{1}>$$

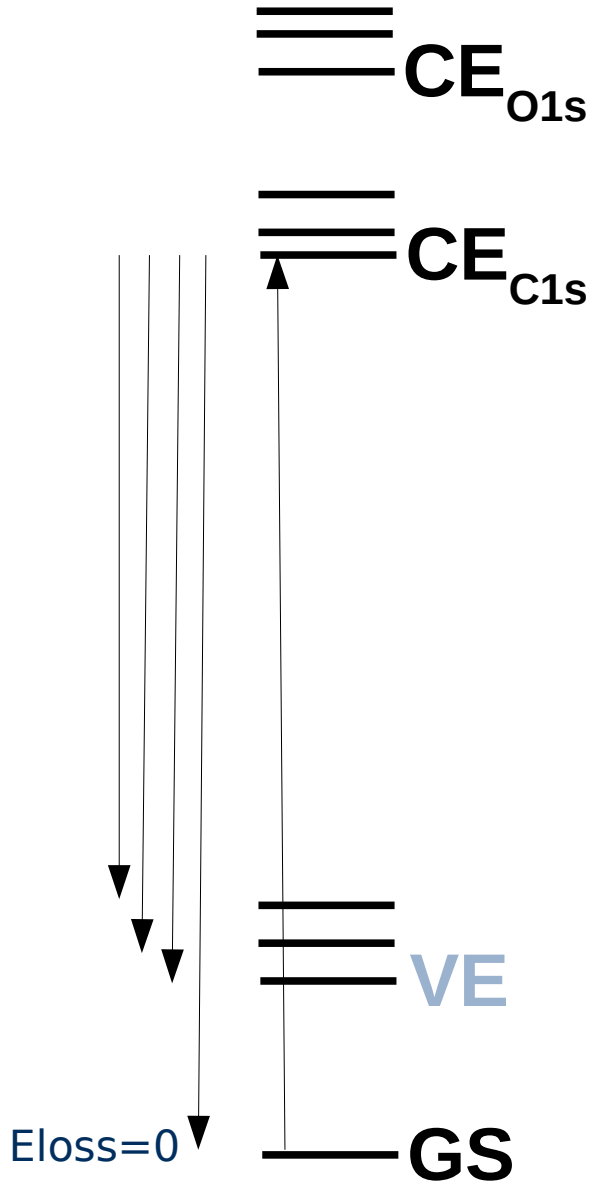
C and O K-edge lowest core-excited states:

$$\Psi_{C1s\ CE} = |\psi_{O1s}^{2}\, \psi_{C1s}^{1} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{1}>$$

$$\Psi_{O1s\ CE} = |\psi_{O1s}^{1}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{1}>$$

Shake-up core-excited states:

$$\Psi_{O1s\ CE} = |\psi_{O1s}^{1}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{1}\, \psi_{LUMO}^{2}>$$



Modelling time-resolved RIXS

Ground state of Methanol:

$$\Psi_{GS} = |\psi_{O1s}^{2}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{0}\rangle$$

Lowest valence-excited state:

$$\Psi_{VE} = |\psi_{O1s}^{2}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{1}\, \psi_{LUMO}^{1}\rangle$$

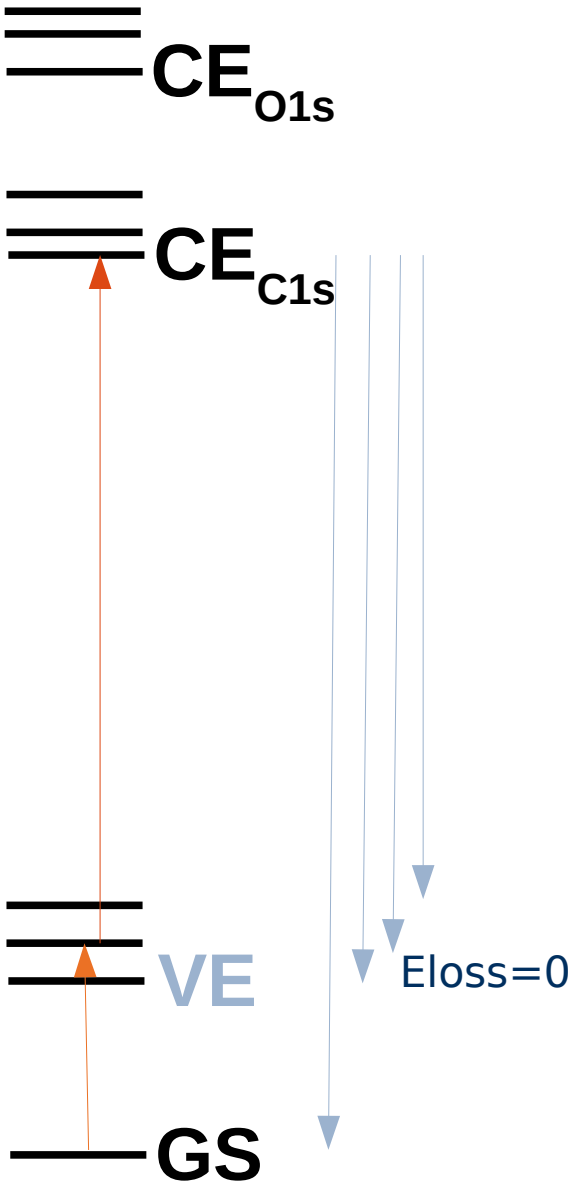
C and O K-edge lowest core-excited states:

$$\Psi_{C1s\ CE} = |\psi_{O1s}^{2}\, \psi_{C1s}^{1} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{1}\rangle$$

$$\Psi_{O1s\ CE} = |\psi_{O1s}^{1}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{2}\, \psi_{LUMO}^{1}\rangle$$

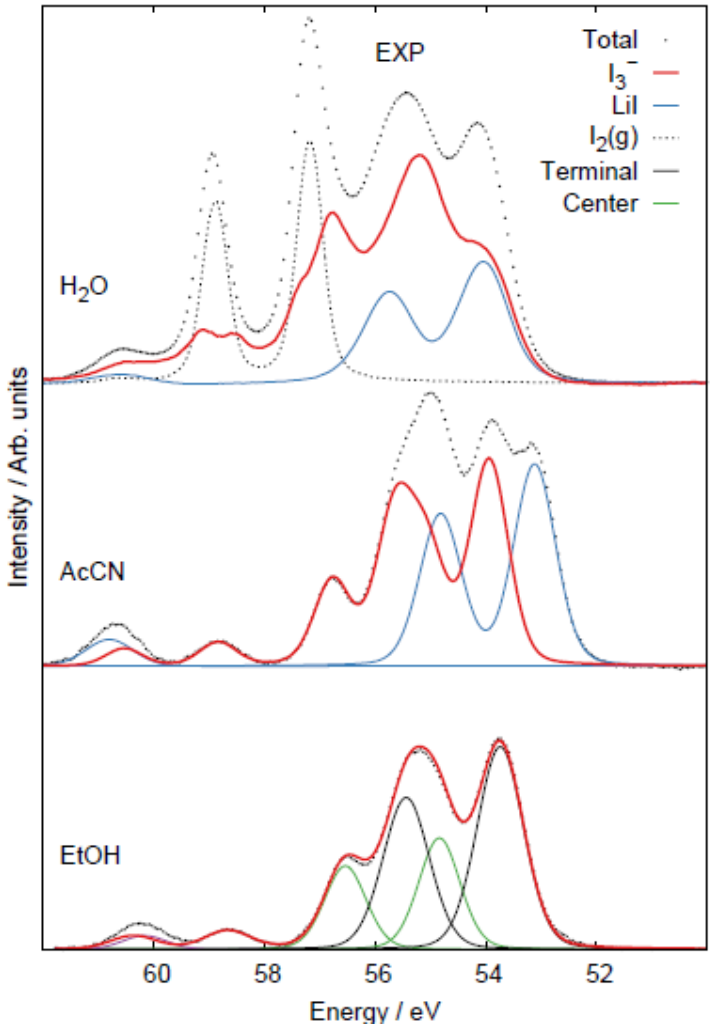
Shake-up core-excited states:

$$\Psi_{O1s\ CE} = |\psi_{O1s}^{1}\, \psi_{C1s}^{2} \ldots \psi_{HOMO}^{1}\, \psi_{LUMO}^{2}\rangle$$



I 4d XPS of solvated I_3^-

Experiment

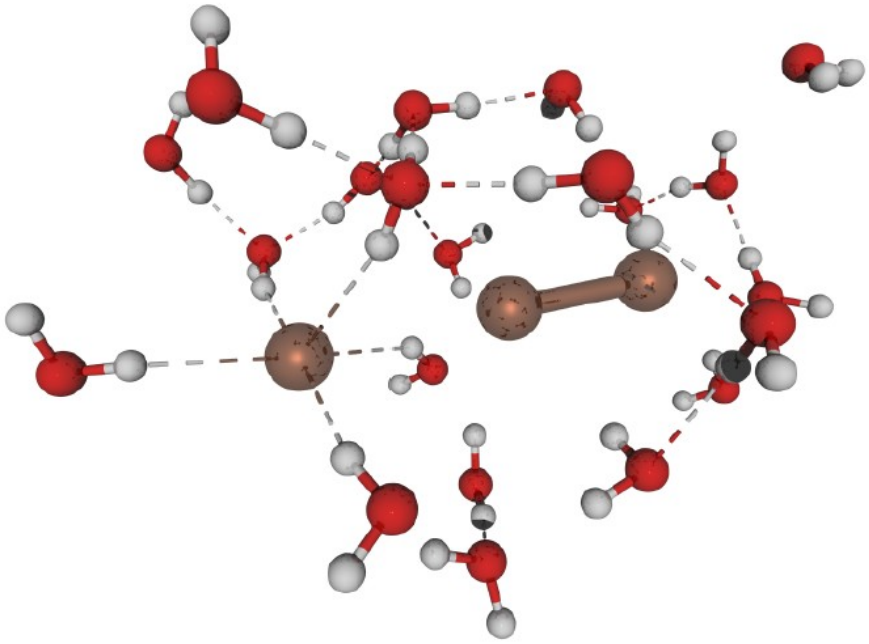


$$E_{binding} = E_{photon} - E_{kin}$$

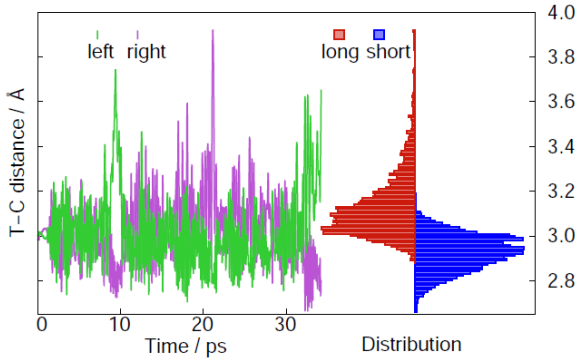
I. Josefsson,et al.. PCCP, 15, 20189 (2013)

Hydration and fluctuations in I_3^-(aq)

