Ultrafast Chemistry: From single site to multi-centre dynamics

Alexander Föhlisch

Institute of Methods and Instrumentation in Synchrotron Radiation Research, Helmholtz-Zentrum Berlin

Institute of Physics and Astronomy University of Potsdam

PSI, 11-12. May 2016, Stockholm

HZB Helmholtz Zentrum Berlin

Universität Potsdam

The projects and the people!

Identification of the dominant photochemical pathways and mechanistic insights to the ultrafast ligand exchange of $Fe(CO)_5$ to $Fe(CO)_4EtOH$

K. Kunnus, I. Josefsson, I. Rajkovic, S. Schreck, W. Quevedo, M. Beye, C. Weniger, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, K. J. Gaffney, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, S. Techert, M. Odelius, Ph. Wernet and A. Föhlisch

Struct. Dyn. 3, 043204 (2016)

Orbital-specific mapping of the ligand exchange dynamics of $Fe(CO)_5$ in solution

P. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, S. Schreck, W. Quevedo, M. Beye, C. Weniger, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. Hartsock, K. Gaffney, W. Schlotter, J. Turner, B. Kennedy, F. Hennies, F. de Groot, S. Techert, M. Odelius, A. Föhlisch, Nature 520 (7545), 78-81 (2015)

Anti-Stokes X-ray Raman Scattering for excited state dynamics

Kristjan Kunnus, Ida Josefsson, Michael Odelius, Philippe Wernet, Alexander Föhlisch, submitted

---

Implications of stimulated resonant X-ray scattering for spectroscopy, imaging, and diffraction in the regime from soft to hard X-rays

S. Schreck, M. Beye, and A. Föhlisch, JMO 62, S41-S51 (2015),

Stimulated X-ray emission for materials science,

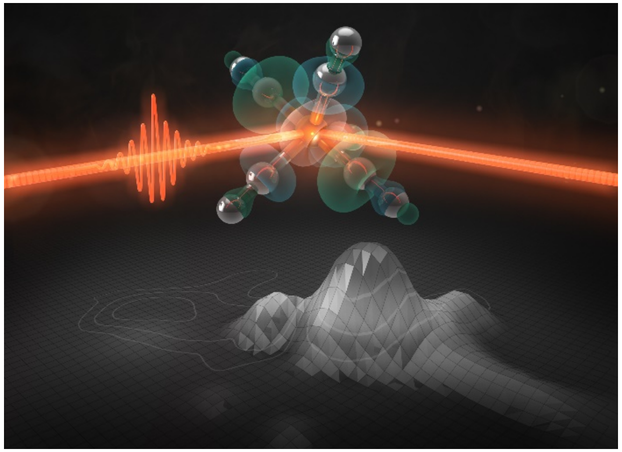
M. Beye, S. Schreck, F. Sorgenfrei, C.Trabant, N. Pontius, C. Schüßler-Langeheine, W. Wurth, and A. Föhlisch Nature 501 191 (2013) DOI: 10.1038/nature12449

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

S Schreck, A. Pietzsch, B. Kennedy, C. Såthe, P. S. Miedema, S. Techert, V. N. Strocov, Th. Schmitt, F. Hennies, J.E. Rubensson, A. Föhlisch,

Scientific Reports | 6:20054 | DOI: 10.1038/srep20054 (2016)

"What controls rate and selectivity in chemistry and catalysis?"
excited state dynamics



Identification of the dominant photochemical pathways and mechanistic insights to the ultrafast ligand exchange of $Fe(CO)_5$ to $Fe(CO)_4EtOH$ Struct. Dyn. 3, 043204 (2016)

Orbital-specific mapping of the ligand exchange dynamics of $Fe(CO)_5$ in solution, Nature 520 (7545), 78-81 (2015)

Anti-Stokes X-ray Raman Scattering for excited state dynamics
submitted

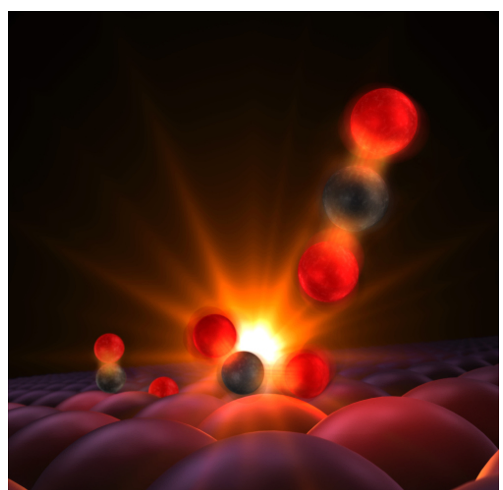
Transition metals key „ingredients“ to (photo-)(bio)-chemistry and Heterogeneous catalysis

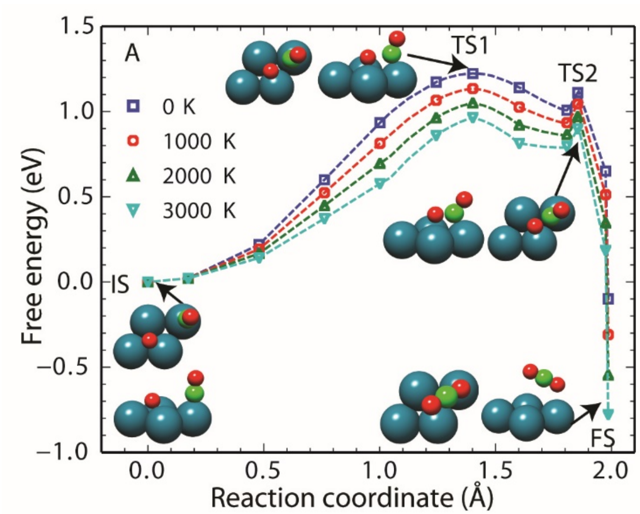
TM K-edge RIXS selective to spin,
L-edge RIXS selective to valence

Probing the transition state region in catalytic CO oxidation on Ru.
H. Öström et al., Science, 12 February 2015 (10.1126/science.1261747)

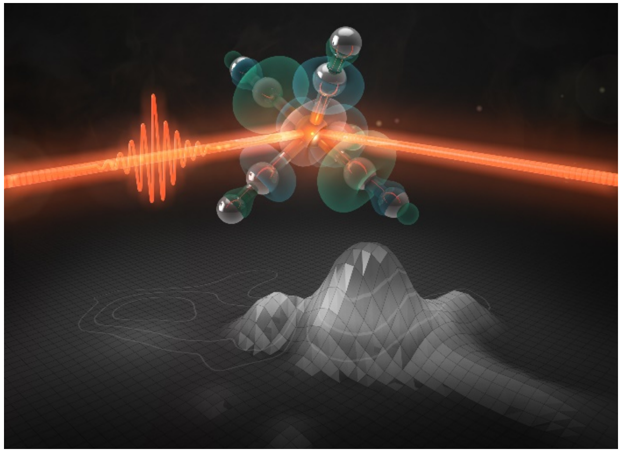
M. Dell'Angela et al., Science 339, 1302-1305 (2013).

A. Nilsson group, J. Norskov group, Pettersson group, W. Wurth group, M. Wolf group





Ligand Substitution: bond breaking and bond creation

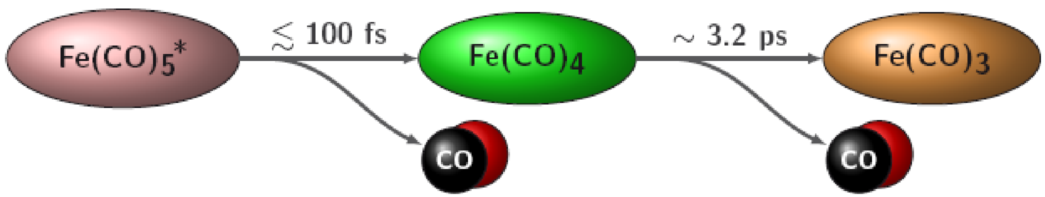


Identification of the dominant photochemical pathways and mechanistic insights to the ultrafast ligand exchange of $Fe(CO)_5$ to $Fe(CO)_4EtOH$ Struct. Dyn. 3, 043204 (2016)

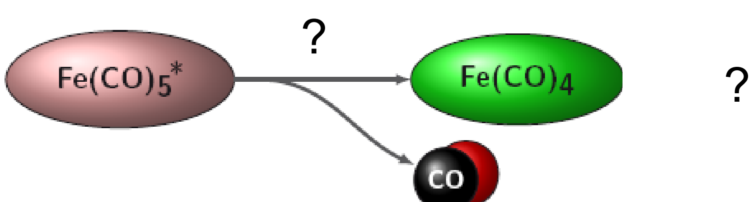
Orbital-specific mapping of the ligand exchange dynamics of $Fe(CO)_5$ in solution, Nature 520 (7545), 78-81 (2015)

Anti-Stokes X-ray Raman Scattering for excited state dynamics submitted

Photodissociation – Gas Phase: $Fe(CO)_5 + h\nu_{pump} \rightarrow Fe(CO)_4 + CO \rightarrow Fe(CO)_3 + CO$



Photodissociation – Solution: $Fe(CO)_5 + h\nu_{pump} \rightarrow Fe(CO)_4 – EtOH + CO$



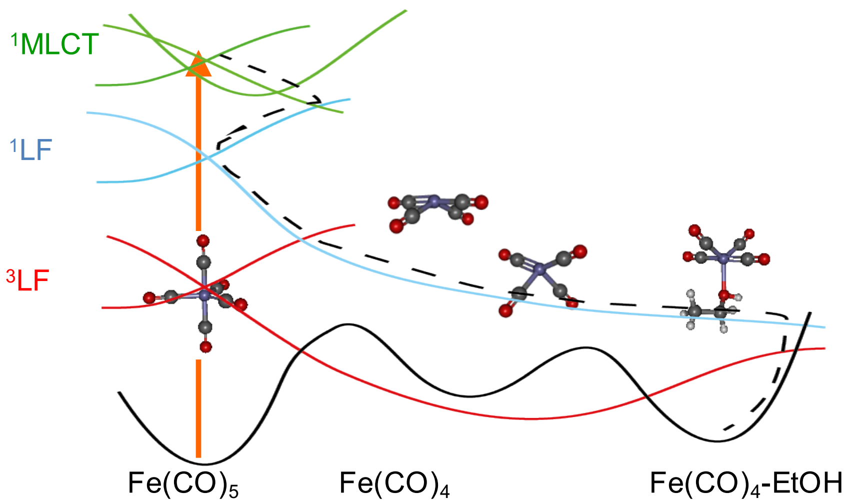
Scenarios of $Fe(CO)_5$ photodissociation/ligand exchange in solution

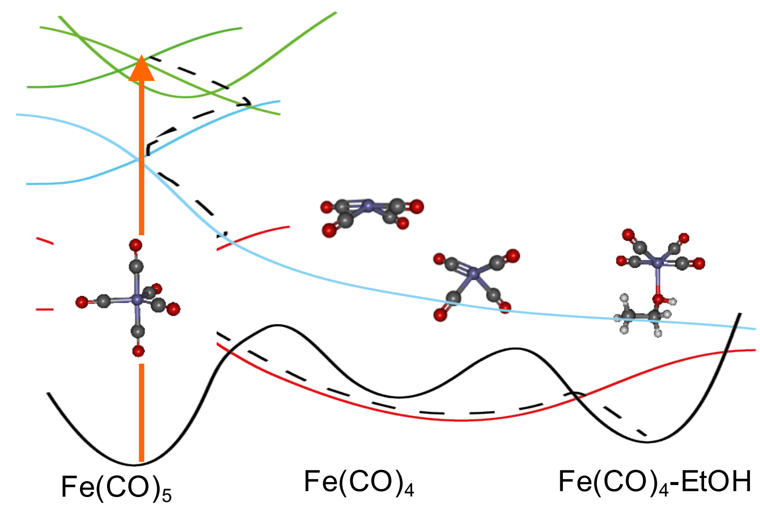
Concentred ligand substitution reaction via singlet pathway

Ahr, Rose-Petruck, et al.,
Phys. Chem. Chem. Phys. 2011, 13, 5590.
Trushin, Fuss, et al.,
J. Phys. Chem. A 2000, 104, 1997.

