Ultrafast dynamics of molecular systems with ultrashort optical and X-ray pulses

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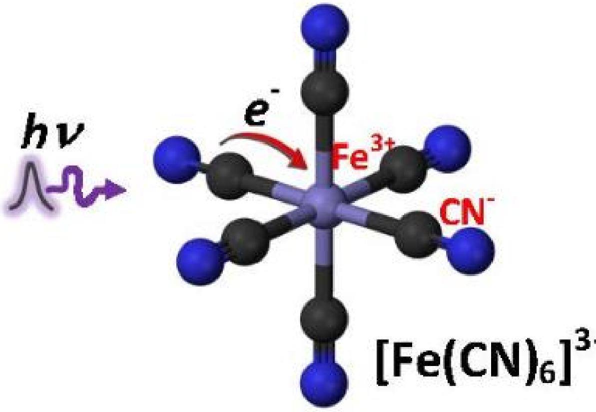
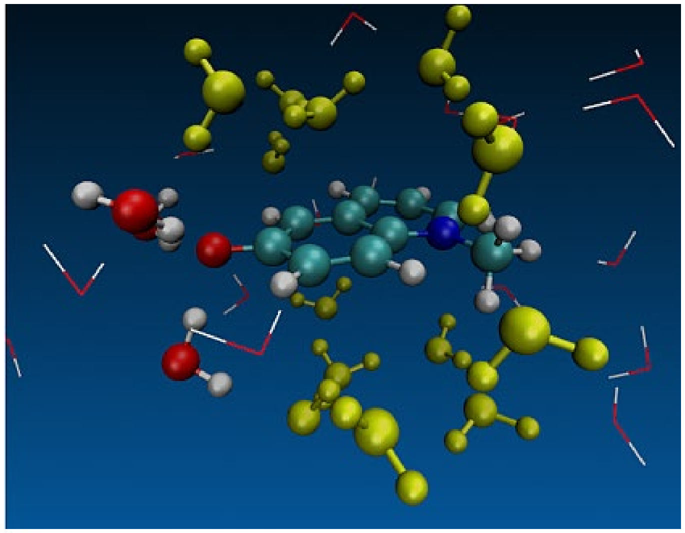
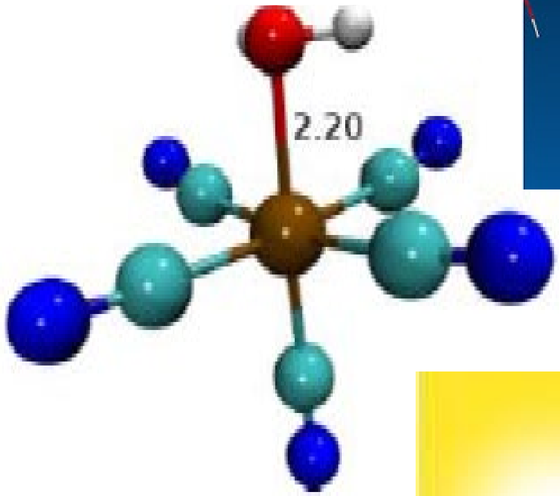
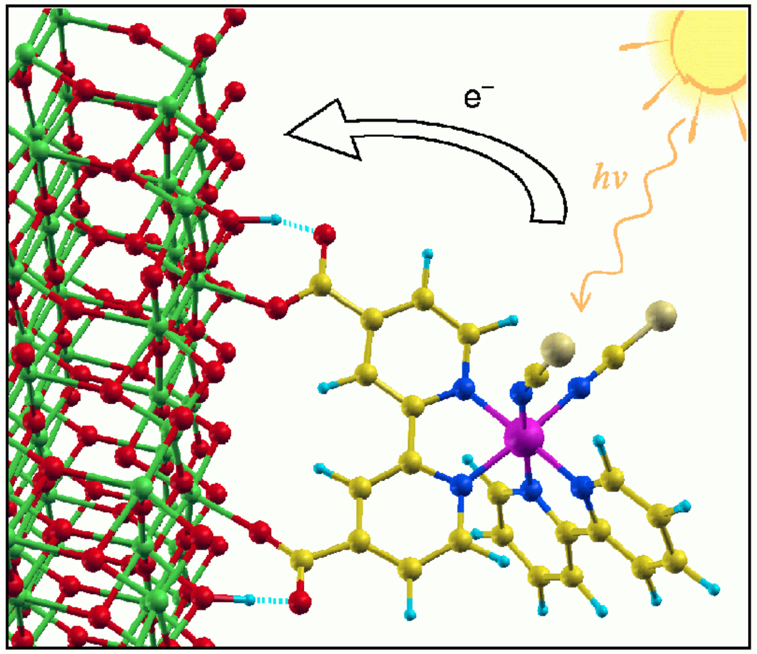
Dynamics of molecular systems



Intramolecular charge transfer dynamics
Spin dynamics
Intramolecular vibrational relaxation
Solvation dynamics
Solute-solvent photochemical reactions

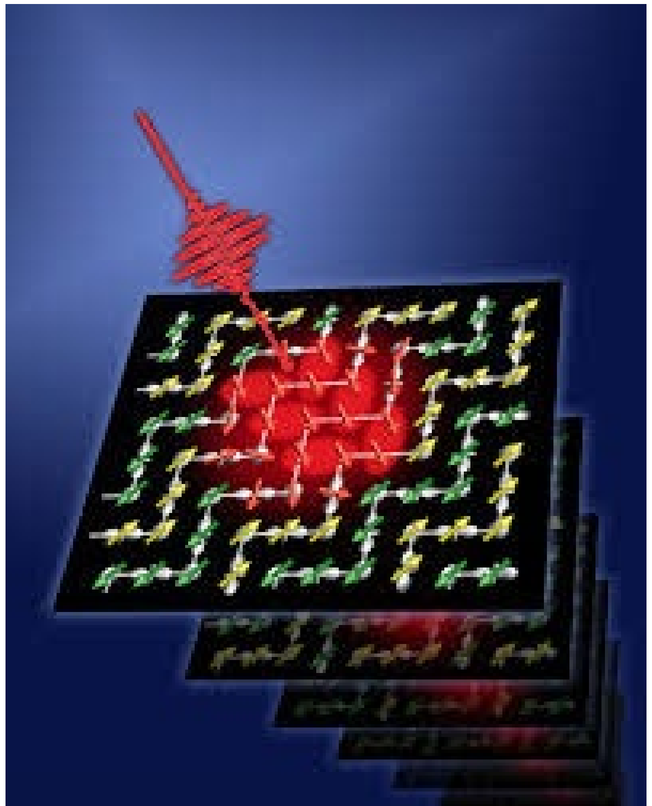


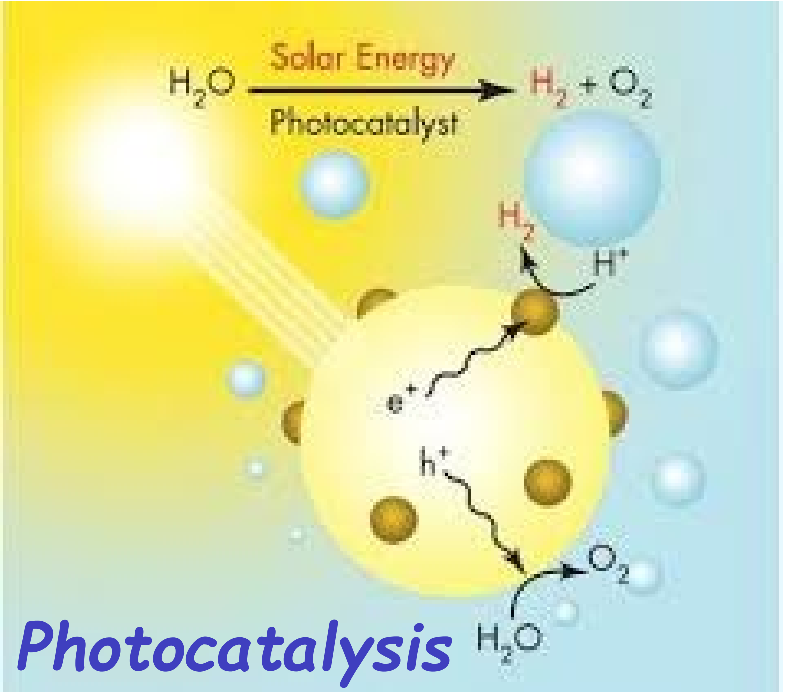




Photovoltaics

Magnetic Data storage





Photocatalysis

Ultrafast Intramolecular Relaxation

- Intramolecular energy redistribution and internal conversion at extremely short times.
- High frequency FC modes dump impulsively their energy to lower frequency ones (often optically silent)

Cannizzo et al., Angew. Chem. Int. Edit. (2006); Gawelda et al, JACS (2007); Cannizzo et al, JACS (2008); Bram et al, Chem . Phys. (2012); Chergui, Acc. Chem. Res. (2015); Messina et al, JPCL (2015)

- Valid for organic dyes

PPO, pTP: Cannizzo et al, Opt. Lett. 2007; Braem et al, PCCP 2012; Retinal in solution: Zgrablic et al, Biophys. J. 2005, JPC B 2009, Chem. Phys. 2011; Tryptophan: JPC A 2010

- Ultrafast Intersystem crossing: No «heavy-atom rule». DOS, SOC and structural dynamics play crucial role at ultrashort times

Dalton Trans. 2012; Acc. Chem. Res. 2015; Cannizzo et al., Angew. Chem. Int. Edit. (2006) and JACS (2008); Gawelda et al, JACS (2007); Bressler et al, Science (2009); van der Veen et al, JACS (2011); Auböck and Chergui, Nat. Chem. (2015), Monni et al, PNAS (2018)

Kasha-Vavilov Rule (*Disc. Faraday Soc.* 1950) very robust!