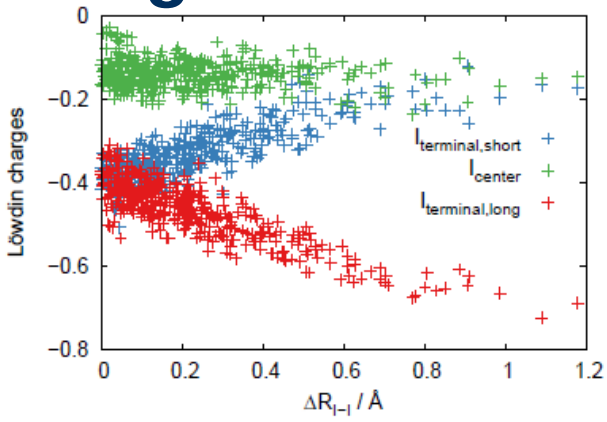
Ab initio Molecular Dynamics



I-I bond asymmetry



Charge localization

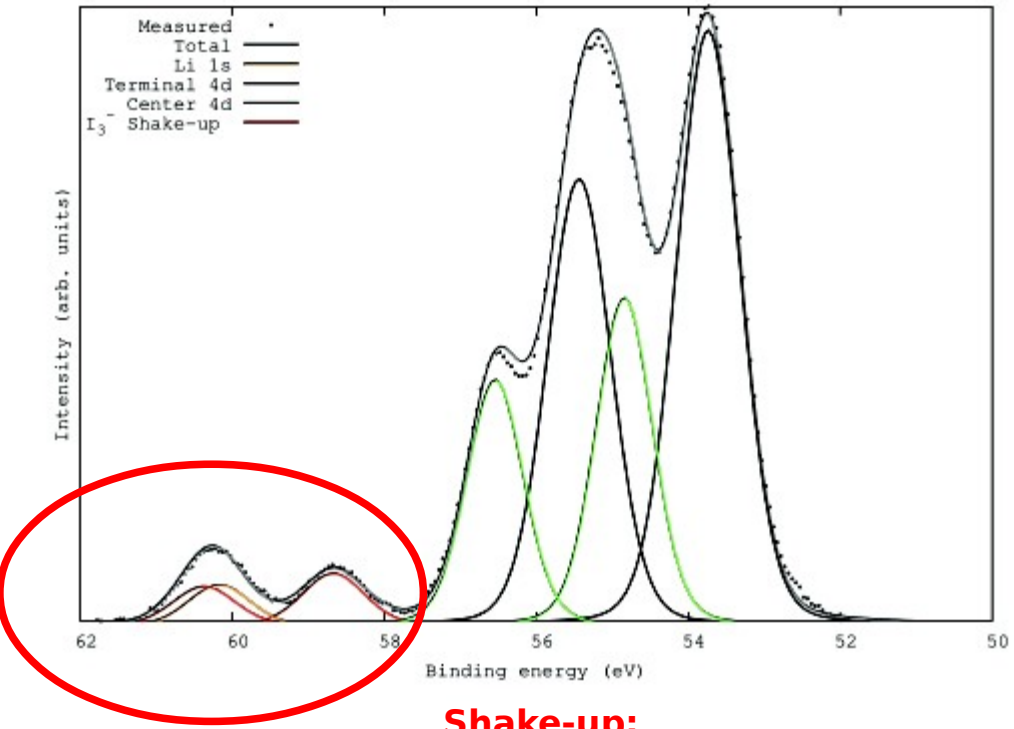


I. Josefsson,et al.. PCCP, 15, 20189 (2013)

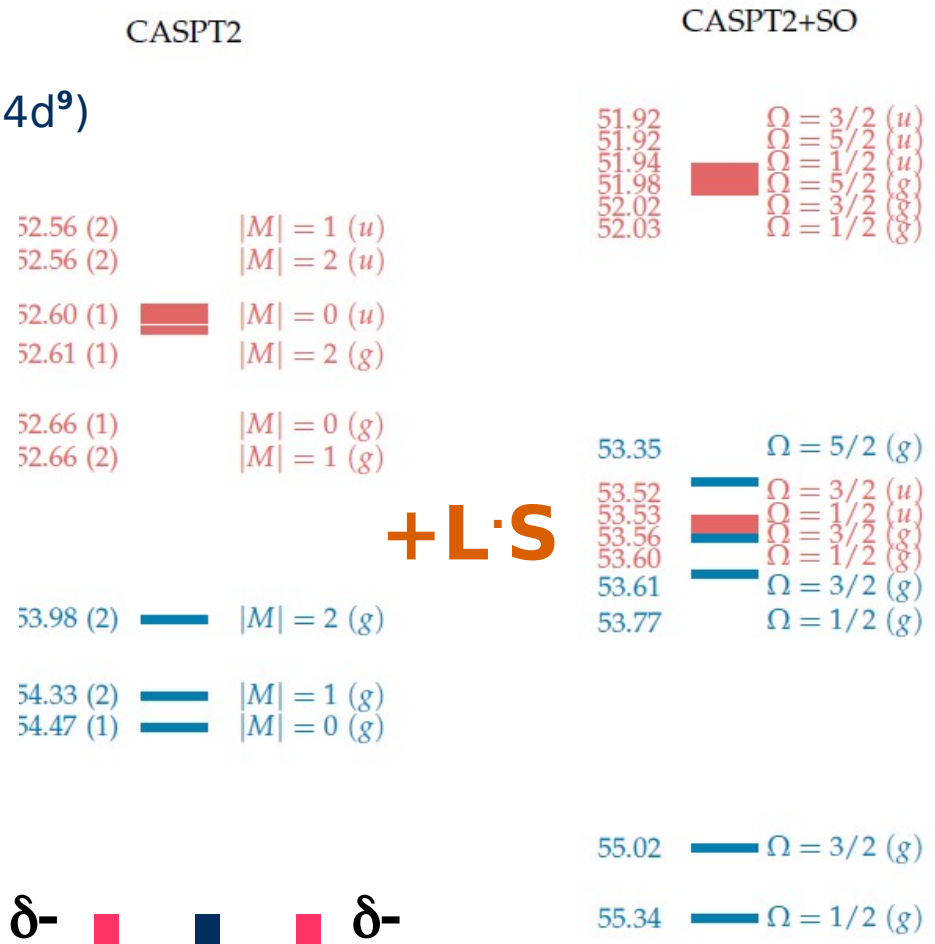
Photo-emission of I_3^-

Multi-configurational SCF

Complete active space CASSCF ($4d^{10}$)-> ($4d^9$)



Shake-up: Simultaneous Core-ionization & valence-excitation





Terminal Center

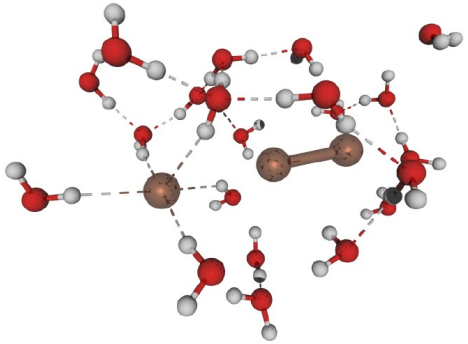
S. Eriksson et al. JPCB, 118, 3164 (2014)
J. Norell et al. PCCP, 20, 19916 (2018)

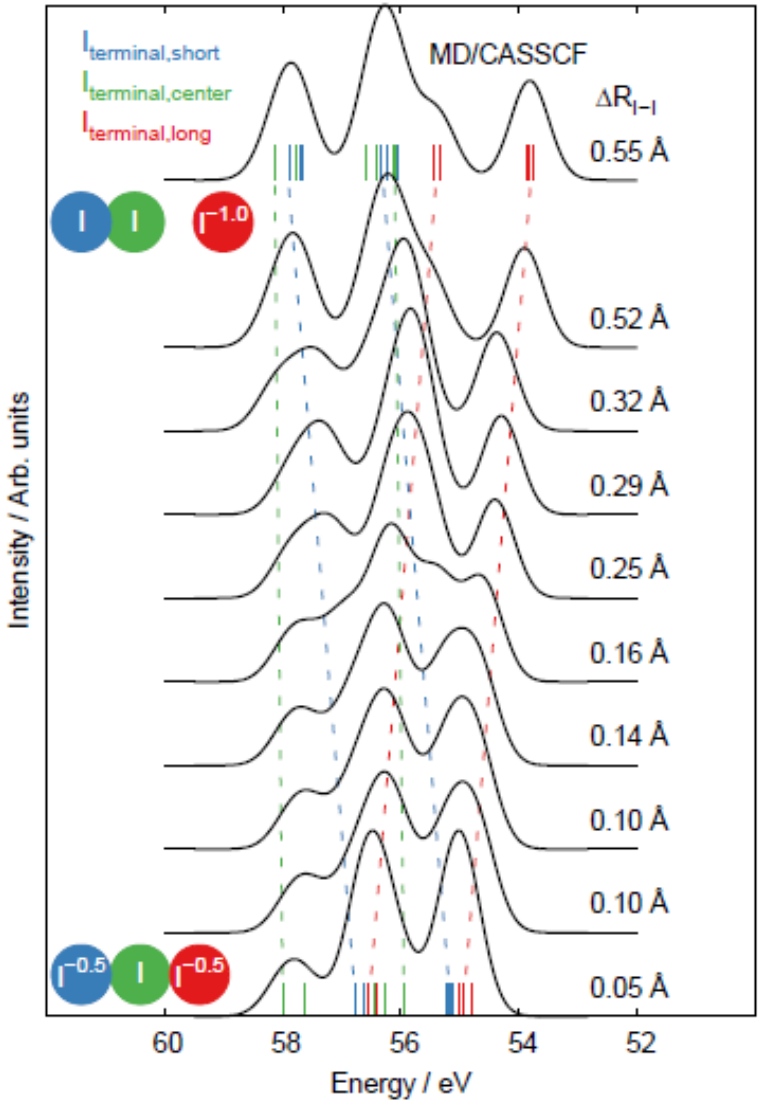
Stockholm University

Electronic structure of I_3^-(aq)

Core-level photo-electron spectroscopy

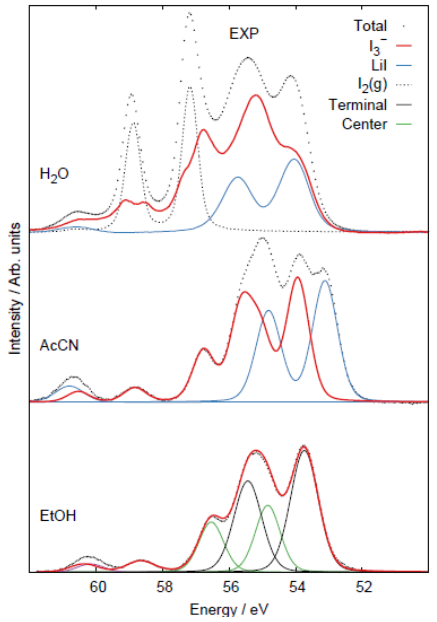
I 4d XPS





$E_{binding} = E_{photon} - E_{kin}$

Experiment

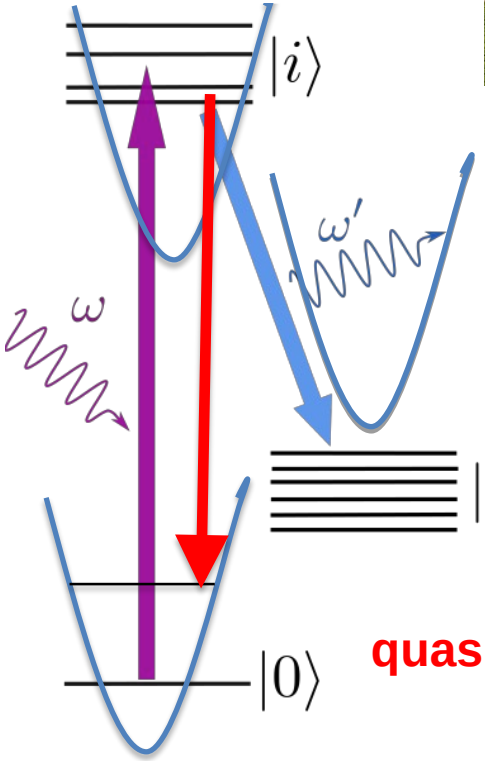


I. Josefsson et al. PCCP, 15, 20189 (2013)

Vibrationally resolved RIXS of liquid water

Experiment (SLS):

