Where Are the Electrons?

New opportunities for mapping local chemical interaction dynamics with time-resolved soft x-ray spectroscopy at FELs

Philippe Wernet

Institute for Methods and Instrumentation for Synchrotron Radiation Research

Helmholtz-Zentrum Berlin für Materialien und Energie

wernet@helmholtz-berlin.de

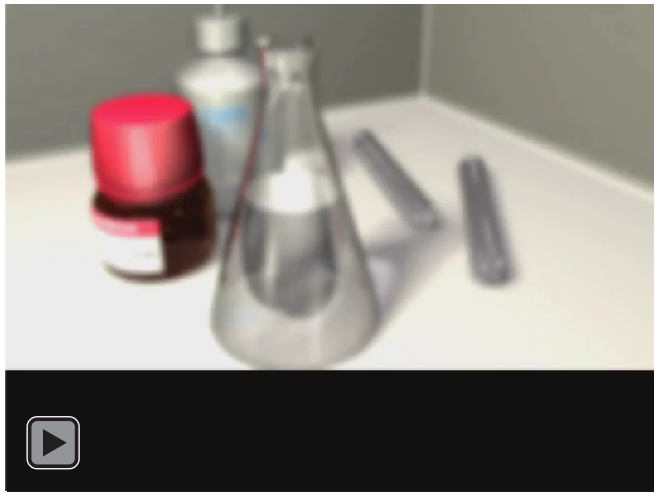
37th International Free Electron Laser Conference (FEL2015), Daejeon, Korea, August 2015

Understand, predict, and control the relationship of structure and function

Mechanistic understanding on atomic length (Å) and time scales (fs)

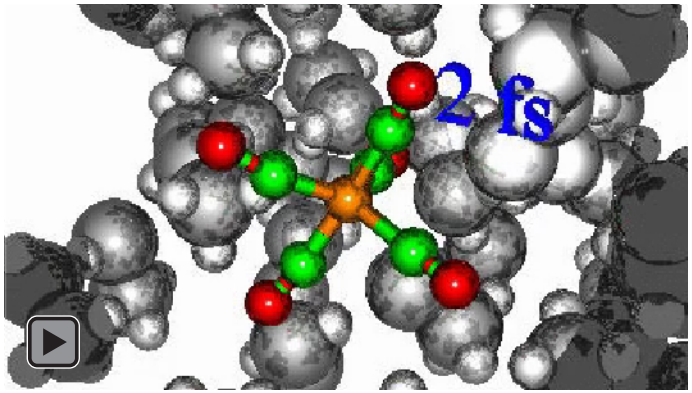
The molecular movie

Organic chemistry



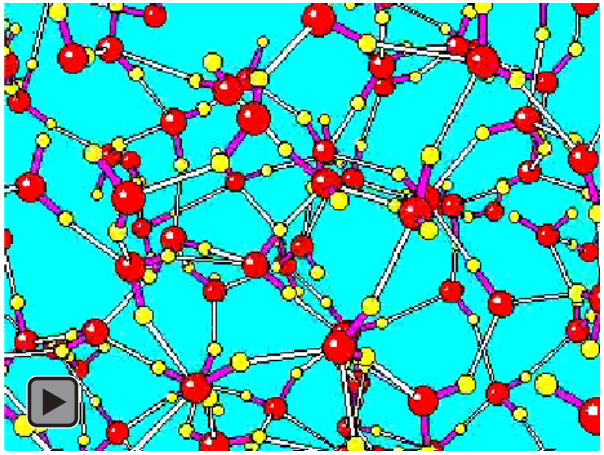
http://www.moleculermovies.com/

Photochemistry



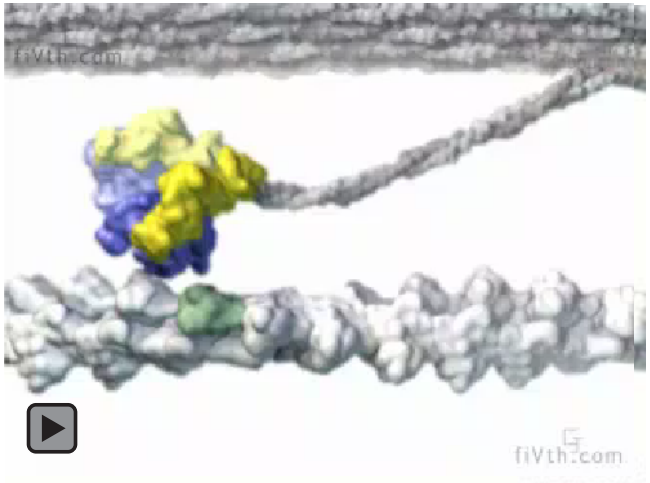
Michael Odelius, Stockholm University , Sweden

Water



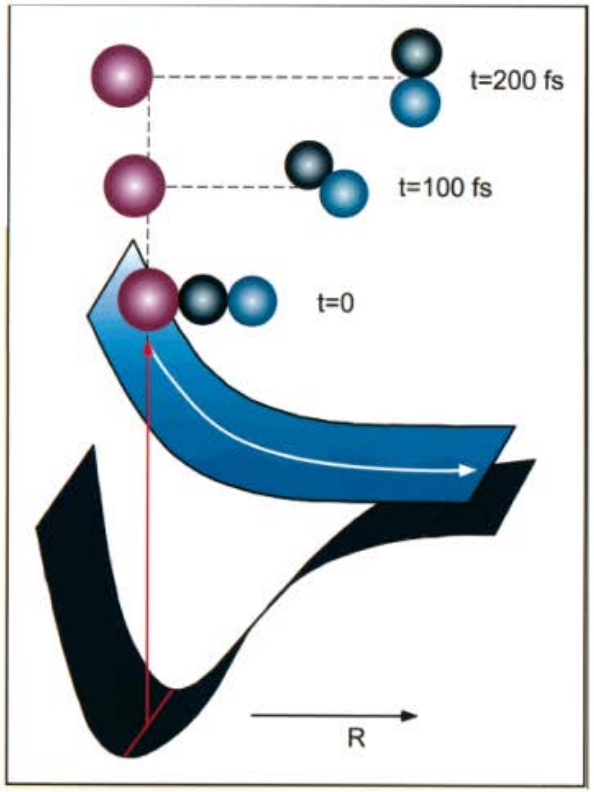
Lars Ojamäe, Linköping University , Sweden