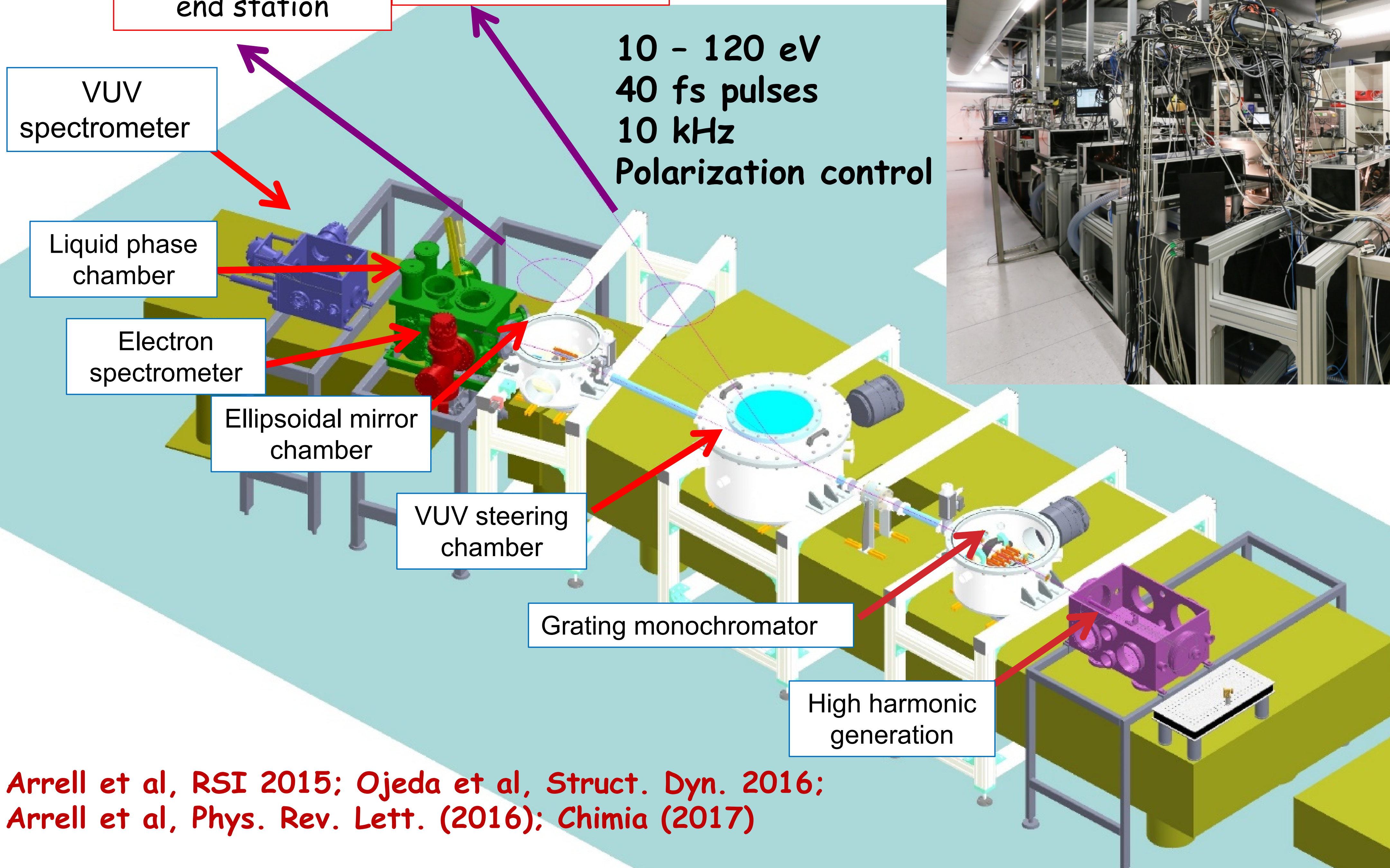
Contents

I. Ultrafast photoelectron spectroscopy of charge transfer reactions: beating the Kasha-Vavilov rule

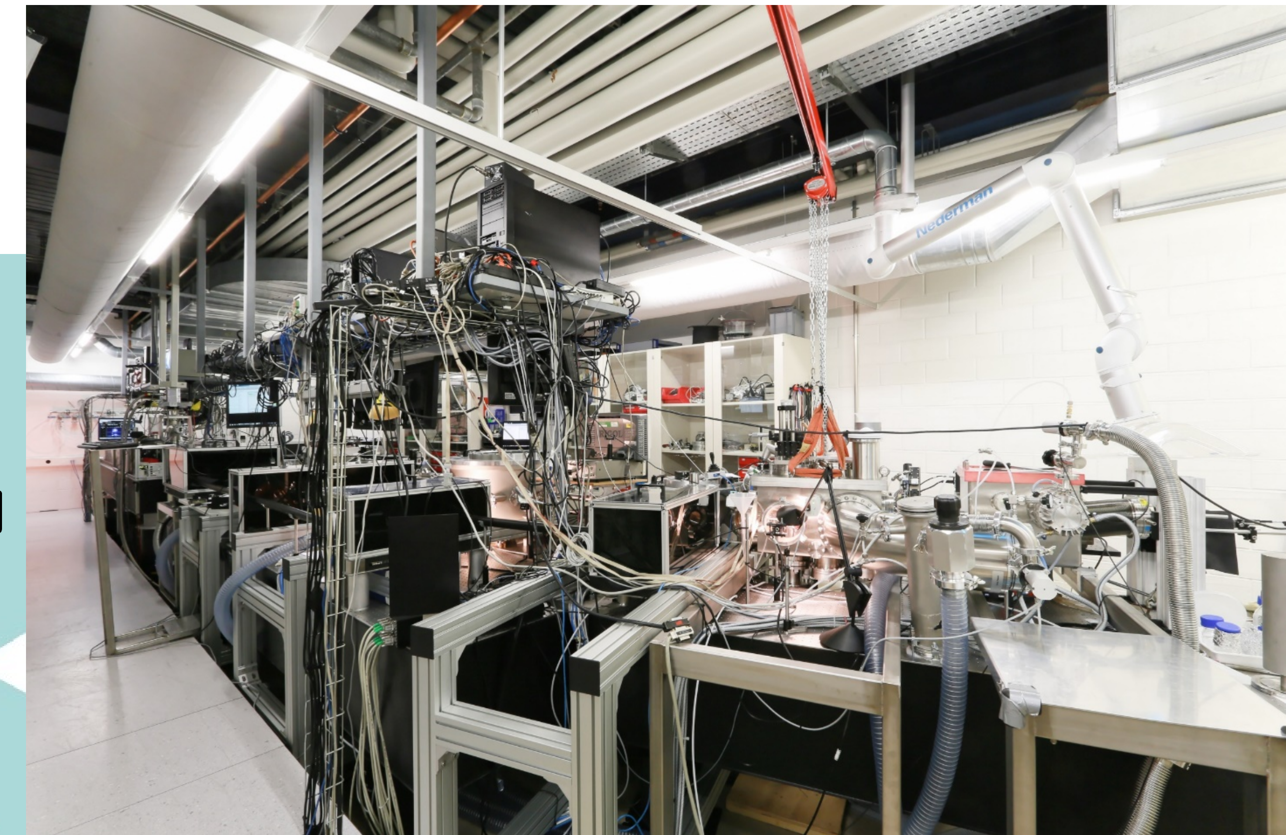
II. X-ray studies of Conical Intersections

Harmonium @

Extreme-UV femtosecond source:
Facility for photoelectron spectroscopy (ESCA) of liquid, gas and solid phases.
Complementary to X-ray studies at the SLS and XFELs



10 – 120 eV
40 fs pulses
10 kHz
Polarization control



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must
erc European Research Council
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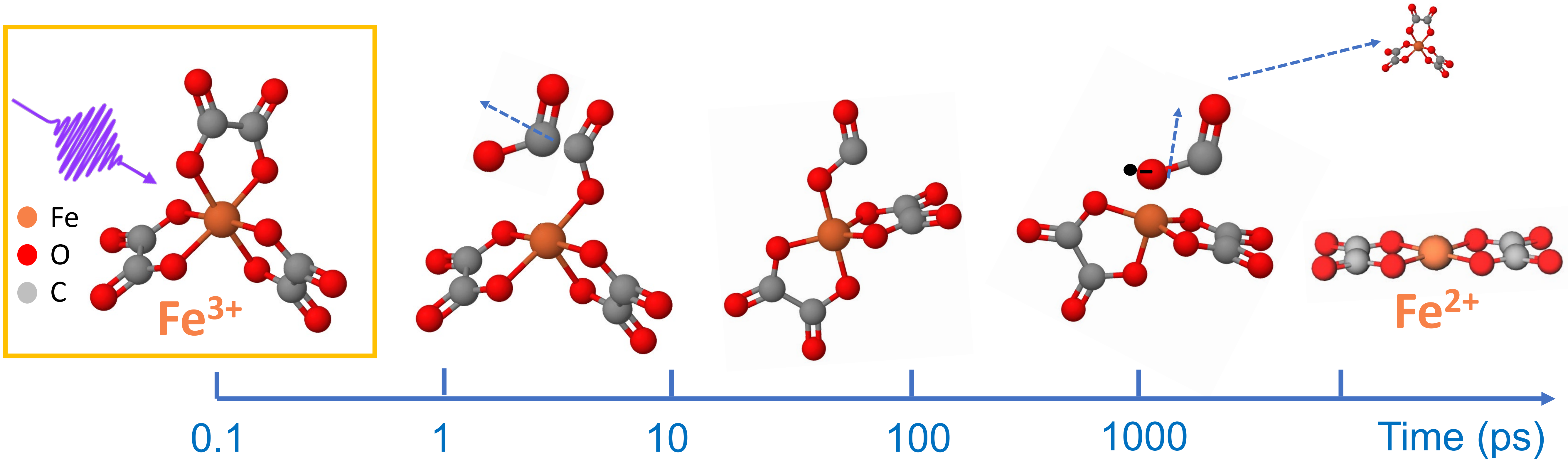
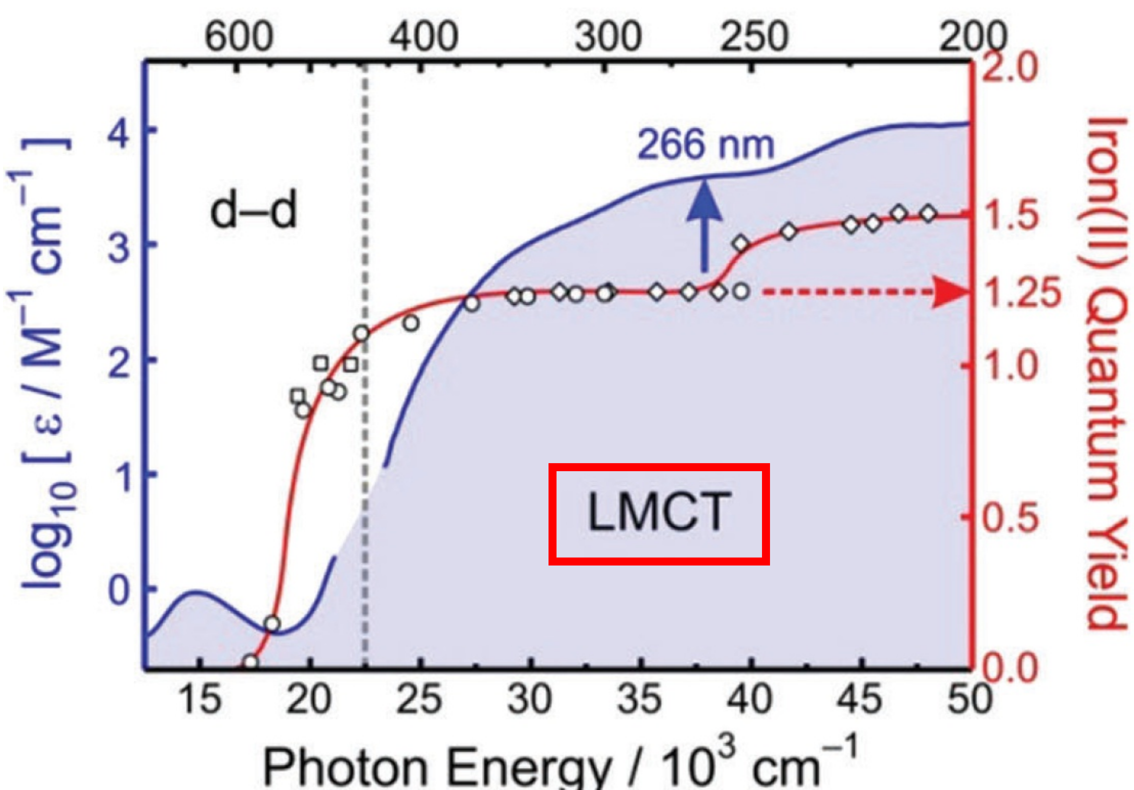
Arrell et al, RSI 2015; Ojeda et al, Struct. Dyn. 2016;
Arrell et al, Phys. Rev. Lett. (2016); Chimia (2017)

Aqueous Ferrioxalate



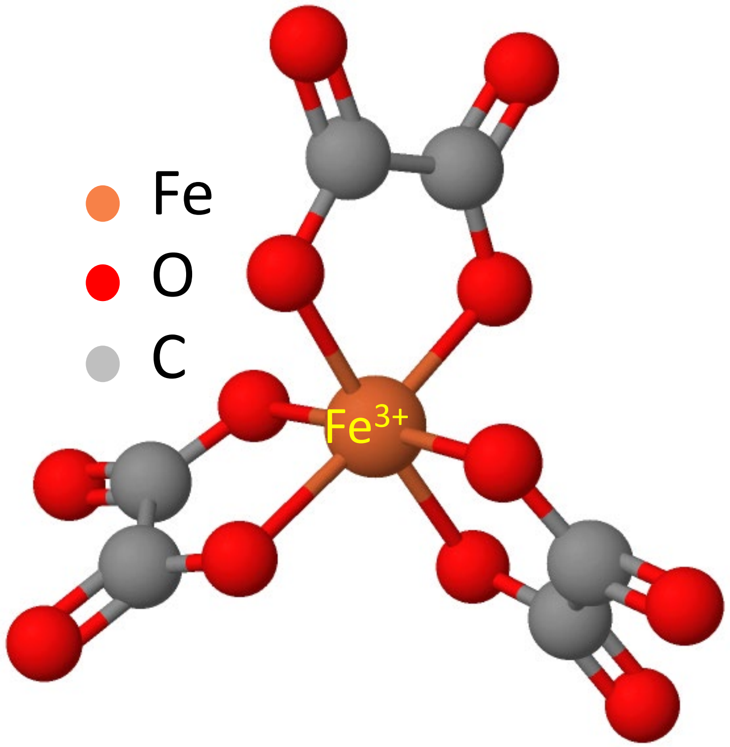
$$[Fe^{III}(C_2O_4)_3]^{3-} + h\nu \rightarrow [(CO_2^{\cdot})Fe^{II}(C_2O_4)_3]^{3-} + CO_2 \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + CO_2 + CO_2^{\cdot -}$$



