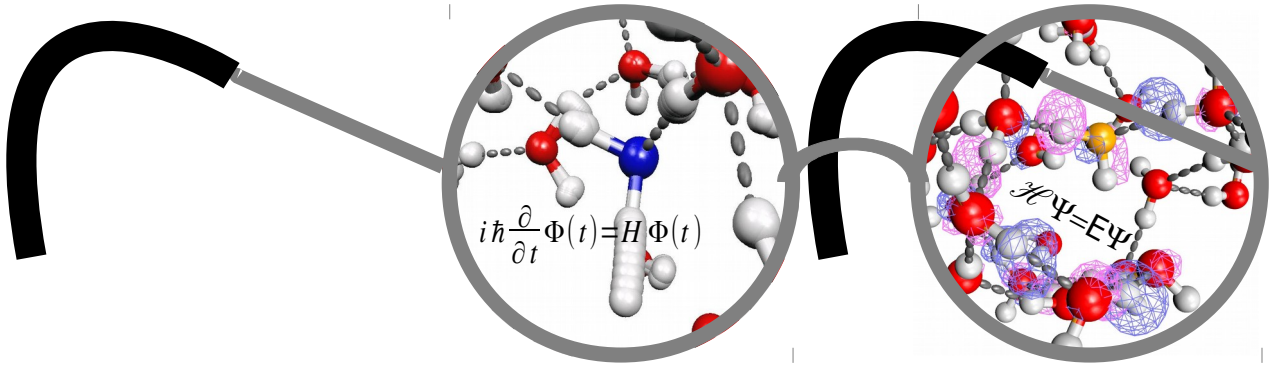


Using RASSCF calculations for Computing Resonant Inelastic X-Ray Scattering (RIXS)

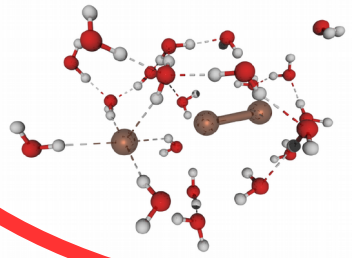
Michael Odelius

odelius@fysik.su.se

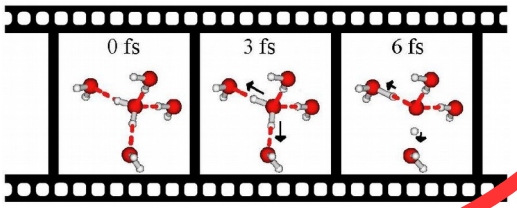
Department of Physics

Stockholm University

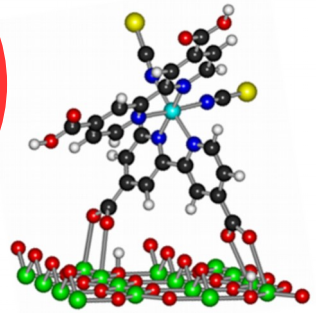
Solution dynamics



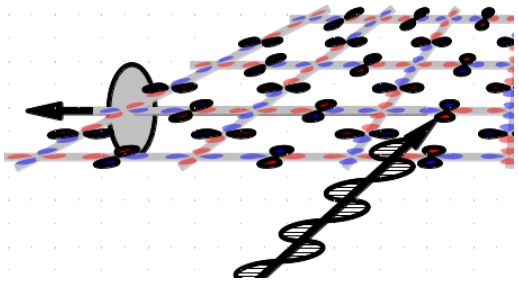
Excited state dynamics



Solar cells



Superconductors



The QCMD group at Fysikum, Stockholm University

Time

SNIC
NSC
C³SE

Money

Carl Tryggers StipendieStiftelse
HZB Helmholtz Zentrum Berlin
Virtual Institute Dynamic Pathways in Multidimensional Landscapes
VETENSKAPSRÅDET THE SWEDISH RESEARCH COUNCIL

Members

Jesper Norell

Dr. Ida Josefsson

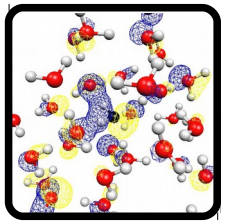
Shehryar Khan

Emelie Ertan

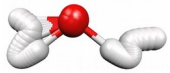
http://www.fysik.su.se/~odelius/qcmd/

Universitet Stockholms
Stockholm University

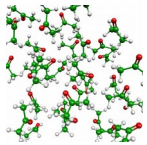
Outline



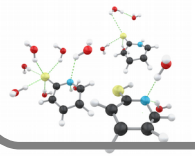
Techniques QC MD RASSCF



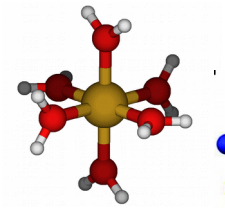
$H_2O(g)$ — O 1s RIXS



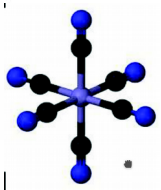
Acetone(l) — O 1s RIXS



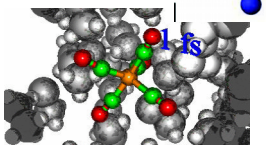
2-MP(aq) — N 1s RIXS(t)



$Ni^{2+}(aq)$ — Ni 2p RIXS



$[Fe(CN)_6]^{3-}(aq)$ — Fe 2p RIXS



$Fe(CO)_5(etoh)$ — Fe 2p RIXS(t)

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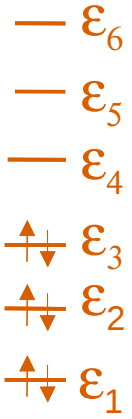
$\mathcal{H}\Psi=E\Psi$

Hartree-Fock

Singlet determinant
Independent particle or Mean-field approximation

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

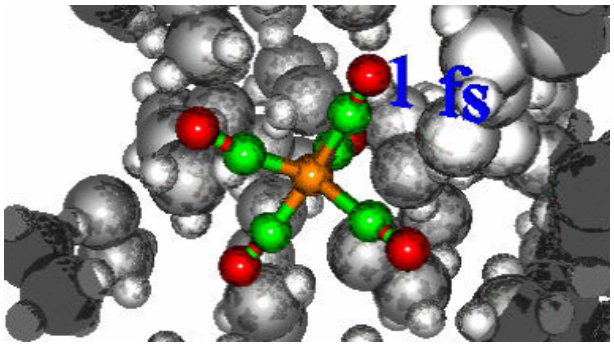
Momentary e^- - e^- correlation missing!



DFT

Singlet determinant

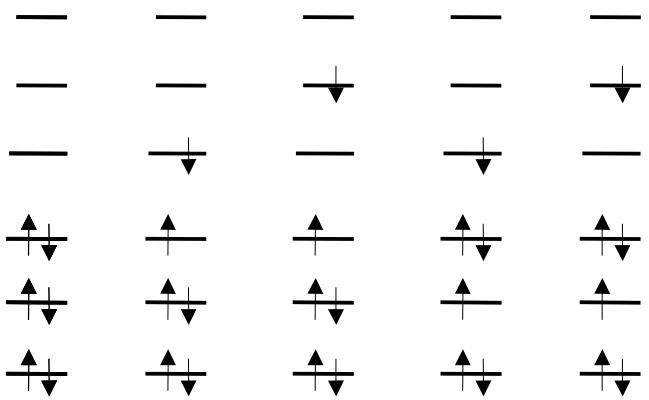
Correlation in $\mathcal{H}$



Post-HF

Multi-determinant

Wave function correlated

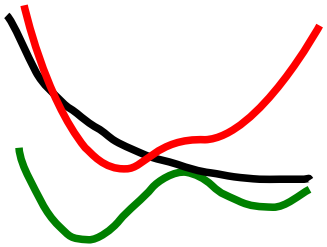


Molecular dynamics

$F=ma \qquad F_I=(-\partial V/\partial r_I)$

Nuclear quantum dynamics

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



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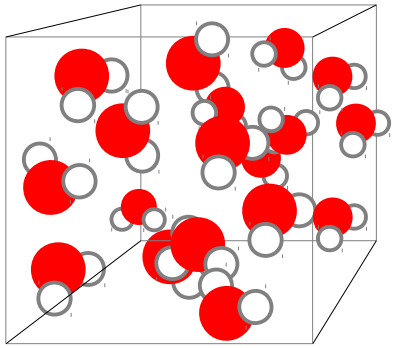
Tool box

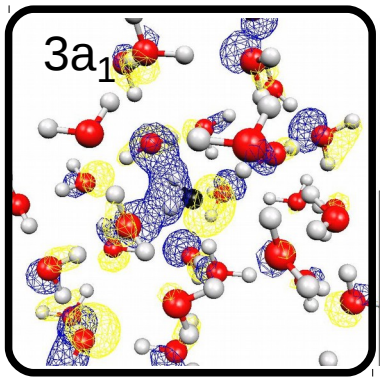
Molecular dynamics simulations



Solution dynamics – CPMD/Cp2k

Quantum dynamics - Victor+Faris

Electronic structure and Spectrum calculations



Density functional theory

- Plane-wave basis - CPMD
- Local Gaussian basis - Cp2k

Post-Hartree-Fock

- Relativistic RASSCF - MOLCAS
  - RASPT2
  - Spin-Orbit Coupling

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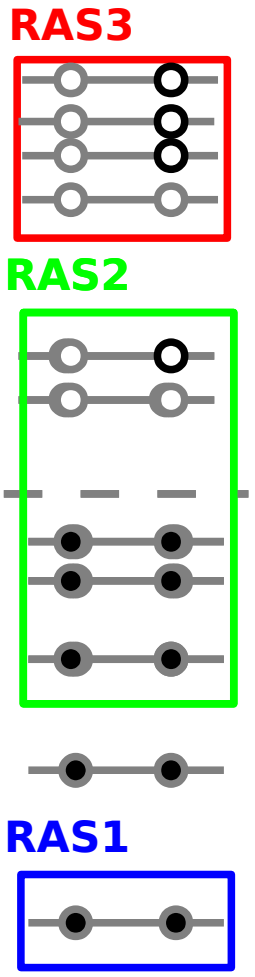
Choice of method



Quantum chemistry of excited states:

Restricted/Complete Active Space SCF

RASSCF

Static correlation

RASSCF+perturbative PT2

Dynamics correlation

RASPT2

Dissociation

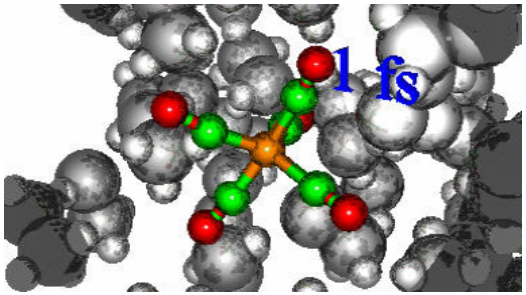
Valence excited states

Core excited states

Scalar Relativistic

Multiplet effects

Spin-orbit coupling



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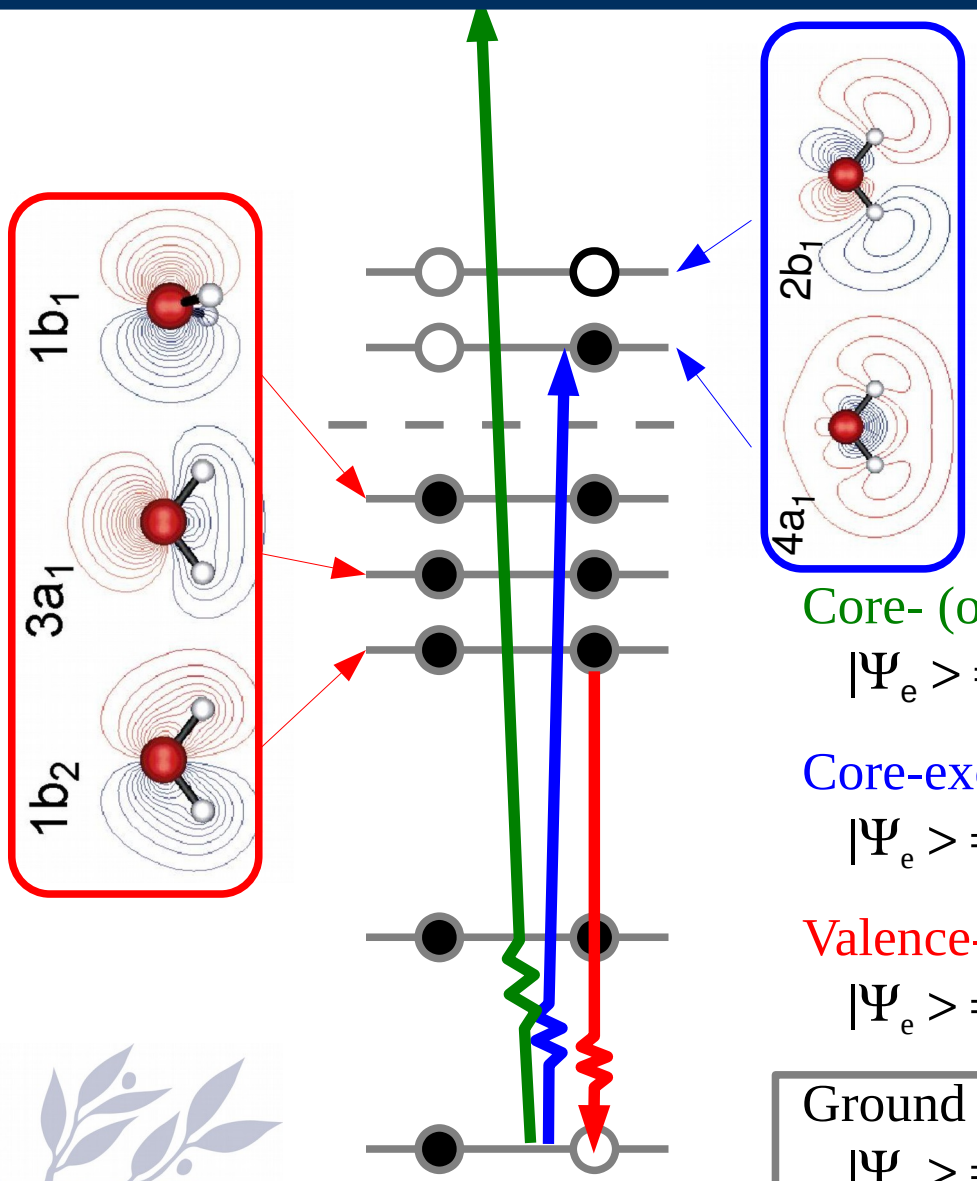
Case study: $H_2O(g)$



$$I(\omega,\omega') \propto \sum_f \left| \sum_c \frac{\langle f|\hat{Q}|c\rangle\langle c|\hat{V}|0\rangle}{\hbar\omega - (E_c - E_0) - i\Gamma_c} \right|^2 \cdot \frac{\Gamma_f/\pi}{(\hbar\omega' - \hbar\omega + (E_f - E_0))^2 + \Gamma_f^2}.$$

Resonant inelastic X-ray scattering RIXS

Core- (or valence-) ionized states:

$$|\Psi_e> = |\ 1a_1^{\ 1}\ 2a_1^{\ 2}\ \ 1b_2^{\ 2}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ \ 4a_1^{\ 0}\ 2b_1^{\ 0}\ >$$

Core-excited state:

$$|\Psi_e> = |\ 1a_1^{\ 1}\ 2a_1^{\ 2}\ \ 1b_2^{\ 2}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ 4a_1^{\ 1}\ 2b_1^{\ 0}\ >$$