Molecular motors

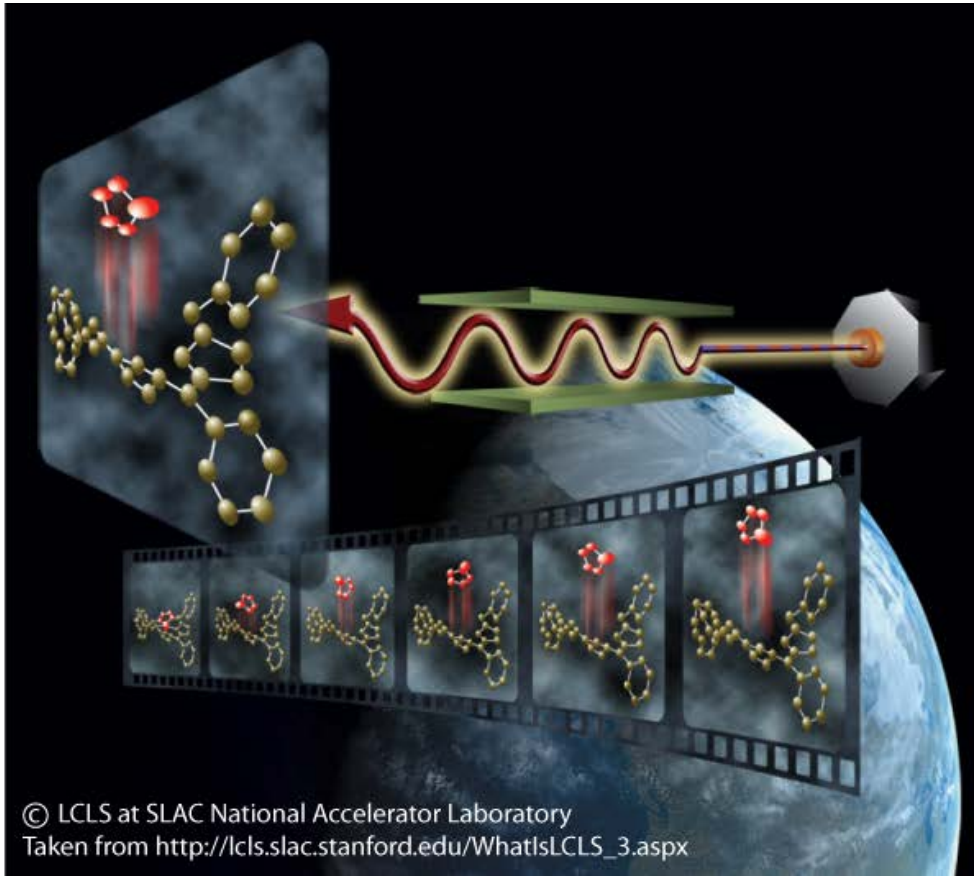


http://www.moleculermovies.com/

The molecular movie

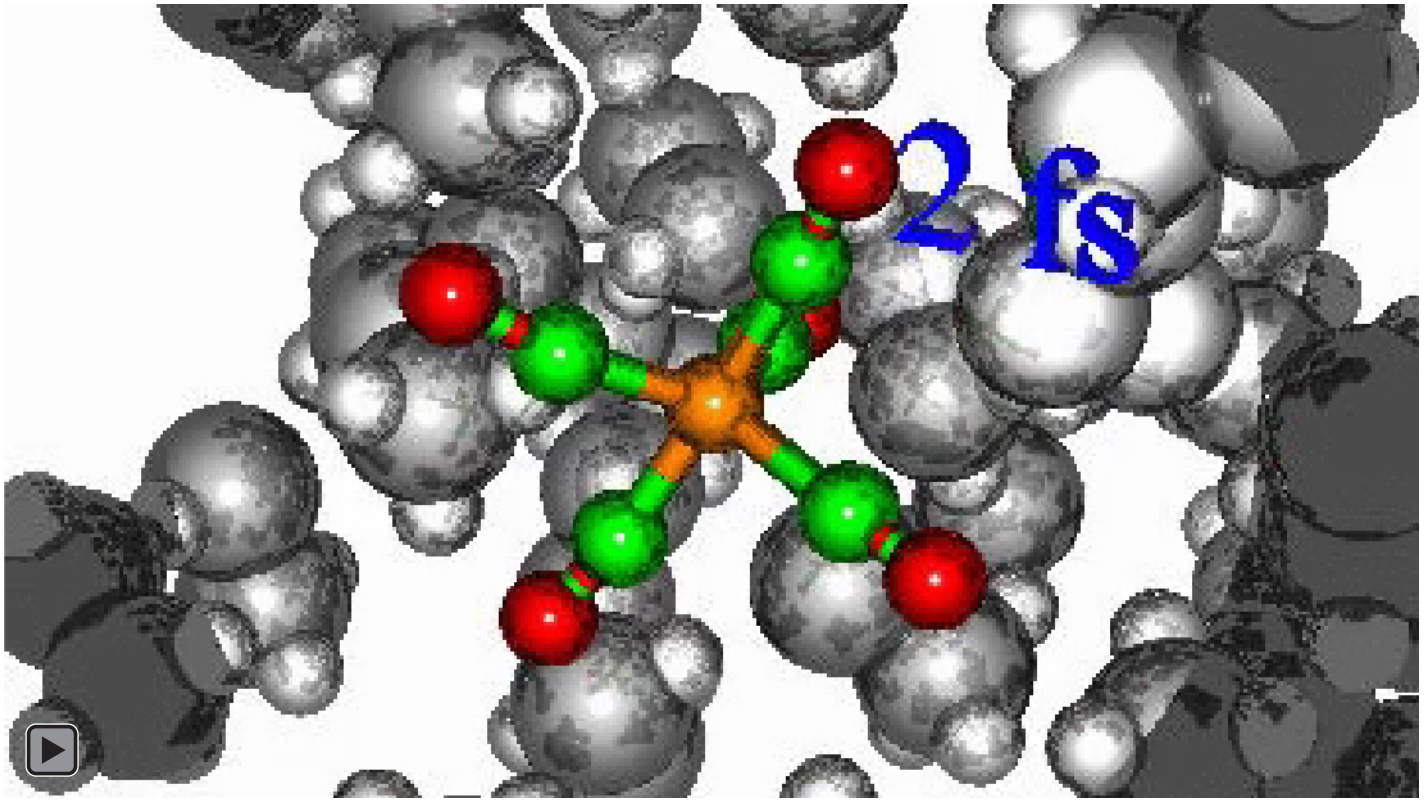