Parker & Hatchard , J. Phys. Chem. 1959

Straub *et al.* PCCP 2018

Aqueous Ferrioxalate

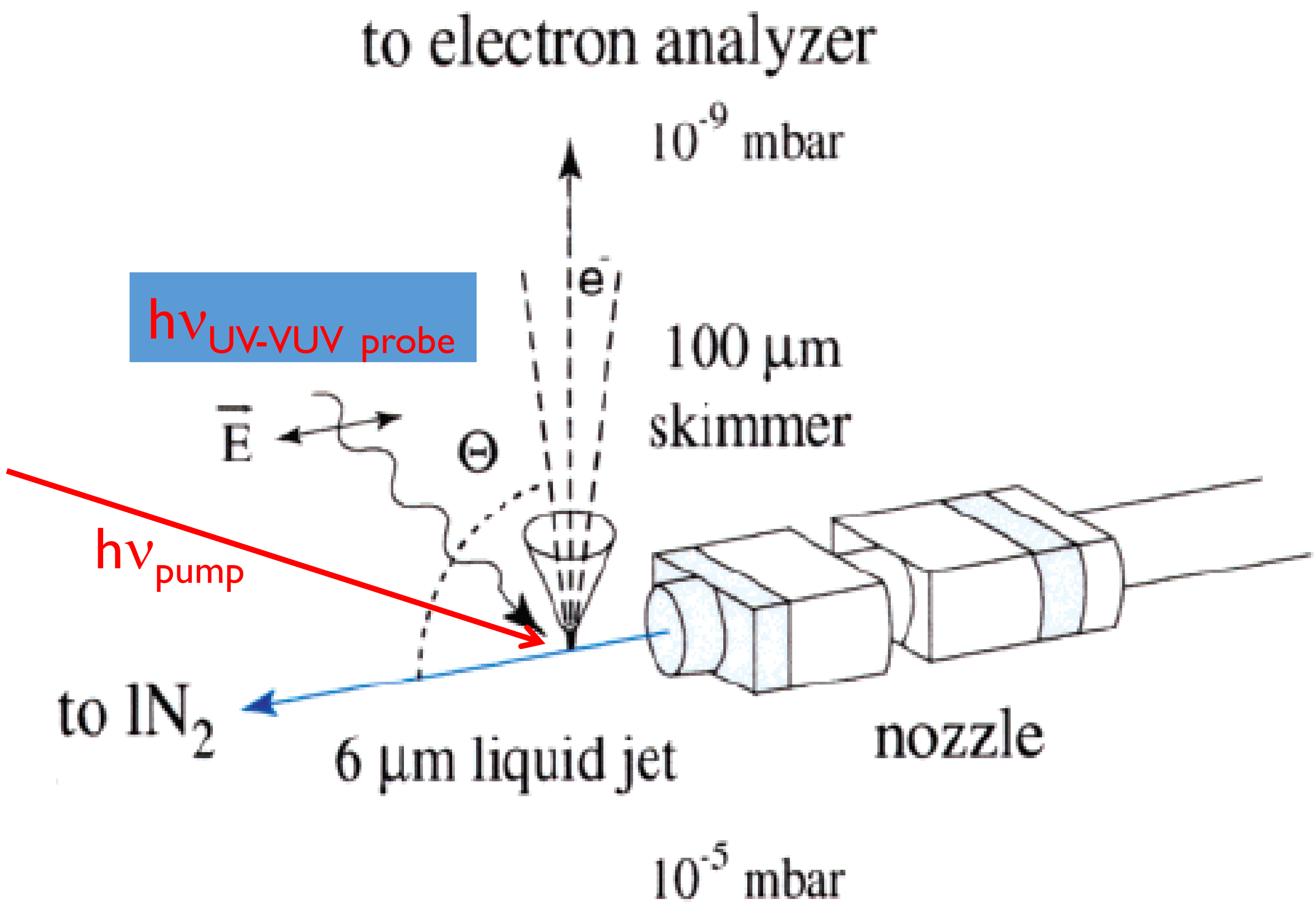


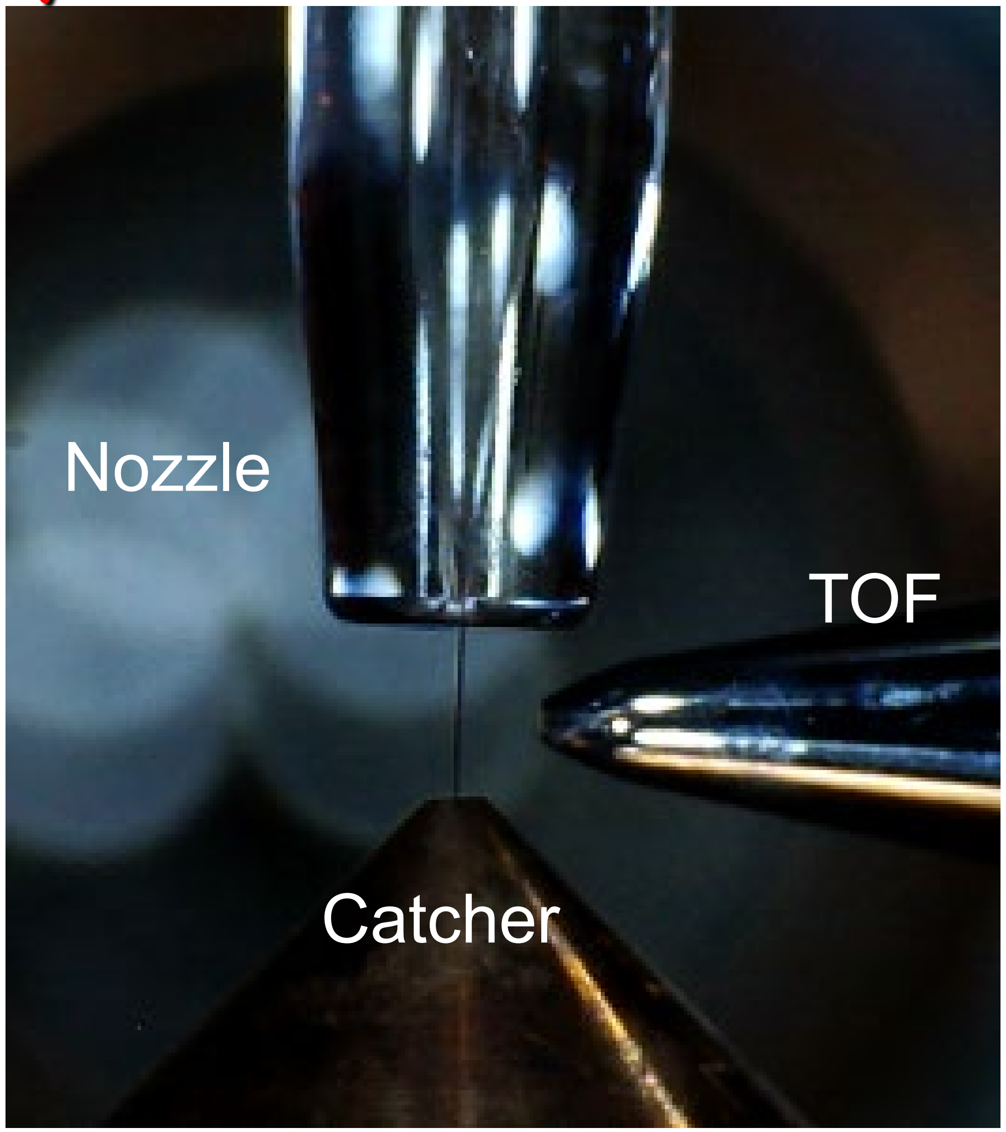
- <u>Initial events</u>:
- How fast is the photoreduction?
- How fast is the first CO_2 dissociation?
- Does reduction trigger dissociation or vice-versa?
- What is the role of the solvent?

<u>Previous ultrafast visible, IR and X-ray absorption TA studies:</u>
- No consensus on the reduction process (<140 fs to > 150 ps)
- No consensus on the initial CO_2 dissociation (<140 fs to 2 ps)
- No consensus on second CO_2 dissociation (2 ps to 1 ns)
- IR TA studies point to ~25-35% recovery of parent molecule in ~ 2 ps. Attributed to intramolecular relaxation.

Rentzepis and co-workers, Inorg. Chem. 2008
Suzuki and co-workers, Struct. Dyn. 2015
Vöhringer and co-workers, PCCP 2018

Ultrafast Vacuum ultraviolet (VUV) photoelectron spectroscopy of solutions

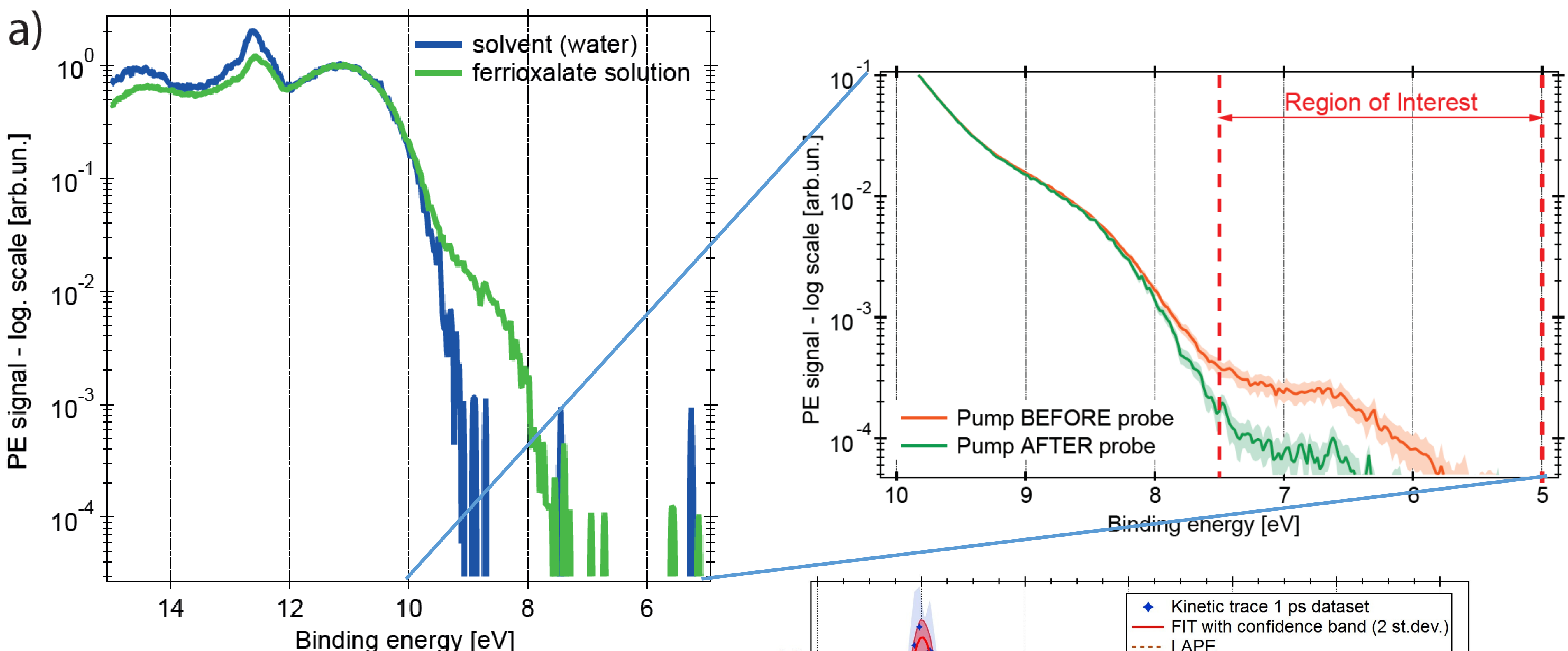




Winter and Faubel, Chem. Rev. 2006
Abel, Faubel et al: First ps studies: Appl Phys A 2009; Nature Chem. 2010; Acc. Chem. Res. 2012