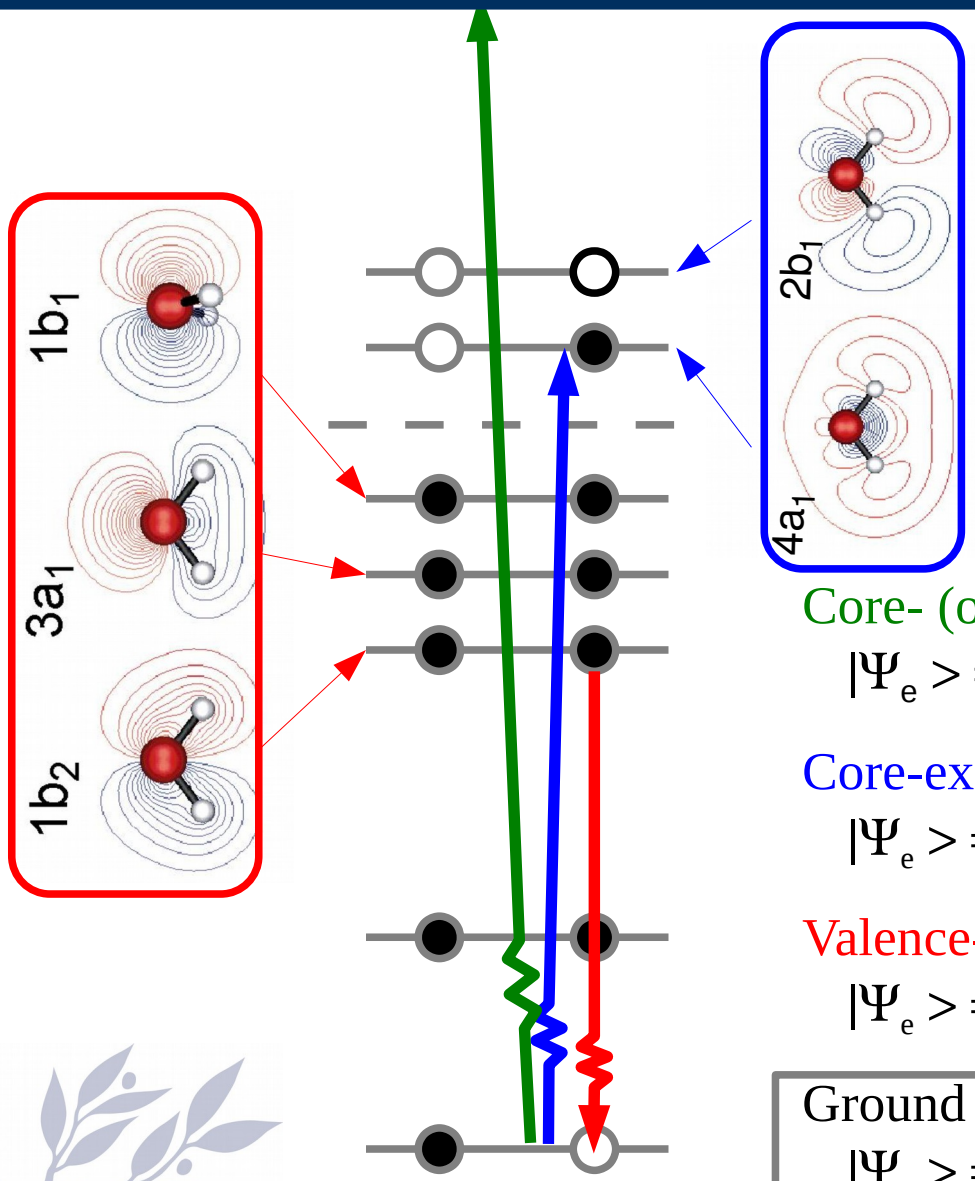
Valence-excited state:

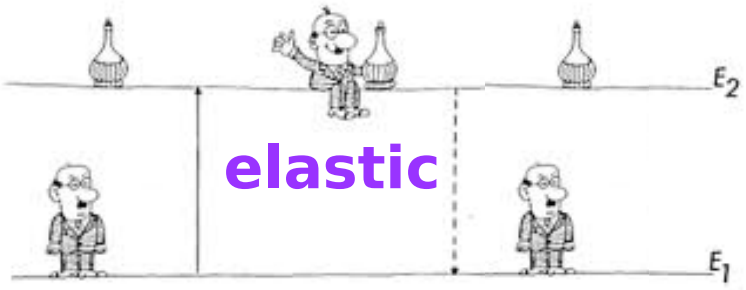
$$|\Psi_e> = |\ 1a_1^{\ 2}\ 2a_1^{\ 2}\ \ 1b_2^{\ 1}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ 4a_1^{\ 1}\ 2b_1^{\ 0}\ >$$

Ground state:

$$|\Psi_e> = |\ 1a_1^{\ 2}\ 2a_1^{\ 2}\ \ 1b_2^{\ 2}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ \ 4a_1^{\ 0}\ 2b_1^{\ 0}\ >$$

Case study: $H_2O(g)$





Resonant inelastic X-ray scattering RIXS

Core- (or valence-) ionized states:

$$|\Psi_e> = |\ 1a_1^{\ 1}\ 2a_1^{\ 2}\ \ 1b_2^{\ 2}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ \ 4a_1^{\ 0}\ 2b_1^{\ 0}\ >$$

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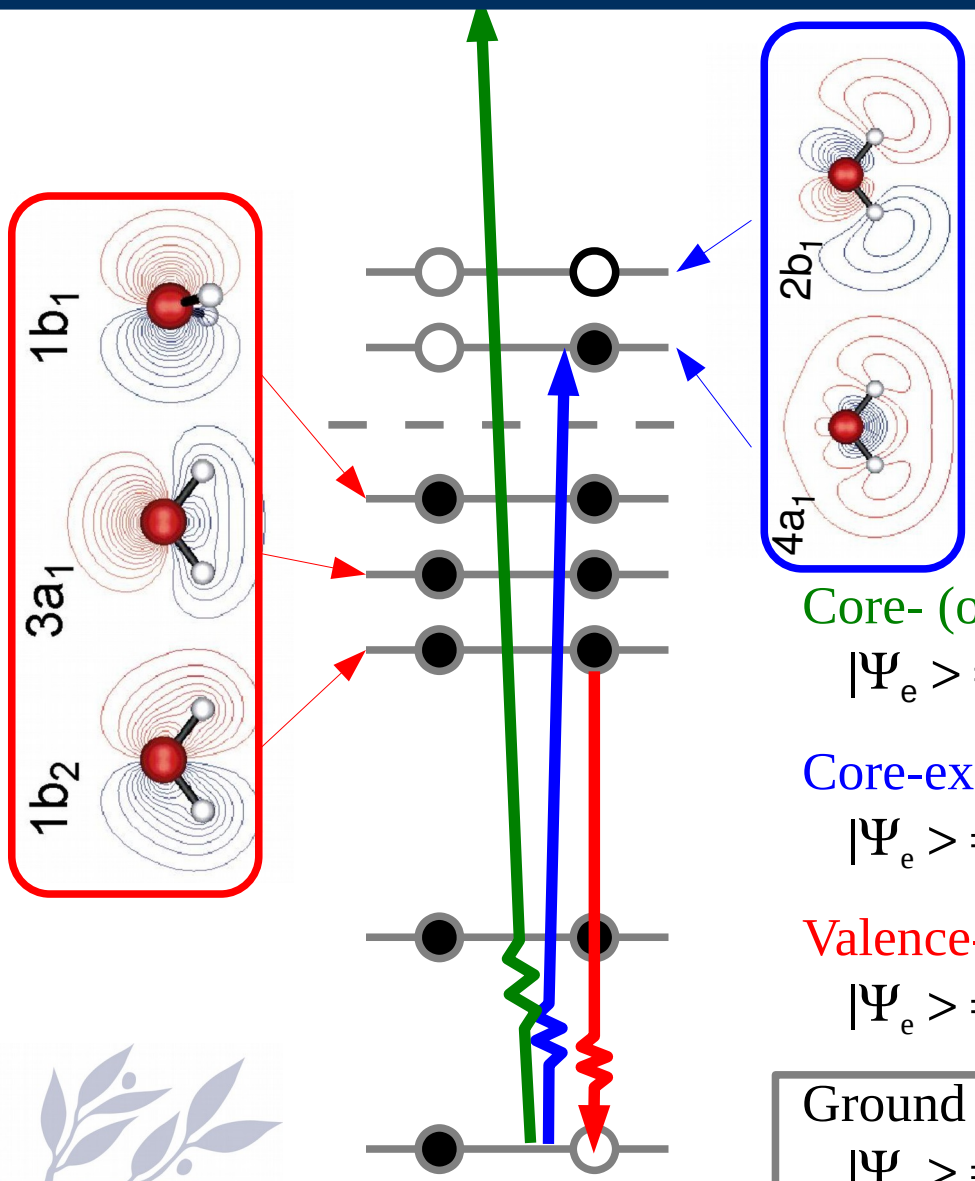
Valence-excited state:

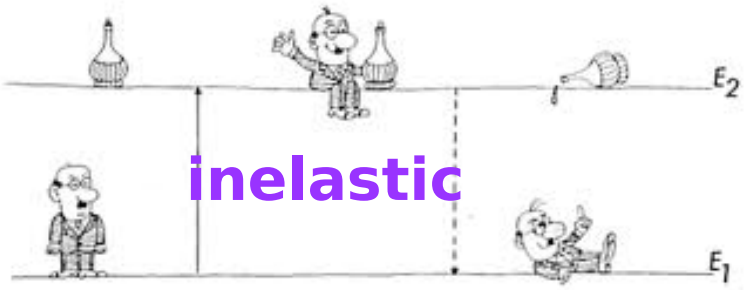
$$|\Psi_e> = |\ 1a_1^{\ 2}\ 2a_1^{\ 2}\ 1b_2^{\ 1}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ 4a_1^{\ 1}\ 2b_1^{\ 0}\ >$$

Ground state:

$$|\Psi_e> = |\ 1a_1^{\ 2}\ 2a_1^{\ 2}\ \ 1b_2^{\ 2}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ \ 4a_1^{\ 0}\ 2b_1^{\ 0}\ >$$

Case study: $H_2O(g)$





inelastic

Resonant inelastic X-ray scattering RIXS

Core- (or valence-) ionized states:

$$|\Psi_e> = |\ 1a_1^{\ 1}\ 2a_1^{\ 2}\ \ 1b_2^{\ 2}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ \ 4a_1^{\ 0}\ 2b_1^{\ 0}\ >$$

Core-excited state:

$$|\Psi_e> = |\ 1a_1^{\ 1}\ 2a_1^{\ 2}\ \ 1b_2^{\ 2}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ \ 4a_1^{\ 1}\ 2b_1^{\ 0}\ >$$

Valence-excited state:

$$|\Psi_e> = |\ 1a_1^{\ 2}\ 2a_1^{\ 2}\ \ 1b_2^{\ 1}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ \ 4a_1^{\ 1}\ 2b_1^{\ 0}\ >$$

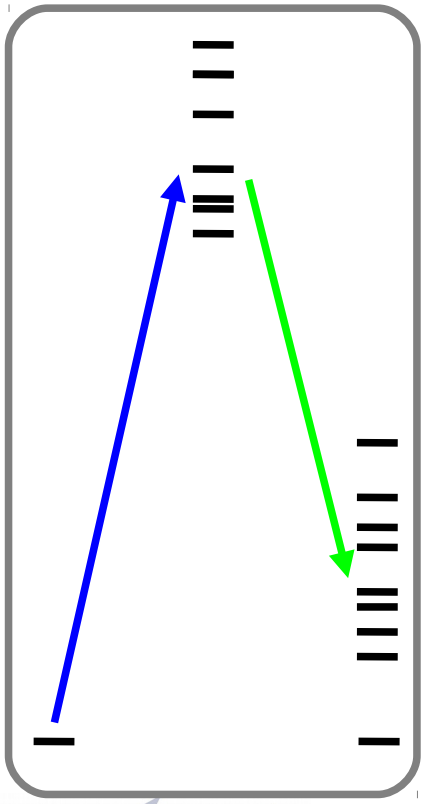
Ground state:

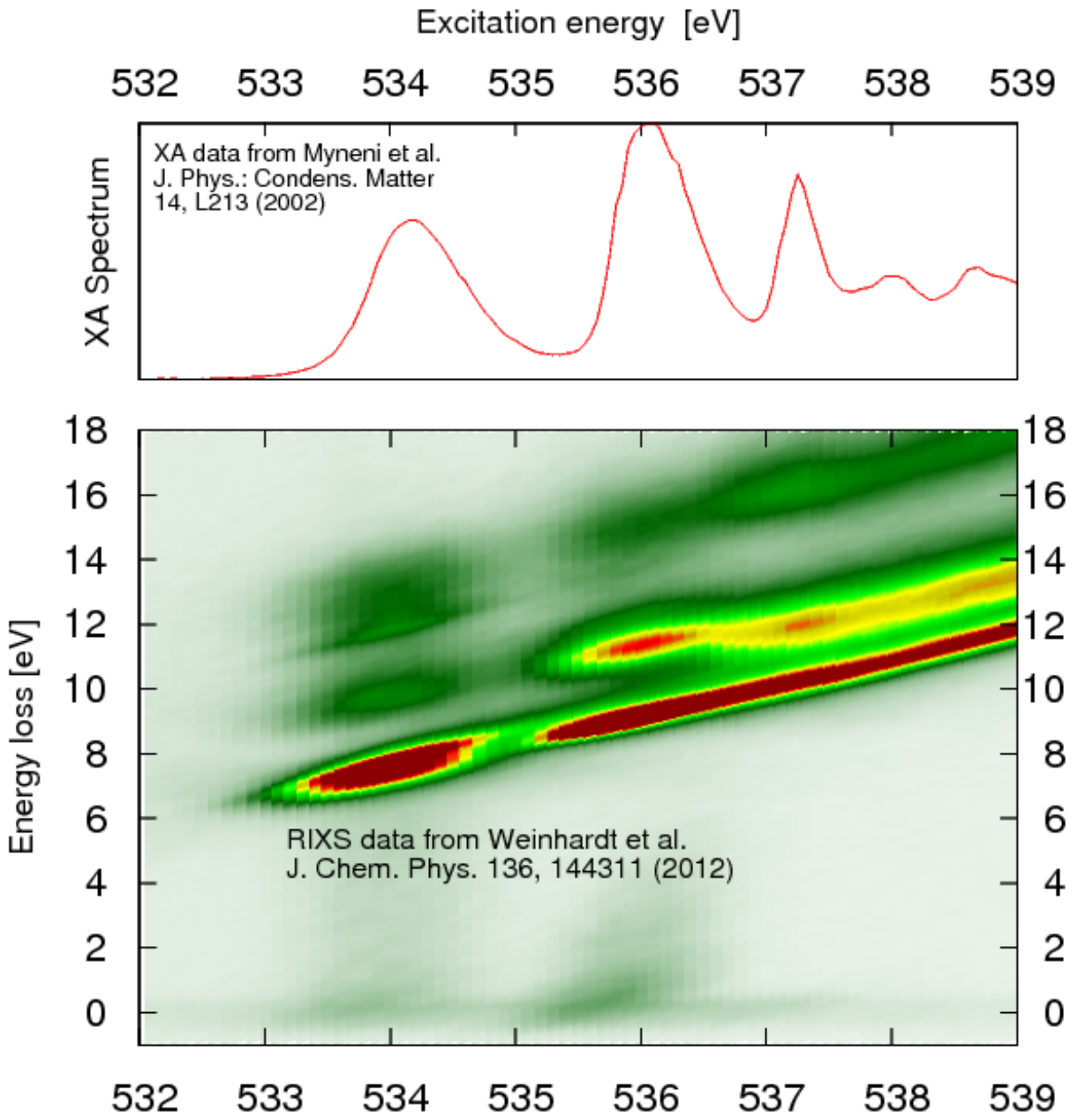
$$|\Psi_e> = |\ 1a_1^{\ 2}\ 2a_1^{\ 2}\ \ 1b_2^{\ 2}\ 3a_1^{\ 2}\ 1b_1^{\ 2}\ \ \ 4a_1^{\ 0}\ 2b_1^{\ 0}\ >$$