A. H. Zewail, *J. Phys. Chem. A.* **104**, 5660 (2000)



Where are the electrons?

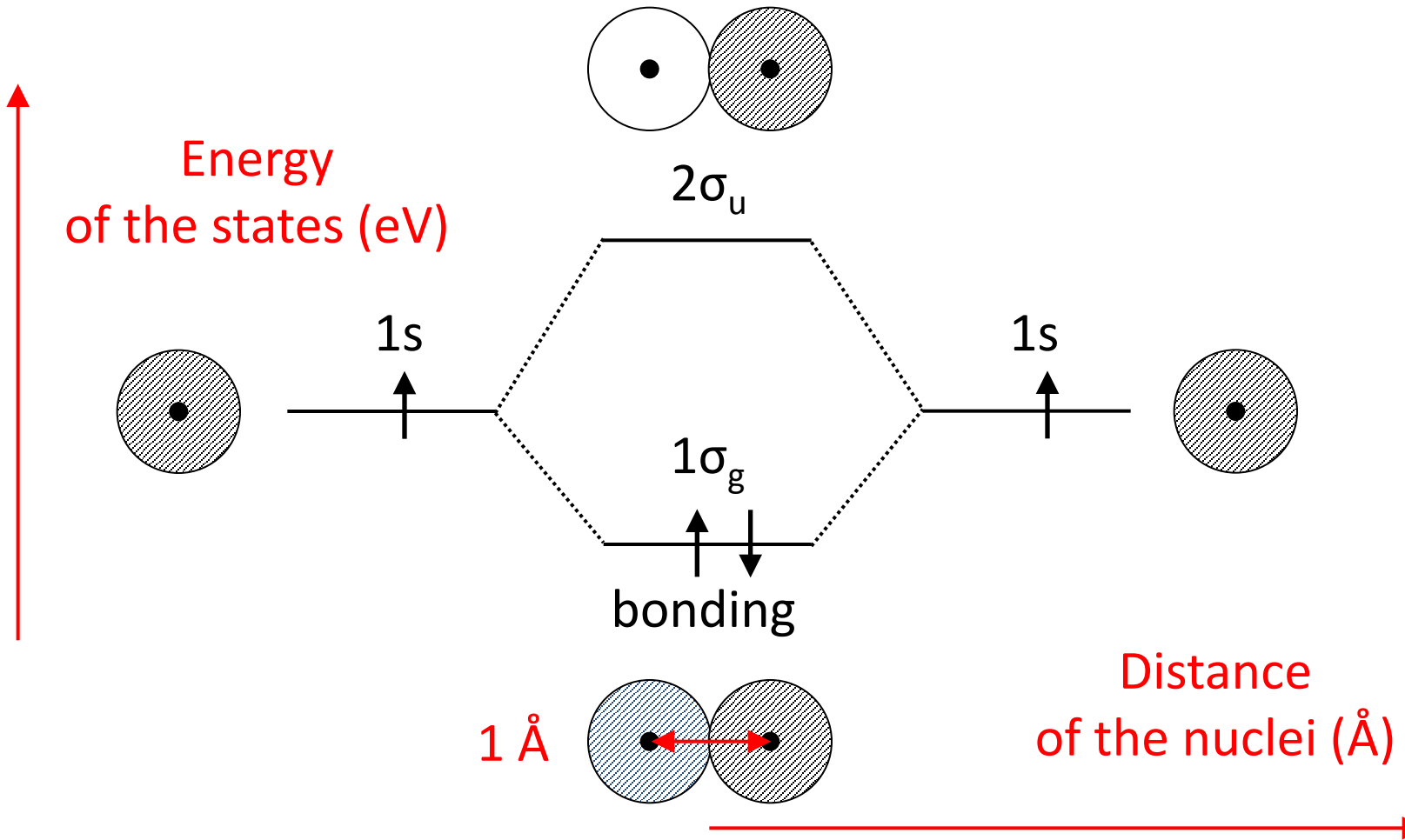
Molecular dynamics simulation
Michael Odelius (Stockholm University)