Reaction via triplet intermediate and diffusion limited complexation

Snee, Harris, et al., JACS. 2001, 123, 6909.
and JACS 2001, 123, 2255.



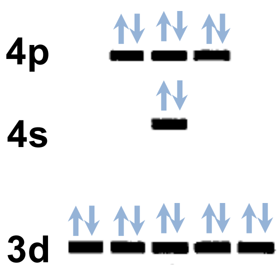


Simplified schemes! More then one nuclear coordinate involved!

18 electron rule of coordinatively saturated 3d transition metal complexes

Kr: $[Ar]3d^{10}\,4s^{2}\,4p^{6}$

Nr. of Valence e^- 18



T. Langmuir, Science 54, 59-67 (1921).
R. Hoffmann, Angew. Chem. Int. Ed. Engl. 21, 711-724 (1982).

18 electron rule of coordinatively saturated 3d transition metal complexes

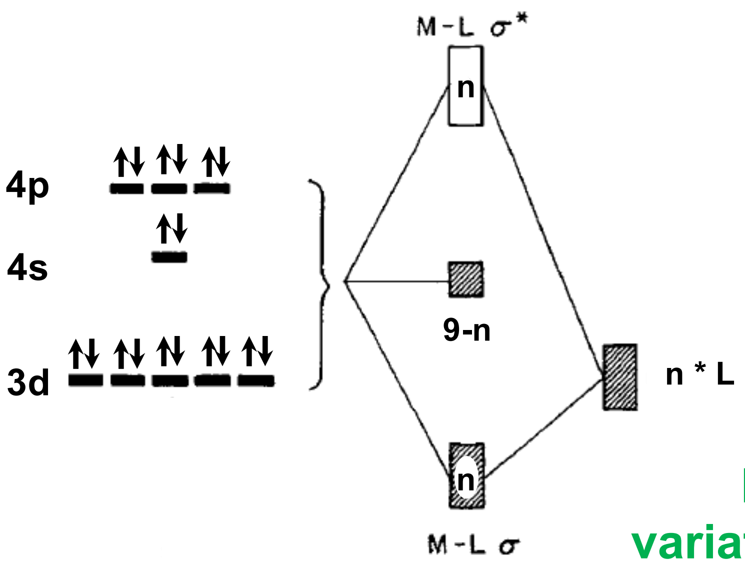
Kr: [Ar]$3d^{10}4s^{2}4p^{6}$

Nr. of Valence e^-: 18

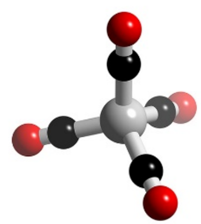
Ni: [Ar]$3d^{8}4s^{2}4p^{0}$
[Ar]$3d^{9}4s^{1}4p^{0}$
10

Fe: [Ar]$3d^{6}4s^{2}4p^{0}$
8

Cr: [Ar]$3d^{5}4s^{1}4p^{0}$
6

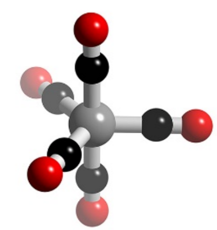


4 CO L donate 8 e^-



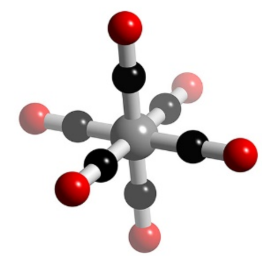
$Ni(CO)_4$

5 CO L donate 10 e^-



$Fe(CO)_5$

6 CO L donate 12 e^-

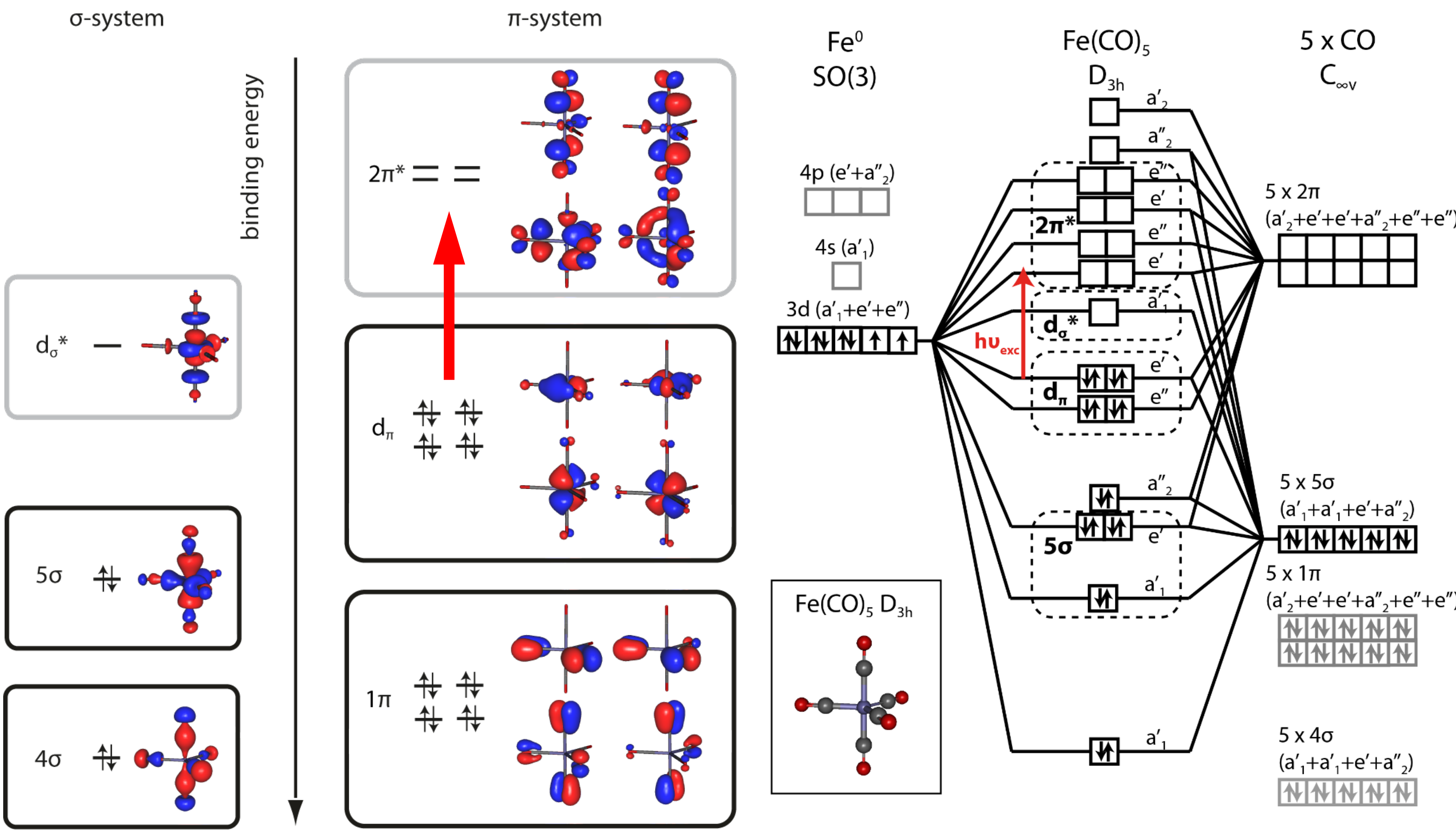


$Cr(CO)_6$

Ligand removal / substitution / chemistry: variation between 18 and 16 electron configuration

T. Langmuir, Science 54, 59-67 (1921).
R. Hoffmann, Angew. Chem. Int. Ed. Engl. 21, 711-724 (1982).

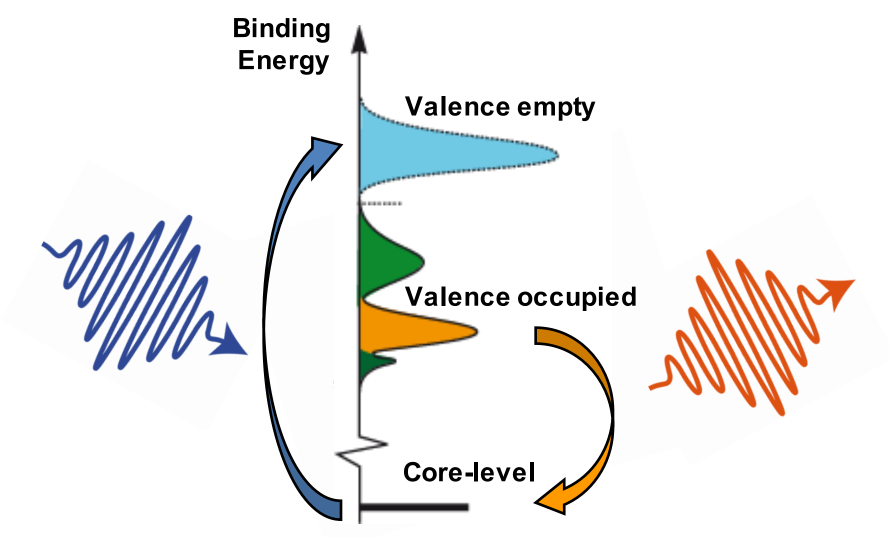
Electronic Structure and optical excitation of $Fe(CO)_5$



A setup for resonant inelastic soft x-ray scattering on liquids at free electron laser light sources. Kunnus et al. Rev. of Sci. Instr., 2012. 83 (12)

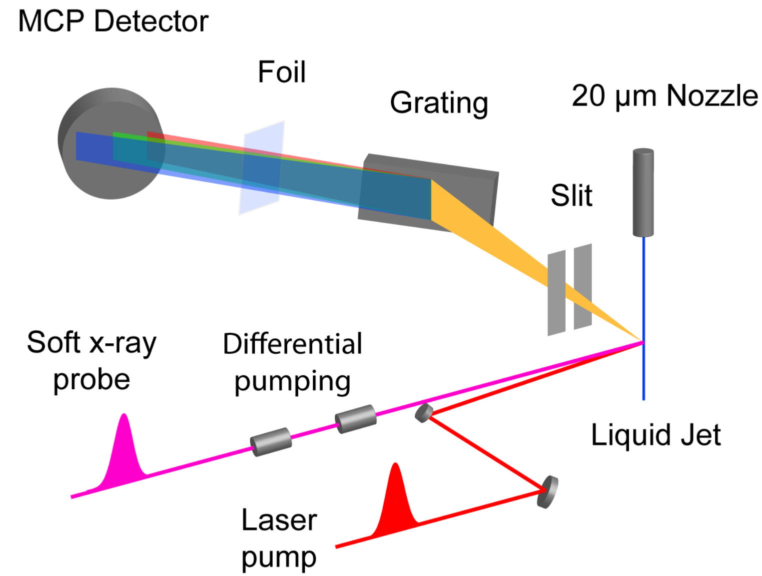
RIXS:

- Valence electronic structure
- Element specific
- Chemical state selective
- Orbital symmetry selective