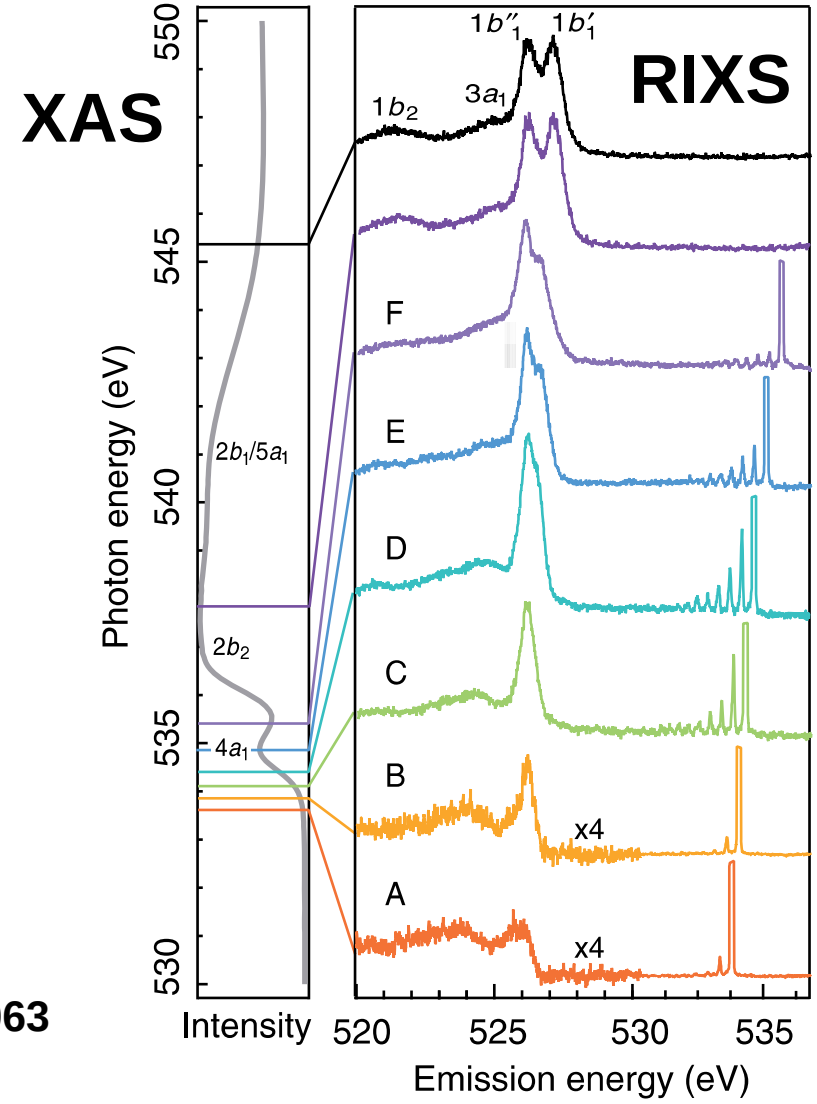




inelastic

quasi-elasic

Liquid water

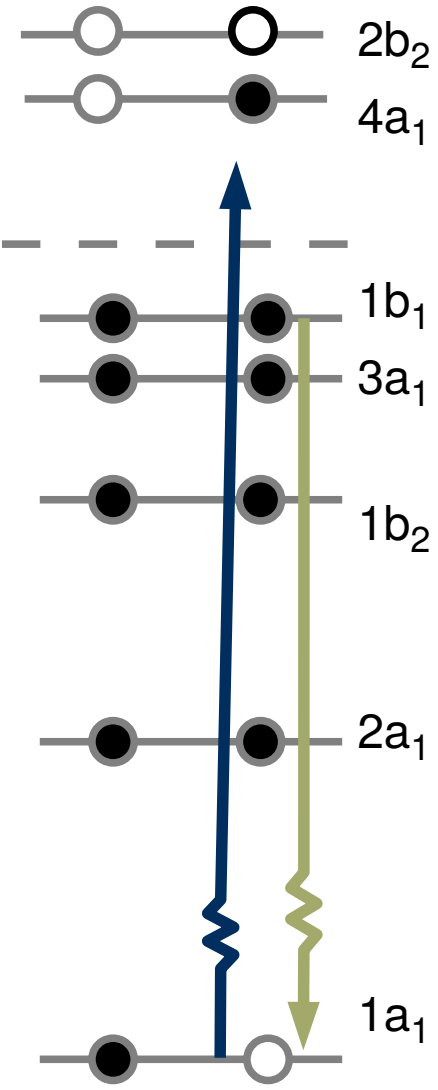


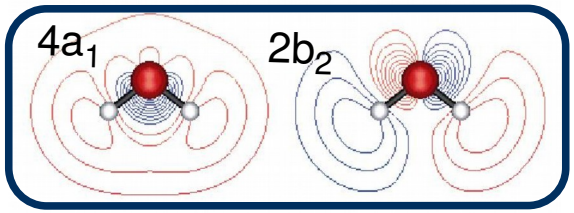
J. Niskanen et al PNAS, 2019 116 (10) 4058-4063

https://doi.org/10.1073/pnas.1815701116

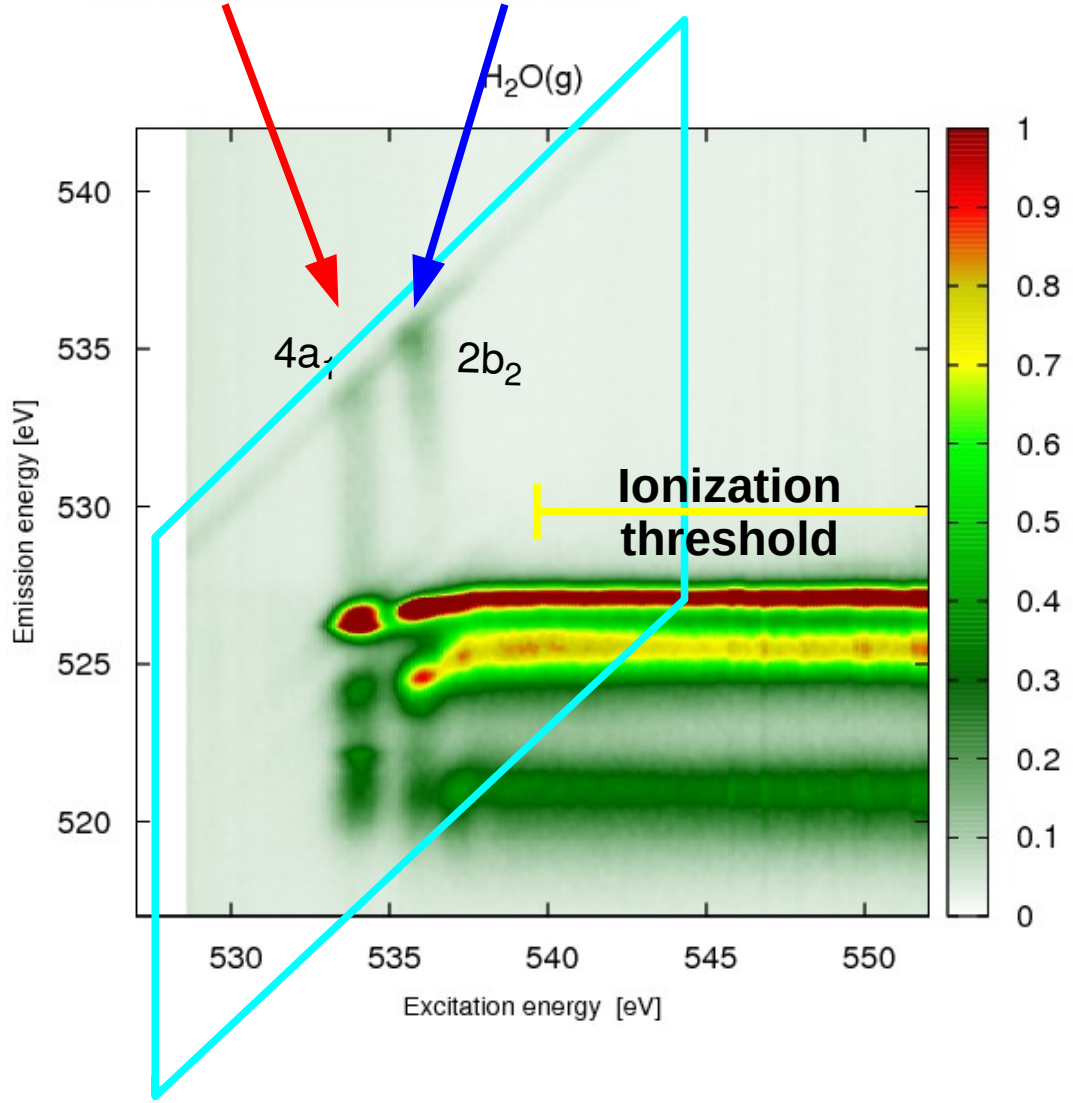
X-ray emission and RIXS of gas phase water

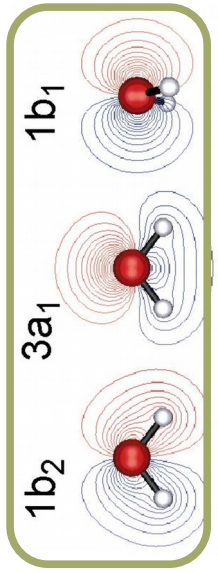
RIXS $H_2O(g)$





RIXS ≠ XAS ⊗ XES

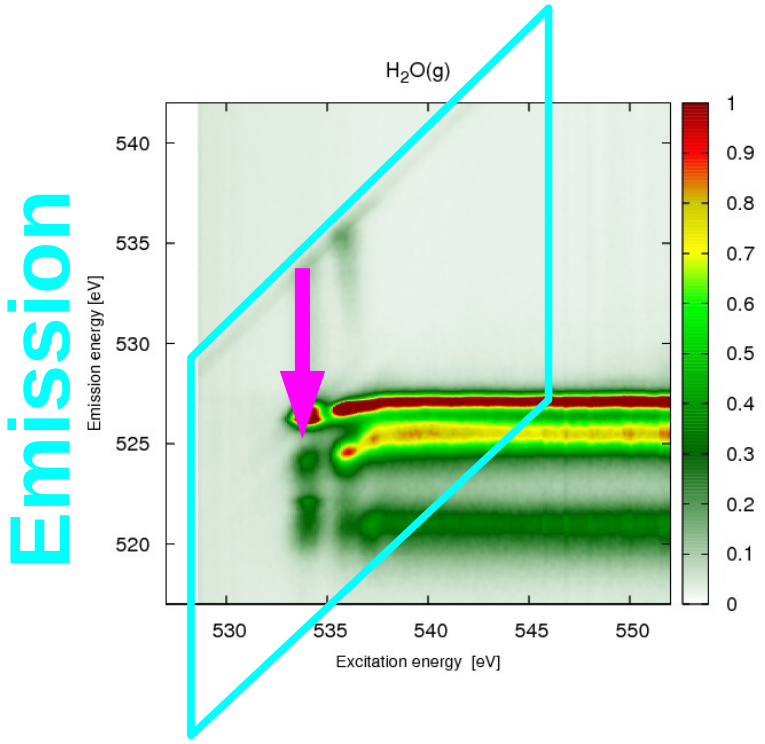


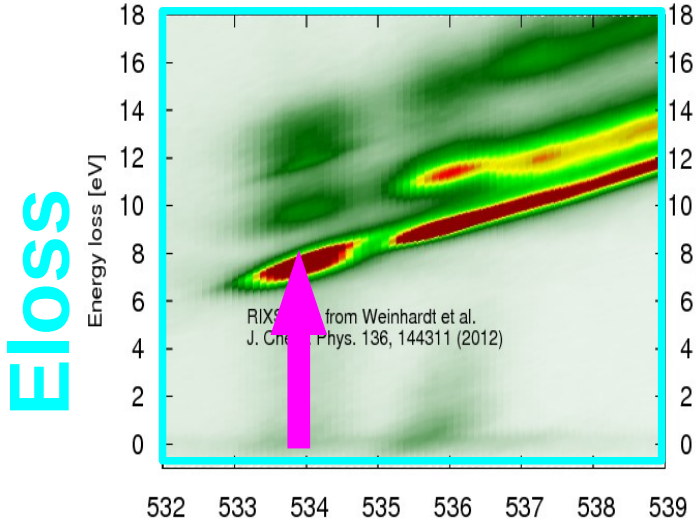


Data from Weinhardt et al. J. Chem. Phys. 136 144311 (2012)