Arrell et al, RSI 2015; Ojeda et al, Struct. Dyn. 2016
Arrell et al, Phys. Rev. Lett. 2016
Ojeda et al, PCCP 2017

Aqueous Ferrioxalate



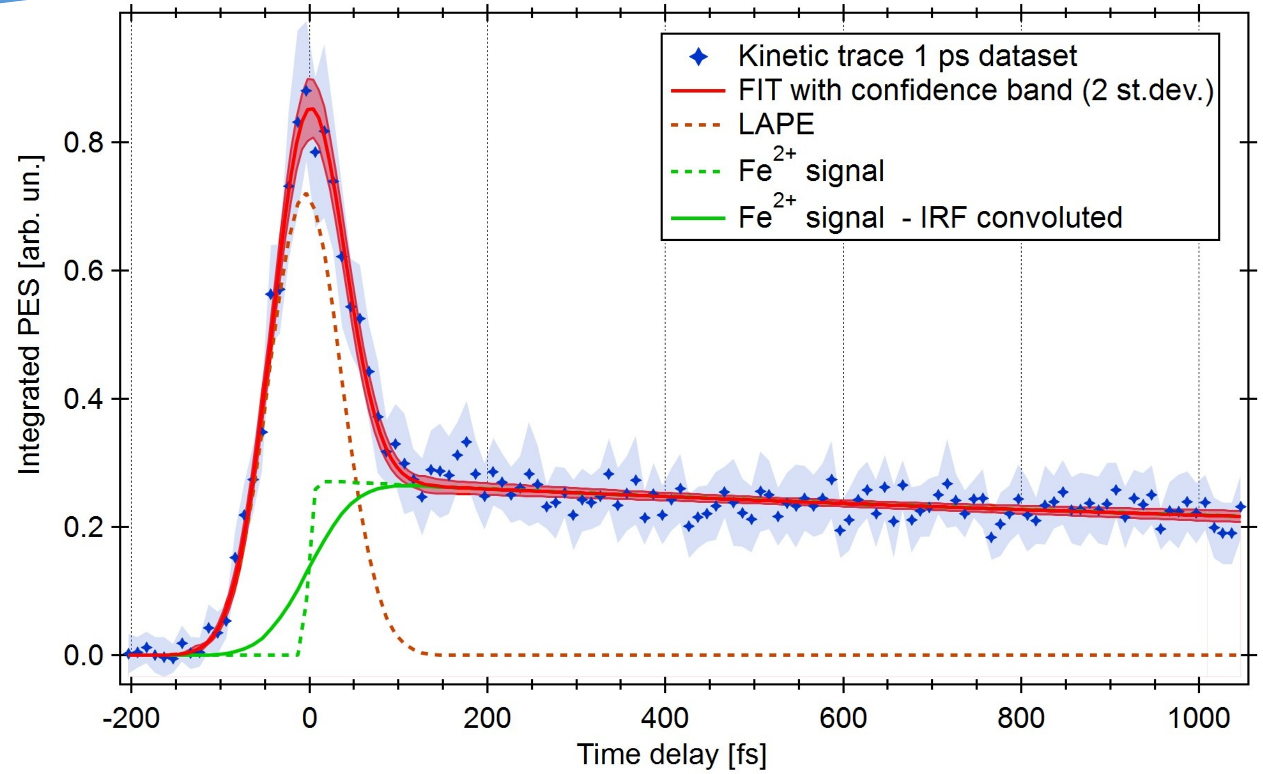
Pump at 4.66 eV

Probe at 34 eV

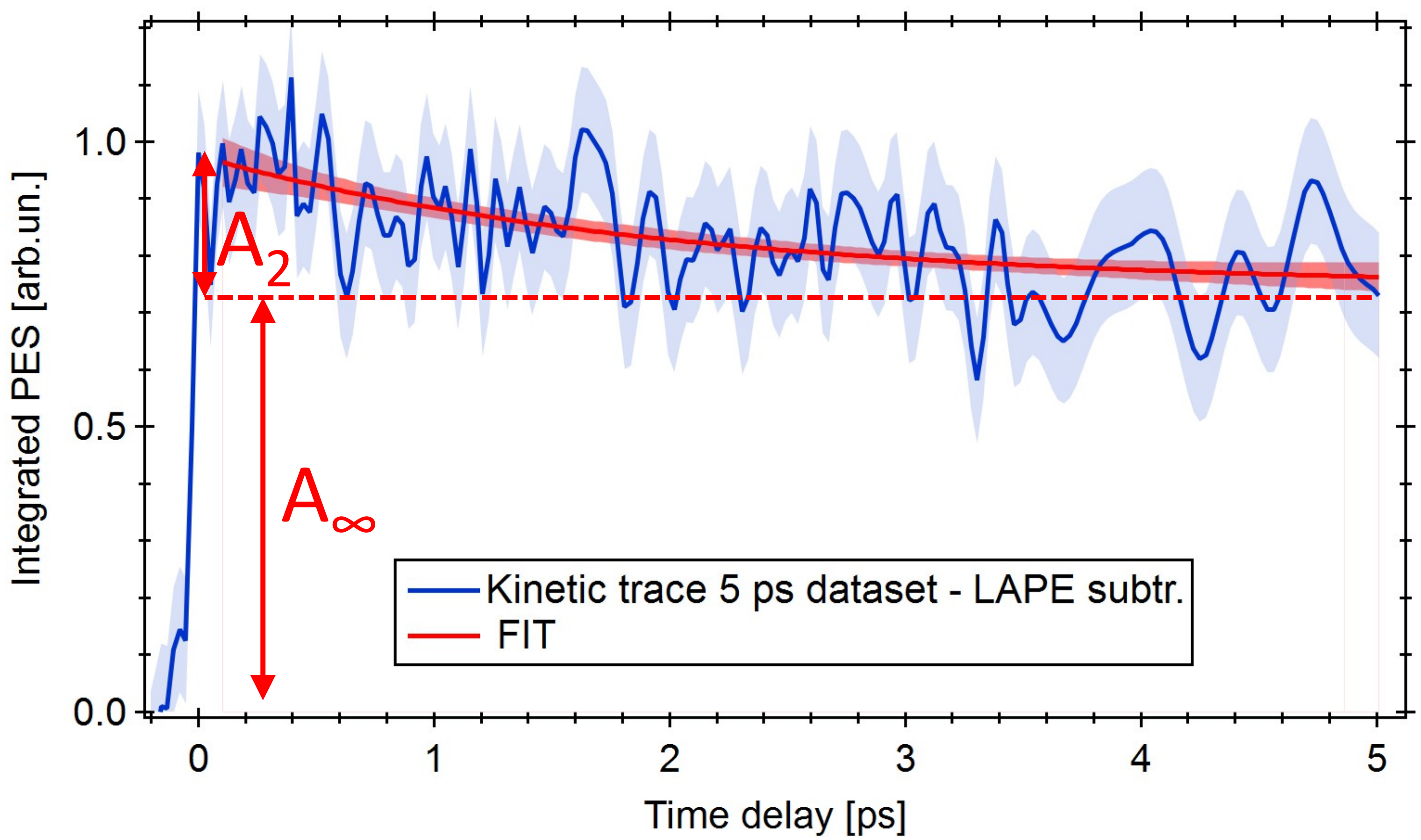
$\tau_R < 30$ fs

(upper limit)

LAPE: Arrell *et al.*, PRL 2016



Transient signal decrease



- Long-lasting signal
- Fast decay

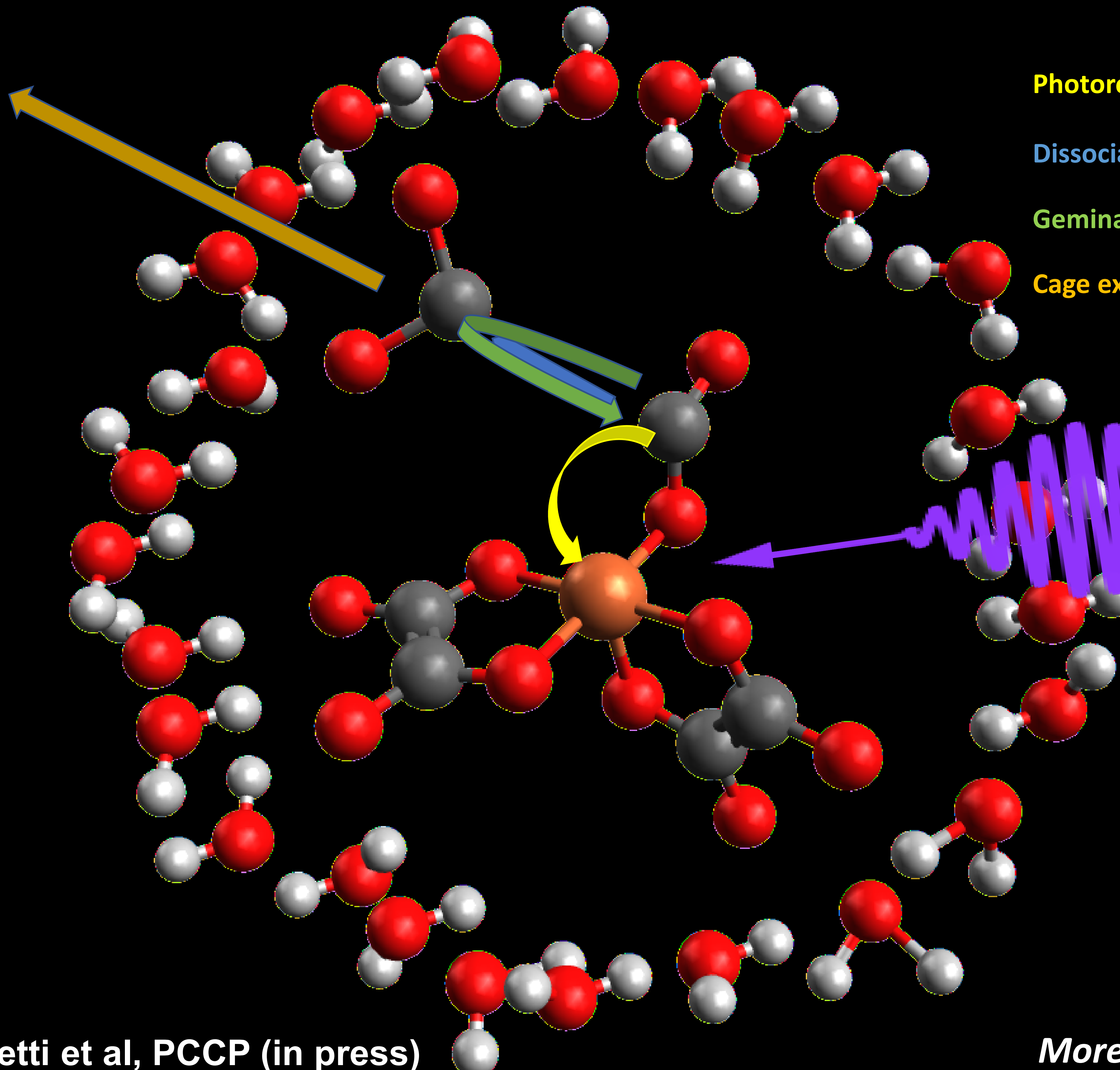
Exponential + plateau

τ_2 = 2 ps

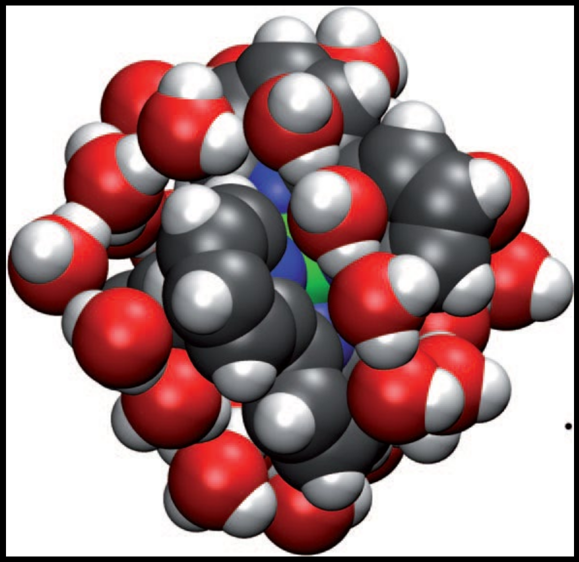
A_2 = 24 % of A(t=0)