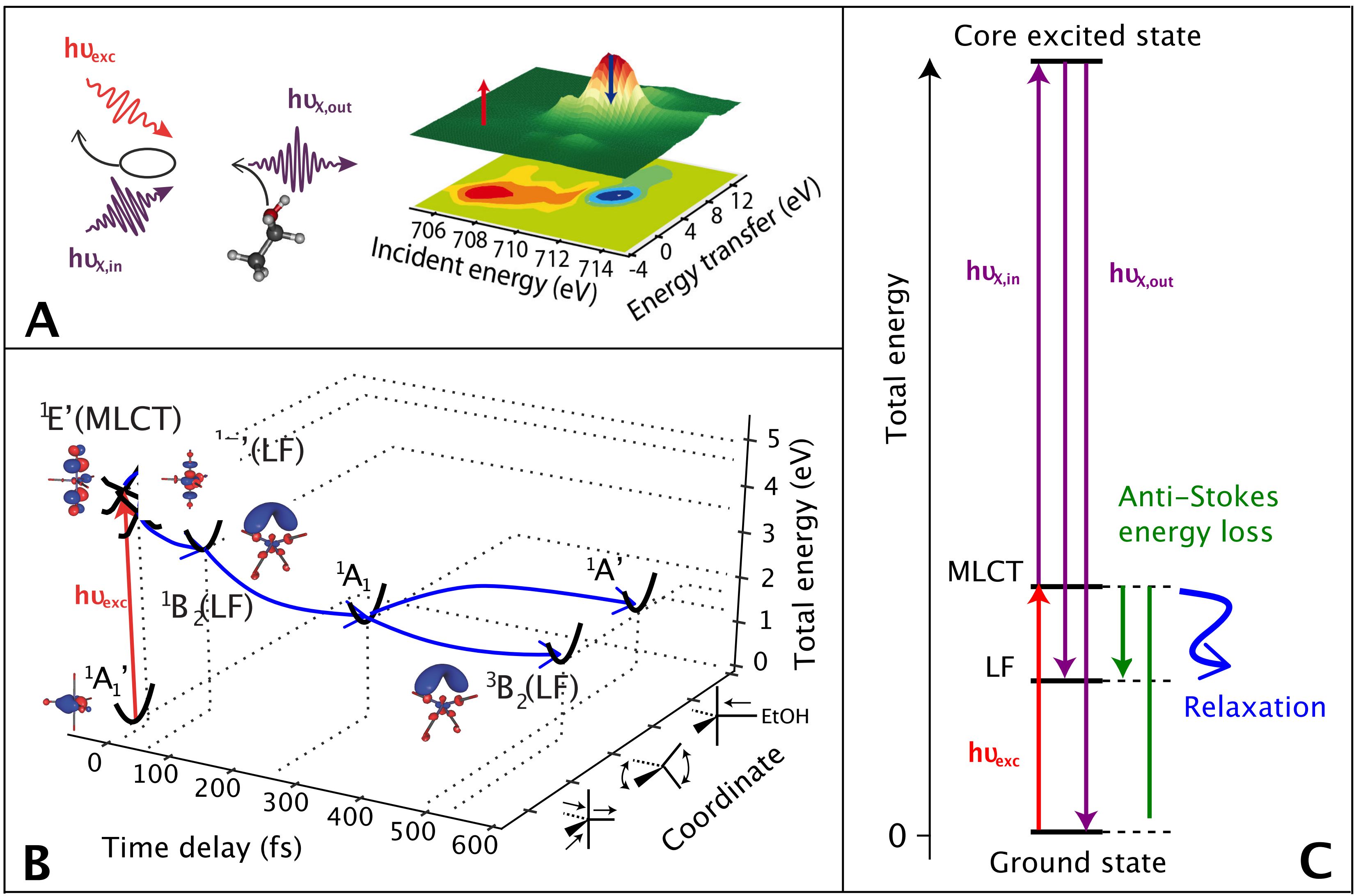


flexRIXS apparatus:

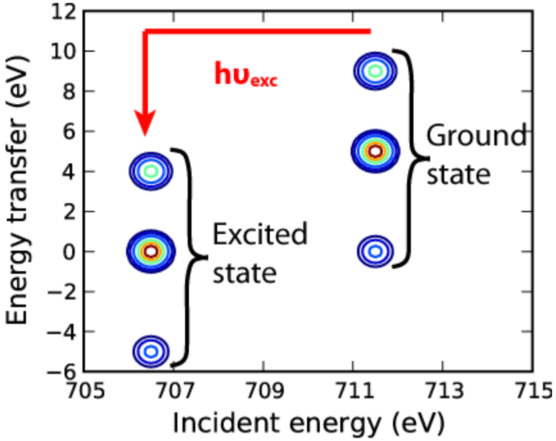
- BESSYII
- LCLS (2*10^{11} W/cm^2 (1.6*10^{10} phot/pulse damage at 6*10^{11} W/cm^2, 160 fs, 120 Hz
- 266 nm, 100 fs, 60 Hz, 10 µJ ~1.5*10^{11} W/cm^2
- 20 µm jet runs at 10 m/s, at 100 Hz: 10 cm between shots

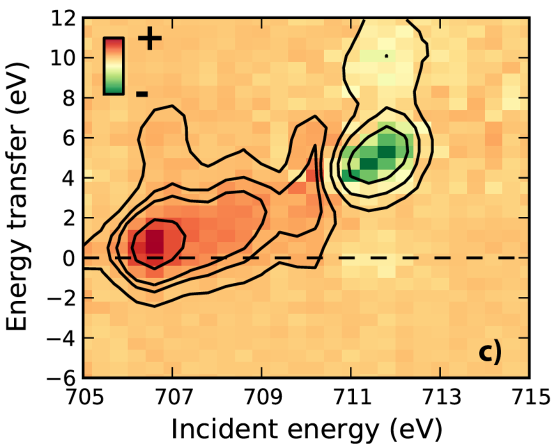


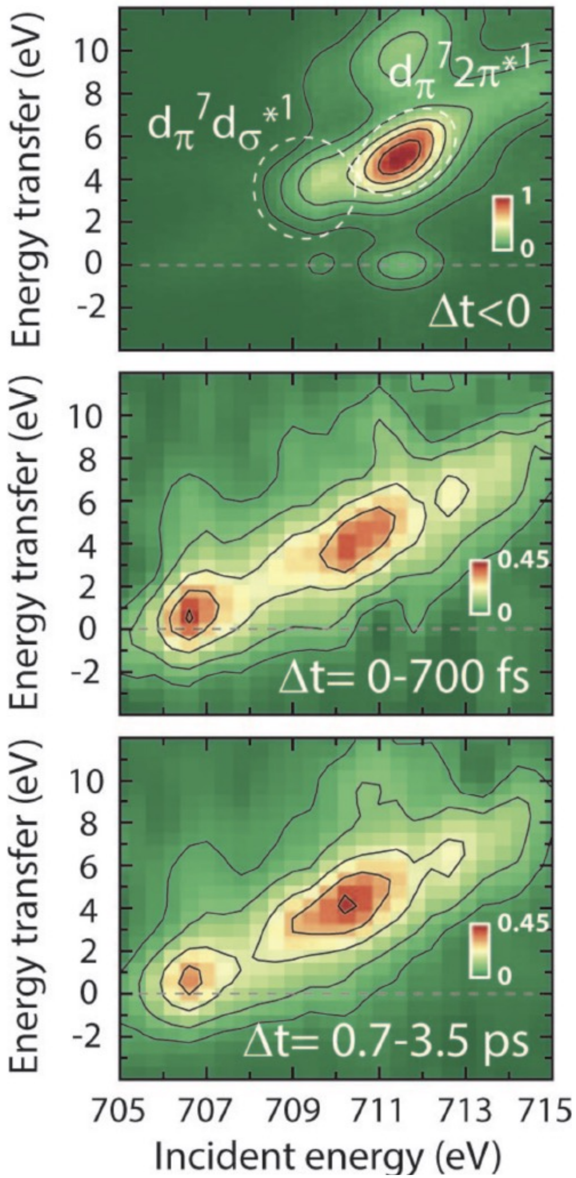
Evolution of excited state dynamics from Anti-Stokes RIXS