Molecular Orbitals → Electronic States

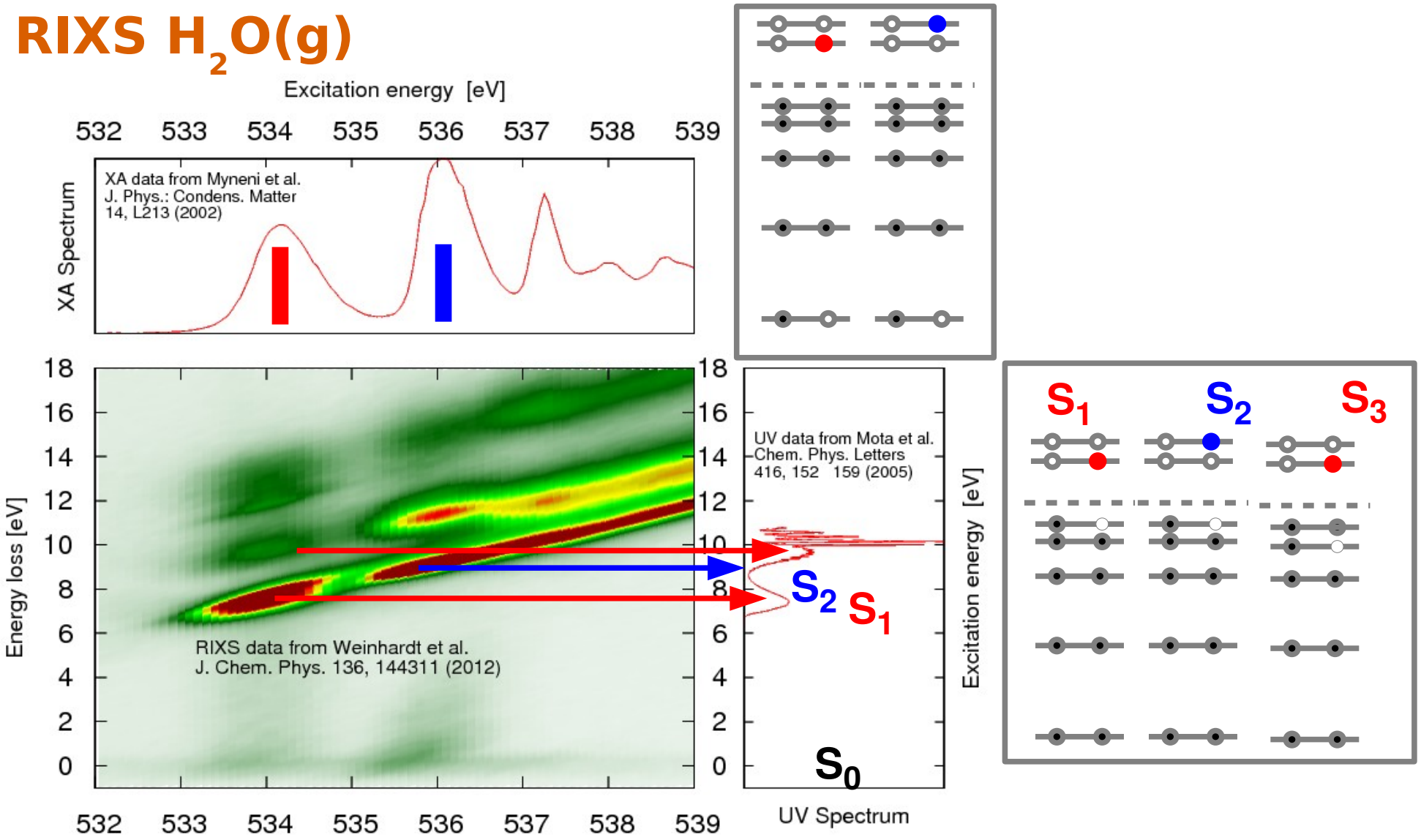
RIXS $H_2O(g)$





RASPT2 calculations of RIXS spectra

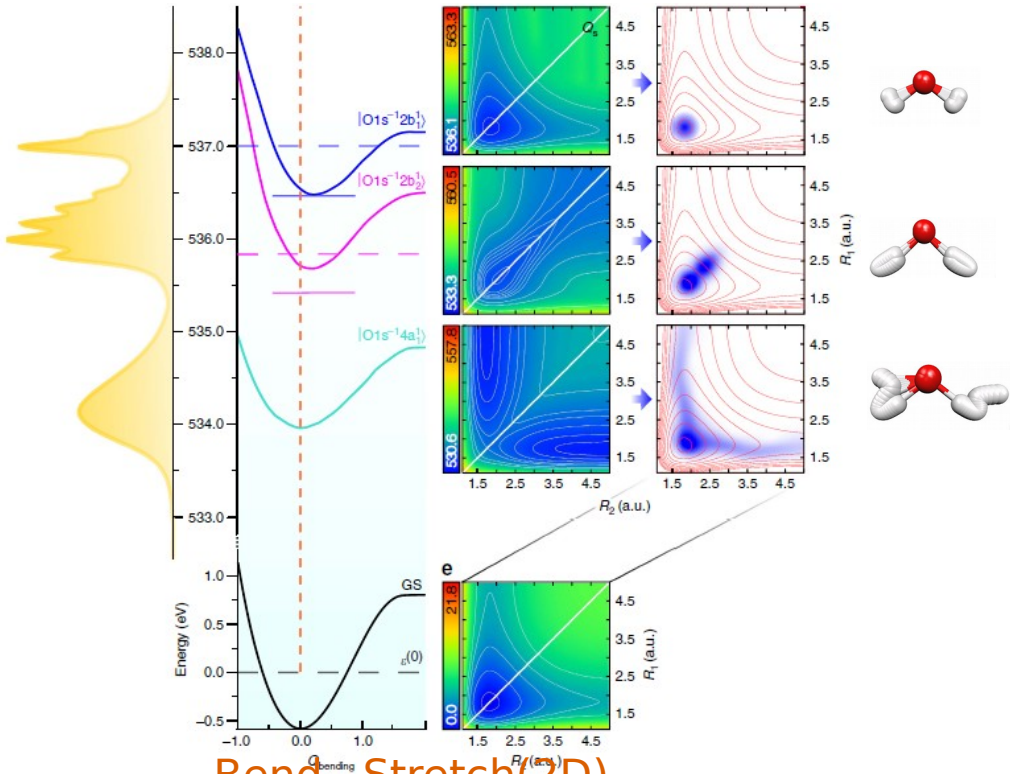
RIXS $H_2O(g)$



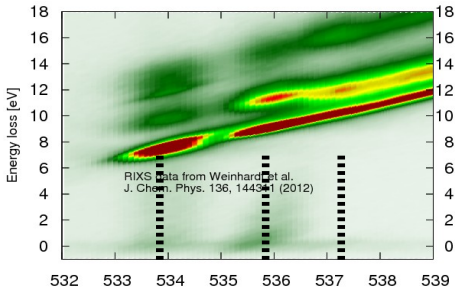
Eloss=Excitation energy – Emission energy

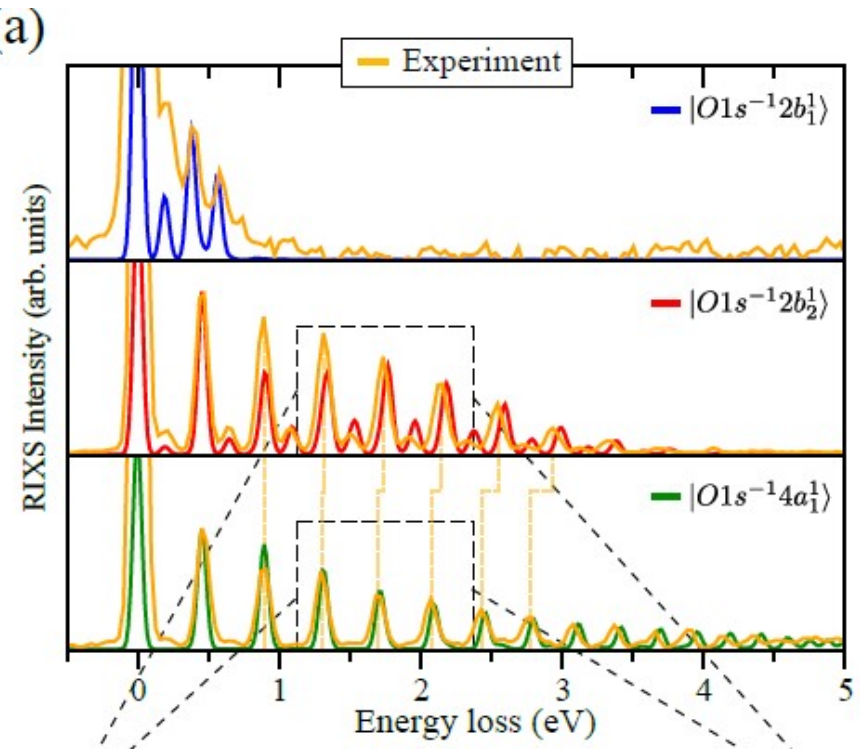
Quasi-elastic RIXS of gas phase water

Multi-configurational electronic wavefunctions
and multi-dimensional nuclear quantum dynamics.



Bend Stretch(2D)



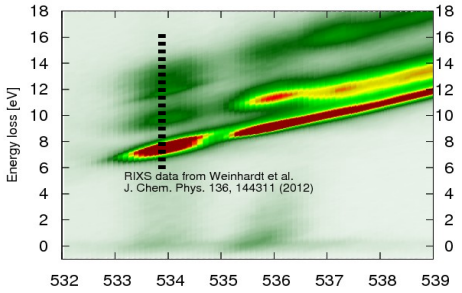


Selective gating to vibrational modes through resonant X-ray scattering

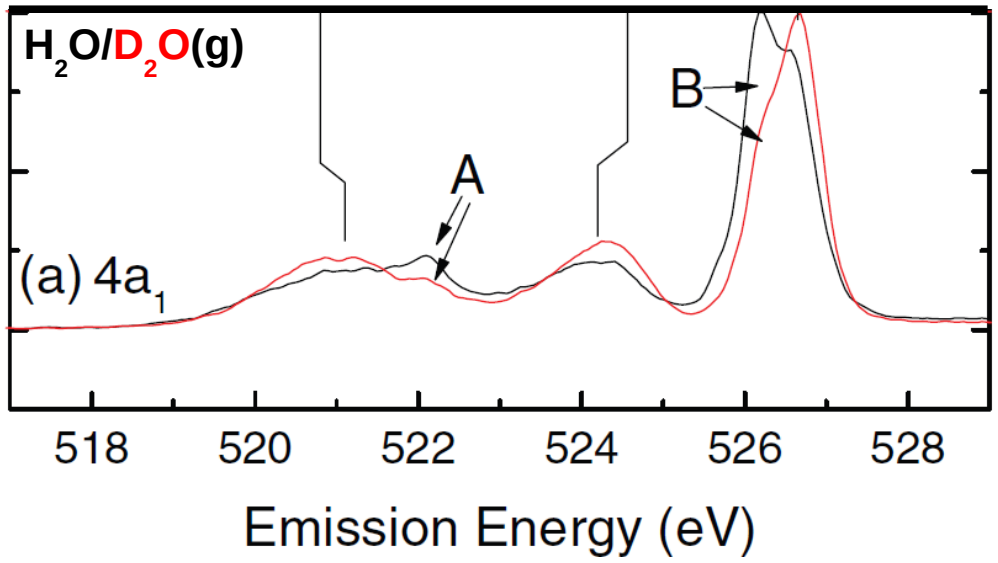
DOI: 10.1038/ncomms14165

Rafael C. Couto[1,2], Vinícius V. Cruz[1], Emelie Ertan[3], Sebastian Eckert[4,5], Mattis Fondell[5], Marcus Dantz[6], Brian Kennedy[5], Thorsten Schmitt[6], Annette Pietzsch[5], Freddy F. Guimarães[2], Hans Ågren[1], Faris Gel'mukhanov[1,7], Michael Odelius[3], Victor Kimberg[1,7] & Alexander Föhlisch[4,5]

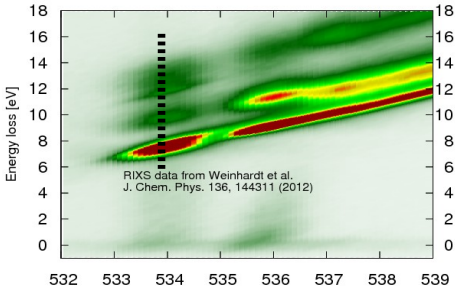
Electronically inelastic RIXS of gas phase water