- 25% of ferrous species are lost in 2 ps
- IR TA: partial (25-35 %) recovery of depleted parent molecule population in ca. 2 ps. Attributed to intramolecular relaxation.
- X-ray TA: <140 fs CO_2 dissociation and 2-3 ps relaxation time, attributed to dissociation of the second fragment (the CO_2^- anion)

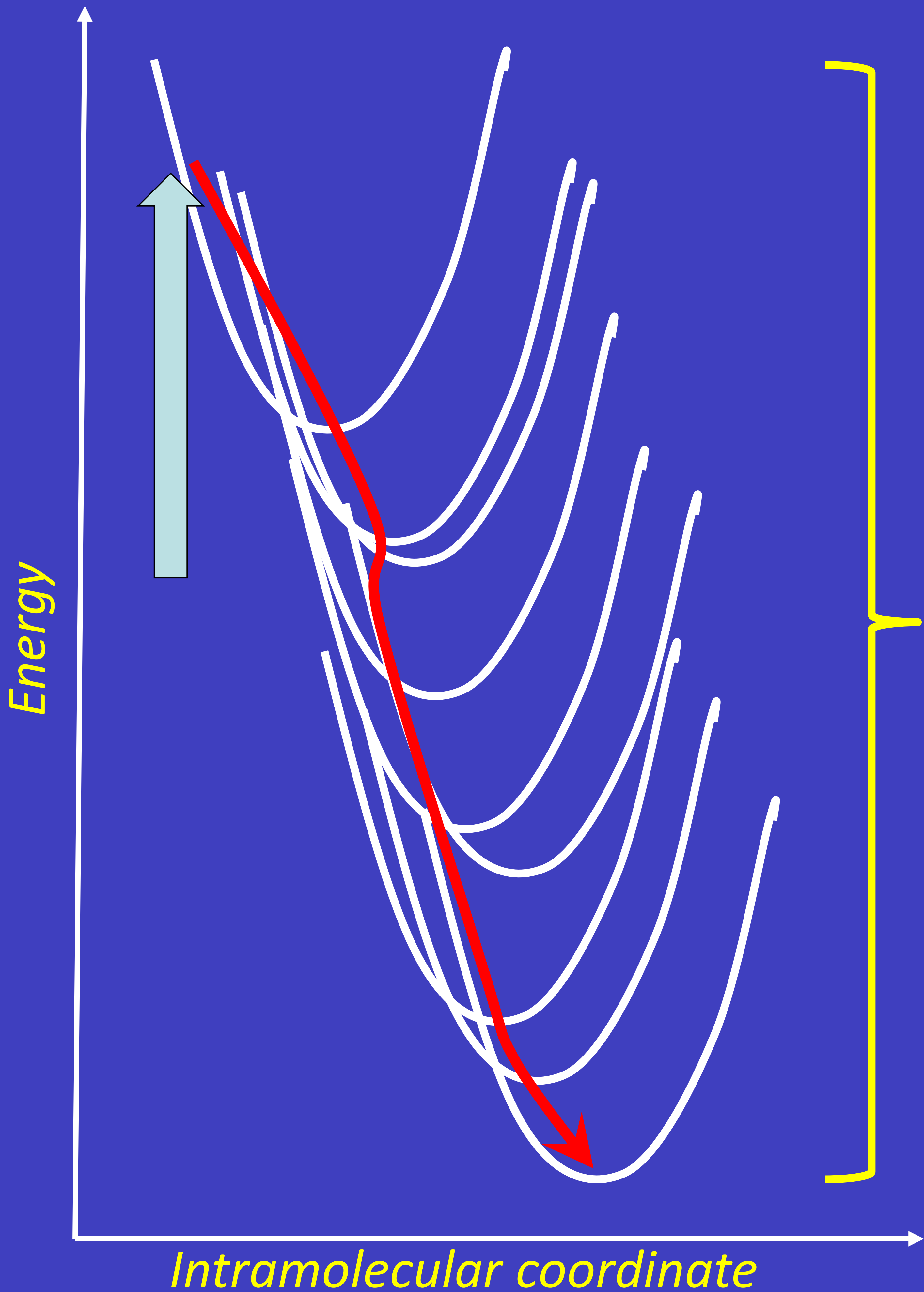
Aqueous Ferrioxalate



Longetti et al, PCCP (in press)



Moret et al, Chem. Eur. J. 2010

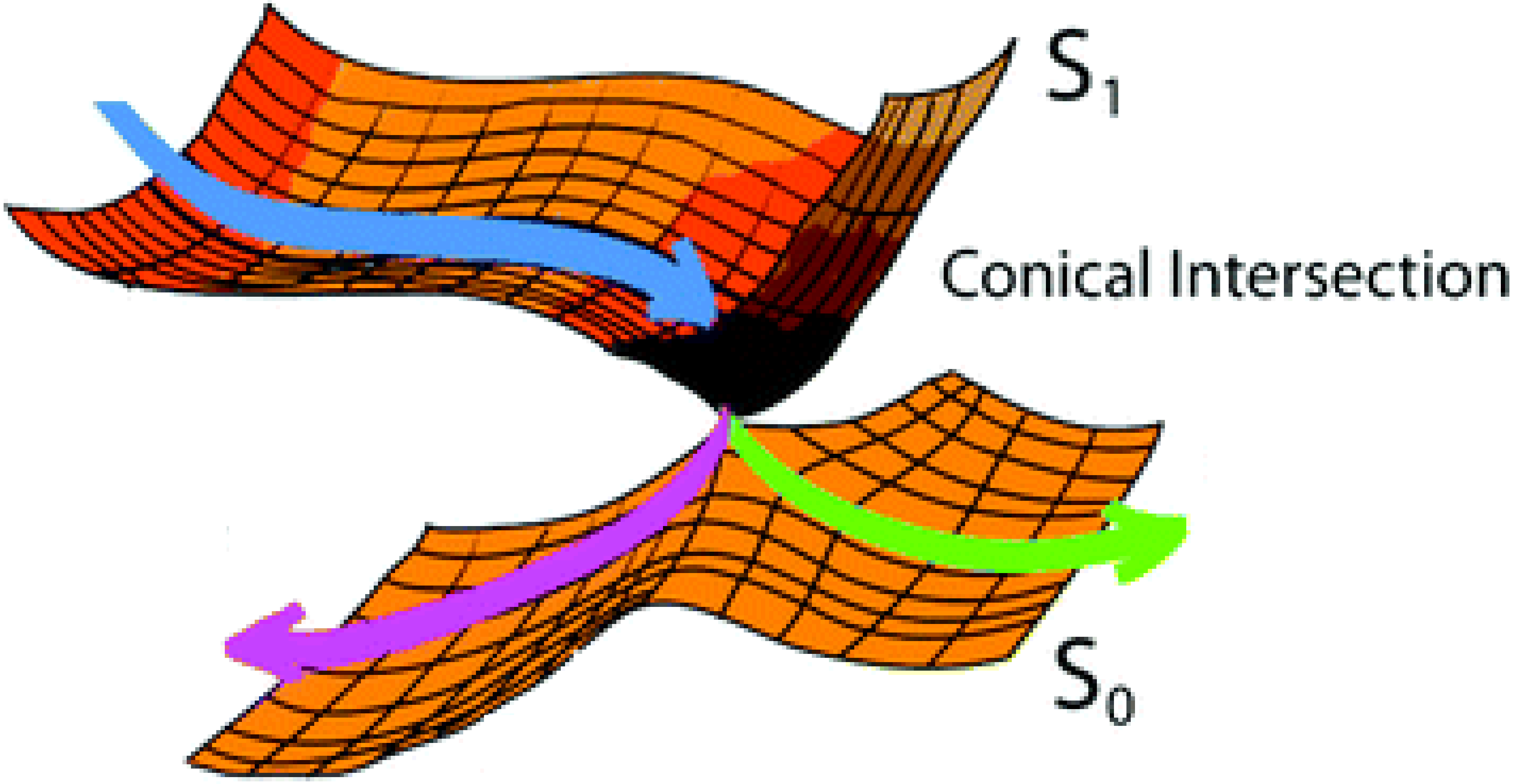


Electronic cooling in <20 fs

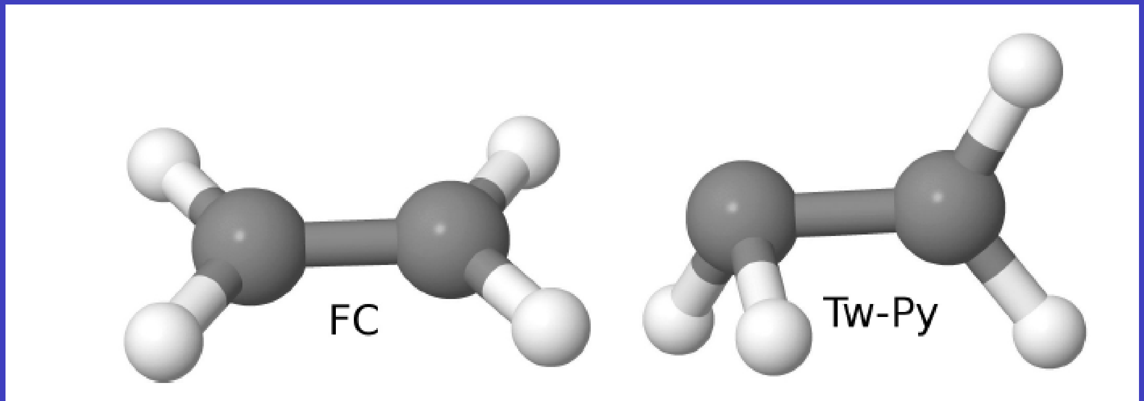
Low freq. non-symmetric modes

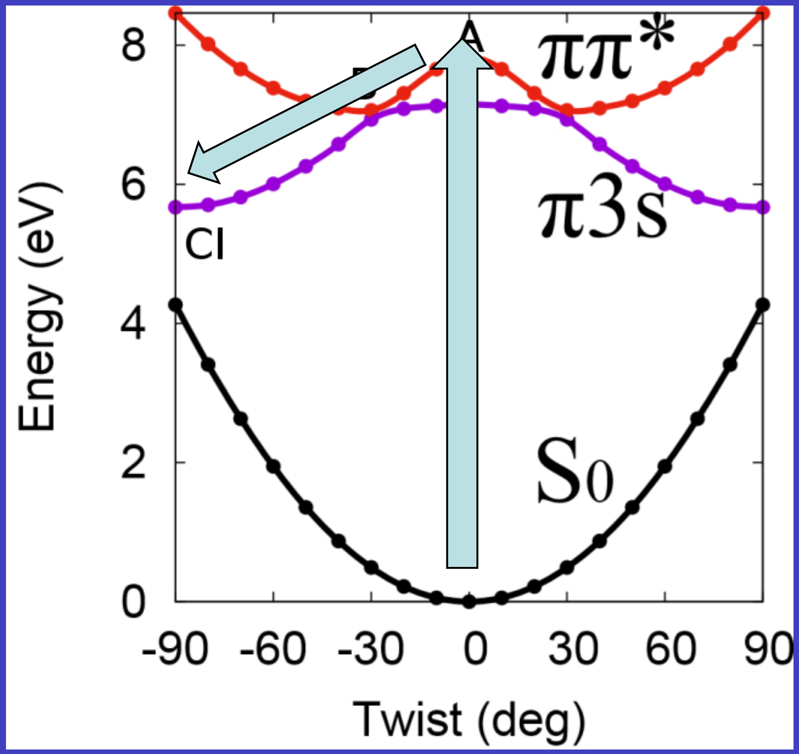
Messina et al, JPCL (2015)