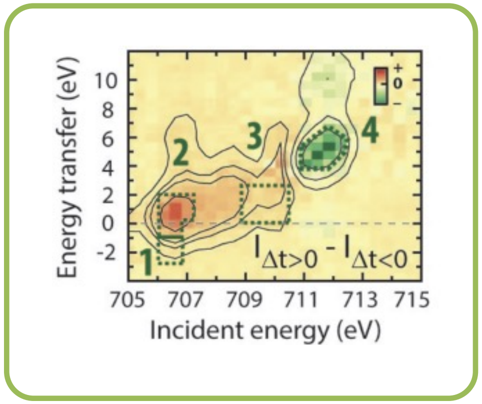
Evolution of excited state dynamics

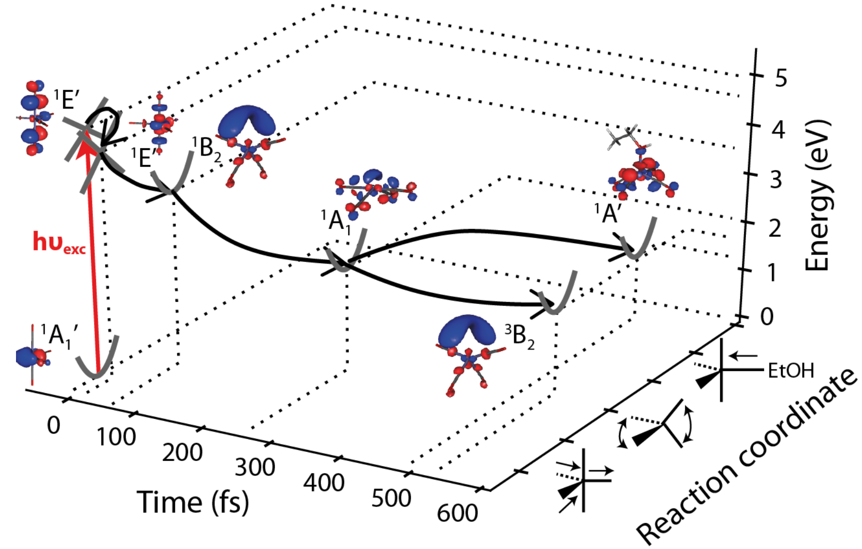


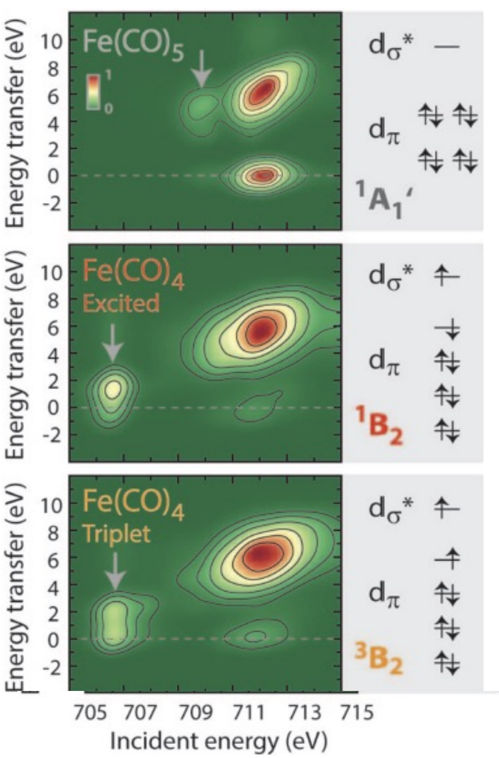


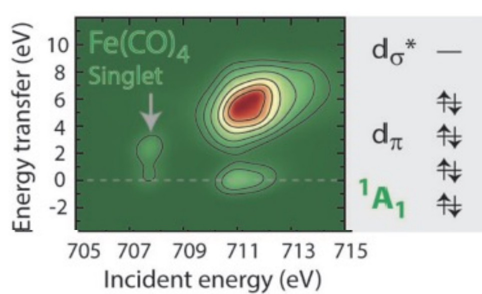


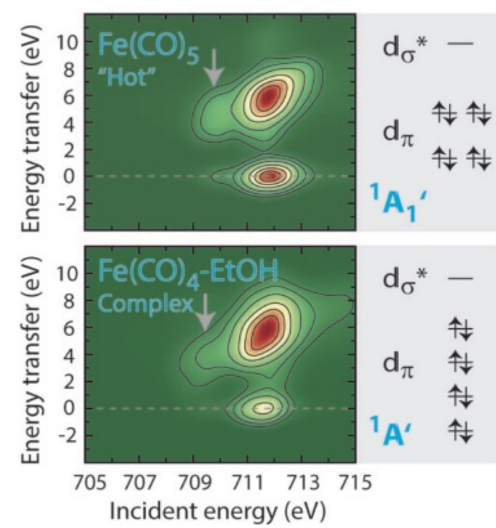
Pathway determination



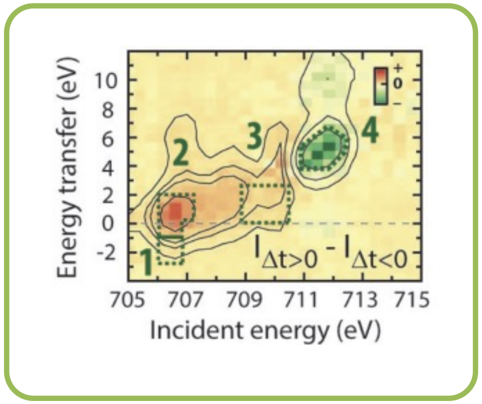


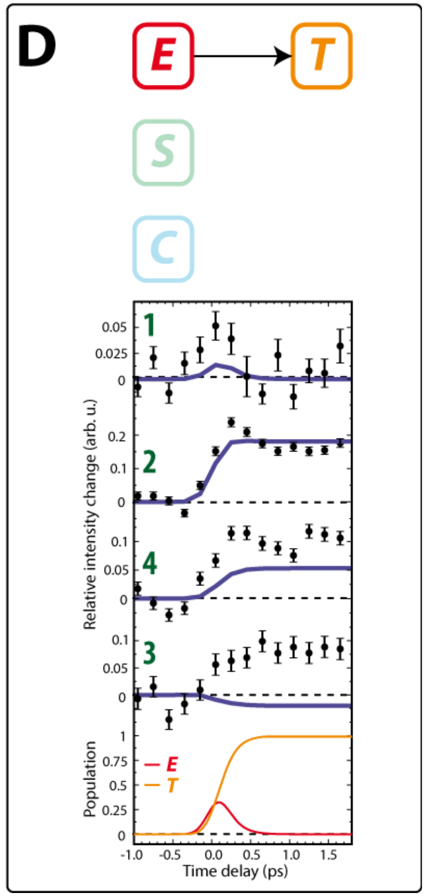


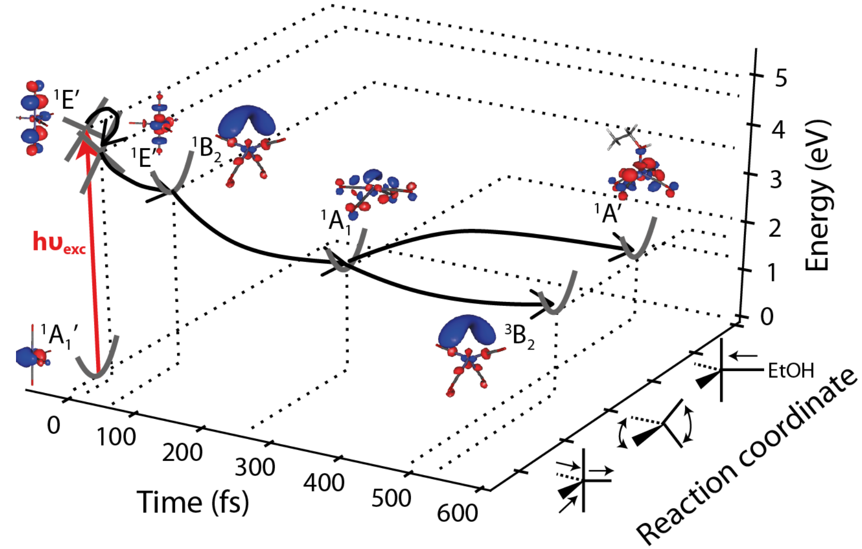


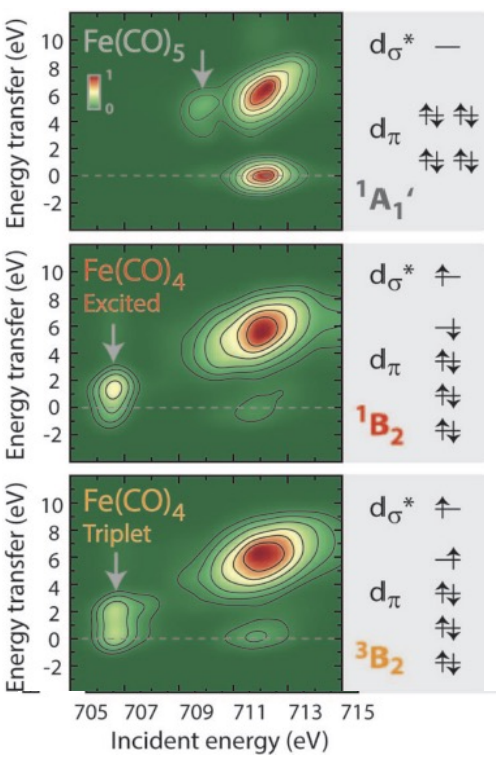


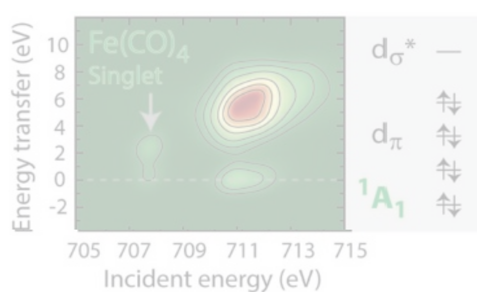
Pathway determination (Reaction via triplet intermediate and diffusion limited complexation, Snee, Harris, et al., JACS. 2001, 123, 6909. and JACS 2001, 123, 2255.)