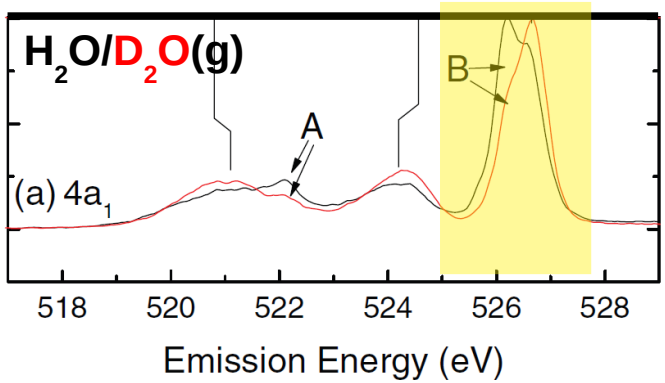
Weinhardt et al. J.Chem.Phys.136 144311 (2012)



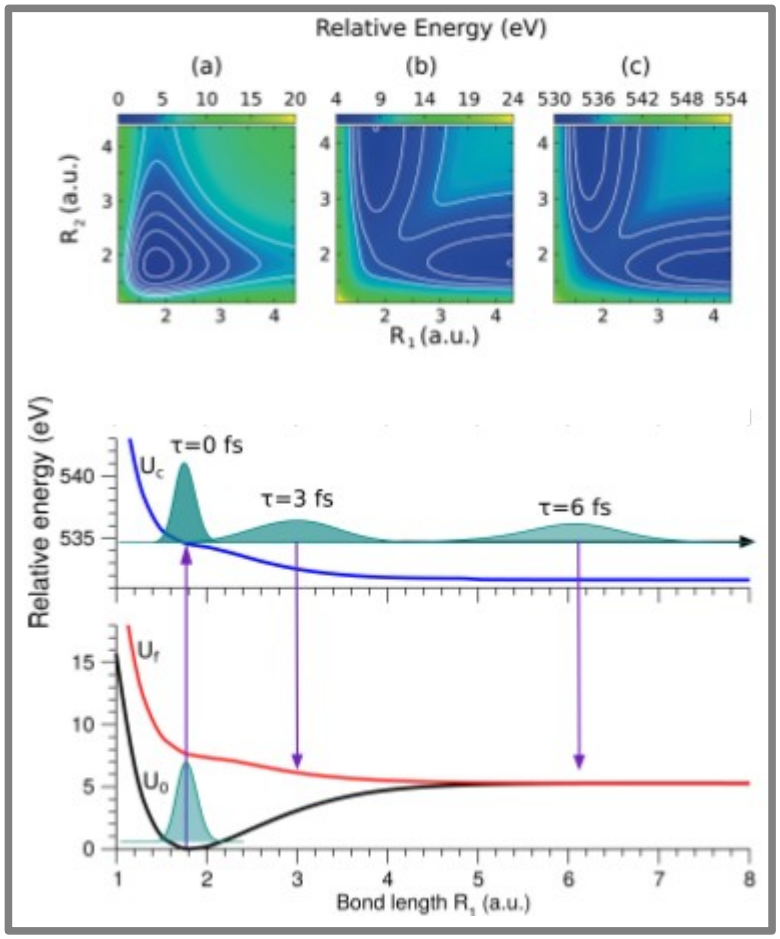
Electronically inelastic RIXS of gas phase water

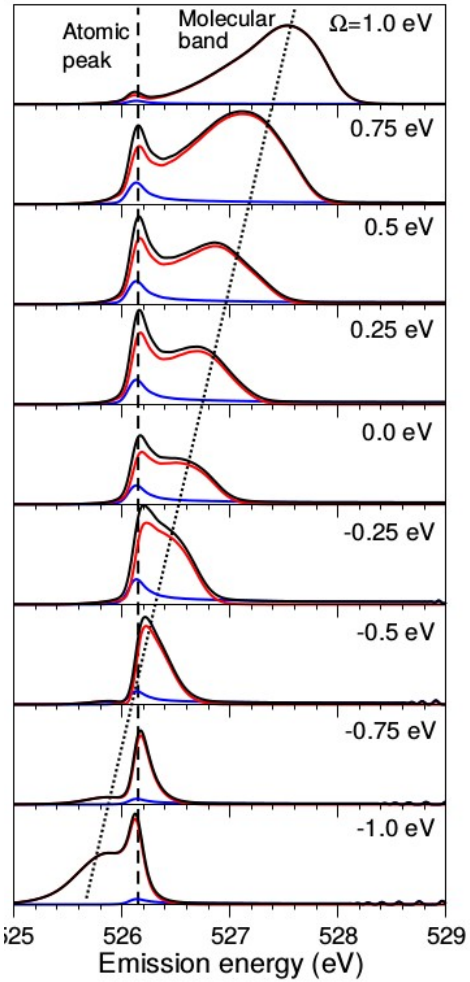


Weinhardt et al. J.Chem.Phys.136 144311 (2012)



$| \ldots \psi_{HOMO}^{-1} \psi_{LUMO}^{1} >$





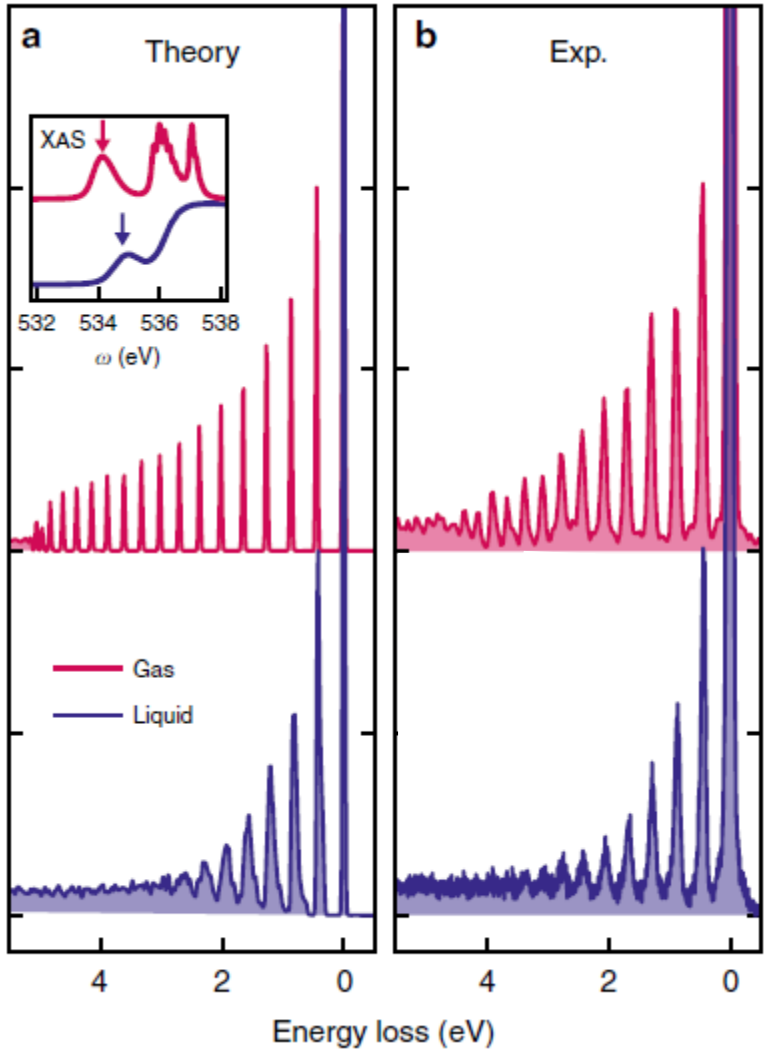
Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2018, 20, 14384

Ultrafast dissociation features in RIXS spectra of the water molecule

Emelie Ertan,[a] Viktoriia Savchenko,[bc] Nina Ignatova,[bc] Vinícius Vaz da Cruz,[b] Rafael C. Couto,[b] Sebastian Eckert,[d] Mattis Fondell,[e] Marcus Dantz,[f] Brian Kennedy,[e] Thorsten Schmitt,[f] Annette Pietzsch,[e] Alexander Föhlisch,[de] Faris Gel'mukhanov,[bc] Michael Odelius[a] and Victor Kimberg[bc]

Quasi-elastic RIXS of liquid water



nature COMMUNICATIONS

Probing hydrogen bond strength in liquid water by resonant inelastic X-ray scattering

Vinícius Vaz da Cruz ✉, Faris Gel'mukhanov, Sebastian Eckert, Marcella Iannuzzi, Emelie Ertan, Annette Pietzsch, Rafael C. Couto, Johannes Niskanen, Mattis Fondell, Marcus Dantz, Thorsten Schmitt, Xingye Lu, Daniel McNally, Raphael M. Jay, Victor Kimberg, Alexander Föhlisch & Michael Odelius ✉

Nature Communications **10**, Article number: 1013 (2019)

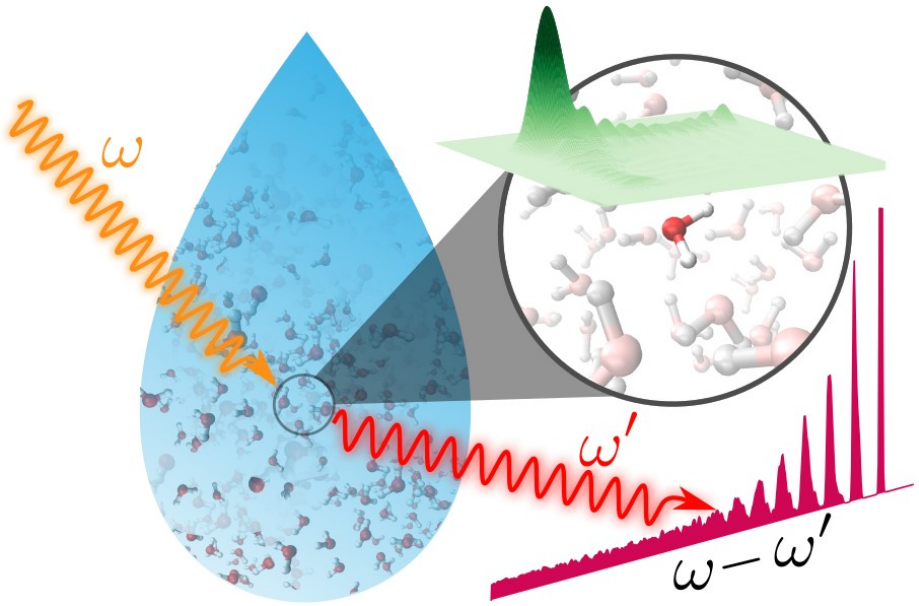
Quasi-elastic RIXS of liquid water

CPMD of liquid water (64 H_2O in PBC)

Scan potential along OH_1 and OH_2 distances for each water molecule (Unrestricted Kohn-Sham BLYP)

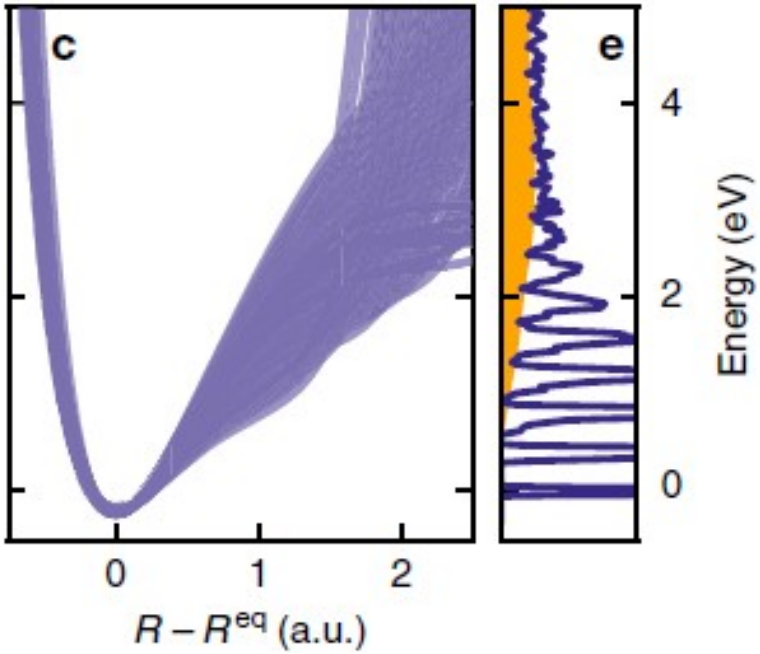
Perform 2D quantum dynamics simulation of the RIXS process