$Fe(CO)_5$ dissociation in ethanol

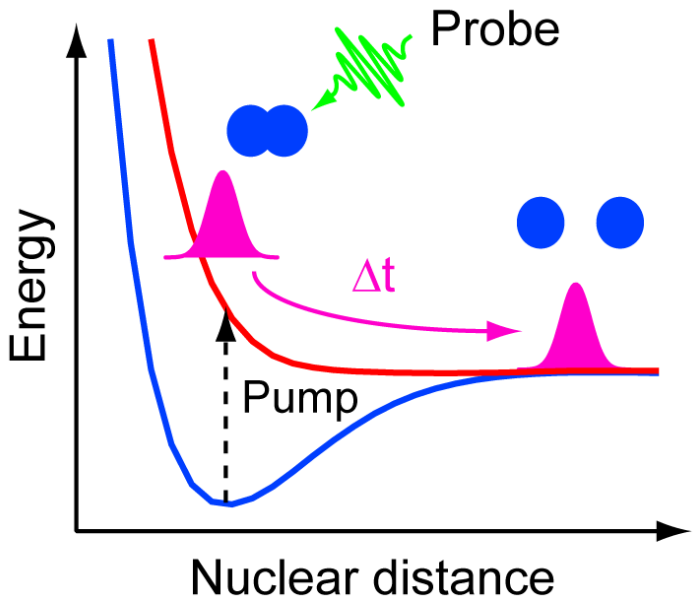
Bonding

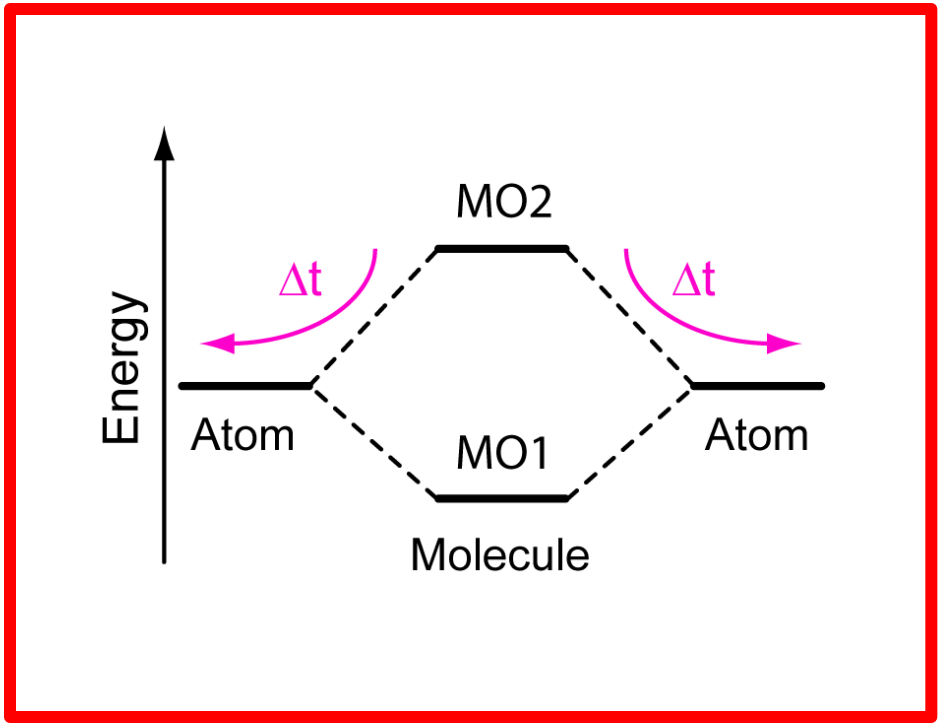
Text book example H_2



The electronic structure molecular movie

Probing chemical interactions and dynamics



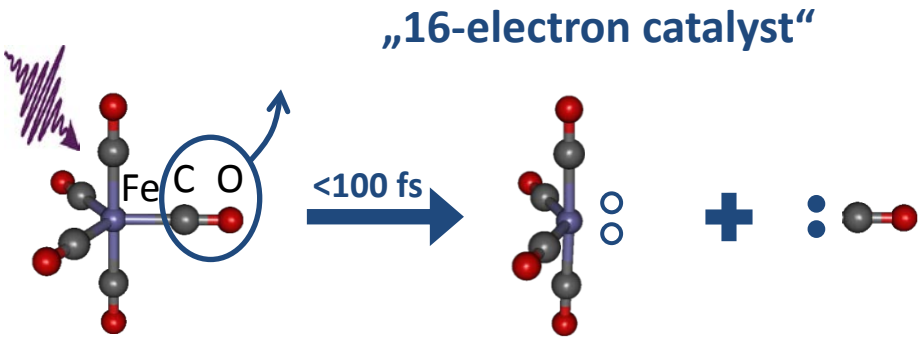


Ph. Wernet, *Electronic structure in real time: Mapping valence electron rearrangements during chemical reactions*, Phys. Chem. Chem. Phys. **13**, 16941 (2011).