Resonant inelastic X-ray Scattering of $H_2O(g)$

$H_2O(g)$

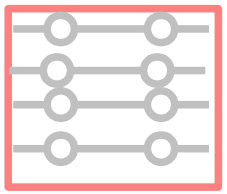
O K-edge



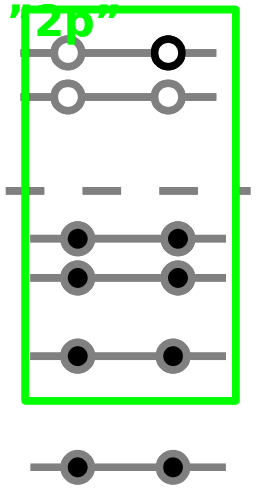


Multi-configurational SCF calculations of $H_2O(g)$

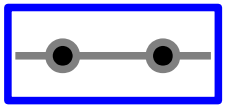
RAS3 Rydberg etc



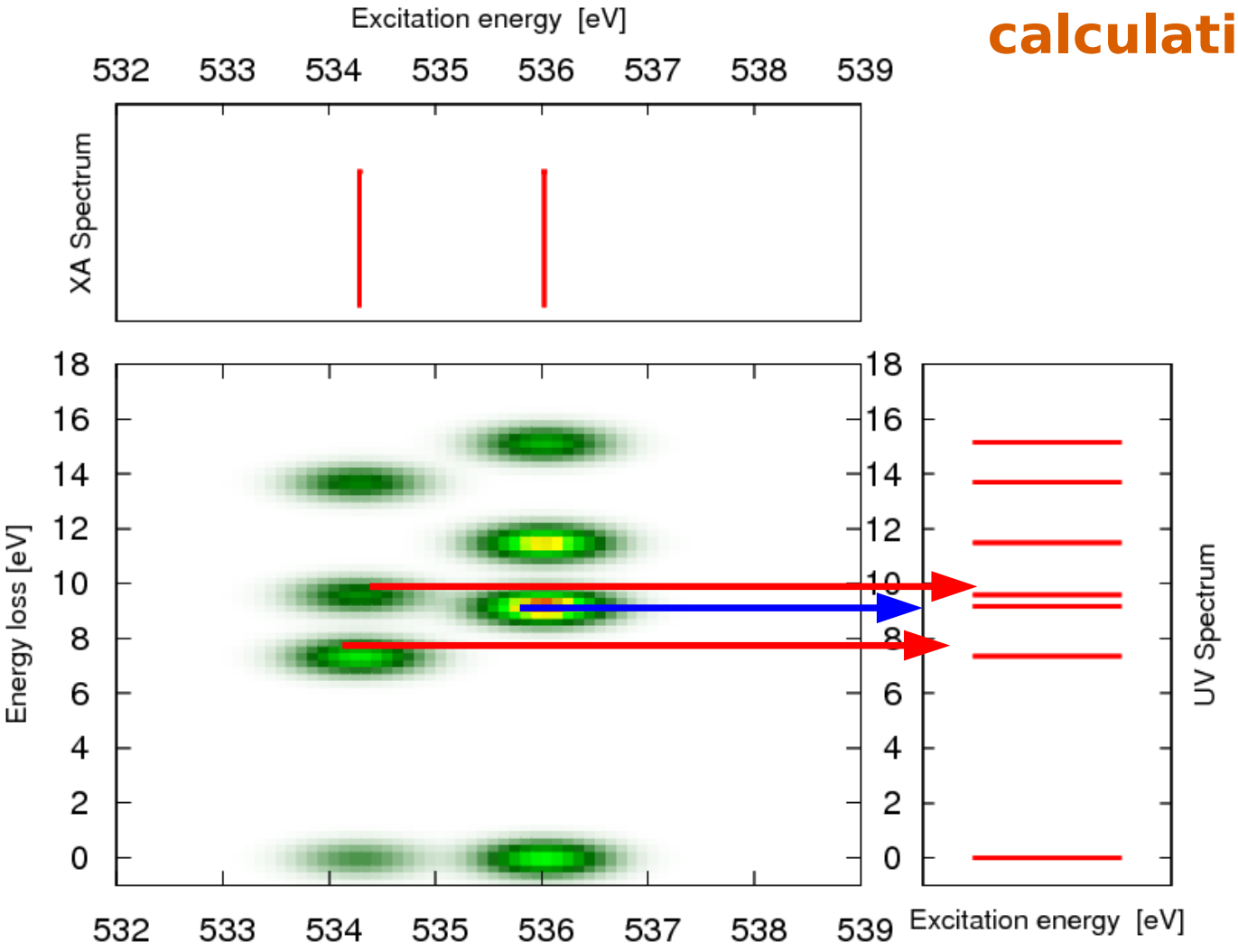
RAS2
"2p"



RAS1 1s



RIXS $H_2O(g)$

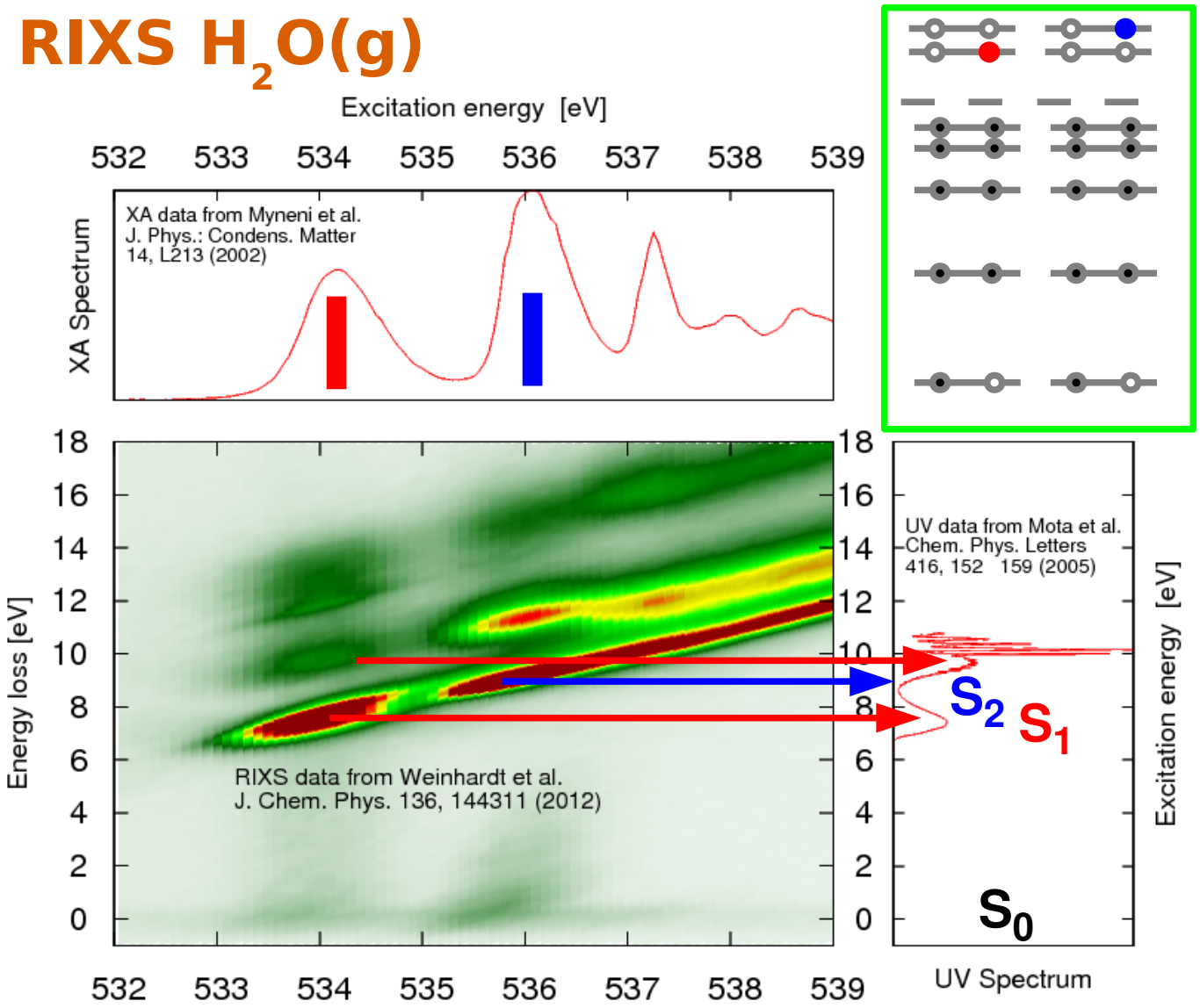


RASPT2 calculations

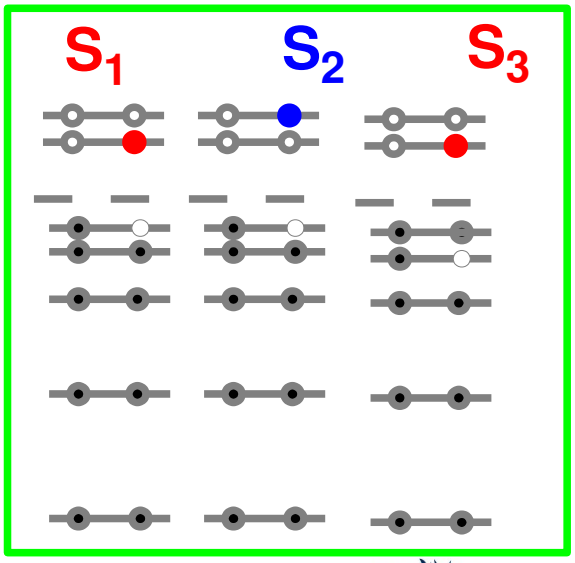
Stockholm University

Resonant inelastic X-ray Scattering of $H_2O(g)$

RIXS $H_2O(g)$



Single dominant determinants motivates using an orbital picture!



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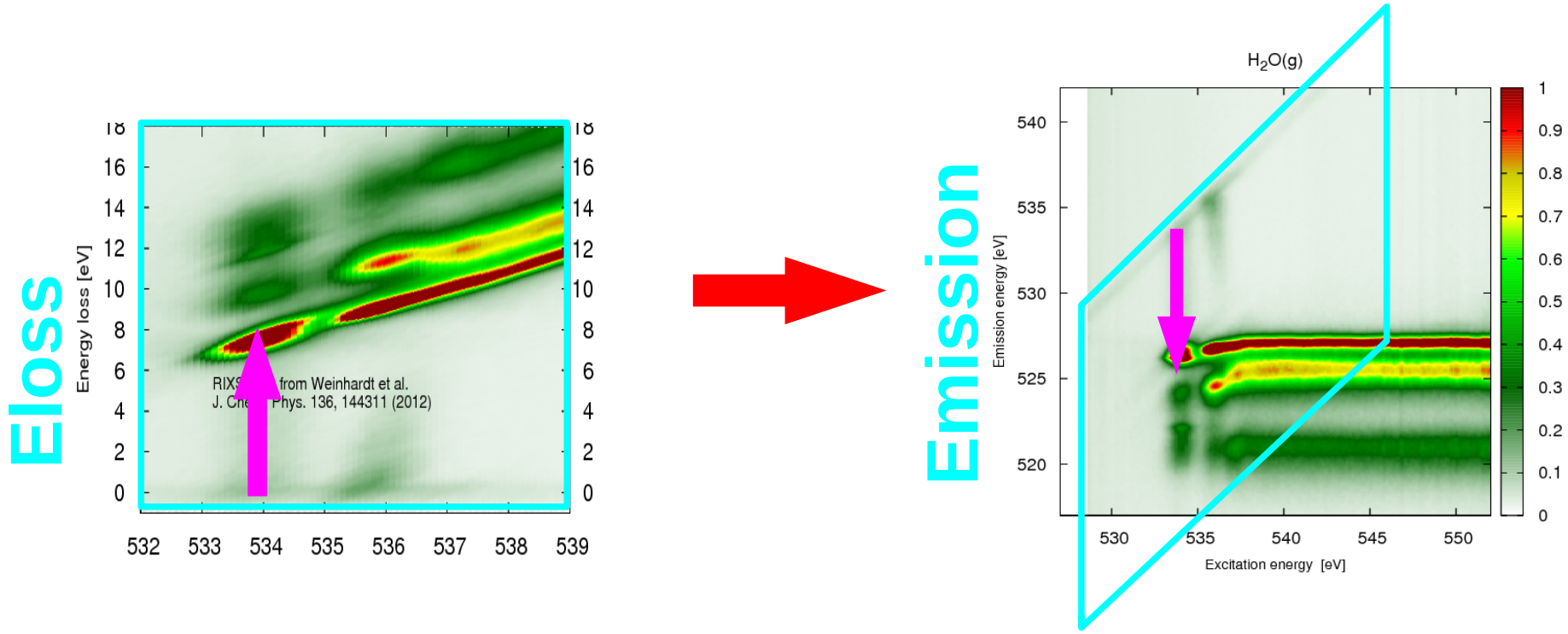
Electronic States → Molecular Orbitals

RIXS $H_2O(g)$



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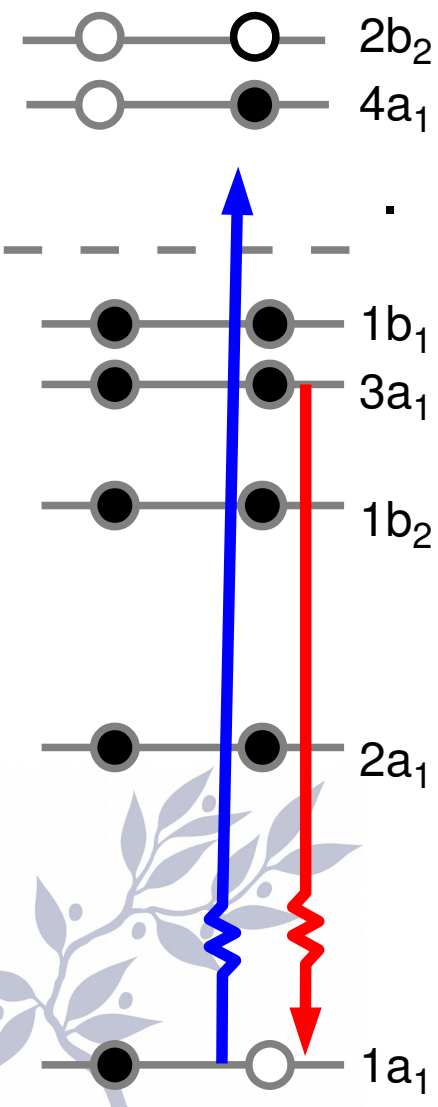
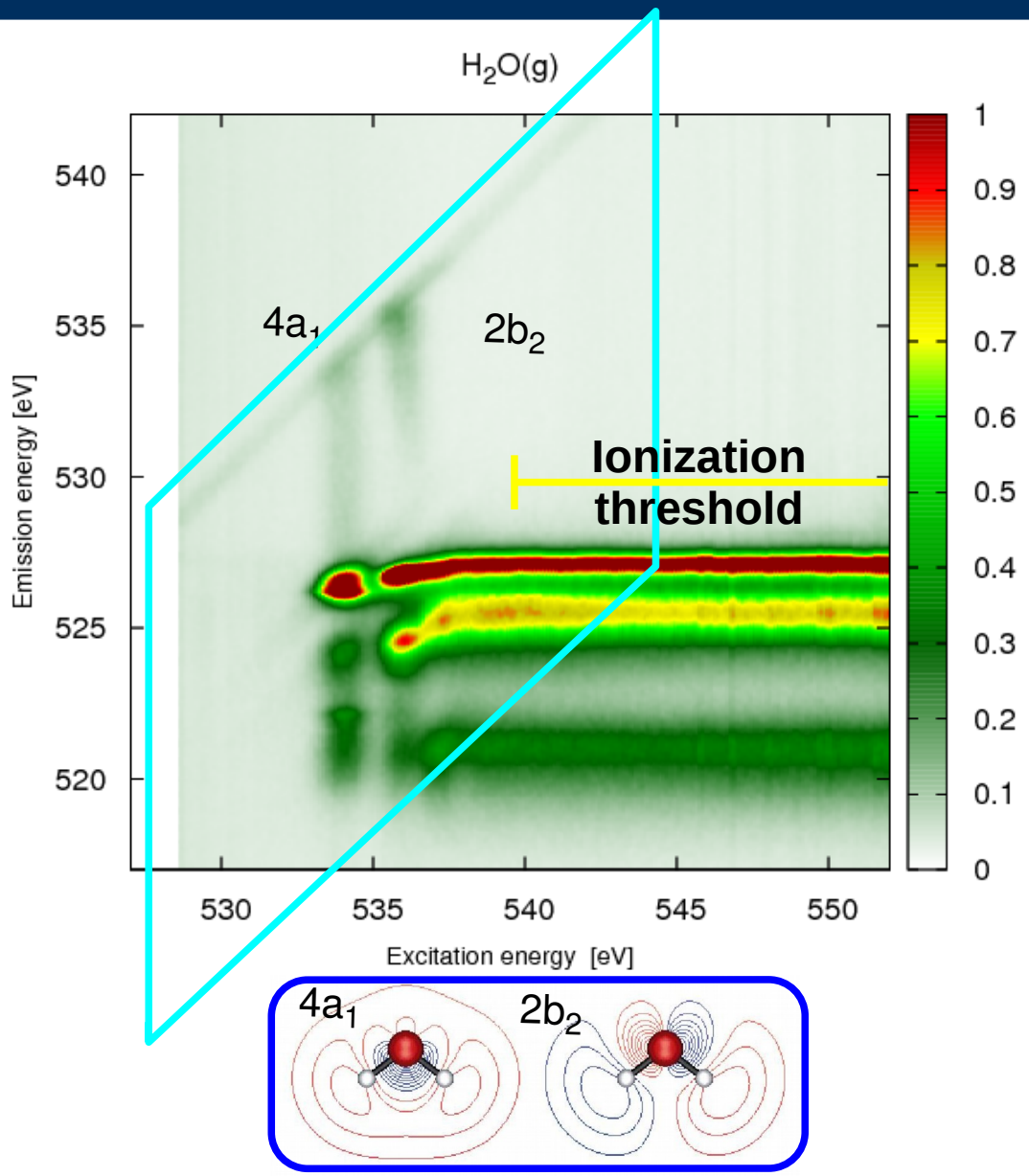
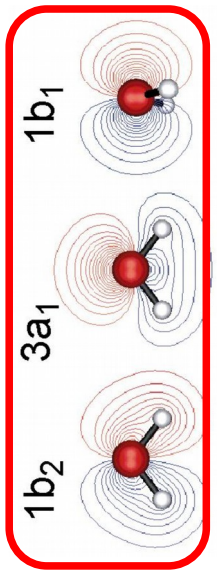
Resonant X-ray emission of $H_2O(g)$