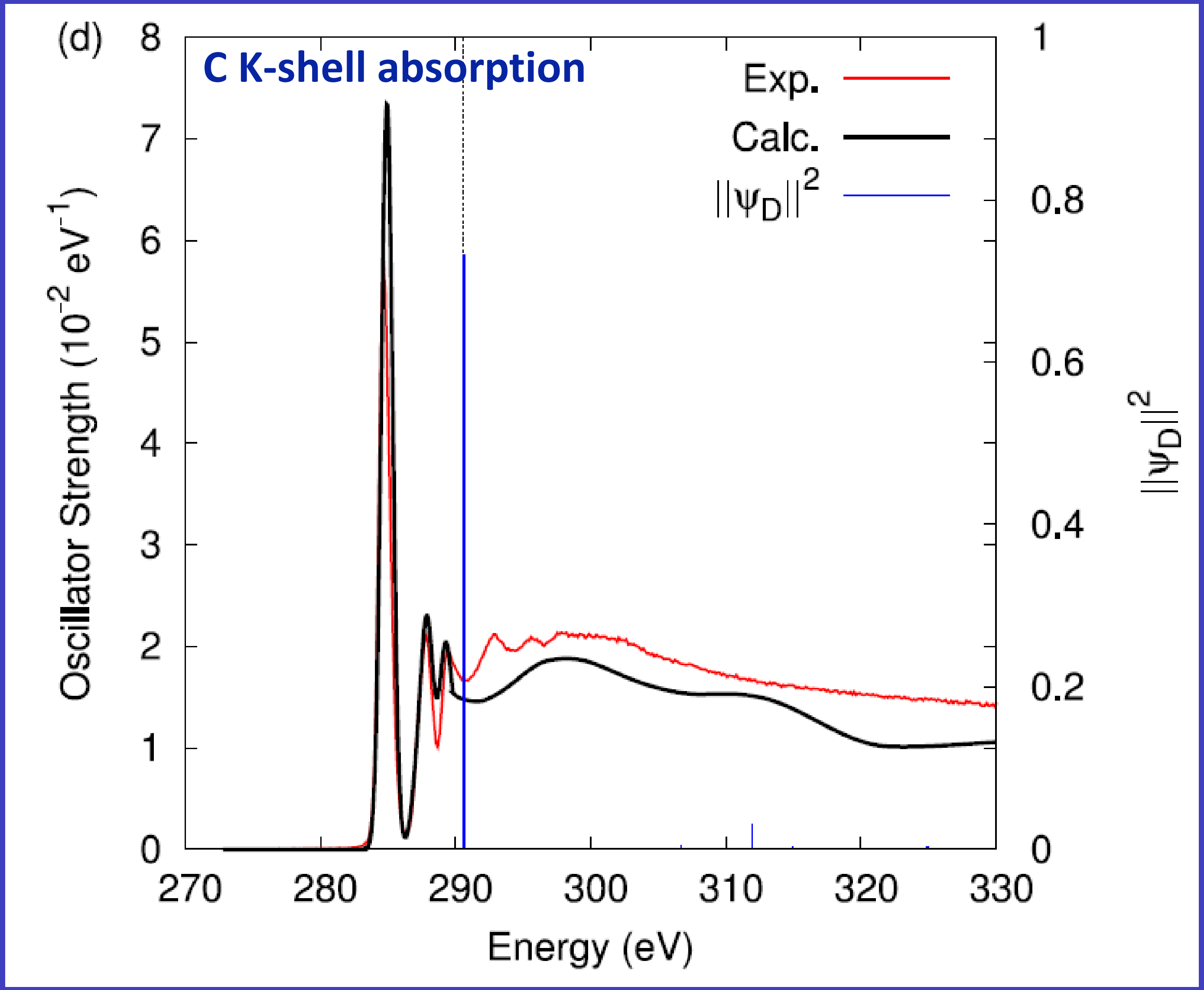
Conical intersections



«Observing» the passage through Conical Intersections (Coll. A. Stolow, M. Schuurman-Ottawa)



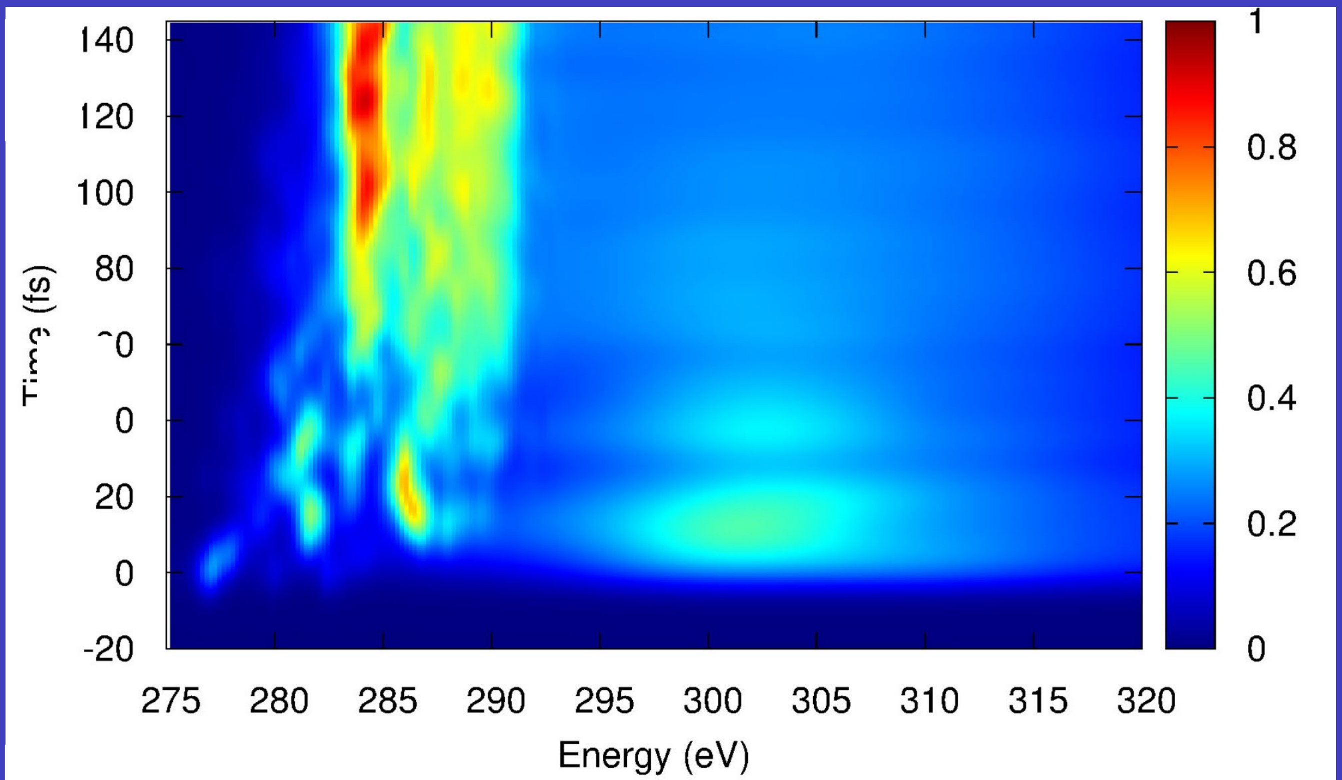


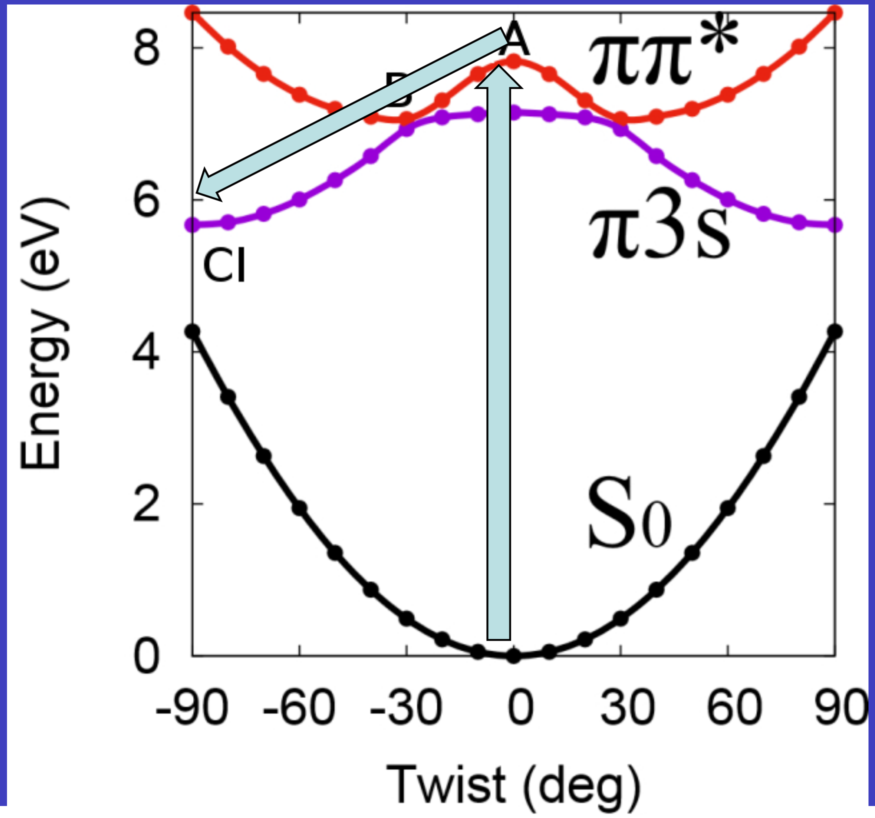


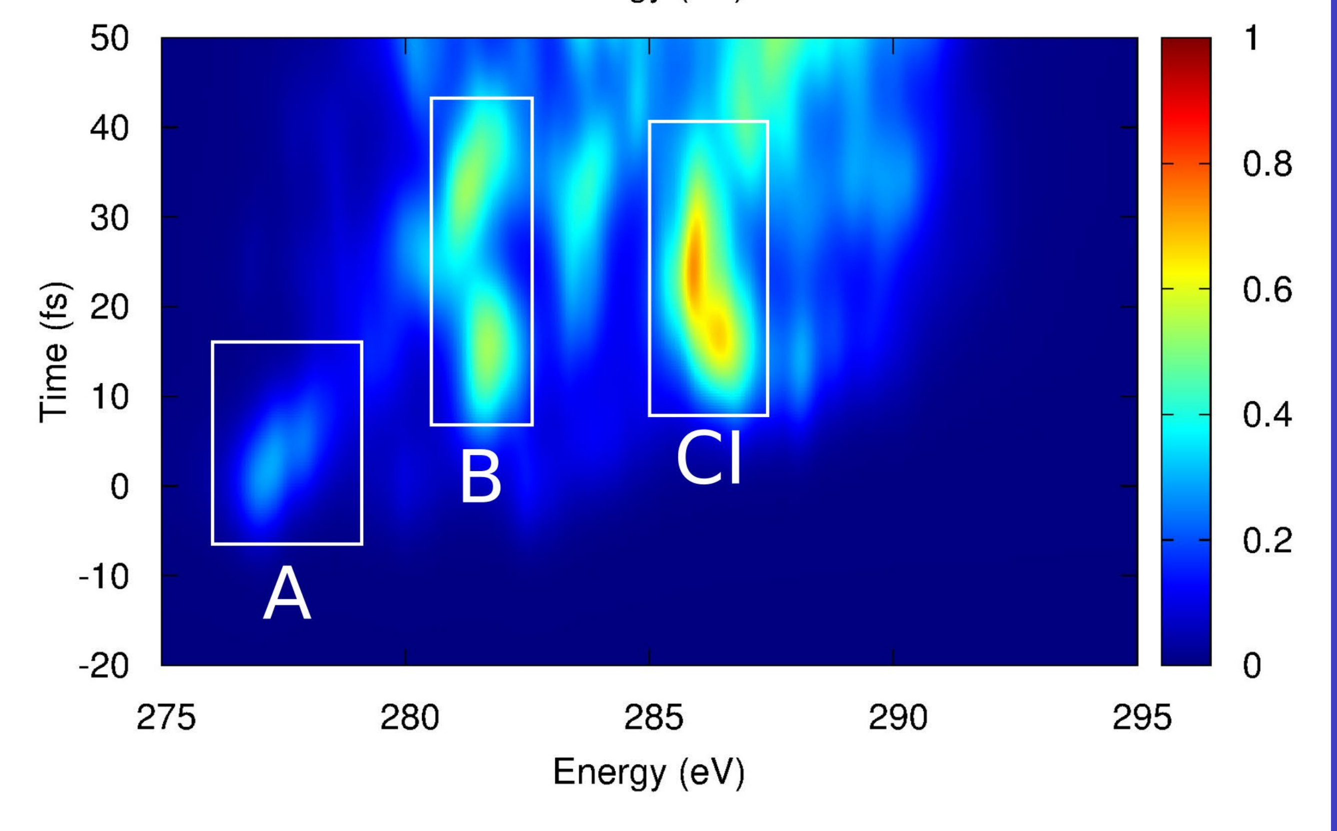
Ab-initio multiple spawning (AIMS) Method:
S. P. Neville, et al, Faraday Discuss. 194, 117 (2016); J. Chem. Phys. 145, 144307 (2016);