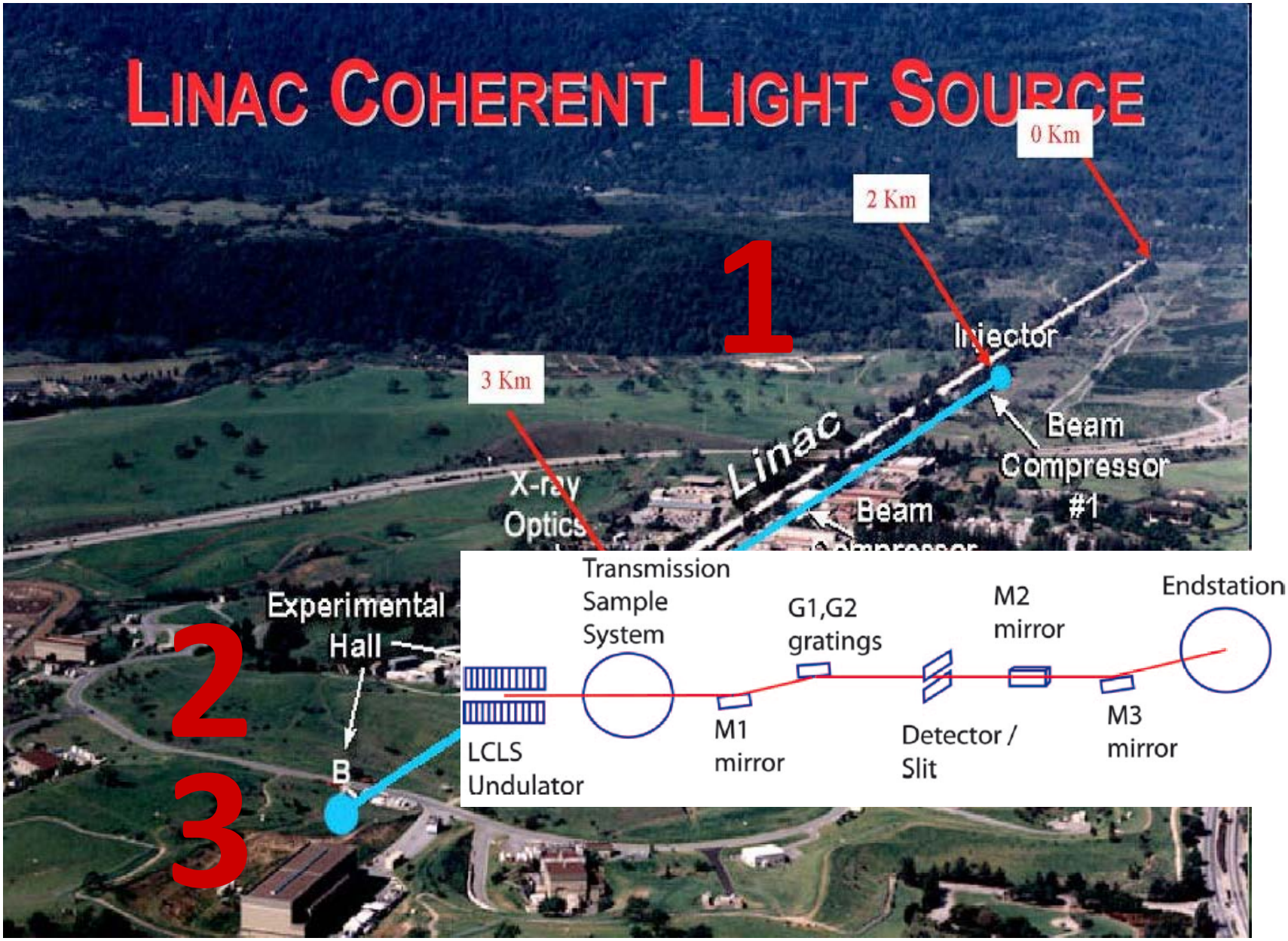
Application 1

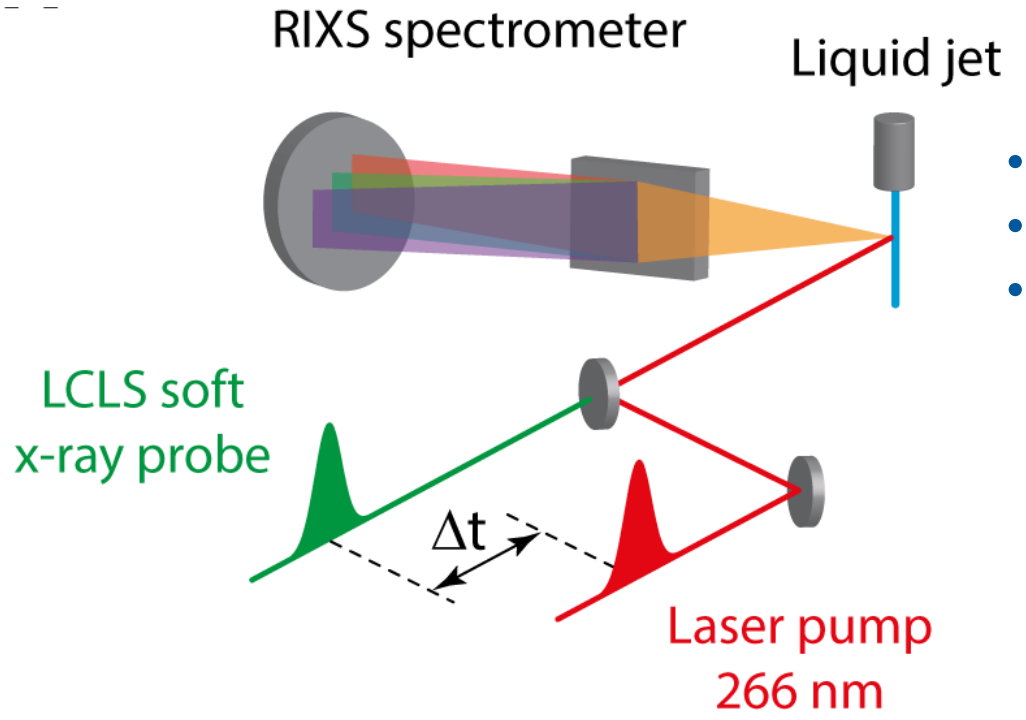
Ultrafast dynamics of a photochemically activated metal complex

$Fe(CO)_5$



MLCT excitation


LINAC COHERENT LIGHT SOURCE
0 Km
2 Km
3 Km
1
Injector
Beam
Compressor
#1
Linac
X-ray
Optics
Beam
Experimental
Hall
2
3
B
Transmission
Sample
System
G1,G2
gratings
M2
mirror
Endstation
LCLS
Undulator
M1
mirror
Detector /
Slit
M3
mirror