Molecular Orbital Picture





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



RIXS ≠ XAS ⊗ XES

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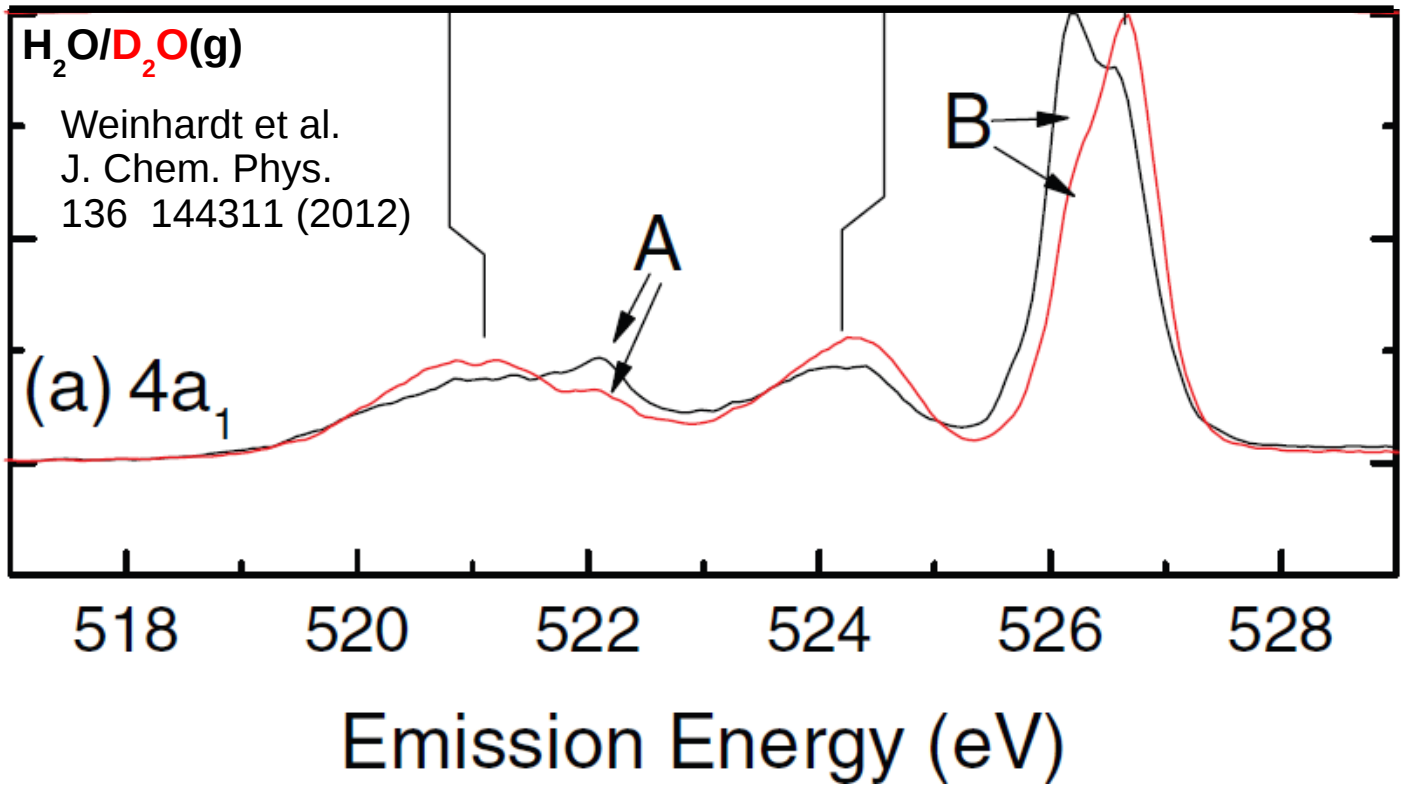
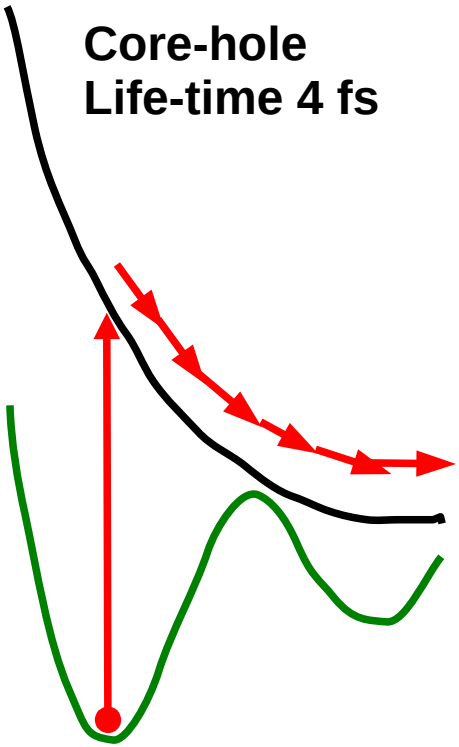
Information content in RIXS

Core-excited state dynamics





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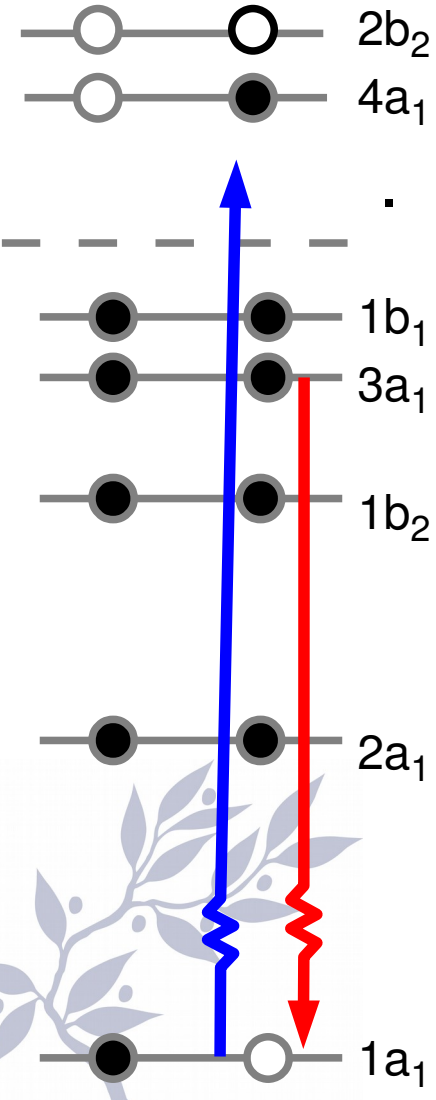
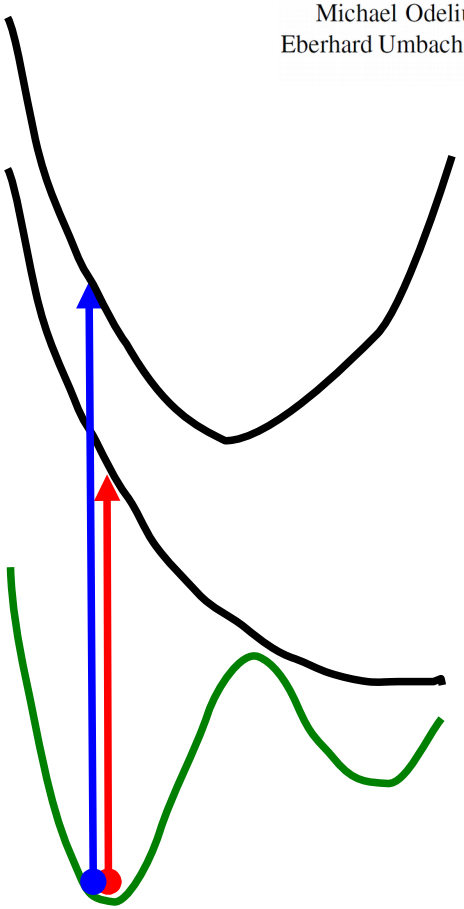
Core-excited state dynamics in $H_2O(g)$

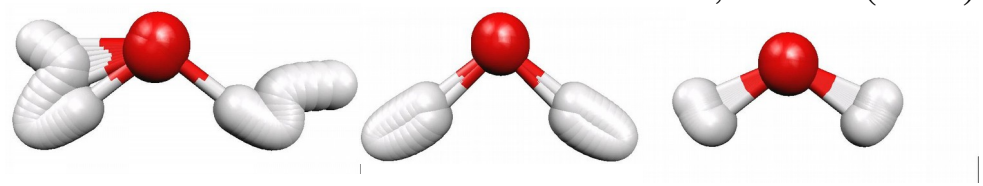


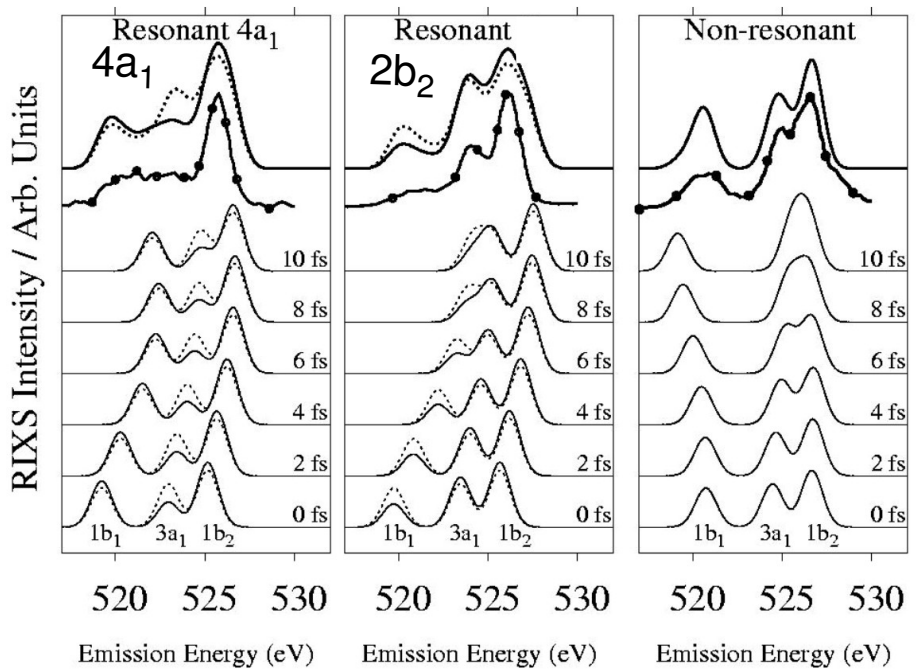


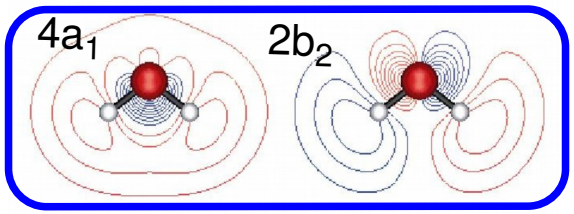
Ultrafast Core-Hole-Induced Dynamics in Water Probed by X-Ray Emission Spectroscopy

Michael Odelius,[1,*] Hirohito Ogasawara,[2] Dennis Nordlund,[1] Oliver Fuchs,[3] Lothar Weinhardt,[3] Florian Maier,[3] Eberhard Umbach,[3] Clemens Heske,[4] Yan Zubavichus,[5] Michael Grunze,[5] Jonathan D. Denlinger,[6] Lars G. M. Pettersson,[1] and Anders Nilsson[1,2]

PRL **94**, 227401(2005)







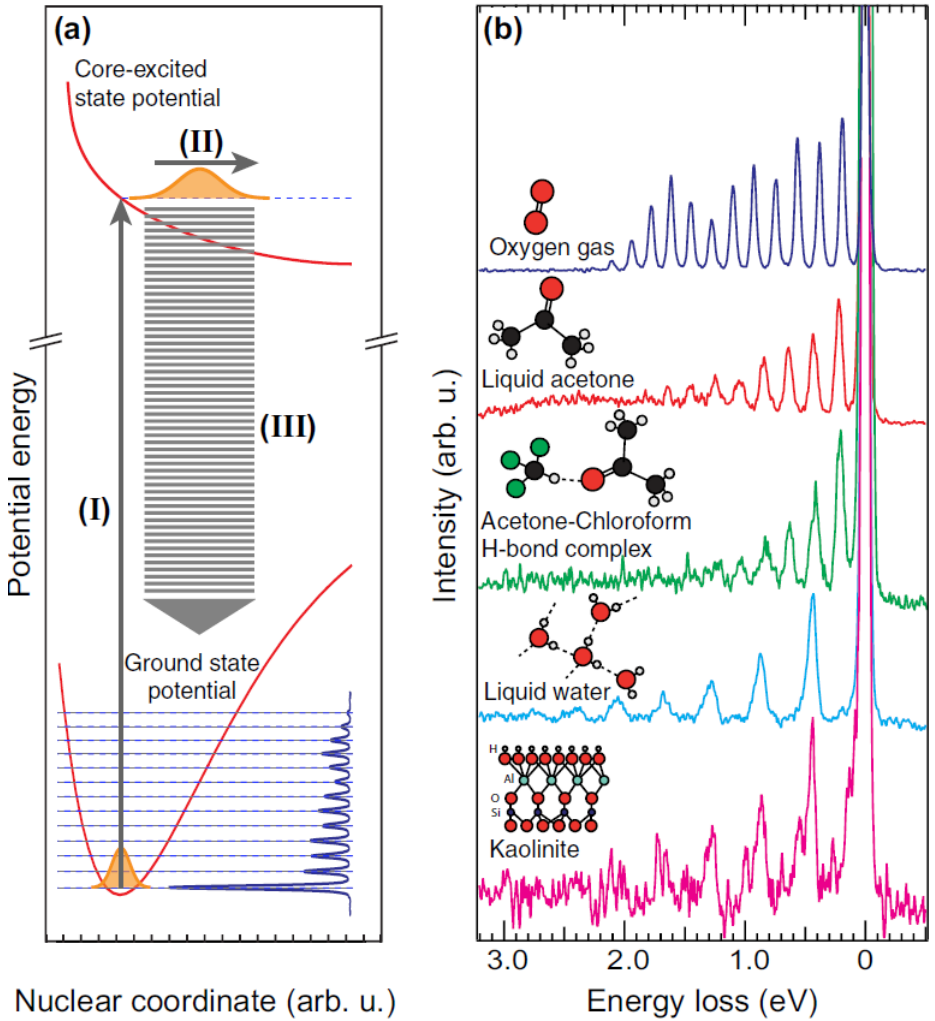
Stockholm University

Vibrationally resolved RIXS

Ground state potential energy surfaces around selected atoms from resonant inelastic x-ray scattering