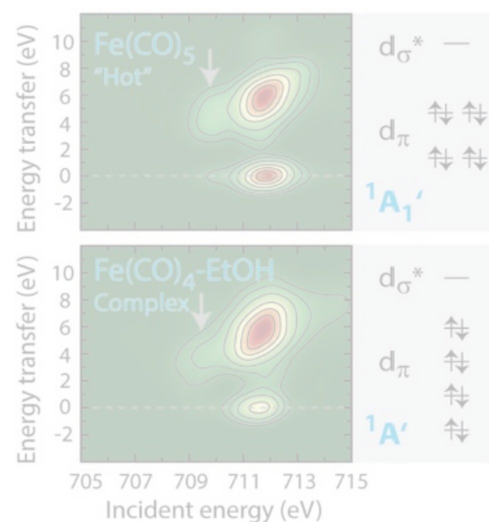




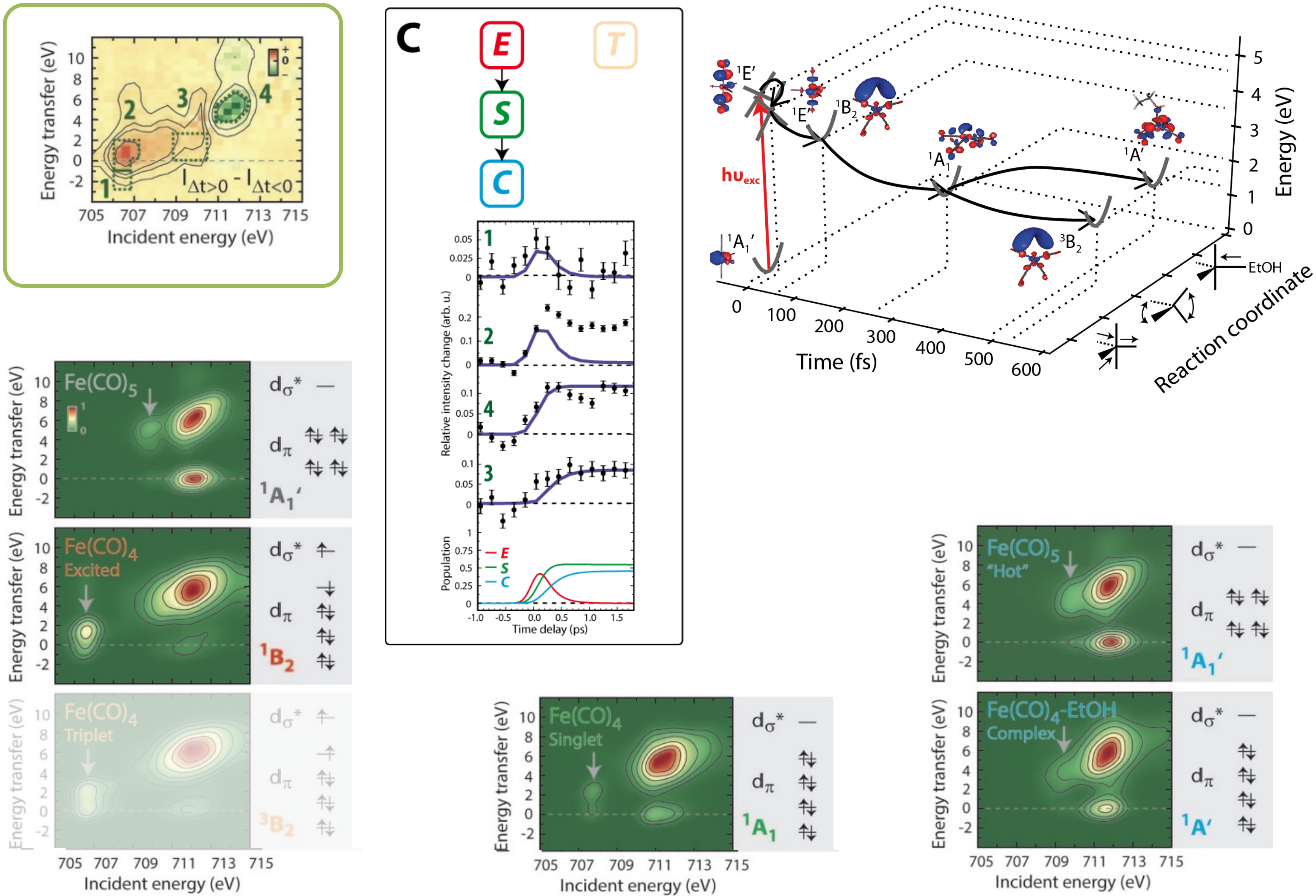




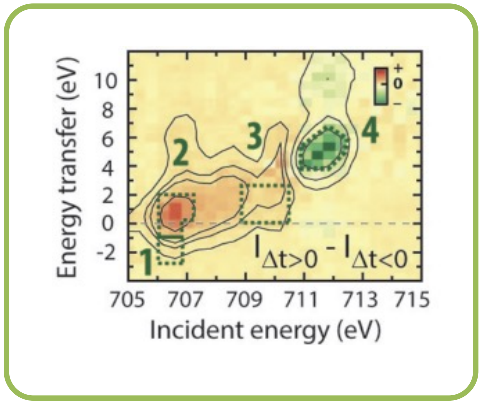


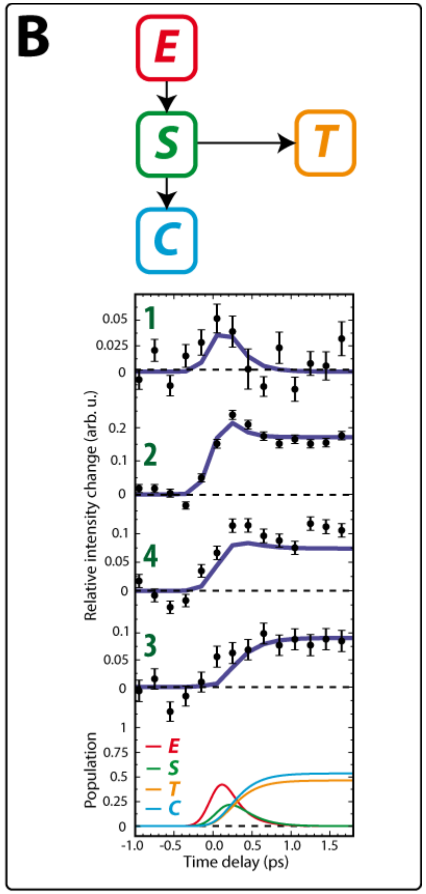


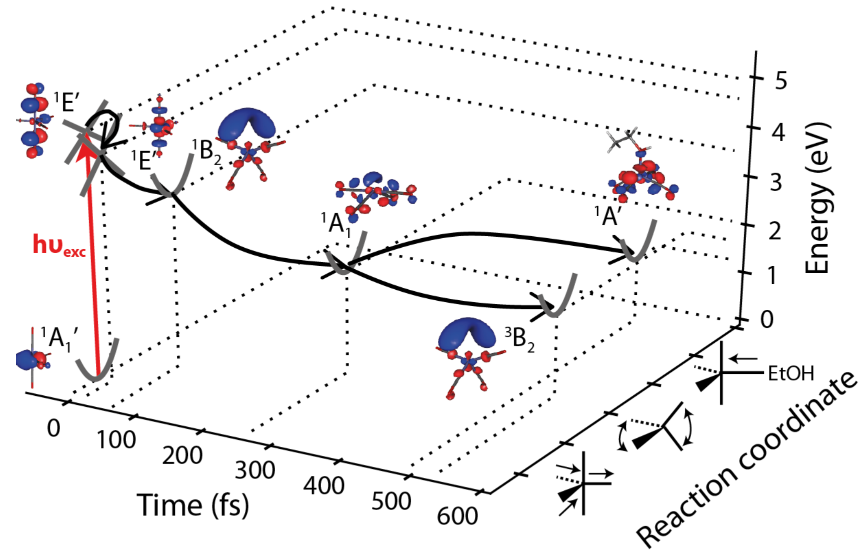
Pathway determination (Concentred ligand substitution reaction via singlet pathway, Ahr, Rose-Petruck, et al., PCCP. 2011, 13, 5590. Trushin, Fuss, et al., J. Phys. Chem. A 2000, 104, 1997.)

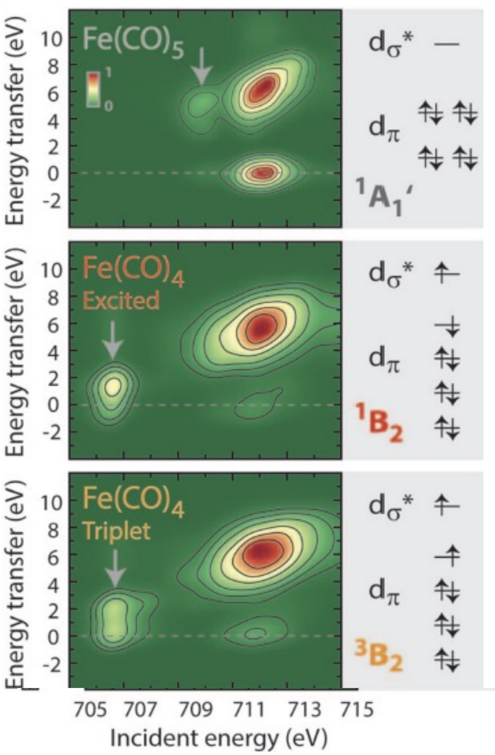


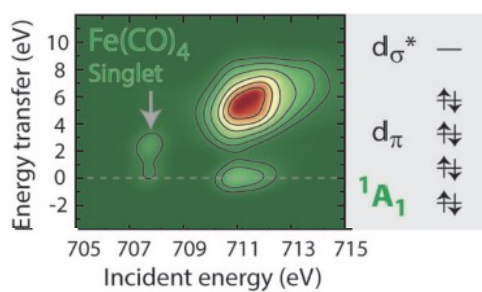
Pathway determination

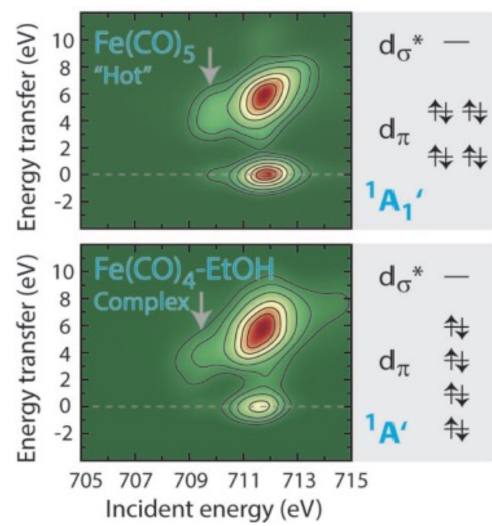






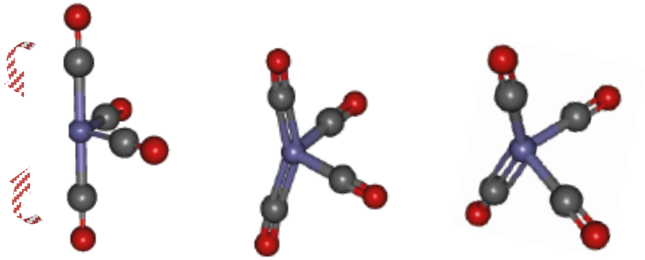




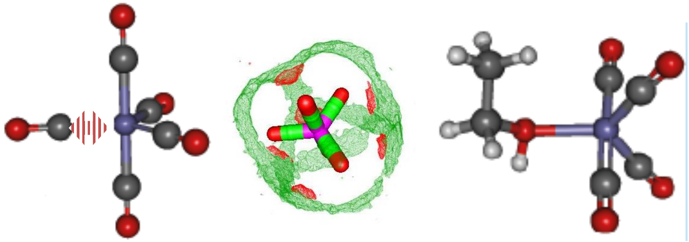


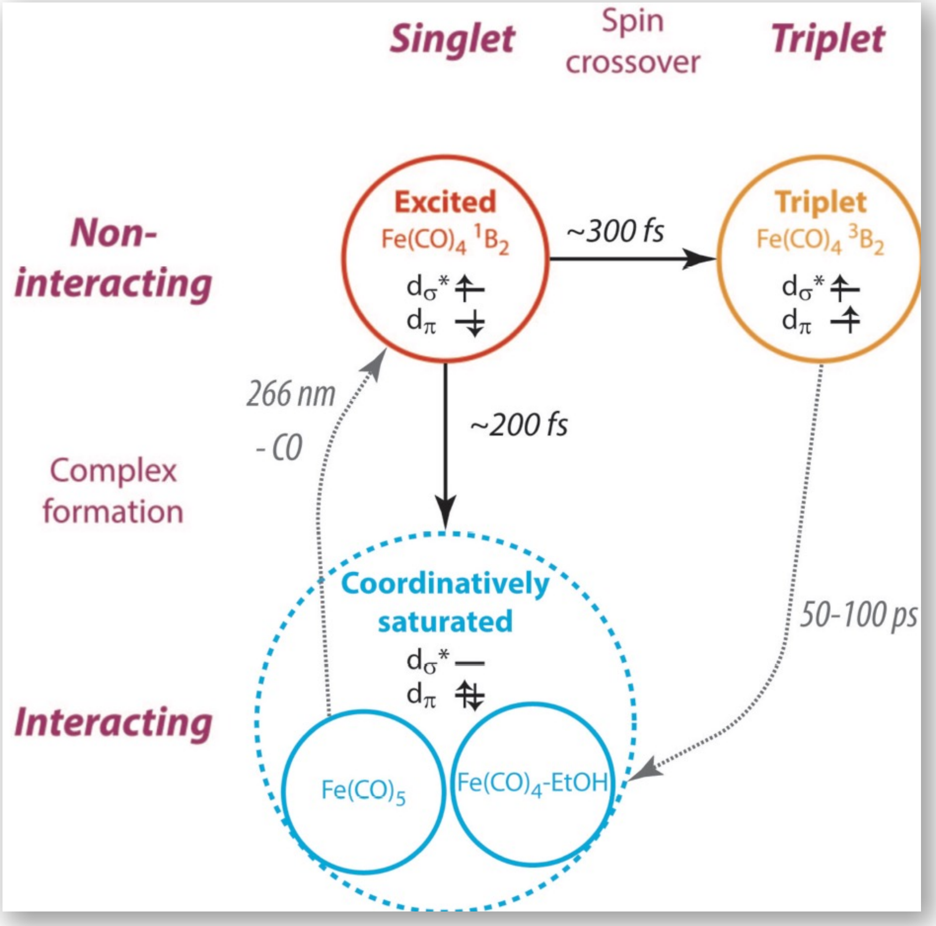
Parallel femtosecond spin-crossover, recombination and ligation