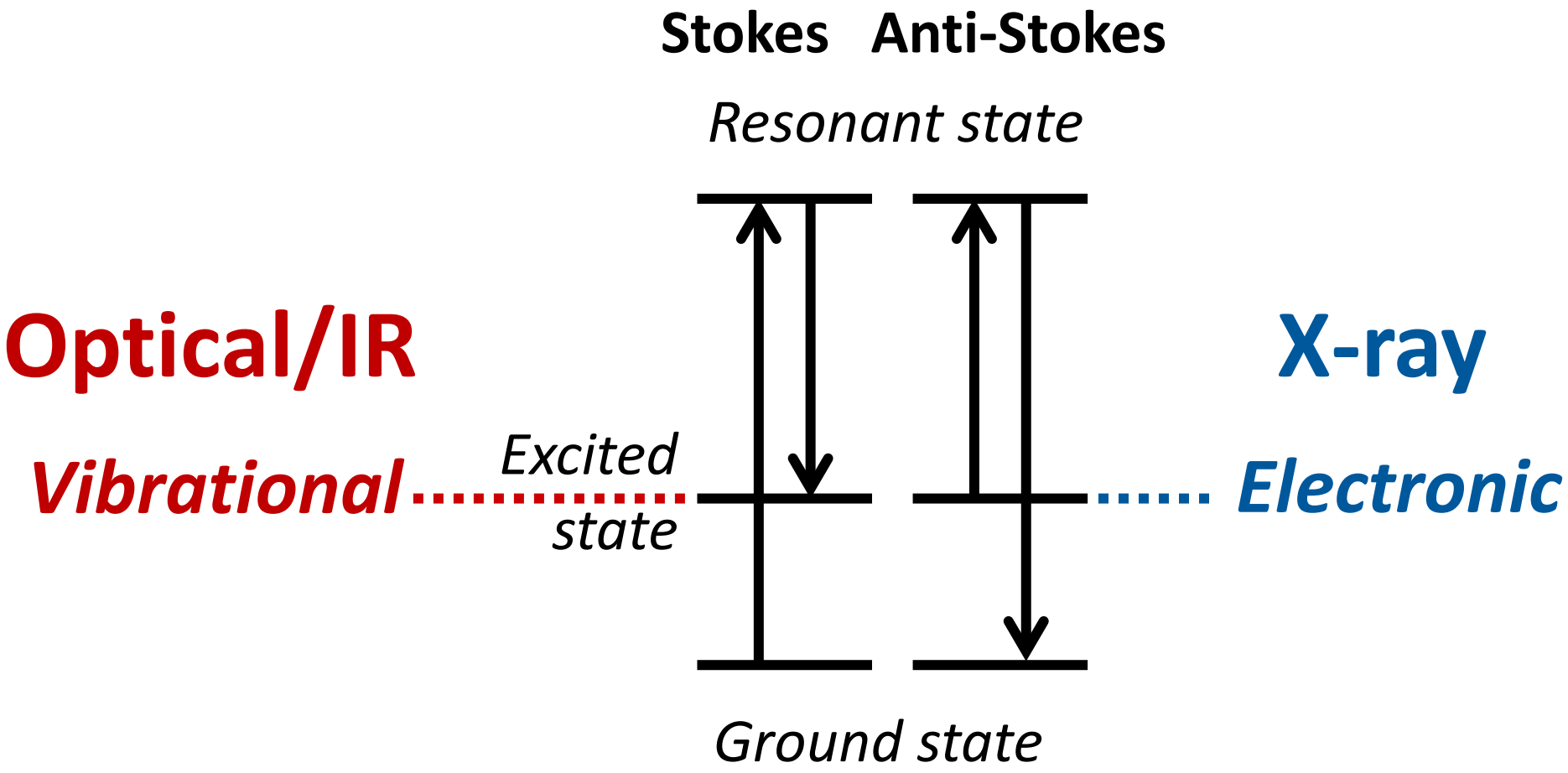


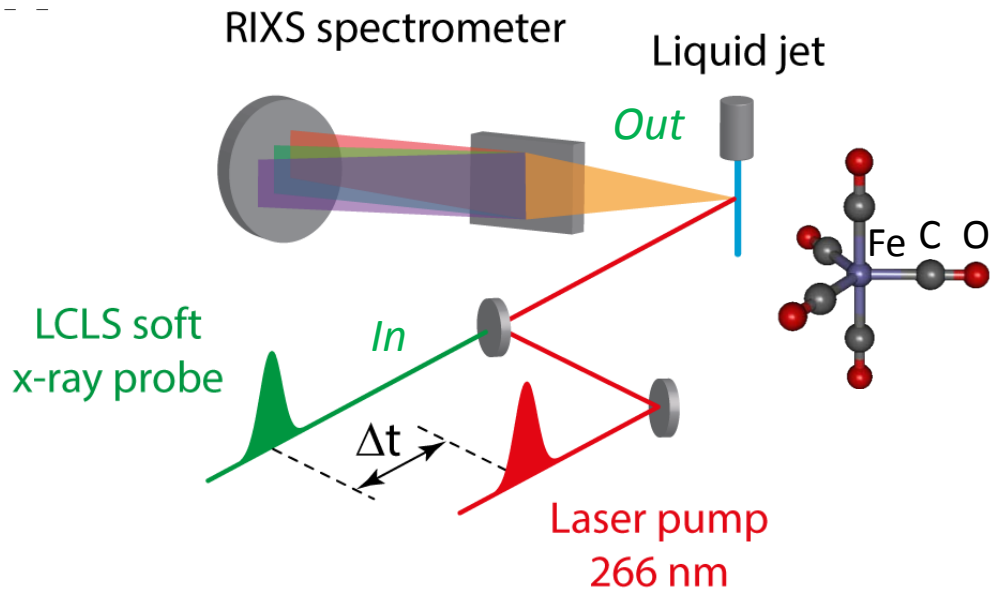
- Flow rate: 1-2 ml/min
- Diameter 20 µm
- Replenishment rate of sample: 0.5-1 MHz (100 µm high cylinder) between x-ray shots

- Concentration 1 mol/l in ethanol
- Repetition rate 60 Hz
- Attenuation factor 10
- X-ray pulse length 160 fs
- Time-resolution 350 fs
- Total accumulation time ~20 h