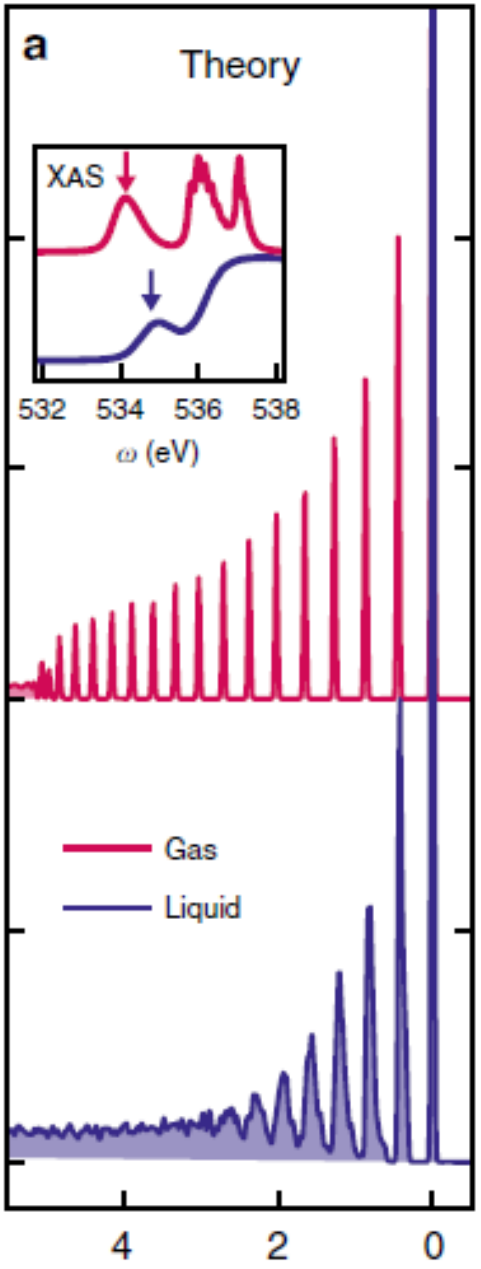
Sum RIXS from different environments



Nature Communications **10**, Article number: 1013 (2019)

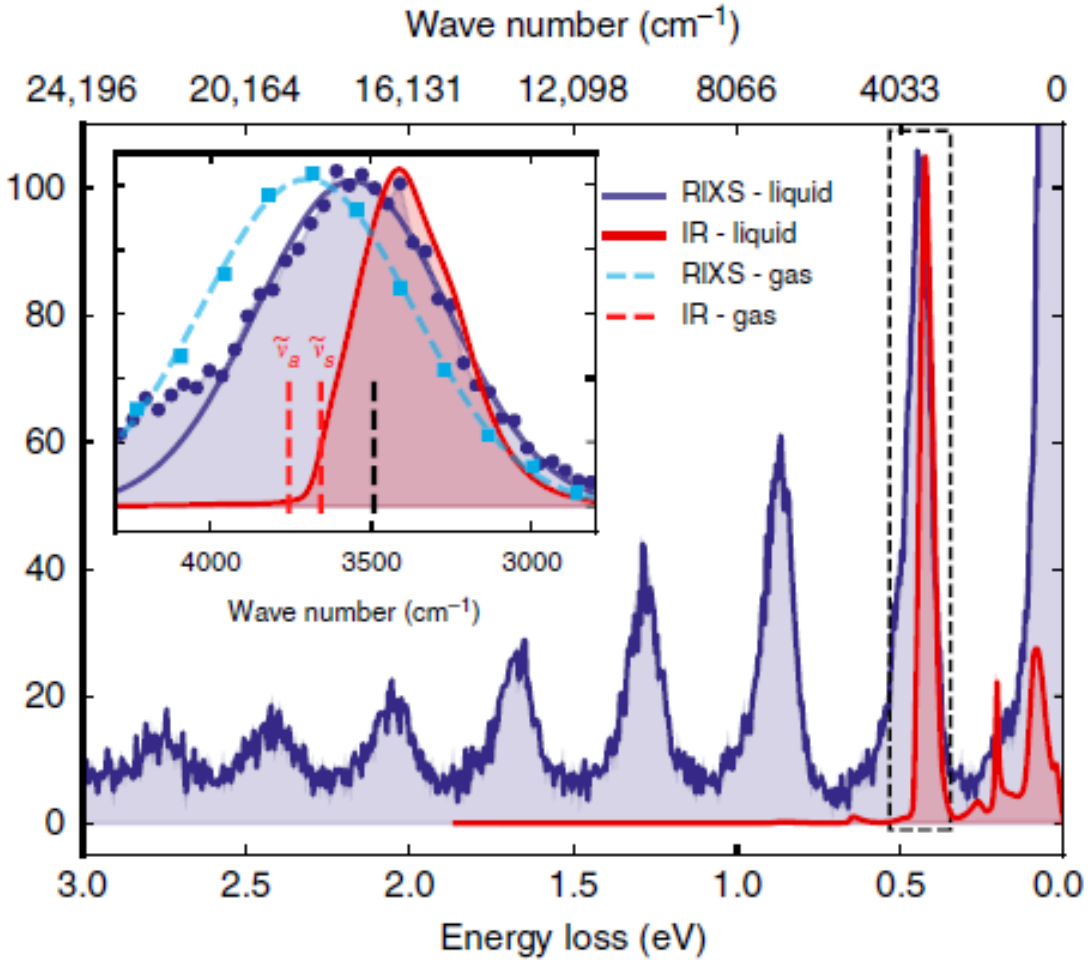
Quasi-elastic RIXS of liquid water

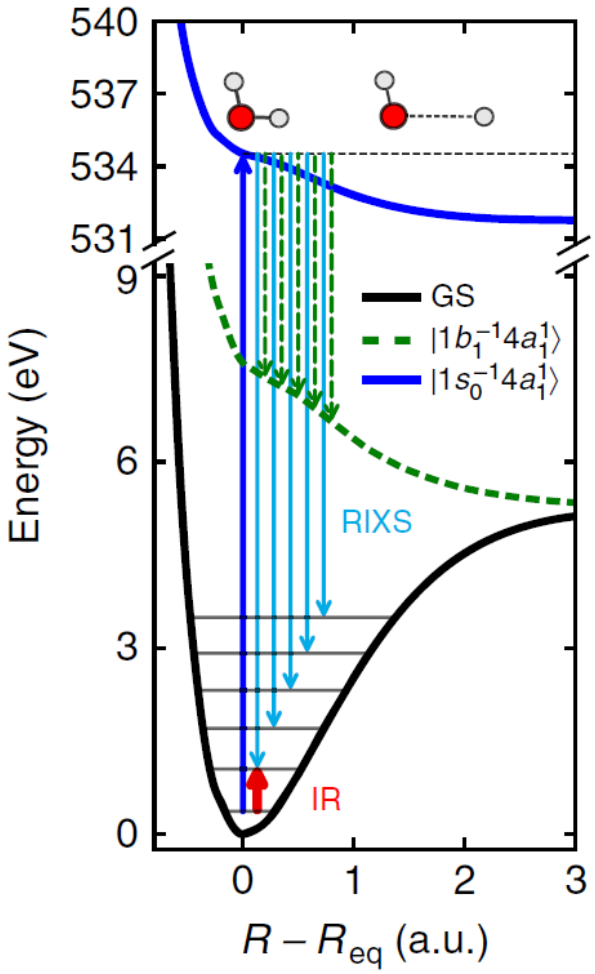




Nature Communications **10**, Article number: 1013 (2019)

IR spectroscopy versus Quasi-elastic RIXS

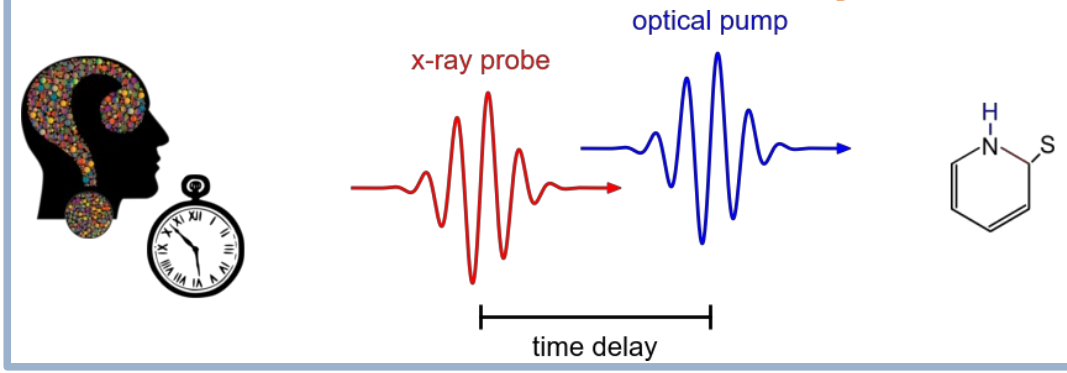


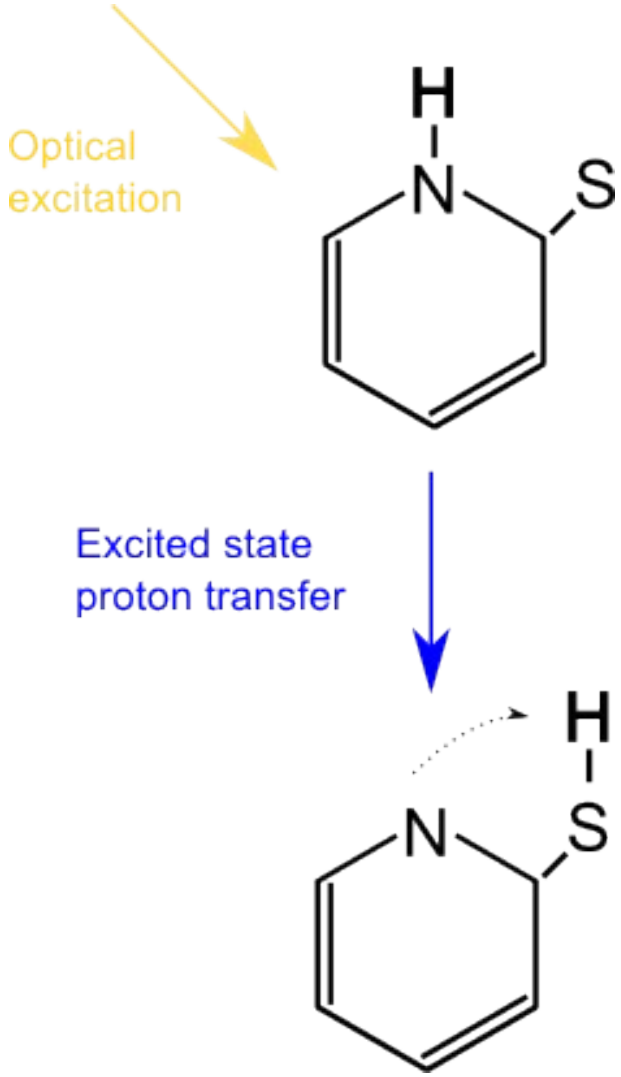


Nature Communications **10**, Article number: 1013 (2019)

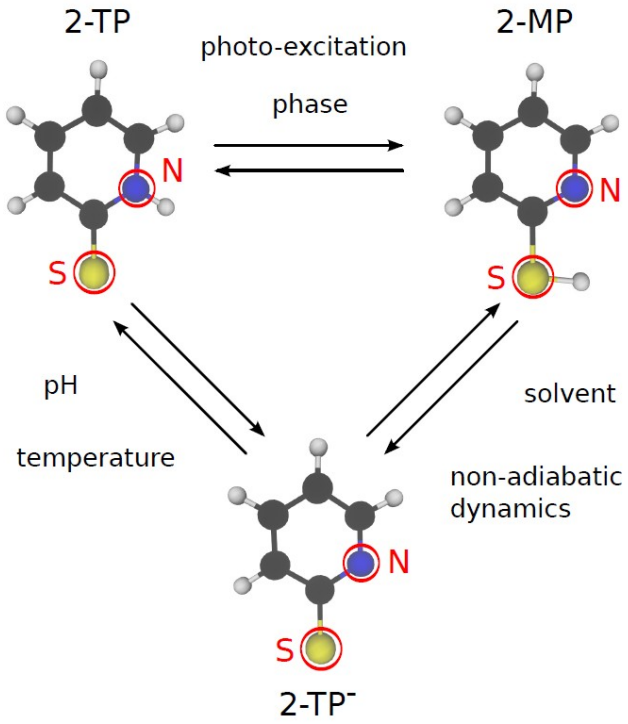
Excited state proton transfer in 2-thiopyridone(aq)