16 e⁻ configuration:
Spin and geometric relaxation

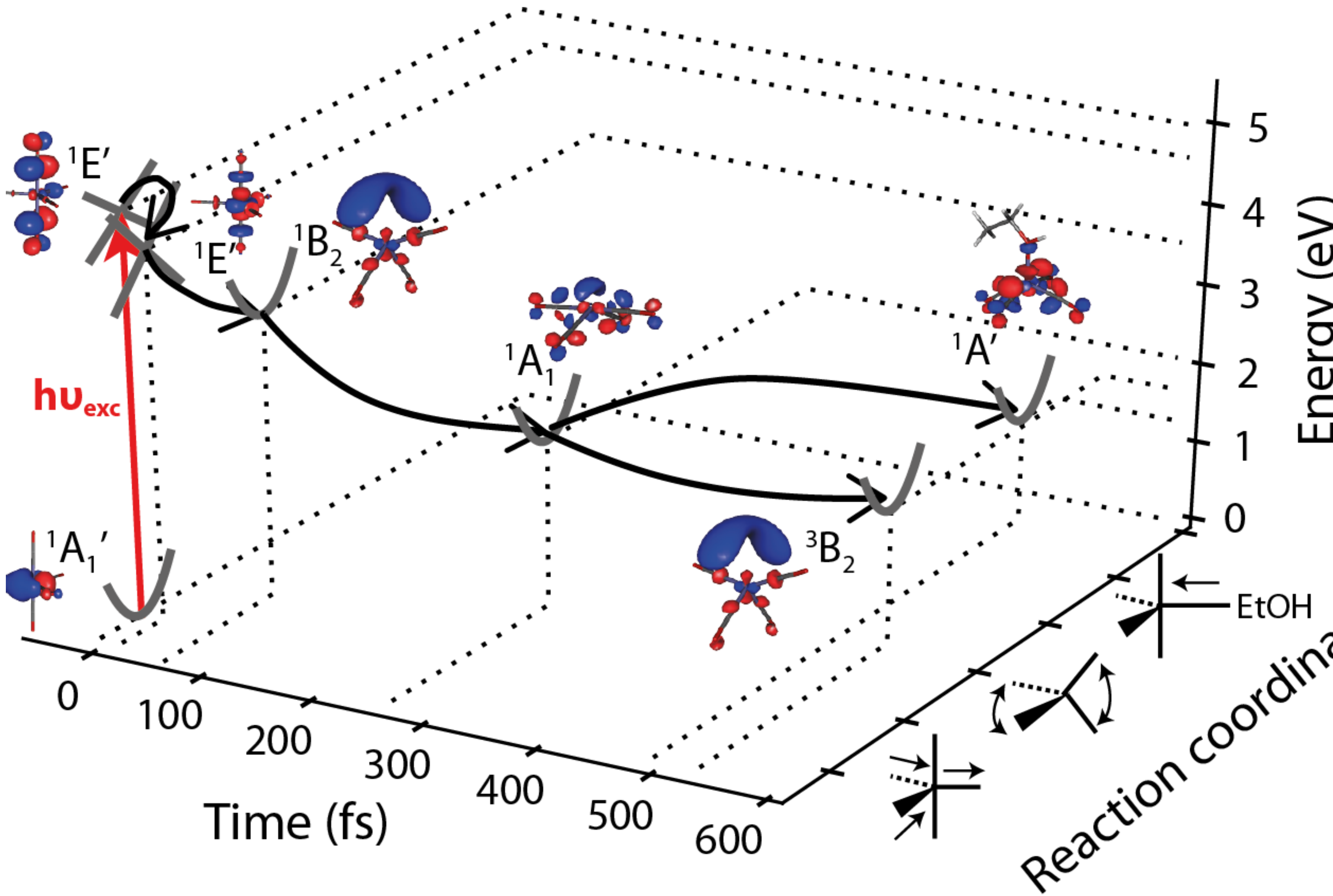


18 e⁻ configuration:
Geminate recombination complexation

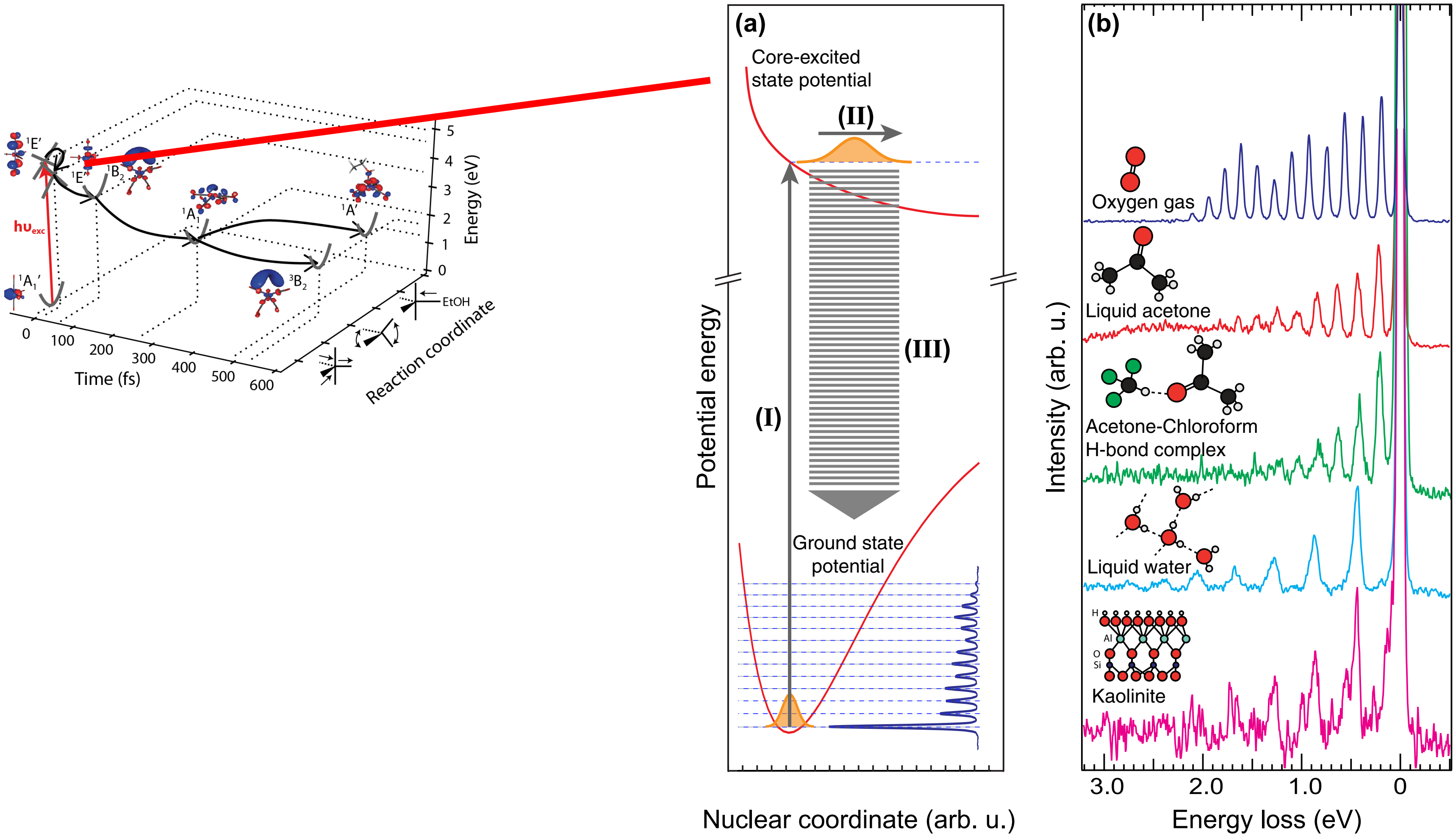




Gedankenexperiment: Can we taylor the X-ray pulse in order to learn about the initial curve crossings of excited states?

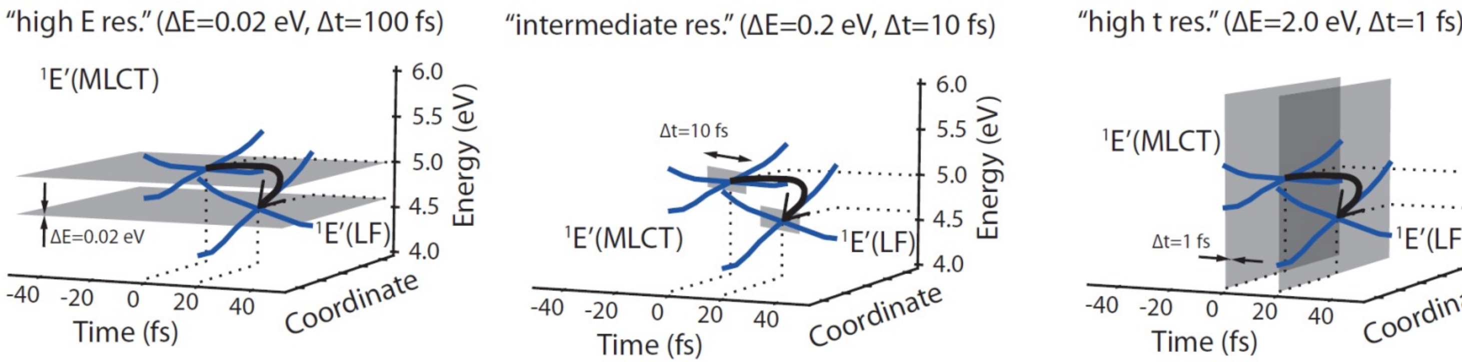


One way: Combine Anti-Stokes at sub-natural linewidth to access relevant curve crossings of excited states

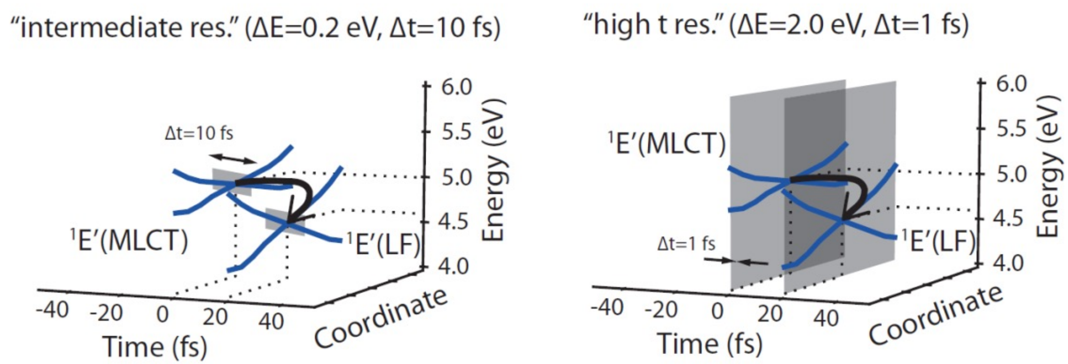


Ground state potential energy surfaces around selected atoms from resonant inelastic x-ray scattering
S Schreck, A. Pietzsch, B. Kennedy, C. Sathe, P. S. Miedema, S. Techert, V. N. Strocov, Th. Schmitt, F. Hennies, J.E. Rubensson, A. Föhlisch, Scientific RepoRts | 6:20054 | DOI: 10.1038/srep20054

RIXS with transform limited pulses – simulation $FeCO_5$ MLCT to LF



Where would SwissFEL come in there?



Low repetition rate < kHz

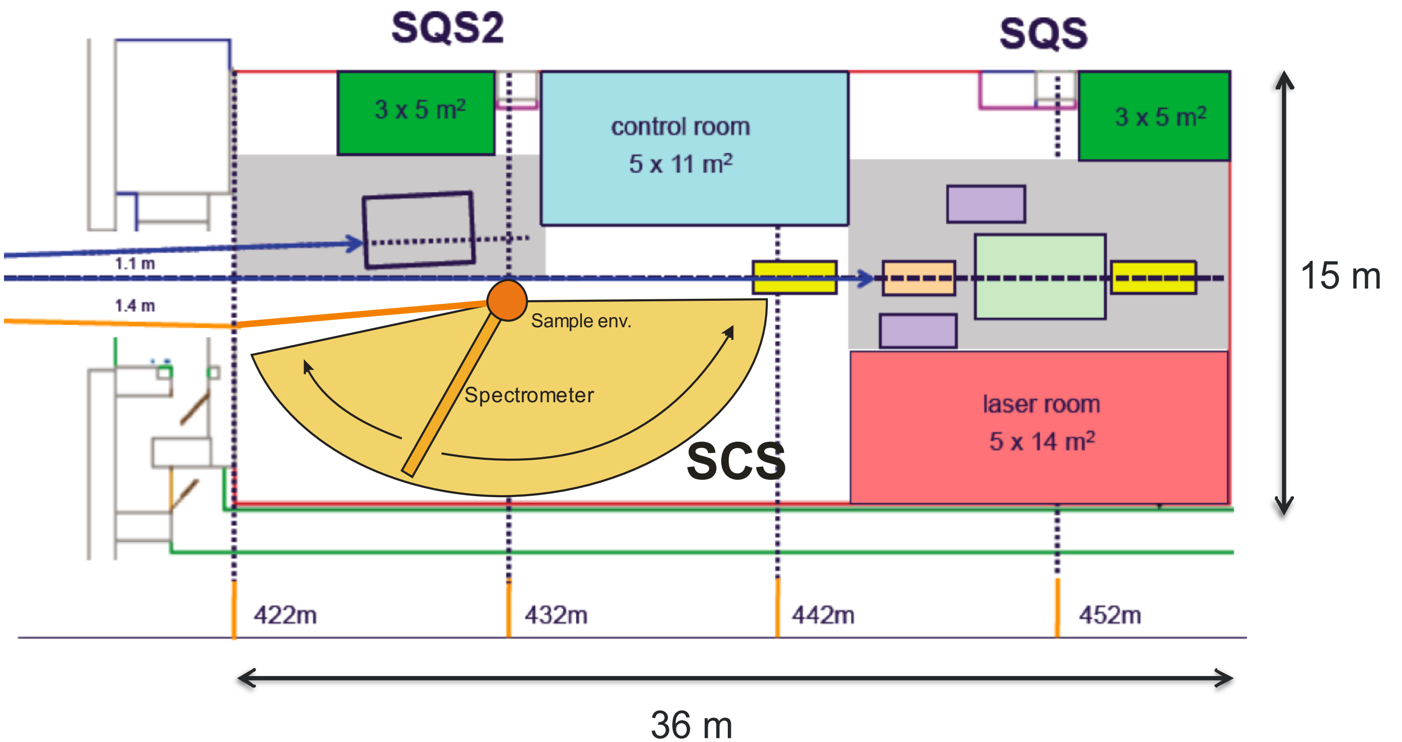
Focus on advanced state preparation

- Taylor the optical, IR and THz pulses to determine/control reaction pathways

- Taylor multi-colour FEL laser pulses for single and multi centre resonant spectroscopy
- synchronized to external Laser-system.