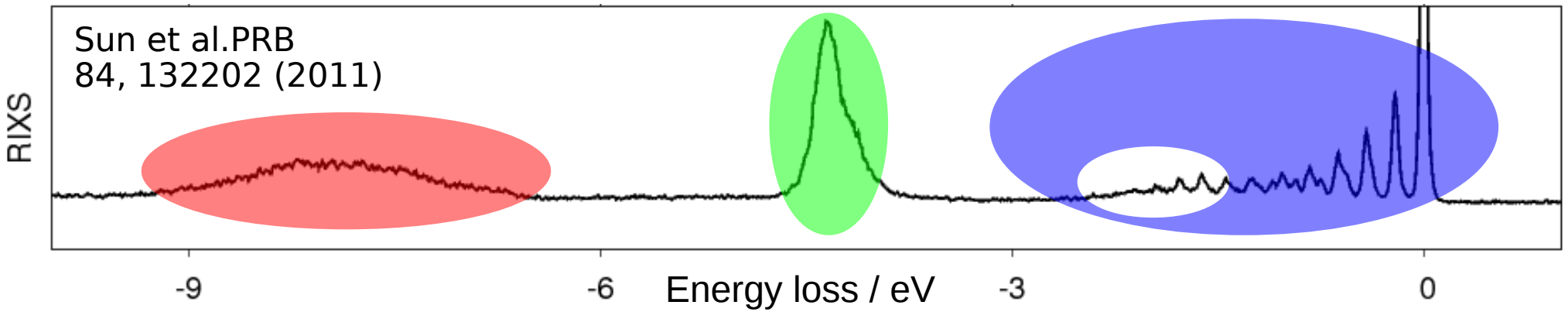
Simon Schreck[1,2,†], Annette Pietzsch[1], Brian Kennedy[1], Conny Såthe[3], Piter S. Miedema[1], Simone Techert[4,5,6], Vladimir N. Strocov[7], Thorsten Schmitt[7], Franz Hennies[3], Jan-Erik Rubensson[8] & Alexander Föhlisch[1,2]

SCIENTIFIC REPORTS | 6:20054 | DOI: 10.1038/srep20054



Stockholm University

Vibrationally resolved RIXS
at the oxygen K-edge(O1s) of liquid acetone
Spectral features in RIXS at the XAS $|O1s^{-1}\pi^{1}>$ resonance



$|f>=|HOMO\text{-}1^{-1}\pi^{1}>$
$+|HOMO\text{-}2^{-1}\pi^{1}>$
$+|HOMO\text{-}3^{-1}\pi^{1}>$

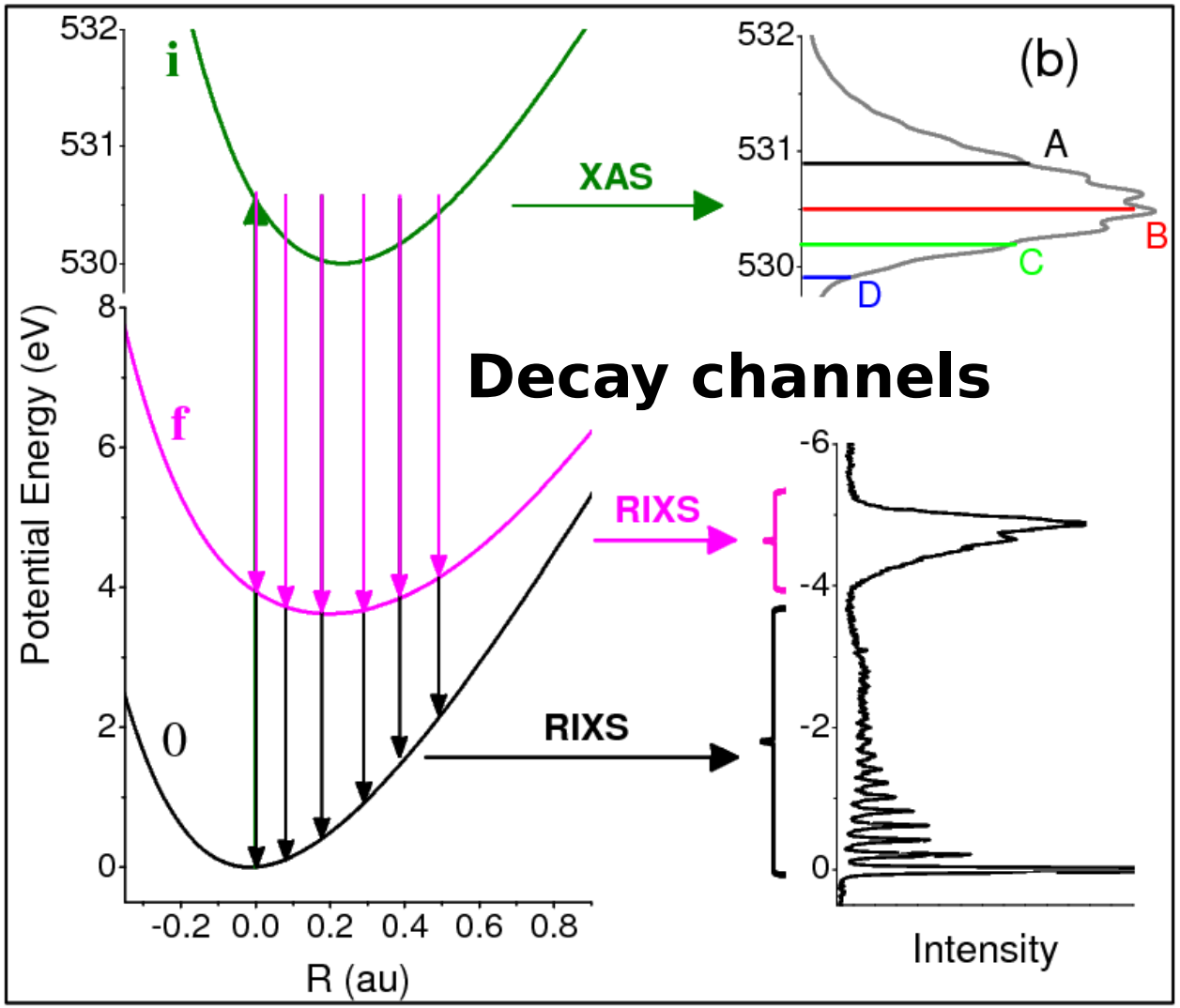
$|f>=|n^{-1}\pi^{1}>$
valence-excitation

$|f>=|0>$
"Quasi-elastic peak"

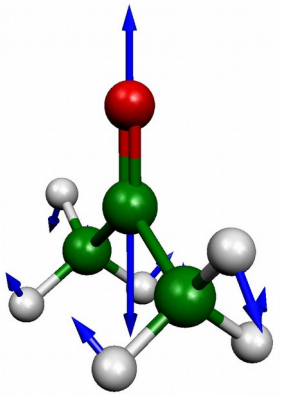
Y.-P. Sun, F. Hennies, A. Pietzsch, B. Kennedy, T. Schmitt,
V. N. Strocov, J. Andersson, M. Berglund,
J.-E. Rubensson, K. Aidas,
F. Gel'mukhanov, M. Odelius, and A. Föhlisch

Stockholm University

Vibrationally resolved RIXS
at the oxygen K-edge(O1s) of liquid acetone



$|i\rangle = |O1s^{-1}LUMO^{1}\rangle$



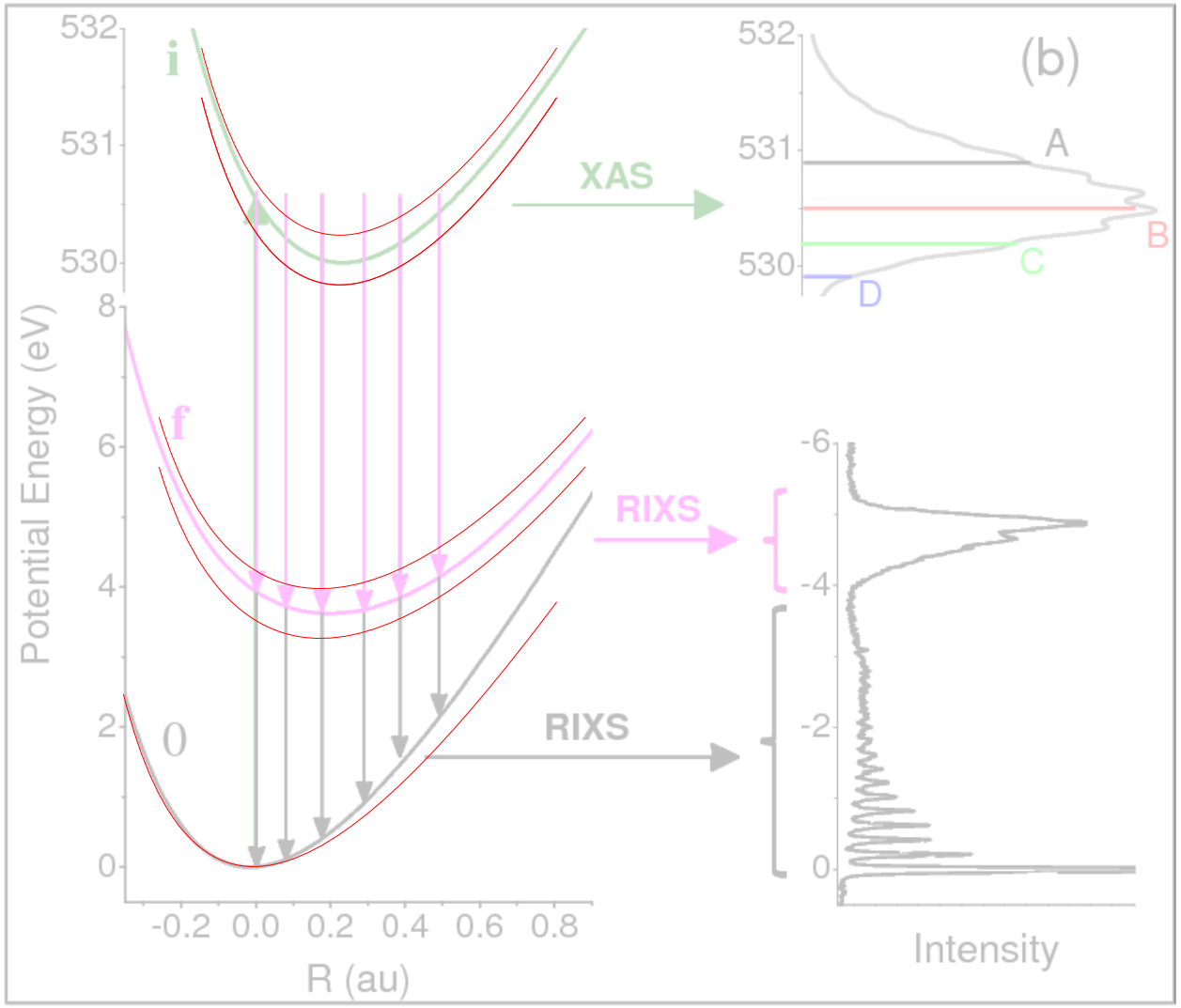
$|f\rangle = |HOMO^{-1}LUMO^{1}\rangle$

$|0\rangle$ = ground state

Sun et al.PRB
84, 132202 (2011)

Stockholm University

Vibrationally resolved RIXS
at the oxygen K-edge(O1s) of liquid acetone



$|i\rangle = |O1s^{-1}LUMO^{1}\rangle$
Variations in core-excitation energy

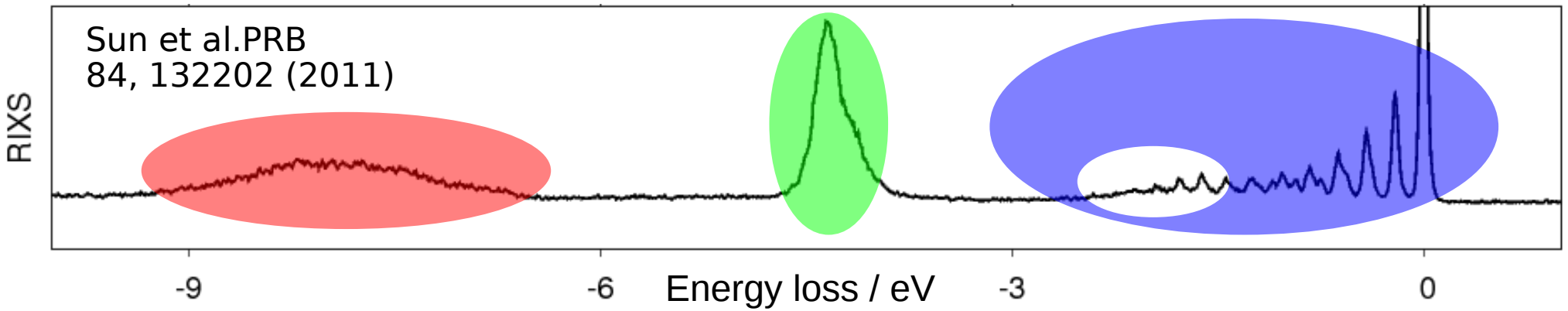
$|f\rangle = |HOMO^{-1}LUMO^{1}\rangle$
Variations in valence-excitation energy

$|0\rangle$ = ground state
Variations in vibrational state
→ potential shape only

Sun et al.PRB
84, 132202 (2011)

Stockholm University

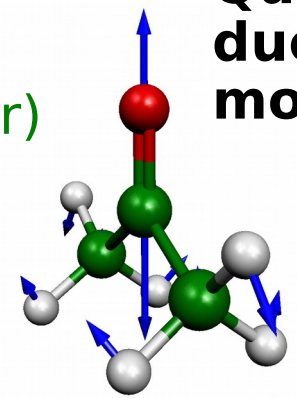
Spectral features in RIXS at the XAS $|O1s^{-1}\pi^{1}>$ resonance



$|f>=|n^{-1}\pi^{1}>$
valence-excitation
energy variations

Inter-molecular
interaction

Vibrational
excitations
(intra-molecular)



$|f>=|0>$
Vibrational excitations

Inter-molecular
influence only
potential shapes

Quasi-continuum due to low-freq modes

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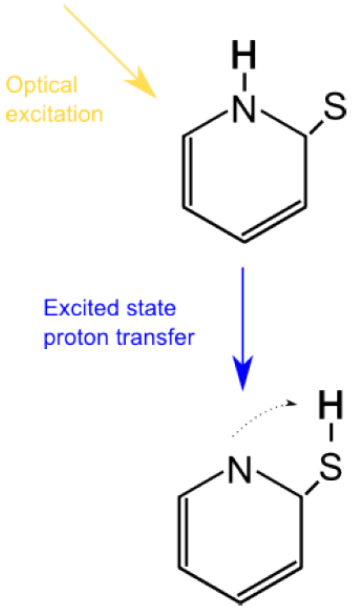
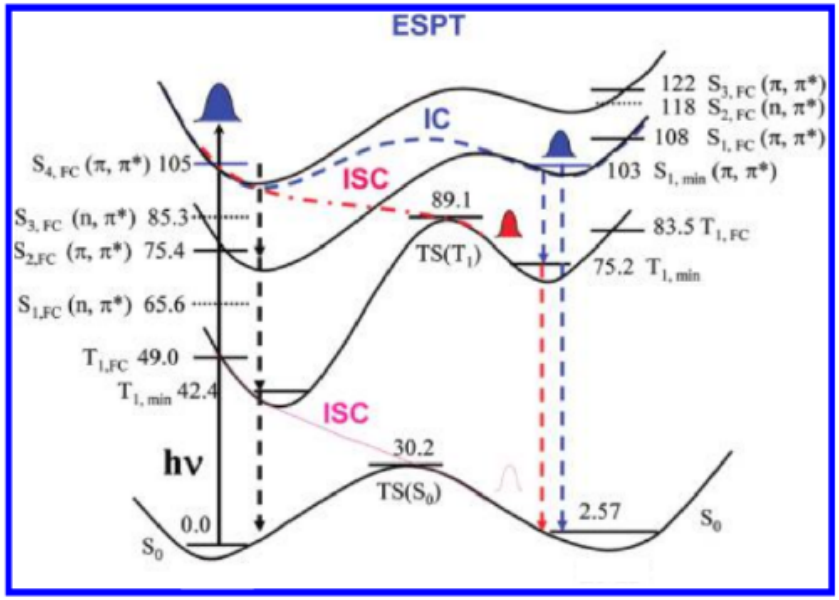
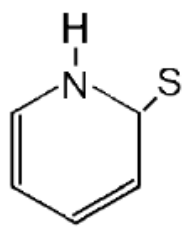
Photochemistry with time-resolved RIXS

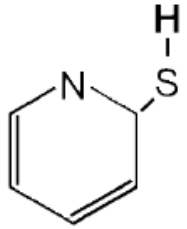
Excited state proton transfer in 2-Mercaptopyridine







2-MP Thione



2-MP Thiol

What can learn about ESPT from time-resolved UV-pump RIXS-probe spectroscopy?