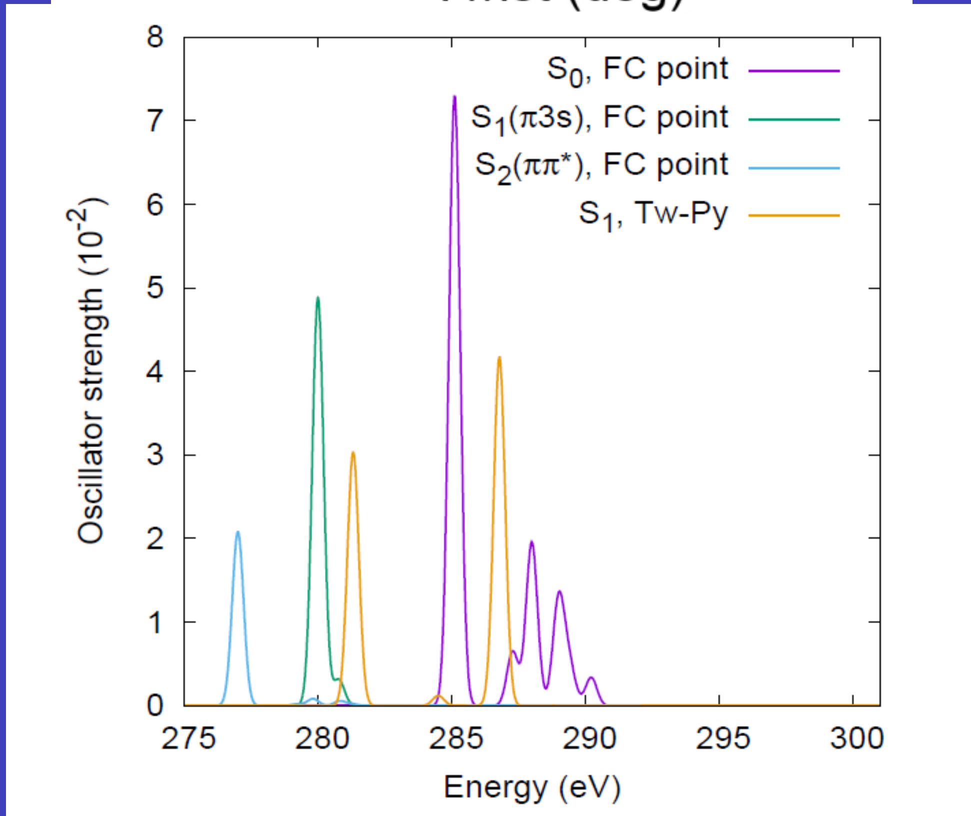
Conical Intersections

Exploiting the sudden polarization at the CI: Neville et al, Phys. Rev. Letters (2018)



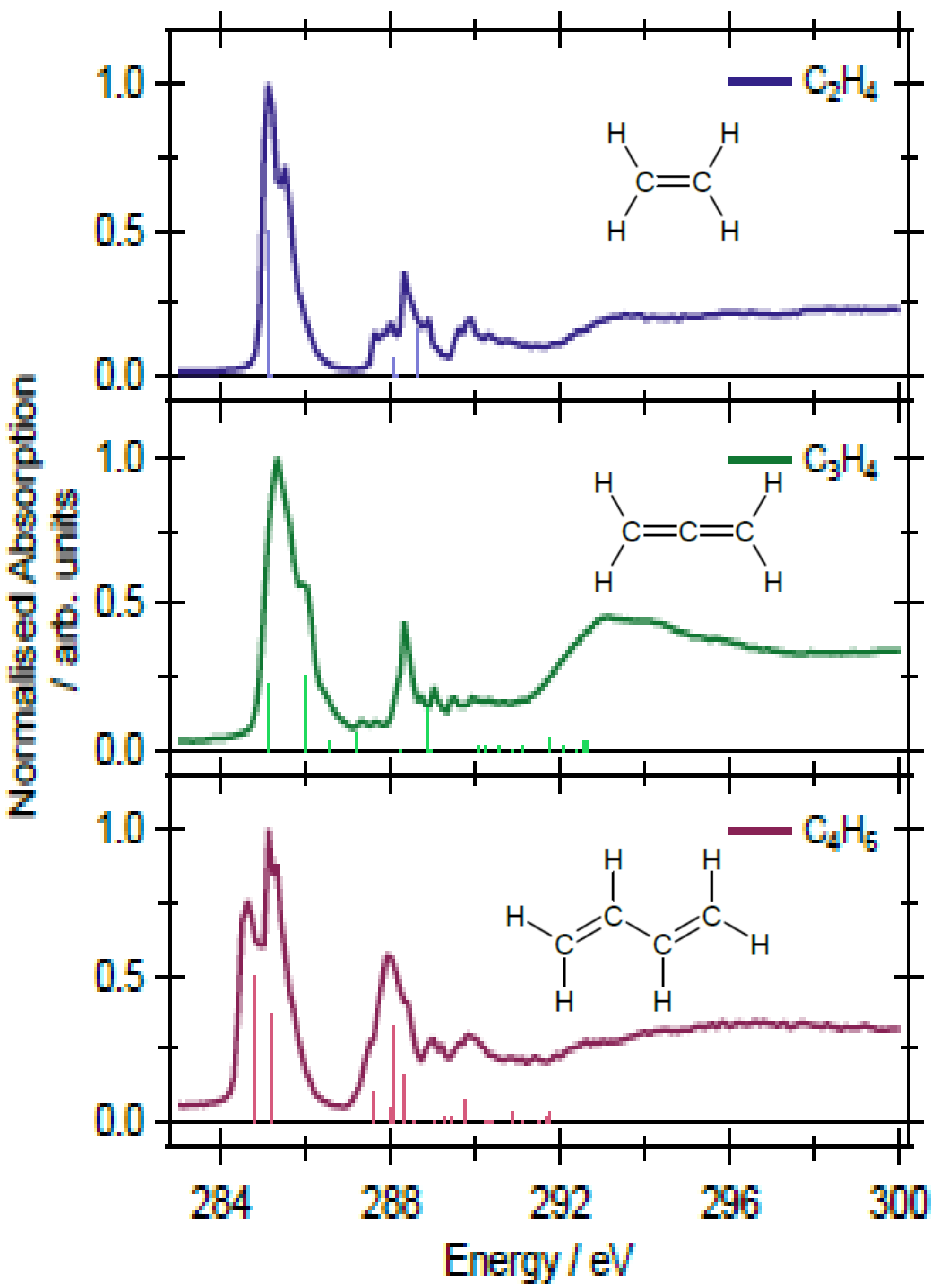






Conical Intersections

Use X-ray emission spectra (XES) rather than X-ray absorption
No photoinduced XES spectra available



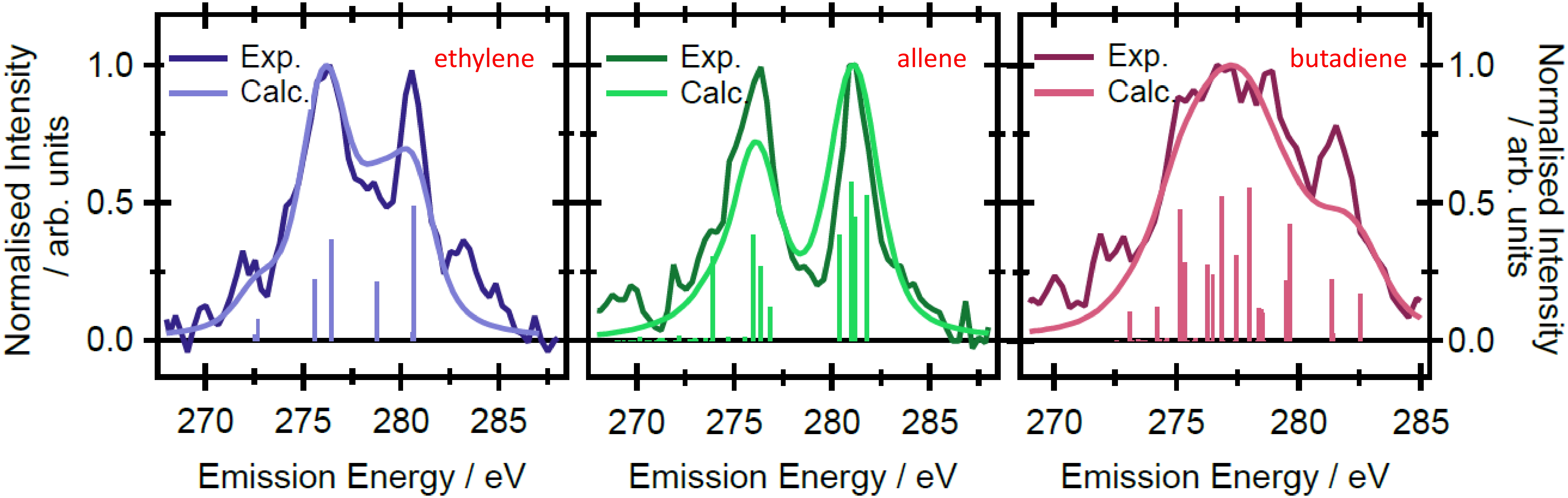
- Only electron-impact XES available (Brammer et al, CPL 1984)

- Photoinduced XES recorded at ELETTRA. Resonant XES excited at ~285 eV Non-resonant XES excited at ~310 eV

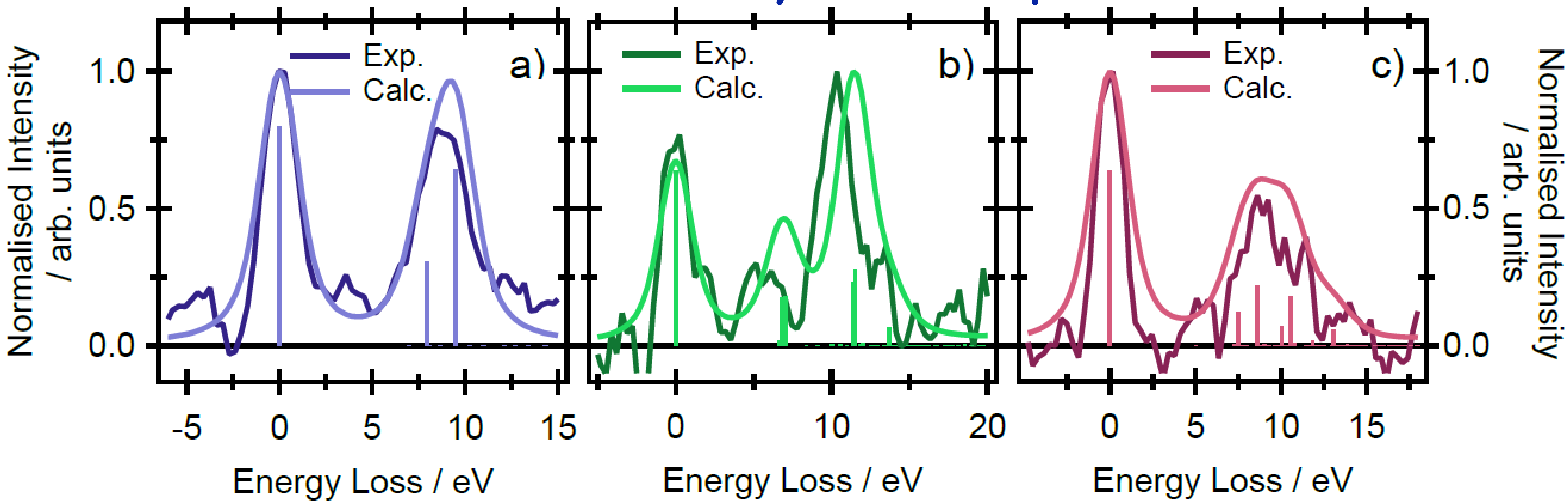
- Simulations using the DFT-ROCIS protocol and the RIXS modeule in ORCA (Coll. M. Odelius, Stockholm)