At XFEL: Get RIXS to the transform limit in time and energy

Beamline extension
- Mono flexible for time and energy resolution
- Focus variable, optimized for RIXS

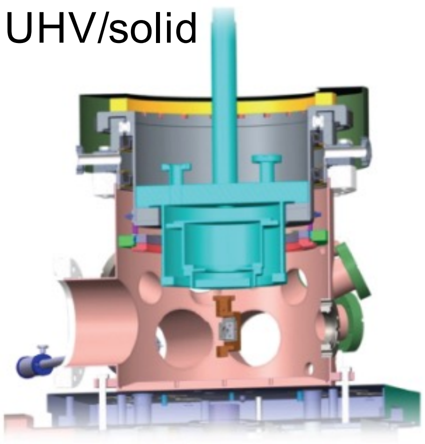


Spectrometer
- Acceptance
- Detection Angle
- combined res.30,000 at Cu-L3
- allow for stimulated processes

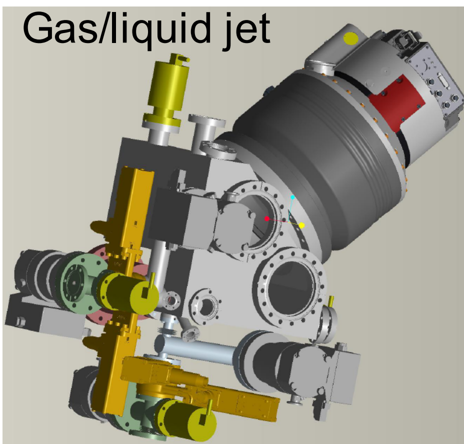
hRIXS consortium:
T. Laarmann, S. Techert, G. Ghiringhelli, F. Senf, A.F. et al.

Modular Sample Environments

UHV/solid

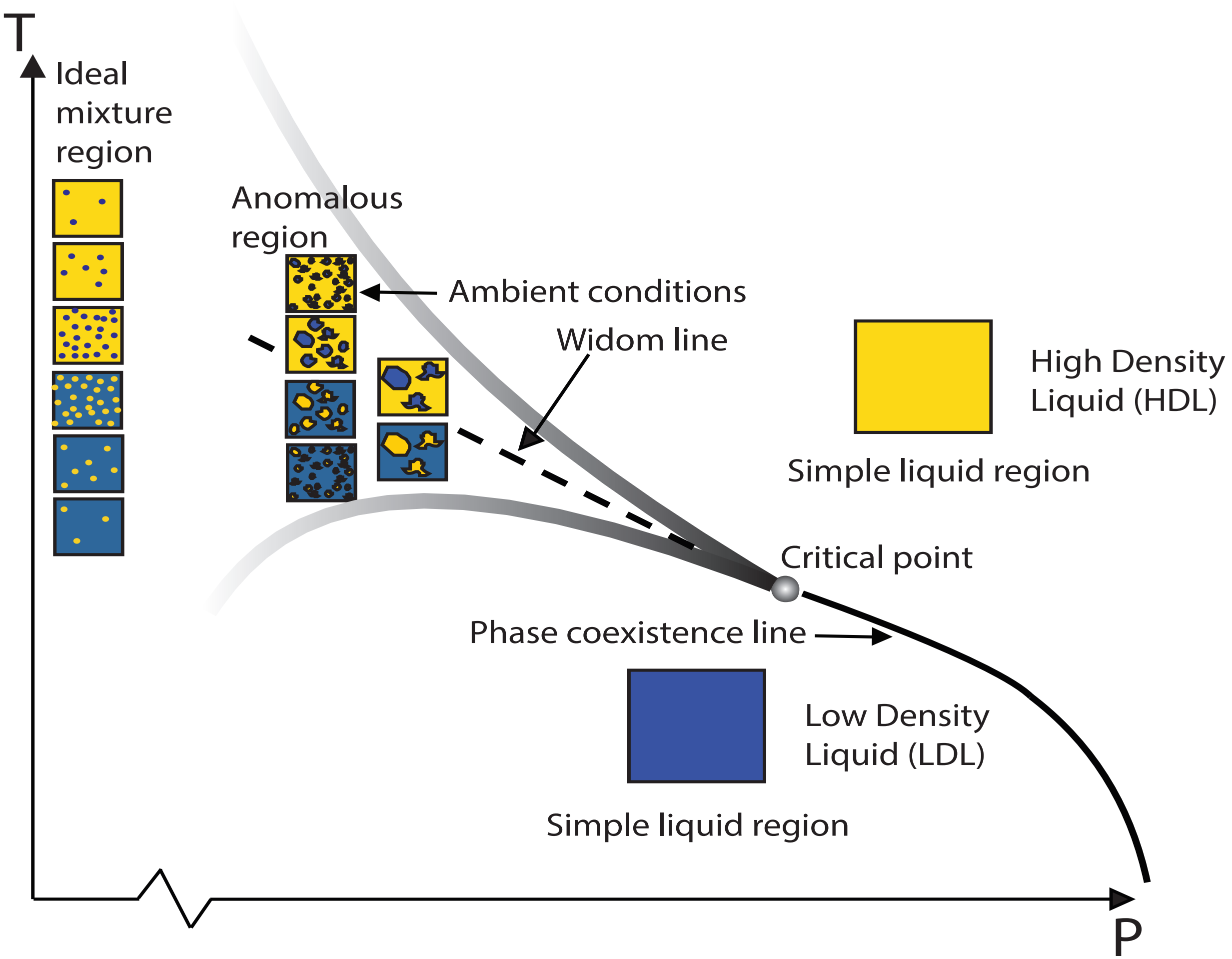


Gas/liquid jet



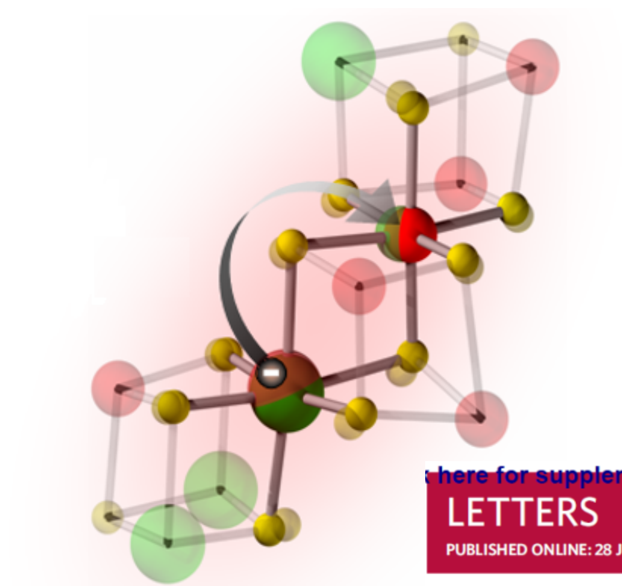
What else would we want? Non local nanoscale aspects in solution environments probed by RIXS and coherent scattering

A. Nilsson and L. G. M. Pettersson, *Nature Comm*. 6, 8998 (2015).



Hypothetical phase diagram of liquid water showing the liquid-liquid coexistence line between LDL and HDL in terms of simple liquid regions, the critical point (real or virtual), the Widom line in the one-phase region and fluctuations on different length scales emanating from the critical point giving rise to local spatially separated regions in the anomalous region. Shaded lines indicate how far fluctuations might extend.

What else would we want?
Transfer of excitation between atomic centers



FLASH & LCLS

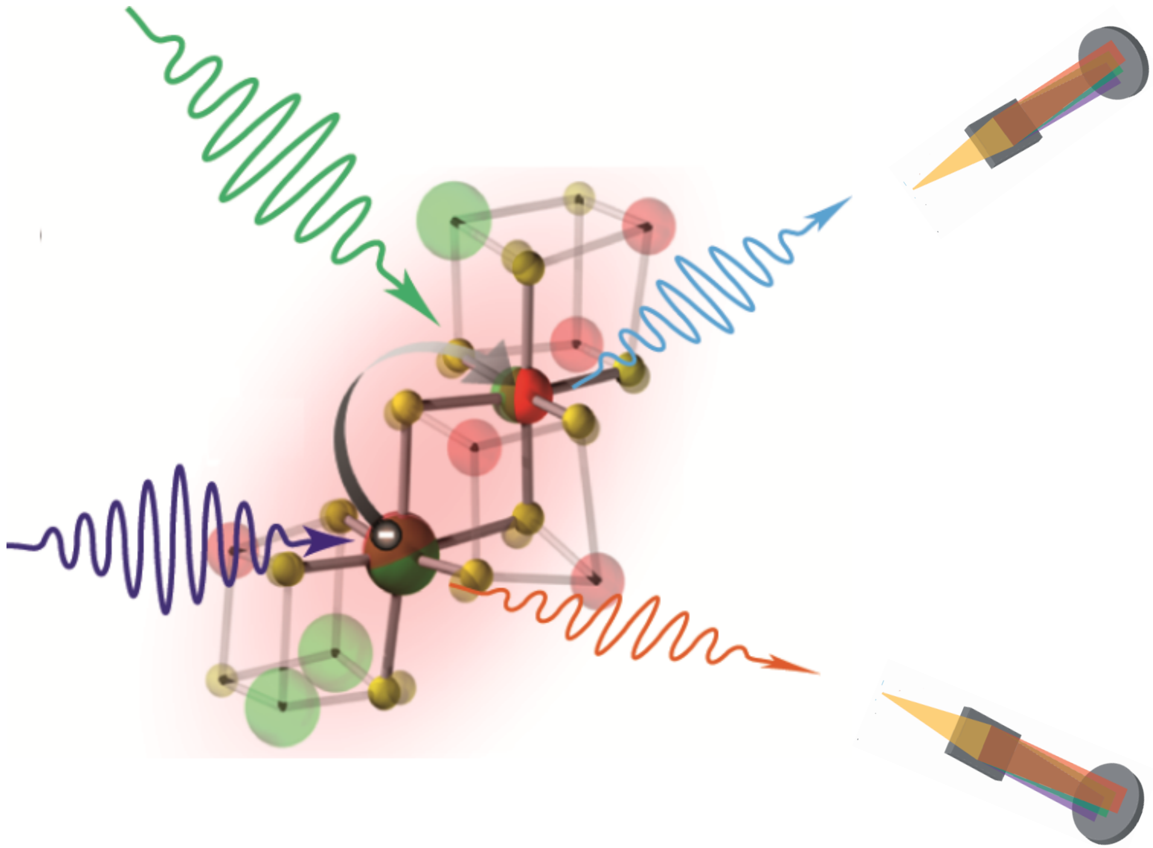
here for supplementary data

LETTERS
PUBLISHED ONLINE: 28 JULY 2013 | DOI: 10.1038/NMAT3718
nature materials

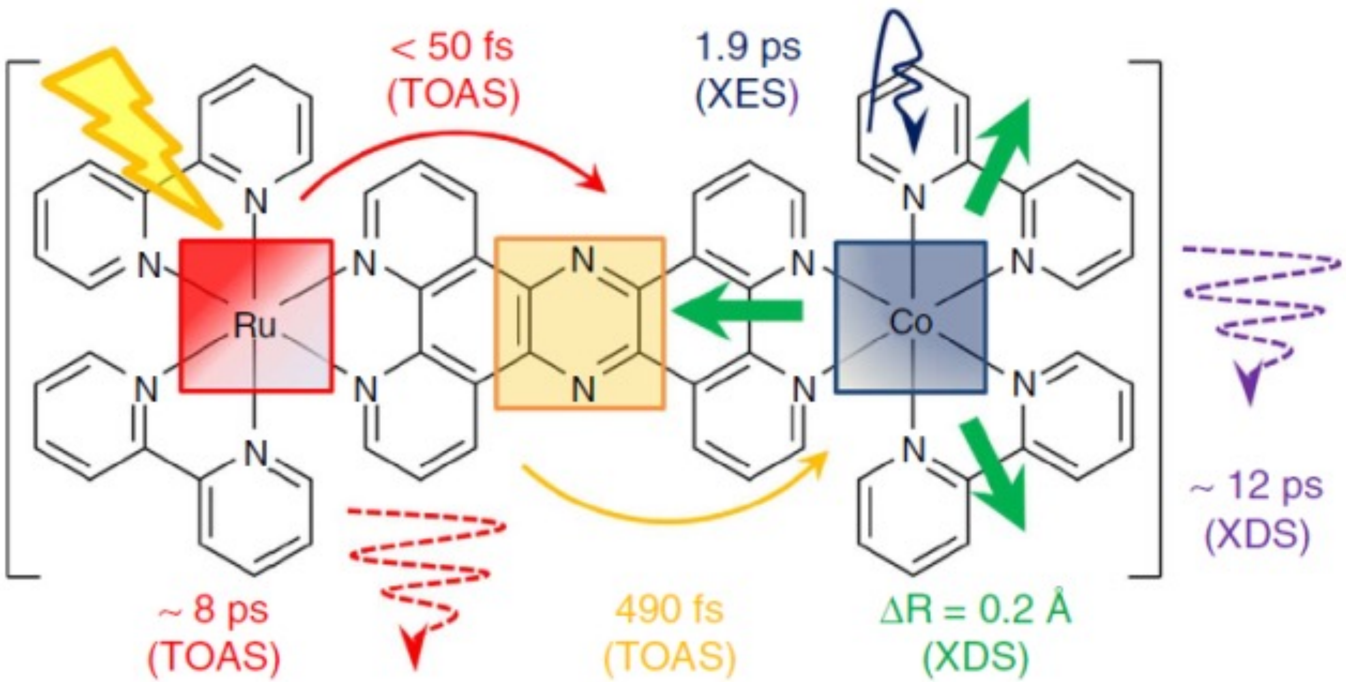
Speed limit of the insulator–metal transition in magnetite