Is the proton-transfer in the core-excited state a limiting issue?

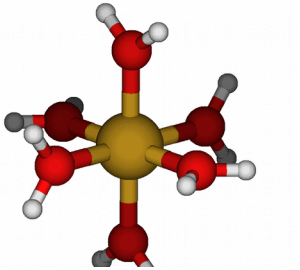
How is the solvent involved?

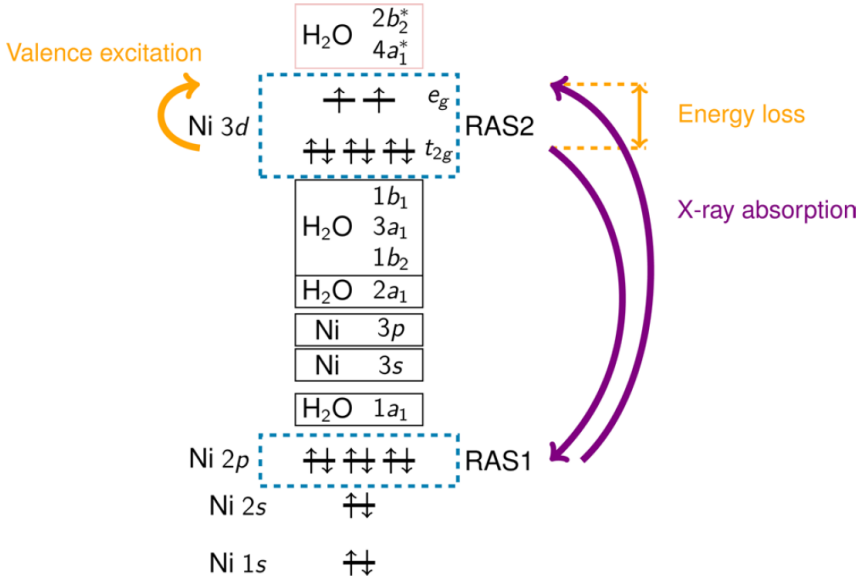
N1s S1s S2p edges

Stockholm University

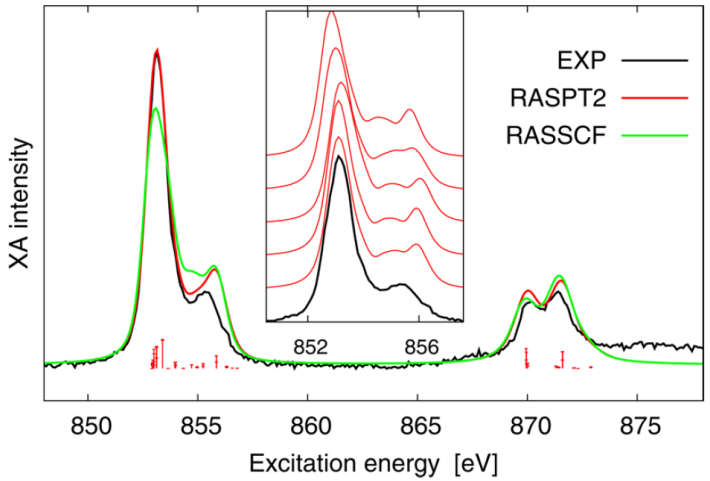
L-edge X-ray Spectroscopy of Transition metal complexes

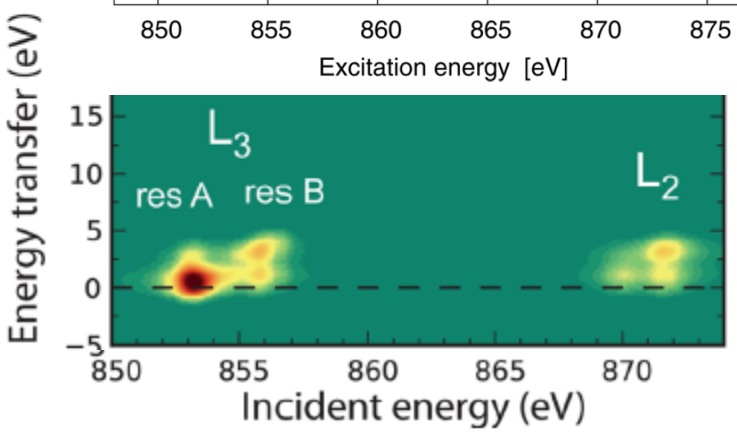
$Ni^{2+}(aq)$





I. Josefsson et al J. Phys. Chem. Lett. 3:3565–3570, 2012
K. Kunnus et al. J. Phys. Chem. B 2013, 117, 16512−16521





Spin-orbit coupling

$^2P_{3/2}(4)$ $^2P_{1/2}(2)$

Core-hole ($2p^5$) XPS

Stockholm University

L-edge X-ray Spectroscopy of Transition metal complexes

$Ni^{2+}(aq)$

With 14 electrons confined to 2p and 3d (16 spinorbitals), there can be only singlet and triplet states.

GS and Fe $2p^6$ $3d^8$

valence exc.

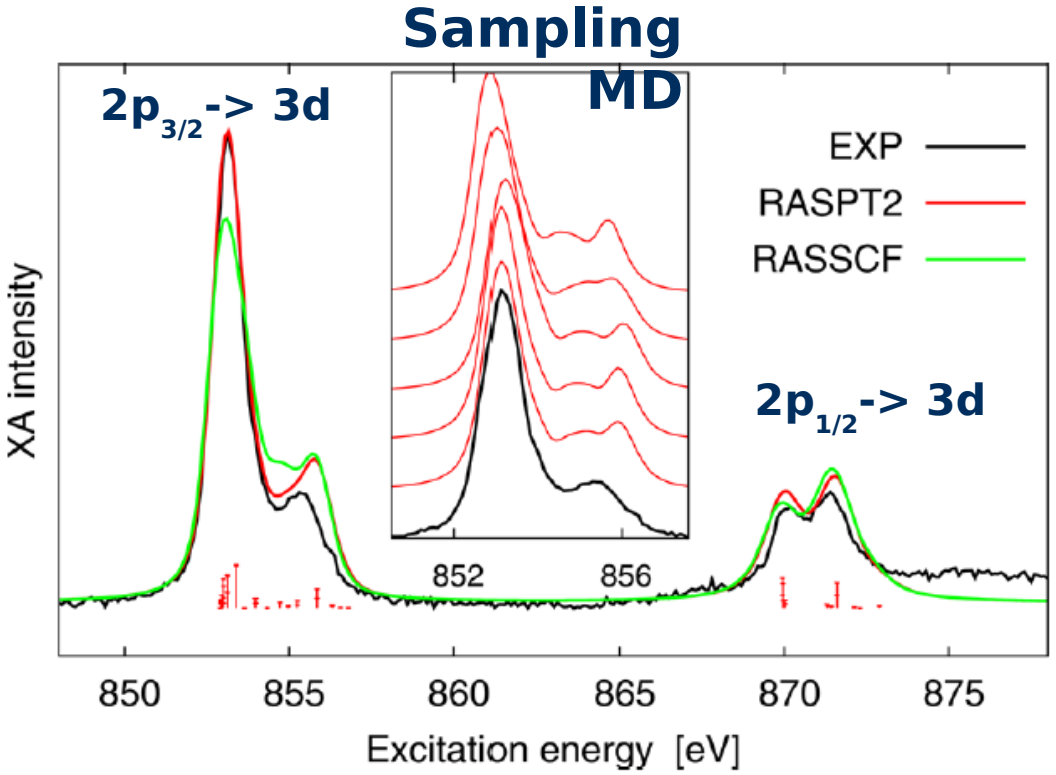
$\binom{10}{8}$=45 microstates

(10 triplets + 15 singlets)

Core-exc. Fe $2p^5$ $3d^9$

$\binom{6}{5} \times \binom{10}{9}$ =60 microstates

(15 core-excited triplets +15 core-excited singlets)



"jj-compling in core"
"LS coupling in valance"
Coupling between core & valence

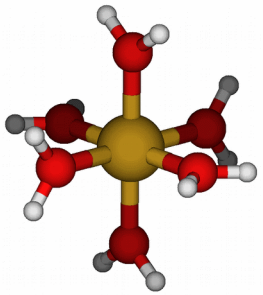
I. Josefsson et al J. Phys. Chem. Lett. 3:3565–3570, 2012

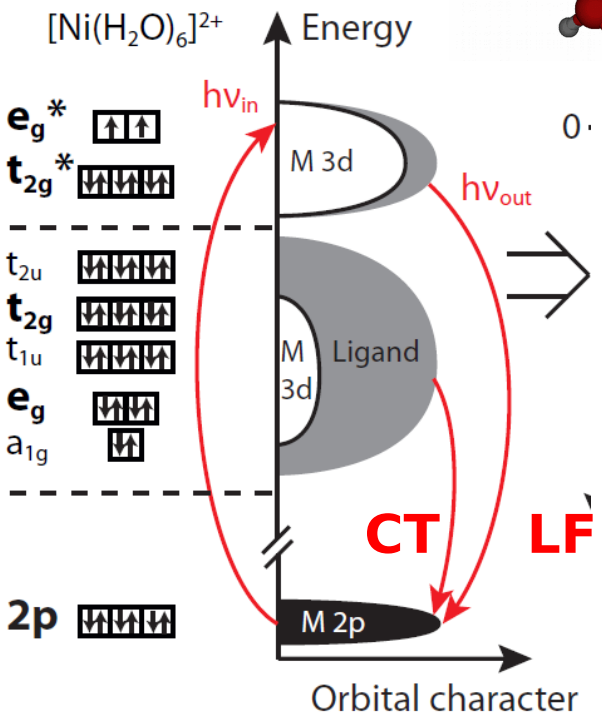
Stockholm University

L-edge X-ray Spectroscopy of Transition metal complexes

$Ni^{2+}(aq)$

High-spin Ni $3d^8$





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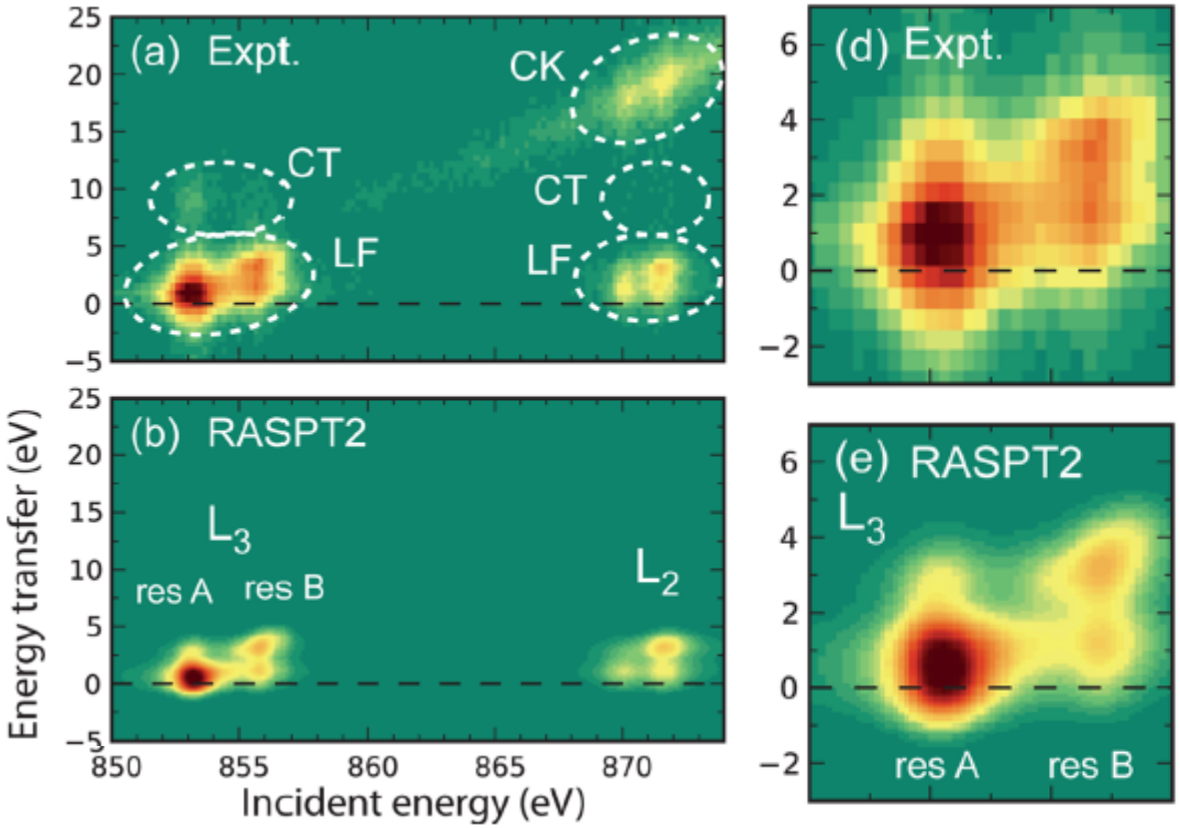
K. Kunnus et al. J. Phys. Chem. B 2013, 117, 16512−16521



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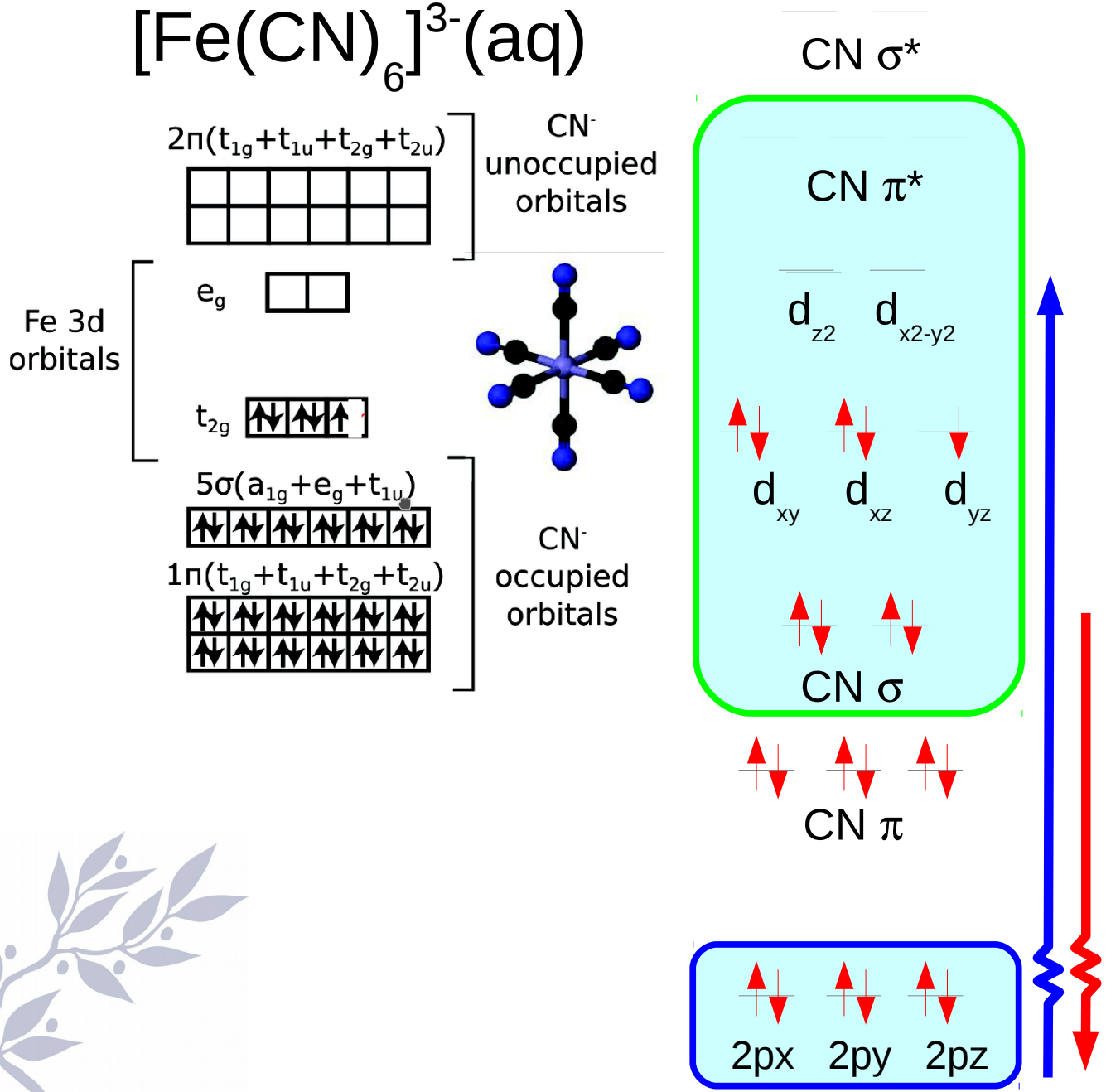
L-edge X-ray Spectroscopy of Transition metal complexes