K. Kunnus et al. Rev. Sci. Instrum. **83**, 123109 (2012).
Ph. Wernet et al. Nature **520**, 78-81 (2015).

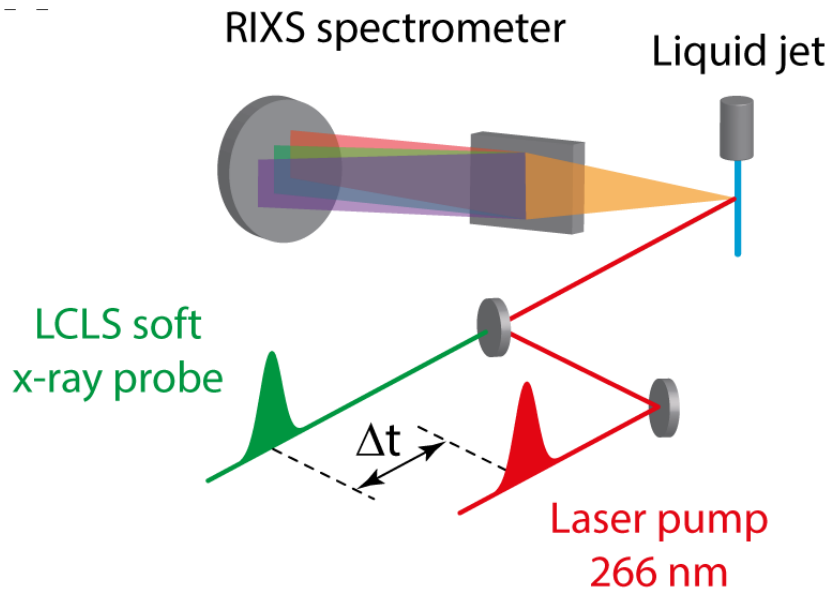
Resonant Raman scattering



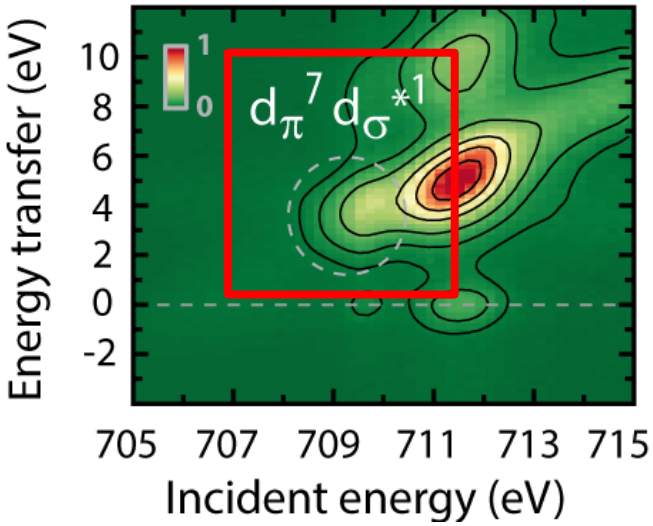


1 mol/l in EtOH

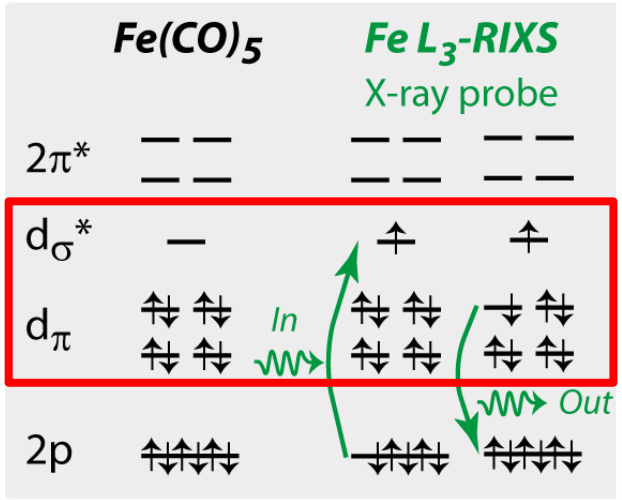
K. Kunnus et al., Rev. Sci. Instrum. **83**, 123109 (2012).
Ph. Wernet et al. Nature **520**, 78-81 (2015).