Time-resolved UV pump - X-ray probe





Excited state proton transfer in 2-thiopyridone(aq)



2-TP($S_{n=1.2}$) **2-MP($S_{n=1,2}$)**

2-TP(T_1) **2-MP(T_1)**

2-TP$^-$(S_0)

- **Energetics**
- **Spectral signature**
- **Peak positions**

Vib. Res.Raman(t) Rui Du et al. , J. Phys. Chem. B, **115**, 8266 (2011) (10.1021/jp203185a)

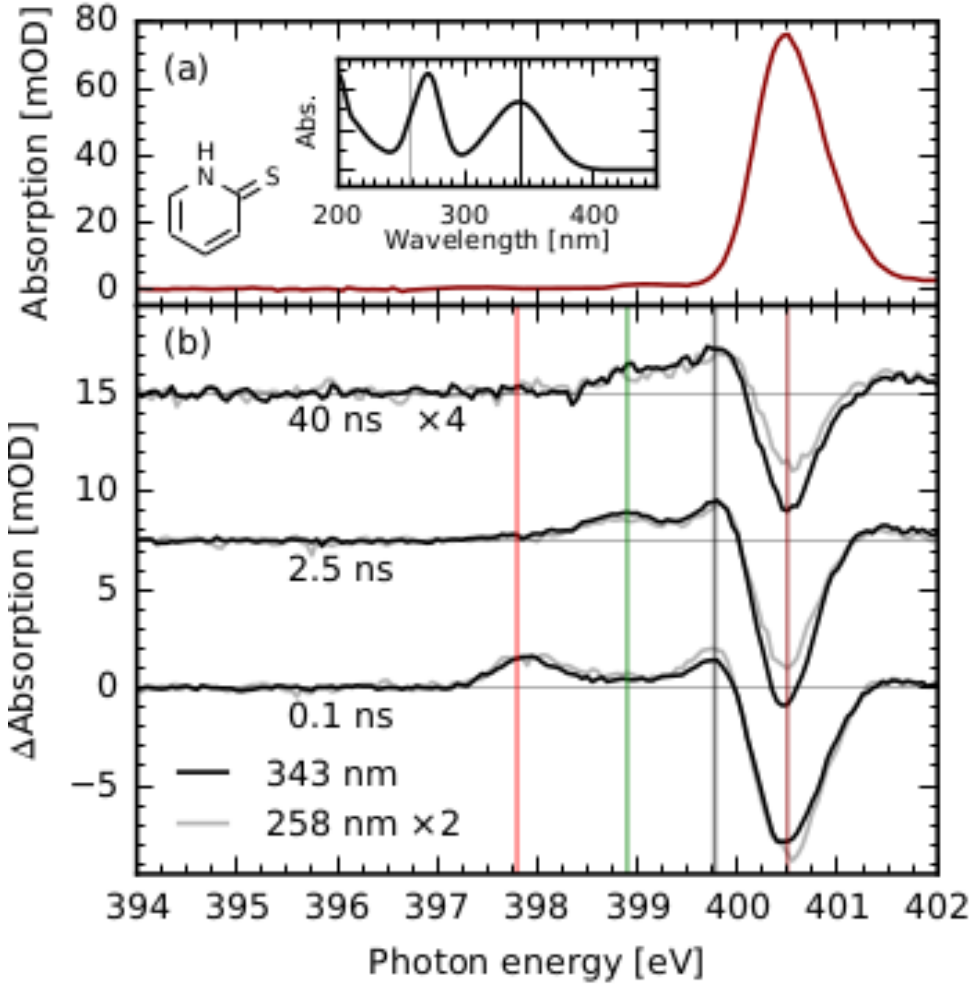
S1s XAS(t) Benjamin E. Van Kuiken, Matthew R. Ross, Matthew L. Strader, Amy A. Cordones, Hana Cho, Jae Hyuk Lee, Robert W. Schoenlein and Munira Khalil, Struct. Dyn. **4**, 044021 (2017) (10.1063/1.4983157)

N1s RIXS(t) Sebastian Eckert et al., Angewandte Chemie, **56**, 6088 (2017) (10.1002/anie.201700239)

N1s XAS(t) Sebastian Eckert, Jesper Norell, Raphael M. Jay, Mattis Fondell, Rolf Mitzner, Michael Odelius, and Alexander Föhlisch, Chem. Eu. J., **25**, 1733 (2019) (10.1002/chem.201804166)

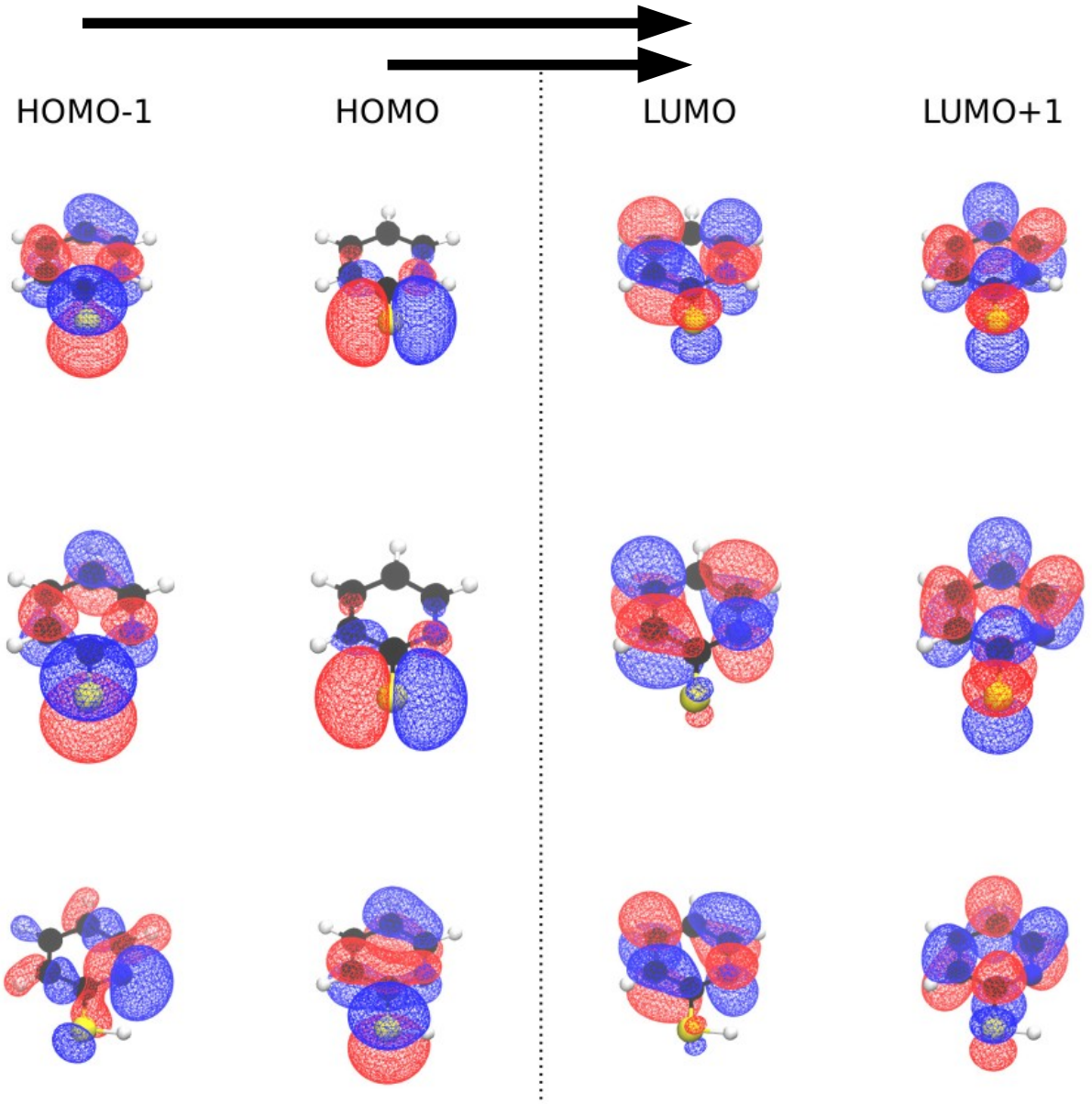
Excited state proton transfer in 2-thiopyridone(aq)

N1s XAS(t) experiments
4.7 3.5 eV



XAS(t) Sebastian Eckert, Jesper Norell, Raphael M. Jay, Mattis Fondell, Rolf Mitzner, Michael Odelius, and Alexander Föhlisch, Chem. Eu. J., **25**, 1733 (2019) (10.1002/chem.201804166)

Low energy electronic transitions in 2-thiopyridone(aq)



Excited state proton transfer in 2-thiopyridone(aq)

Total energy calculations RASPT2+PCM (eV)

State[†]	2-TP$_{FC}$	2-TP$_{R}$	2-MP$_{R}$	2-TP$^{-}_{R}$
S_0	0.00	0.00	0.58	0.00 [‡]
$S_1(n,\pi^*)$	3.87	2.94	5.38	3.50 [‡]
$S_2(\pi,\pi^*)$	3.89	3.15	5.12	3.46 [‡]
$T_1(\pi,\pi^*)$	3.16	2.66	4.42	3.20 [‡]
$T_2(n,\pi^*)$	3.60	2.95	4.85	3.40 [‡]
$S_3(n,\pi^*)$	5.08	-	-	-
$S_4(\pi,\pi^*)$	5.13	-	-	-

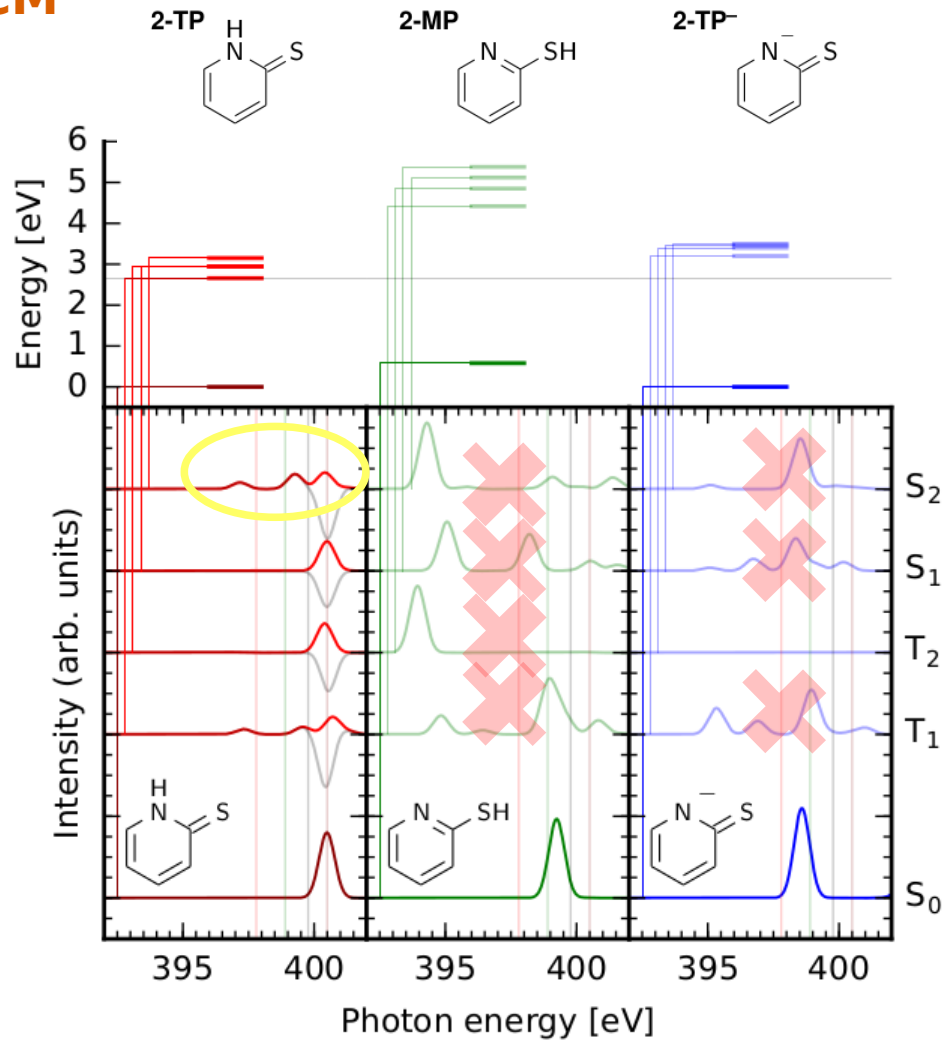
FC=Vertical excitation energy **R=Adiabatic energy**