RASPT2
Jesper Norell
Marcus Lundberg
Rahul V. Pinjari
Mickael G. Delcey
Meiyuan Guo

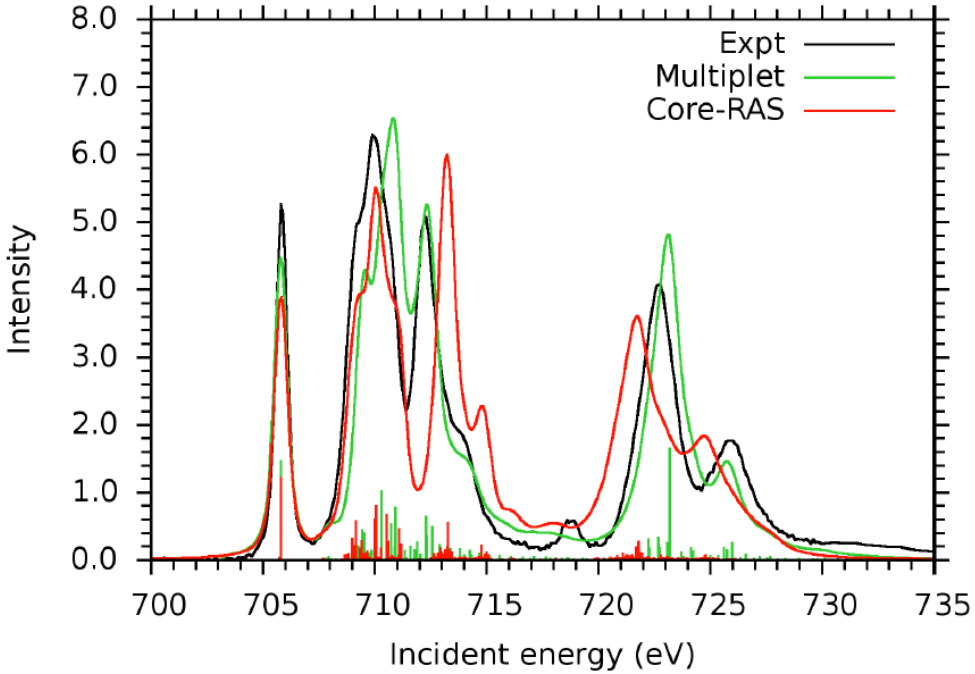
RIXS
Kristjan Kunnus
Simon Schreck
...
Philippe Wernet
Kelly Gaffney
Alexander Föhlisch

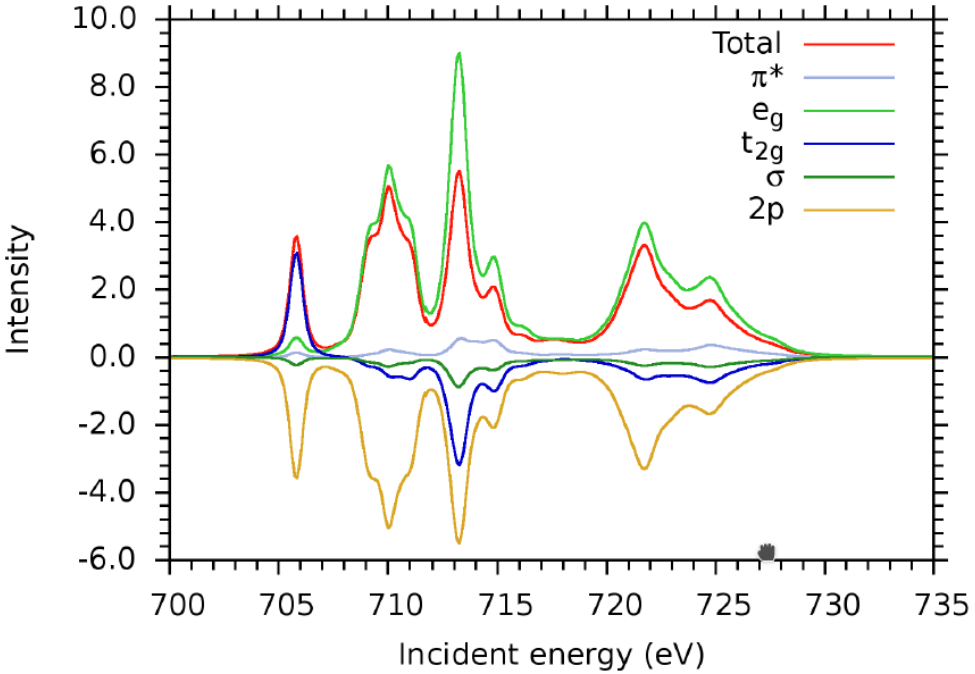
Stockholm University

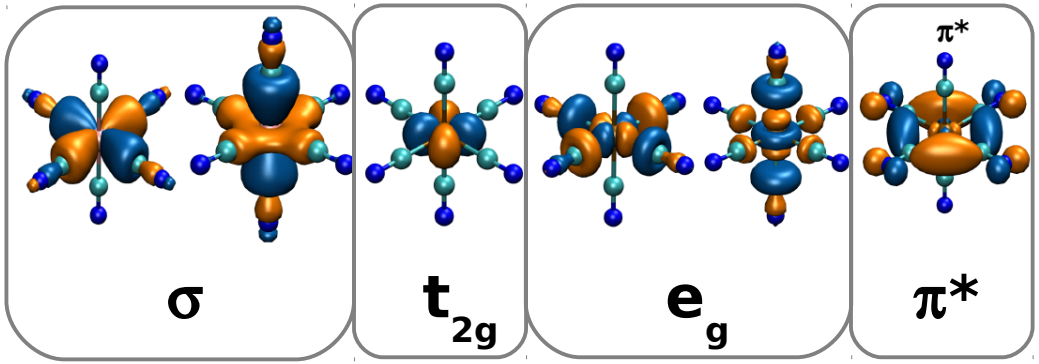
L-edge X-ray Spectroscopy of Transition metal complexes

Restricted active space calculations of L-edge X-ray absorption spectra: From molecular orbitals to multiplet states

R. V. Pinjari, M. G. Delcey, M. Guo, M. Odelius, and M. Lundberg, J. Chem. Phys. **141**, 124116 (2014).







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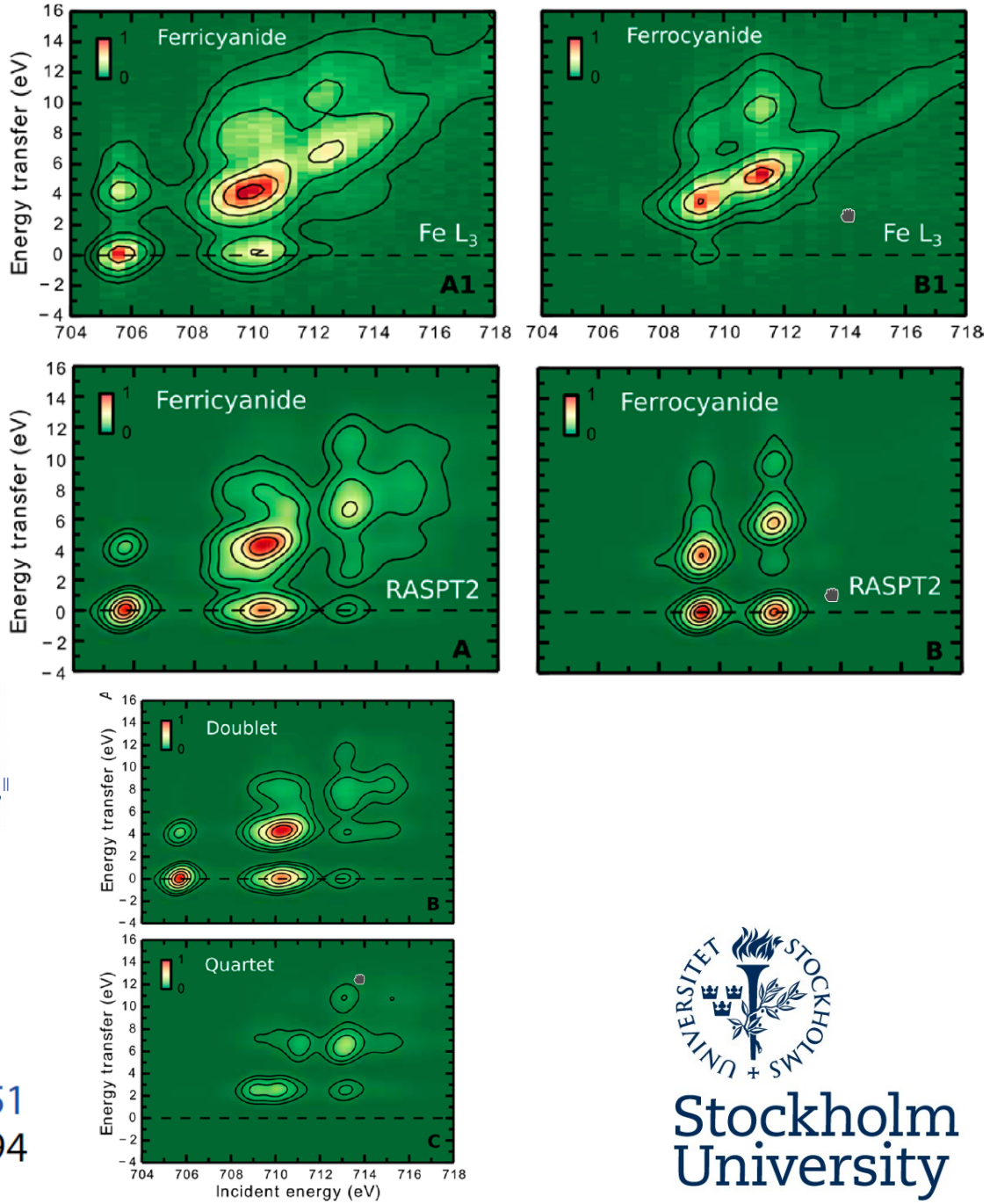
L-edge X-ray Spectroscopy of Transition metal complexes

$[Fe(CN)_6]^{3-}(aq)$

$[Fe(CN)_6]^{4-}(aq)$



Viewing the Valence Electronic Structure of Ferric and Ferrous Hexacyanide in Solution from the Fe and Cyanide Perspectives

Kristjan Kunnus,[*,†,‡,§] Wenkai Zhang,[∥,⊥] Mickaël G. Delcey,[#] Rahul V. Pinjari,[#] Piter S. Miedema,[†] Simon Schreck,[†,‡,▽] Wilson Quevedo,[†] Henning Schröder,[†,‡] Alexander Föhlisch,[†,‡] Kelly J. Gaffney,[∥] Marcus Lundberg,[#] Michael Odelius,[○] and Philippe Wernet[*,†]

DOI: 10.1021/acs.jpcb.6b04751
J. Phys. Chem. B 2016, 120, 7182−7194

Stockholm University

Photo-dissociation of $FeCO_5$ in ethanol solution

HZB: Philippe Wernet, Martin Beye, Simon Schreck, Christian Weniger, Christian Kalus, Kerstin Kalus, Edlira Suljoti, Alexander Föhlisch

MPI-BPC: Ivan Rajkovic, Sebastian Grübel, Wilson Quevedo, Mirko Scholz, Simone Techert
MAX-lab: Brian Kennedy, Franz Hennies

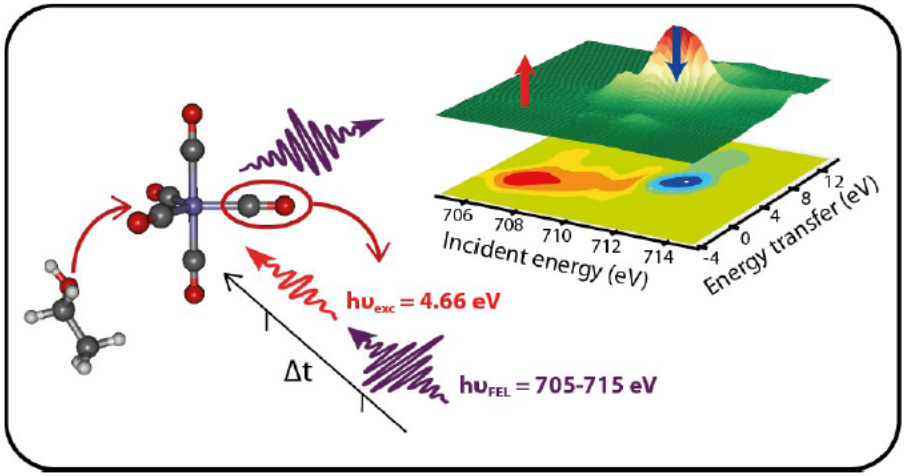
SSRL/SLAC: Dennis Nordlund

PULSE/SLAC: Kelly Gaffney, Robert Hartsock, Wenkai Zhang
LCLS/SLAC: Bill Schlotter, Josh Turner

Utrecht University: Frank de Groot (Theory)

Stockholm Uni.: Ida Josefsson, M. Odelius (Theory)