Elettra Sincrotrone Trieste

Non-resonant X-ray emission spectra



Resonant X-ray emission spectra



Ingle et al, J. Phys. B (submitted)

Very good agreement theory-experiment

Allows identifying which atoms contribute to the XES

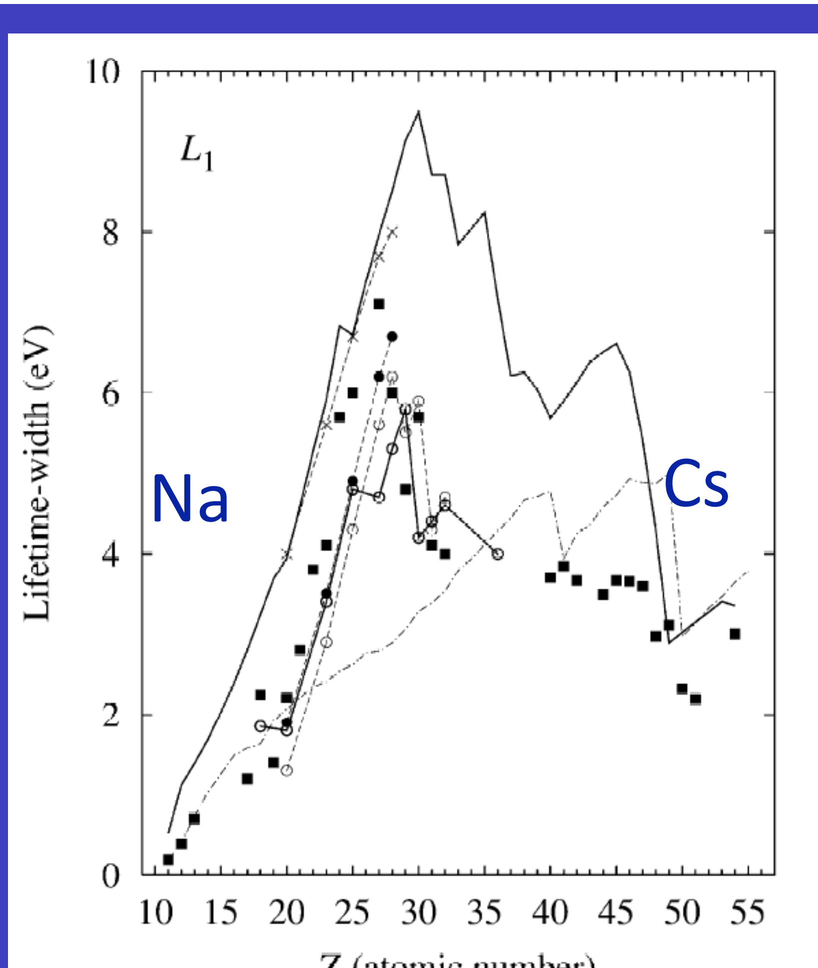
Competition between dynamics through CI and core-hole lifetime of Carbon.

Dynamics vs core-hole lifetime

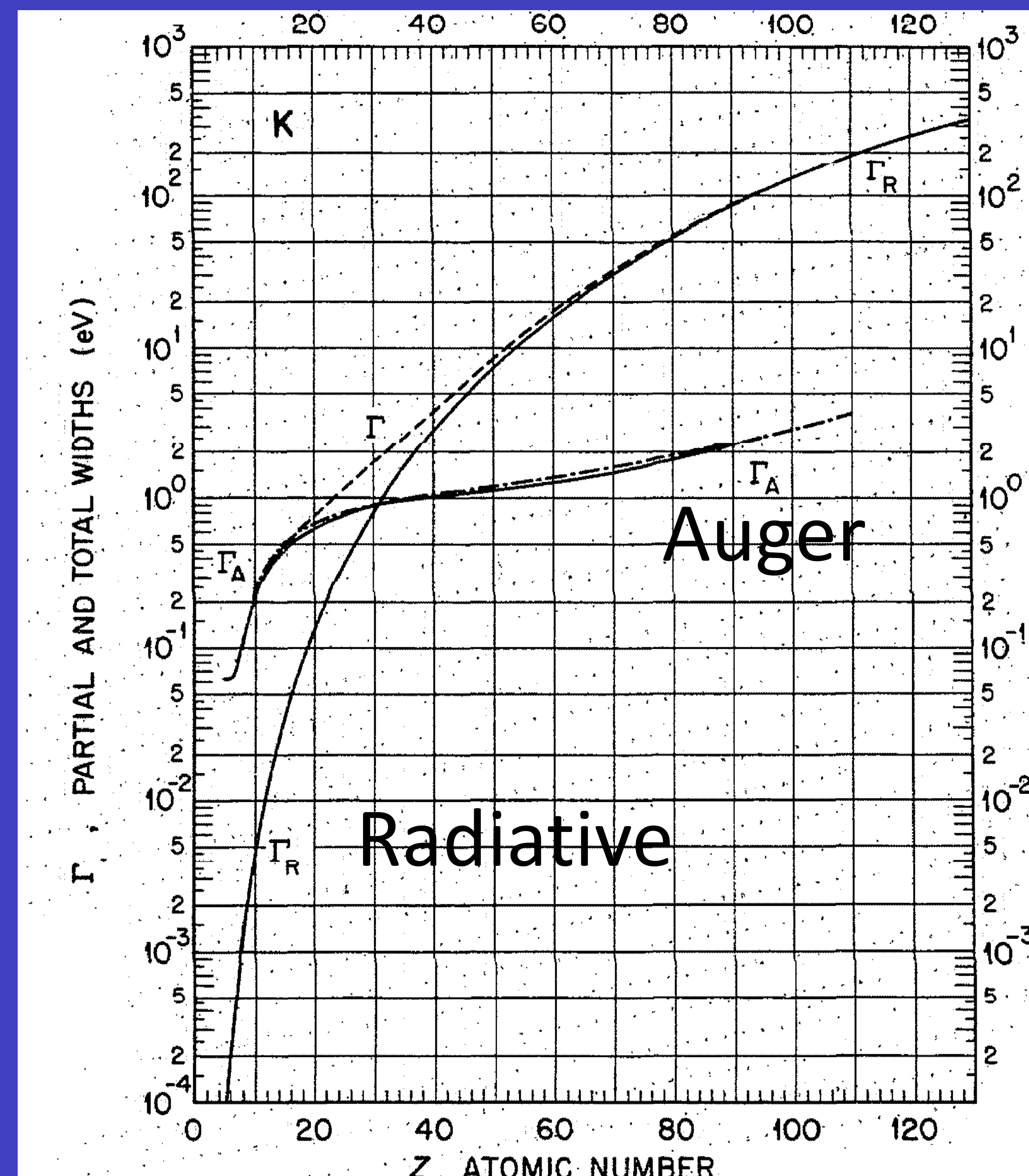
First, it should be mentioned that in XAS, the processes of ejection, backscattering, and interference are extremely fast. For inner shell electrons with ionization energies above 1 keV, these processes are mostly completed well within ~1 fs, as can be seen from the measured homogeneous line widths of the absorption edges.[103] This means that XANES and EXAFS take a truly instantaneous snapshot of immobile atoms, even during a violent chemical reaction. Therefore, implementing ultrafast time-resolved XAS via the pump–probe scheme (Figure 1) is straightforward.

Bressler & Chergui, Chem. Rev. (2004)

1 eV= 1.52 fs



Ohno & van Riessen, JESRP (2003)



Krause, JPCRD (1978)

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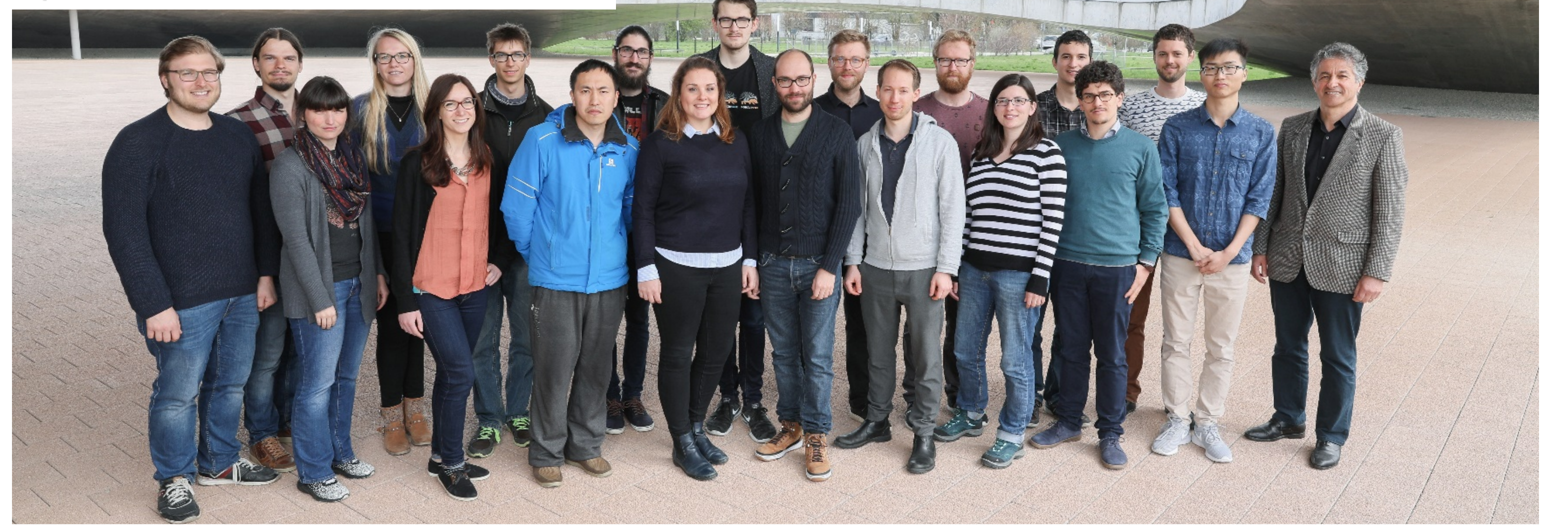
C. Bacellar, Th. Barillot, O. Cannelli, R. Ingle, D. Kinschel, L. Longetti, G. Mancini, H. Marroux, M. Oppermann, S. Polishchuk, M. Puppin, J. Rouxel, L. Wang.



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Experimental strategies at the

Method	Type of information
Deep-UV to visible probe (270-700 nm) Transient absorption	Electronic
Polychromatic Fluorescence up-conversion IR to UV (300 nm to 2 μm)	Electronic
Ps and fs X-ray (2 to 20 keV) absorption spectroscopy (XANES and EXAFS)	Electronic and geometric
Ps and fs X-ray emission and inelastic scattering spectroscopy (coll. XFEL)	Electronic, spin, momentum
Multidimensional TA Ultraviolet and coherent visible spectroscopies	Geometric, electronic and correlations
Deep-UV circular dichroism	Geometric and correlations
Ultrafast energy and angle resolved photoelectron spectroscopies	Momentum, electronic