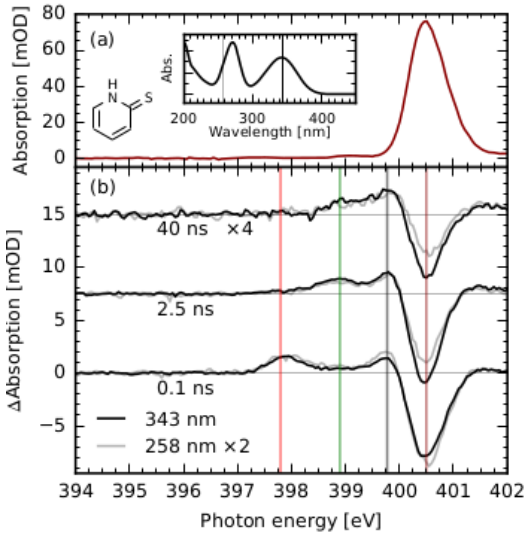
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Excited state proton transfer in 2-thiopyridone(aq)

N1s XAS simulations
RASPT2+PCM

$S_2(\pi \rightarrow \pi^*)$
$S_1(n \rightarrow \pi^*)$
$T_2(n \rightarrow \pi^*)$
$T_1(\pi \rightarrow \pi^*)$



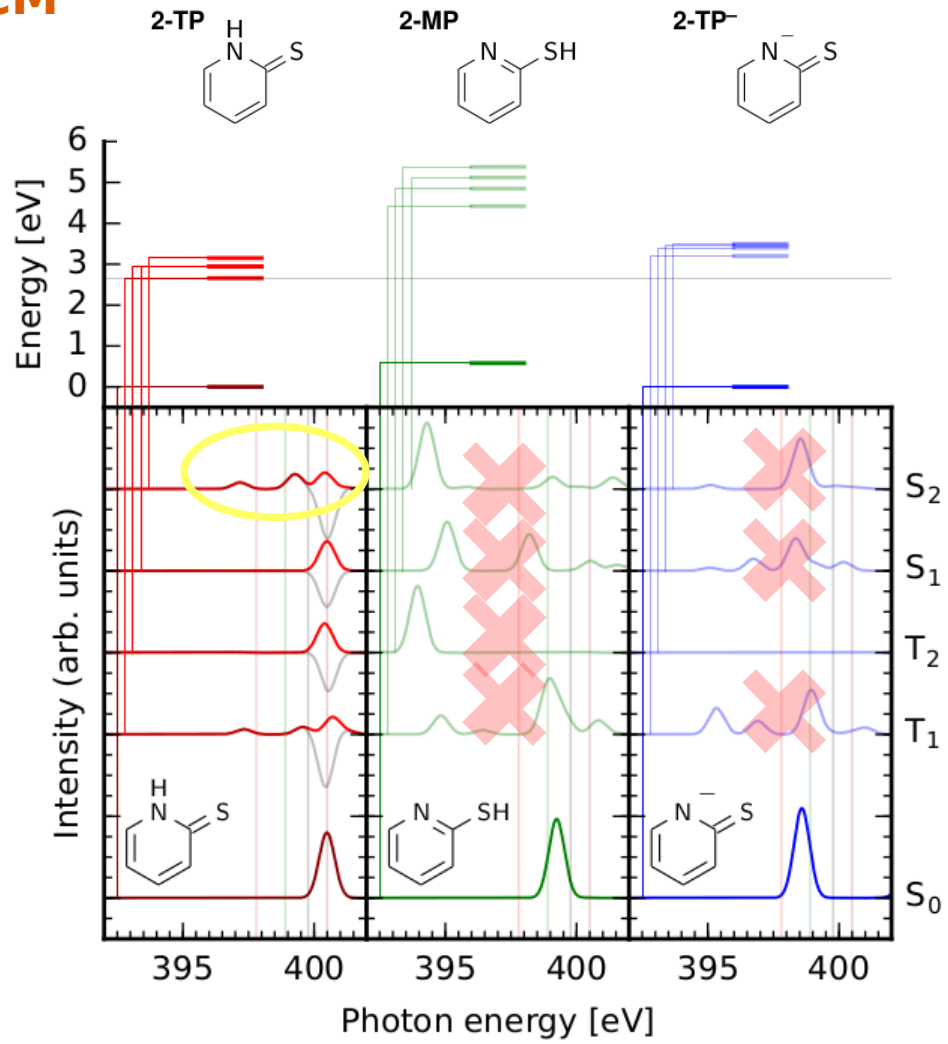


XAS(t) Sebastian Eckert, Jesper Norell, Raphael M. Jay, Mattis Fondell, Rolf Mitzner, Michael Odelius, and Alexander Föhlisch, Chem. Eu. J., **25**, 1733 (2019) (10.1002/chem.201804166)

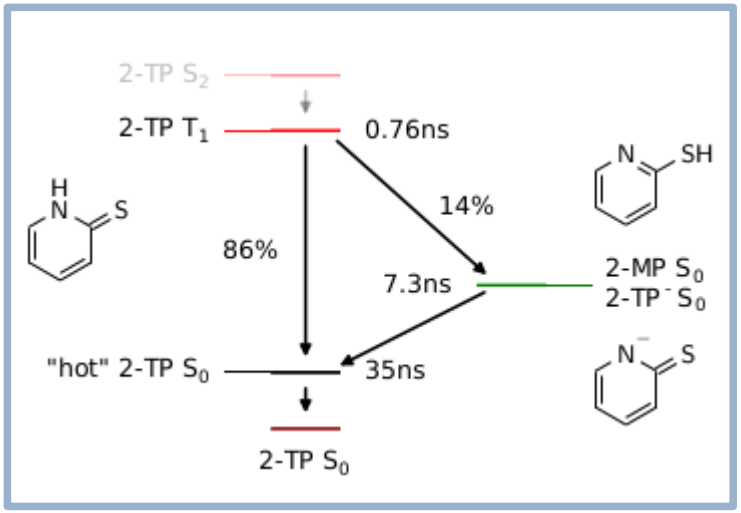
Excited state proton transfer in 2-thiopyridone(aq)

N1s XAS simulations RASPT2+PCM

$S_2(\pi \rightarrow \pi^*)$
$S_1(n \rightarrow \pi^*)$
$T_2(n \rightarrow \pi^*)$
$T_1(\pi \rightarrow \pi^*)$



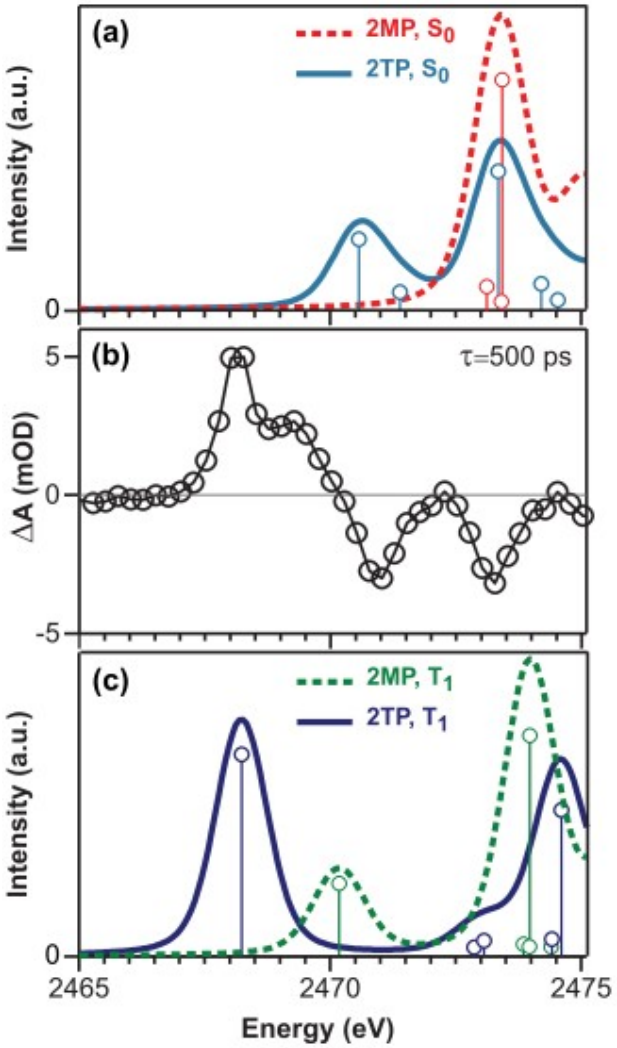
Energetic and spectroscopic conclusions

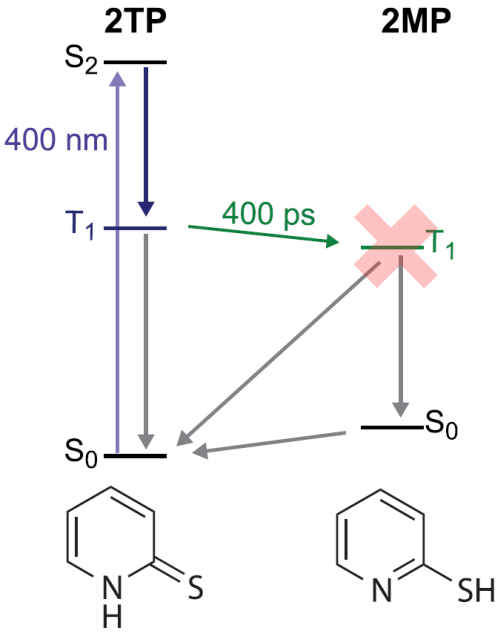


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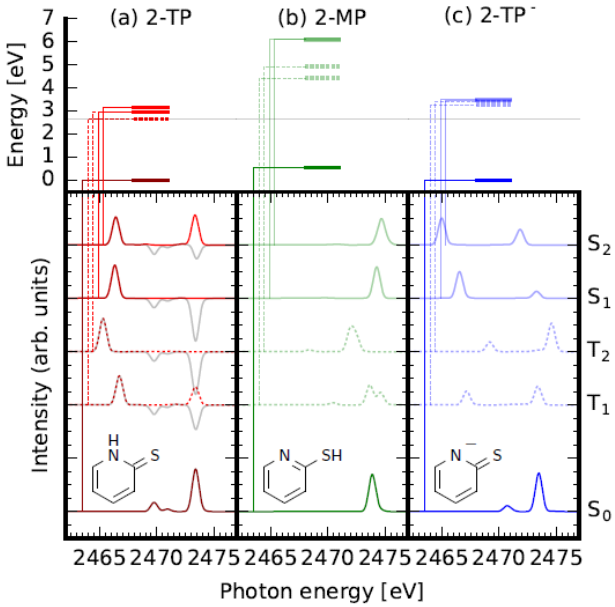
S1s XAS TDDFT(g)





Van Kuiken et al. Struct. Dyn. 4, 044021 (2017)

S1s XAS simulations RASPT2+PCM



Summary

Molecular orbital approach

Modeling and assignment of XPS, XAS, XES, RIXS

Electronic states approach

State specific electron relaxation

High-resolution spectral features

Relativistic and dynamical effects

Excited state X-ray spectra



Stockholm University