Time-resolved Fe L-edge RIXS



LCLS

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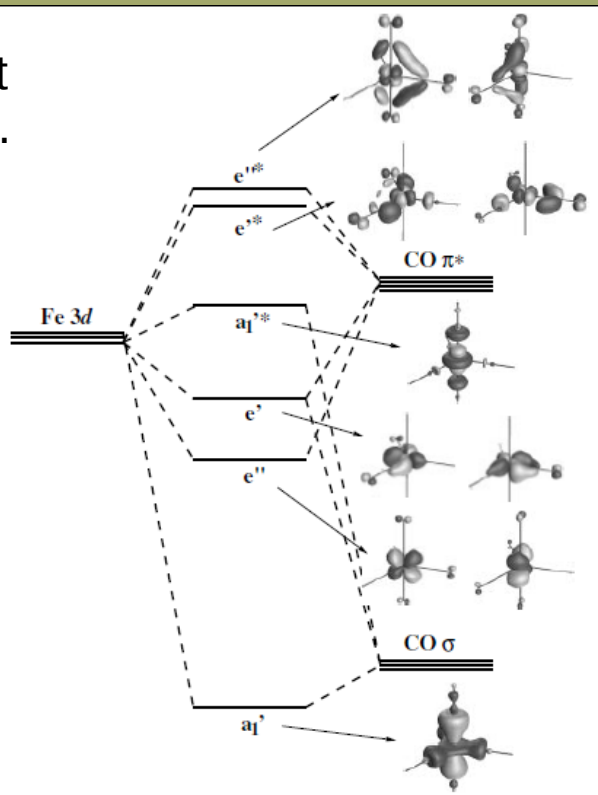
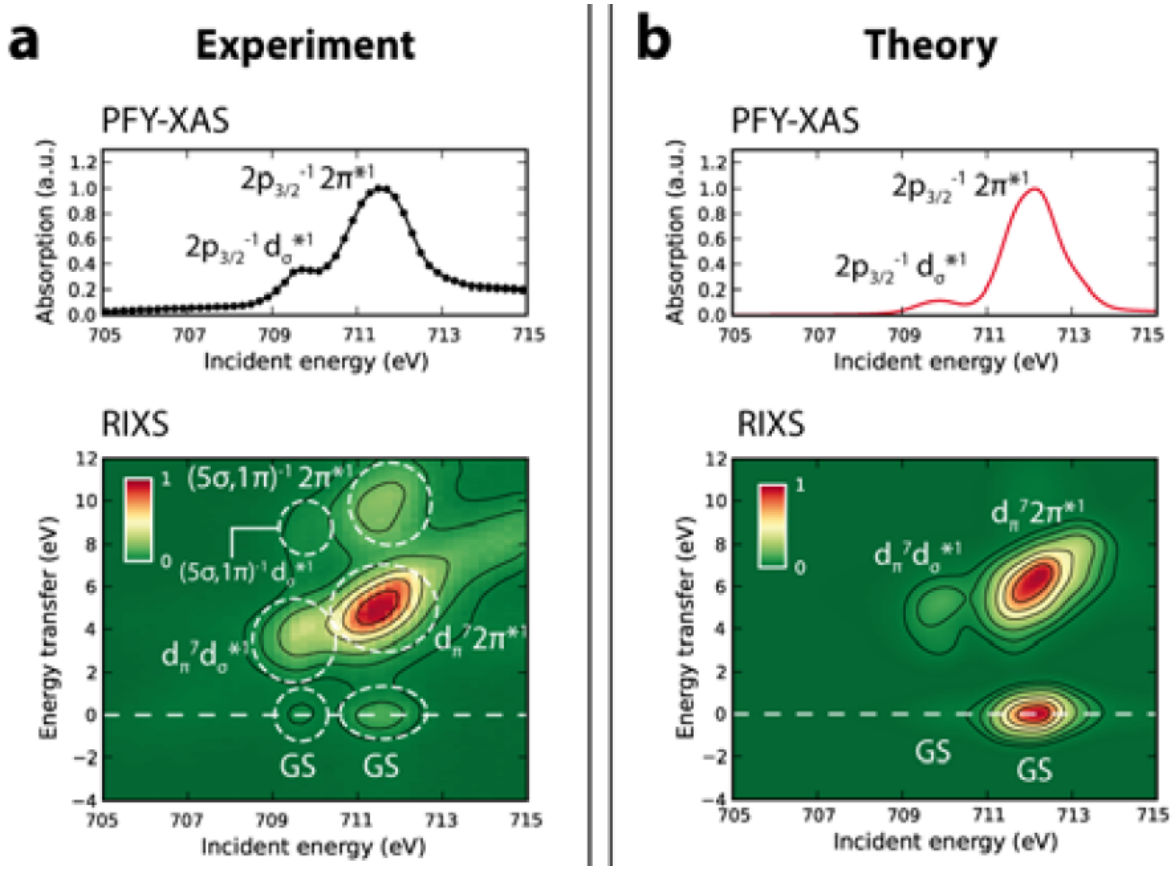
RASSCF calculations of $Fe(CO)_5$

K. Pierloot
Mol. Phys.
101, 2083
(2003)



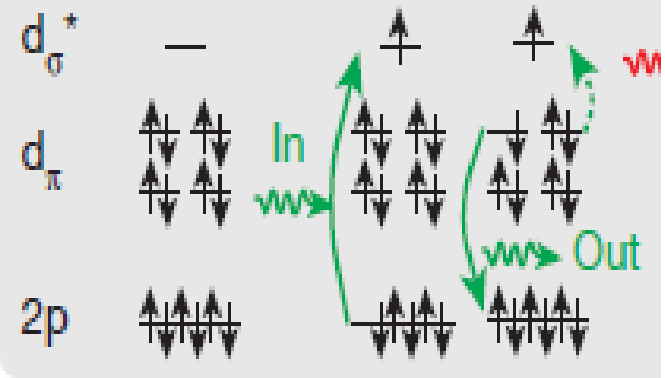
Evaluation of RIXS calculation

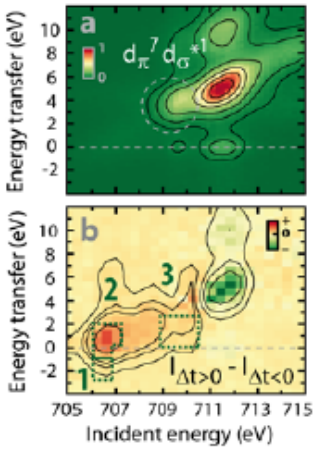
RASSCF RAS1=2p RAS2=4 RAS3=7 (2e-)



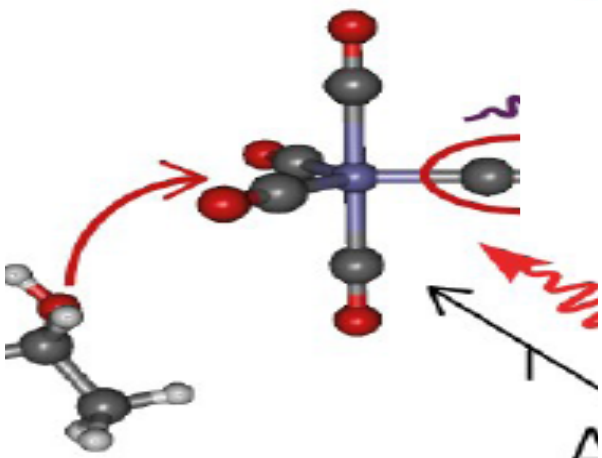
Ph. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, W. Quevedo, M. Beye, S. Schreck, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, K. J. Gaffney, S. Techert, M. Odelius, and A. Föhlisch. Nature 520, 78–81 [2015]

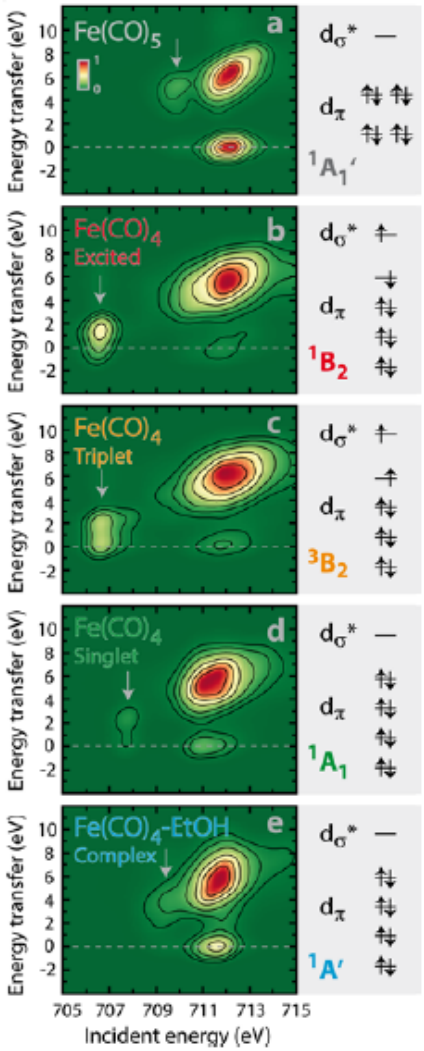
Dissecting the information in time-resolved Iron L-edge RIXS





$^1Fe(CO)_5(EtOH)$ +hν:





RIXS simulations

MOLCAS (RASSCF)
RAS1=3,RAS2=4,
RAS3=7, 2e- TVZP

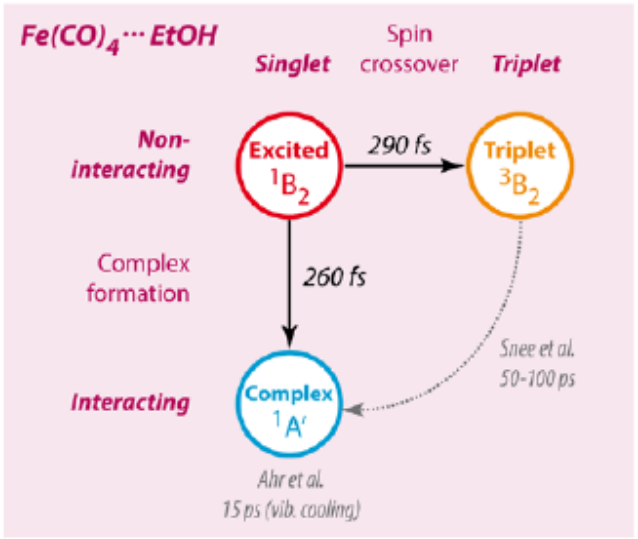
Possible reaction pathways were investigated with a library of ~80 RIXSsimulations Giving fingerprints of various reaction intermediates and electronic states.

Stockholm University

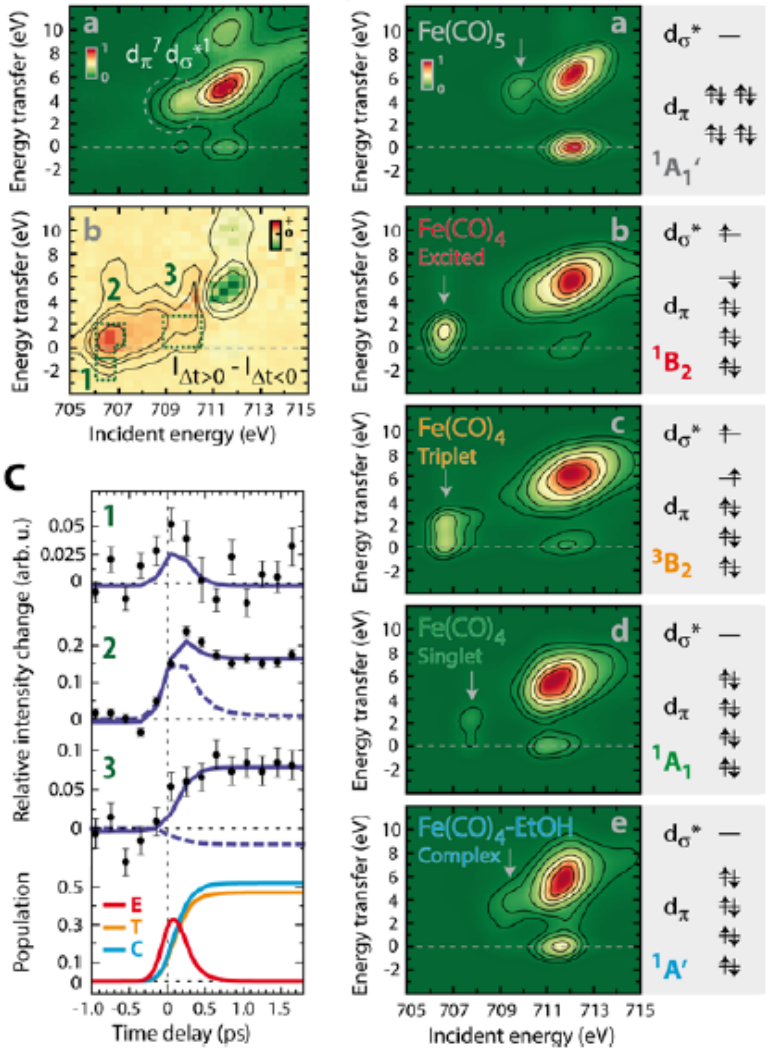
Solvent complexation and Intersystem crossing

Competing pathways in the photodissociation of $Fe(CO)_5$

$^1Fe(CO)_5(etoh) + h\nu$:

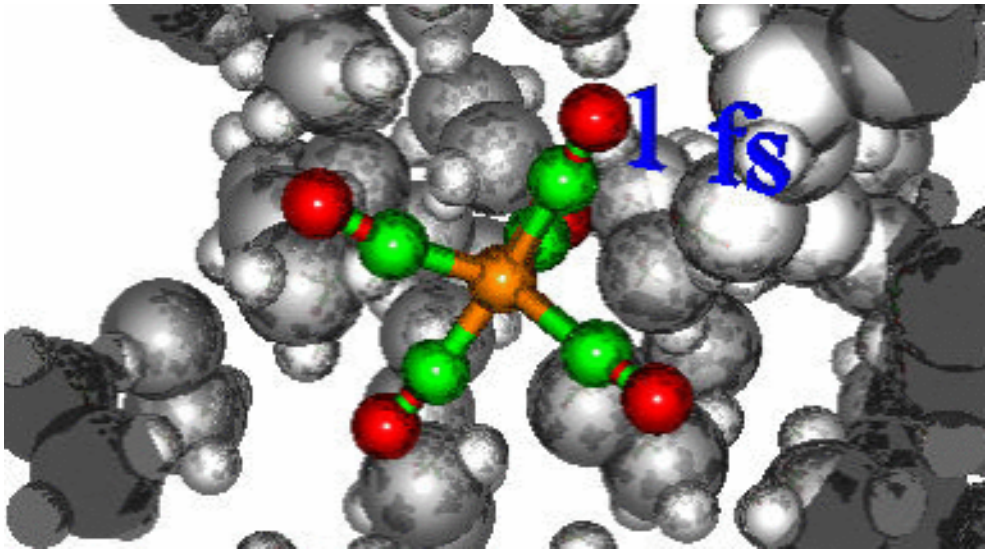


Initially excited state
Solvent complexation
Intersystem crossing



Ph. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, W. Quevedo, M. Beye, S. Schreck, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, K. J. Gaffney, S. Techert, M. Odelius, and A. Föhlisch. Nature 520, 78–81 [2015]

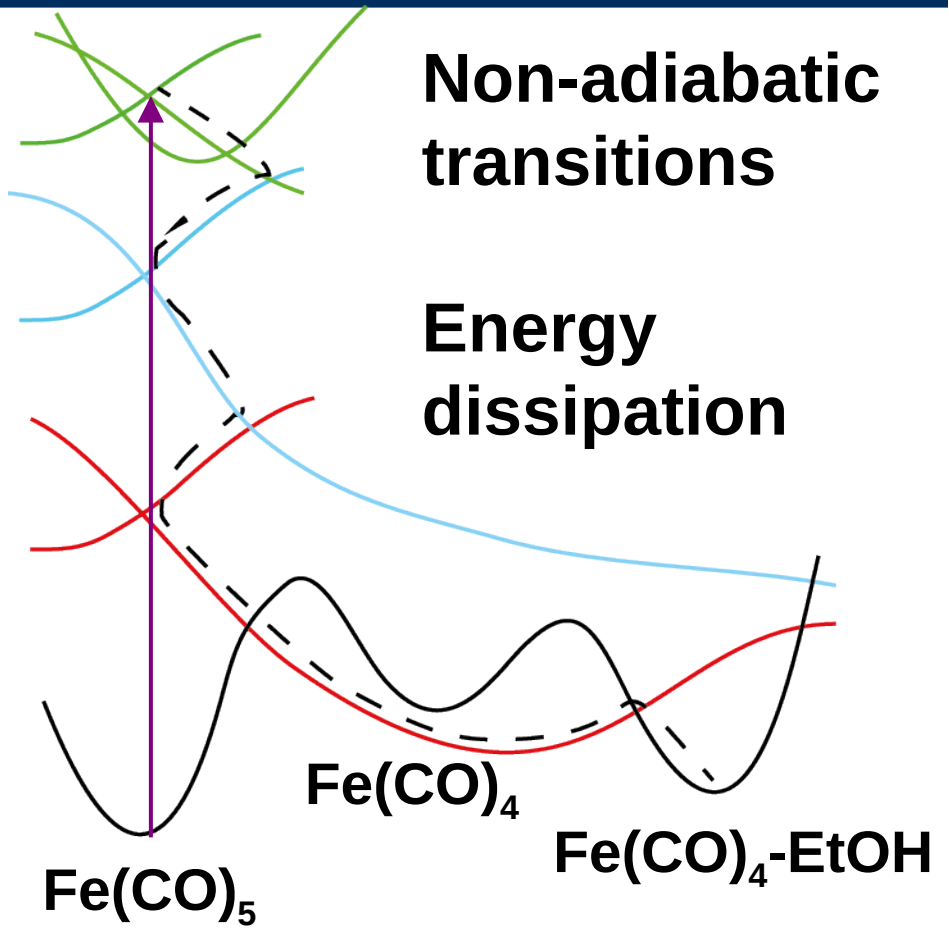
Spectroscopy of transient excited-states:
Challenges & Opportunities for Theory.



High-level Quantum Chemistry

Ab initio Molecular Dynamics

Quantum Dynamics



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