S. de Jong[1†], R. Kukreja[1,2†], C. Trabant[3,4,5], N. Pontius[4], C. F. Chang[3,6], T. Kachel[4], M. Beye[4], F. Sorgenfrei[4,7], C. H. Back[1,8], B. Bräuer[1], W. F. Schlotter[9], J. J. Turner[9], O. Krupin[9,10], M. Doehler[3], D. Zhu[1], M. A. Hossain[1], A. O. Scherz[1,10], D. Fausti[11,12], F. Novelli[12], M. Esposito[11,12], W. S. Lee[1], Y. D. Chuang[13], D. H. Lu[14], R. G. Moore[1], M. Yi[1], M. Trigo[1], P. Kirchmann[1], L. Pathey[15], M. S. Golden[1,16], M. Buchholz[3], P. Metcalf[17], F. Parmigiani[11,12], W. Wurth[7], A. Föhlisch[4,5], C. Schüßler-Langeheine[3,4]★ and H. A. Dürr[1]★

Multi centre dynamics between atomic moities
Non-linear soft X-ray spectroscopy: 4 wave mixing



Multi centre dynamics between atomic moities
Transfer of excitation between atomic centers



SACLA

nature COMMUNICATIONS

ARTICLE

Received 7 Oct 2014 | Accepted 23 Jan 2015 | Published 2 Mar 2015 DOI: 10.1038/ncomms7359 OPEN

Visualizing the non-equilibrium dynamics of photoinduced intramolecular electron transfer with femtosecond X-ray pulses

Sophie E. Canton[1,*], Kasper S. Kjær[2,3,*], György Vankó[4], Tim B. van Driel[3], Shin-ichi Adachi[5], Amélie Bordage[4,†], Christian Bressler[6,7], Pavel Chabera[8], Morten Christensen[3], Asmus O. Dohn[9], Andreas Galler[6], Wojciech Gawelda[6], David Gosztola[10], Kristoffer Haldrup[3], Tobias Harlang[8], Yizhu Liu[11], Klaus B. Møller[9], Zoltán Németh[4], Shunsuke Nozawa[5], Mátyás Pápai[4], Tokushi Sato[5,†], Takahiro Sato[12,†], Karina Suarez-Alcantara[1,†], Tadashi Togashi[13], Kensuke Tono[13], Jens Uhlig[8], Dimali A. Vithanage[8], Kenneth Wärnmark[11], Makina Yabashi[12], Jianxin Zhang[11,†], Villy Sundström[8] & Martin M. Nielsen[3]

Non linear X-ray optics has been dealt with already in „dark ages“

VOLUME 25, NUMBER 18 PHYSICAL REVIEW LETTERS 2 NOVEMBER 1970

Optically Modulated X-Ray Diffraction

Isaac Freund and B. F. Levine
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 26 August 1970)

PRL 25,1241 (1970)

PHYSICAL REVIEW A VOLUME 3, NUMBER 3 MARCH 1971

Mixing of X-Ray and Optical Photons

P. M. Eisenberger and S. L. McCall
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
(Received 26 August 1970)

PRA 3,1145 (1971)

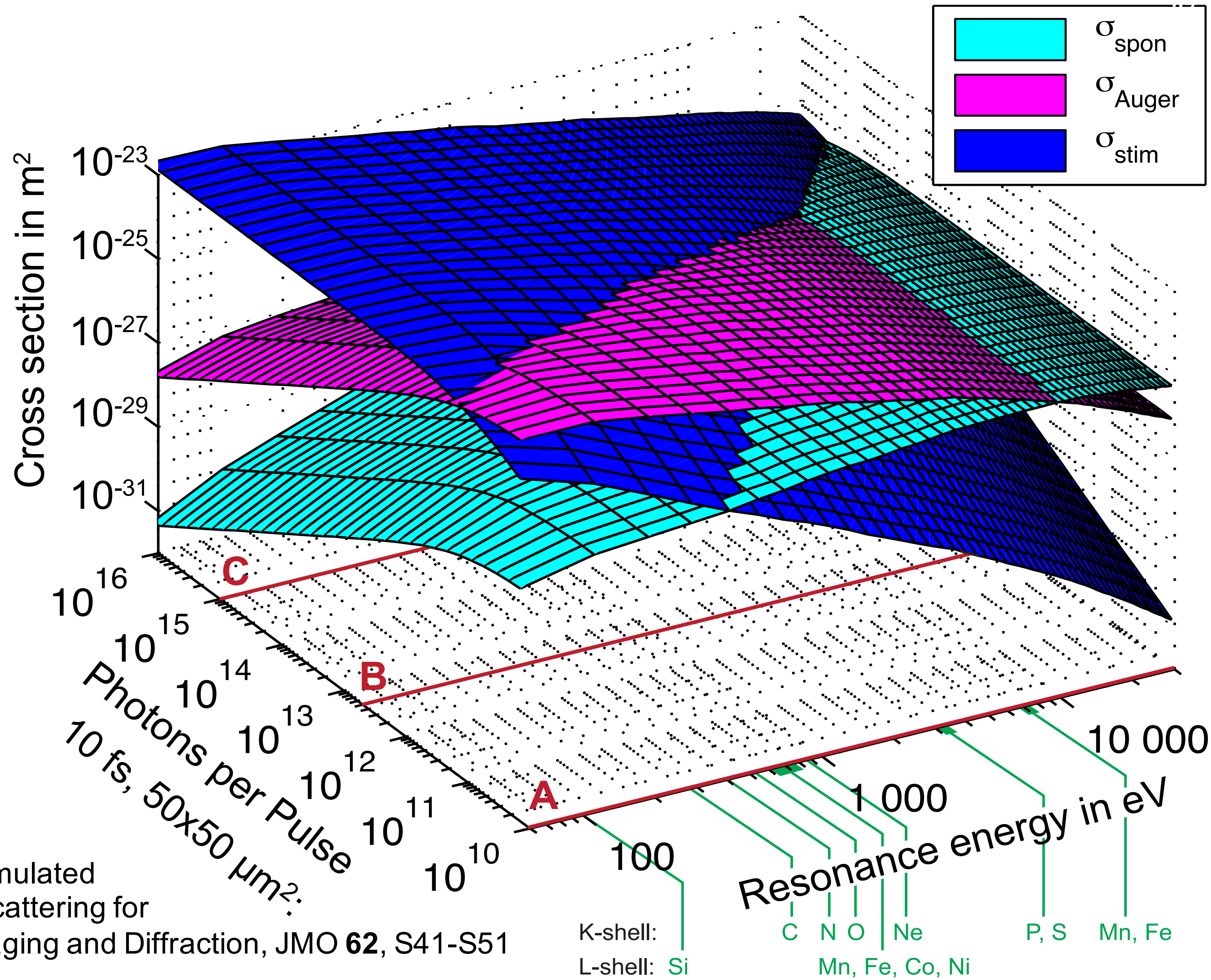
Nonlinear effects involving x-ray and optical photons are described with particular emphasis on the generation of sum and difference frequencies. Efficiencies for sum and difference frequency generation are calculated and found to be large enough to be observable. The expected advent of x-ray lasers should enhance the usefulness of such mixing techniques in the measurement of excited-state wave functions. Under favorable circumstances, the mixing technique may provide a means of efficiently tuning x-ray laser outputs.

A unified view of Raman, resonance Raman and fluorescence spectroscopy,
D Lee and AC Albrecht,
Adv. IR and Raman Spect, Wiley, 12, 179 (1985)

Multiple core-hole coherence in x-ray four-wave-mixing spectroscopies
Shaul Mukamel
PRB 72, 235110 (2005)

Resource Letter on Stimulated Inelastic X-ray Scattering at an XFEL
B. D. Patterson
SLAC technical Note SLAC-TN-10-026 (2010)

Stimulated X-ray scattering sizeable with soft X-rays, less with hard X-rays



Implications of Stimulated Resonant X-ray Scattering for Spectroscopy, Imaging and Diffraction, JMO **62**, S41-S51 (2015)

Conclusions

- Beat complexity through the selectivity of resonant X-ray spectroscopy

- New selectivities/opportunities from non-linear spectroscopy with X-rays:
  - stimulated processes strong for soft, less for hard X-rays
  - multi-center dynamics
- Is there a science case for nano scale order and RIXS/coherent scattering in solution environments?

- At SwissFEL take advantage of low repetition rate < kHz
  - Focus on advanced state preparation
    - Taylor the optical, IR and THz pulses to determine/control reaction pathways
    - Taylor multi-colour FEL laser pulses for single and multi centre resonant spectroscopy
    - synchronized to external Laser-system.

- Highest rep rate at XFEL Heisenberg RIXS with transform limited pulses will reveal in combination with sub-natural linewidth RIXS currently unaccessible dynamics. i.e. the MLCT to LF transition.

The projects and the people!

Identification of the dominant photochemical pathways and mechanistic insights to the ultrafast ligand exchange of $Fe(CO)_5$ to $Fe(CO)_4EtOH$

K. Kunnus, I. Josefsson, I. Rajkovic, S. Schreck, W. Quevedo, M. Beye, C. Weniger, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, K. J. Gaffney, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, S. Techert, M. Odelius, Ph. Wernet and A. Föhlisch

Struct. Dyn. 3, 043204 (2016)

Orbital-specific mapping of the ligand exchange dynamics of $Fe(CO)_5$ in solution

P. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, S. Schreck, W. Quevedo, M. Beye, C. Weniger, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. Hartsock, K. Gaffney, W. Schlotter, J. Turner, B. Kennedy, F. Hennies, F. de Groot, S. Techert, M. Odelius, A. Föhlisch, Nature 520 (7545), 78-81 (2015)

Anti-Stokes X-ray Raman Scattering for excited state dynamics

Kristjan Kunnus, Ida Josefsson, Michael Odelius, Philippe Wernet, Alexander Föhlisch, submitted

---

Implications of stimulated resonant X-ray scattering for spectroscopy, imaging, and diffraction in the regime from soft to hard X-rays

S. Schreck, M. Beye, and A. Föhlisch, JMO 62, S41-S51 (2015),

Stimulated X-ray emission for materials science,

M. Beye, S. Schreck, F. Sorgenfrei, C.Trabant, N. Pontius, C. Schüßler-Langeheine, W. Wurth, and A. Föhlisch Nature 501 191 (2013) DOI: 10.1038/nature12449

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

S Schreck, A. Pietzsch, B. Kennedy, C. Såthe, P. S. Miedema, S. Techert, V. N. Strocov, Th. Schmitt, F. Hennies, J.E. Rubensson, A. Föhlisch,

Scientific Reports | 6:20054 | DOI: 10.1038/srep20054 (2016)