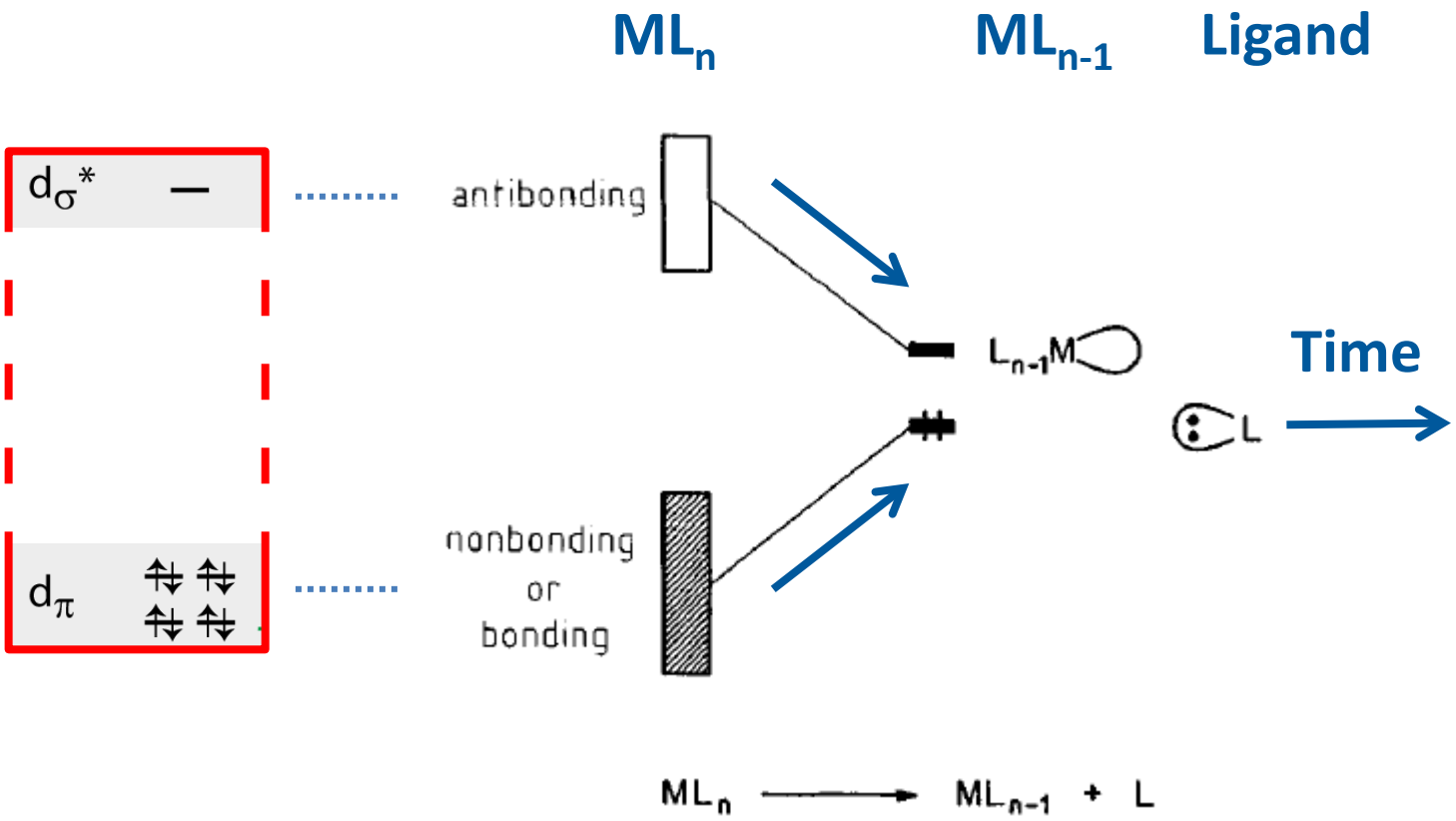
Fe L_3-absoprtion edge



Energy transfer = E_{In} - E_{out}

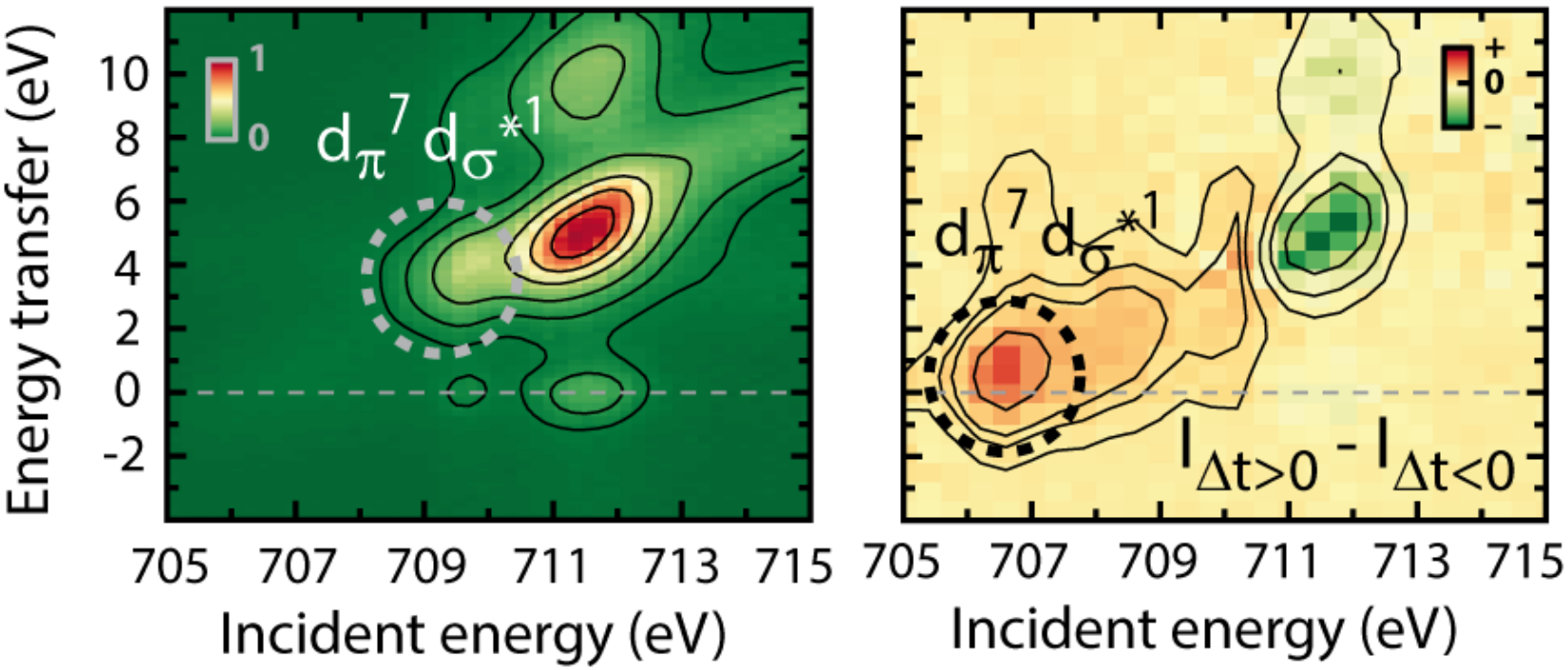


- Probing the ligand-field excited states that determine excited-state behavior
- Probing the frontier orbitals
- Locally at the Fe center
- Probing valence charge density

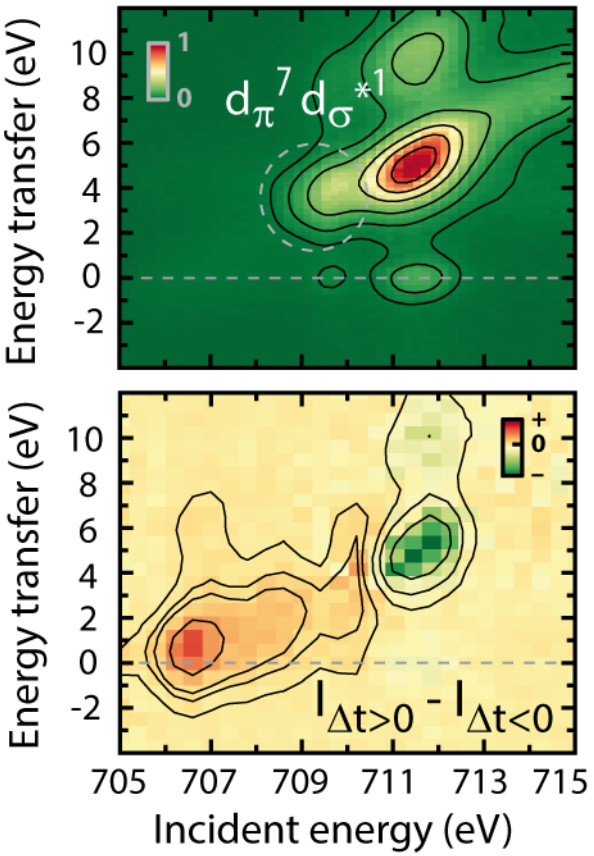


R. Hoffmann, Angew. Chem. Int. Ed. Engl. **21**, 711-724 (1982).

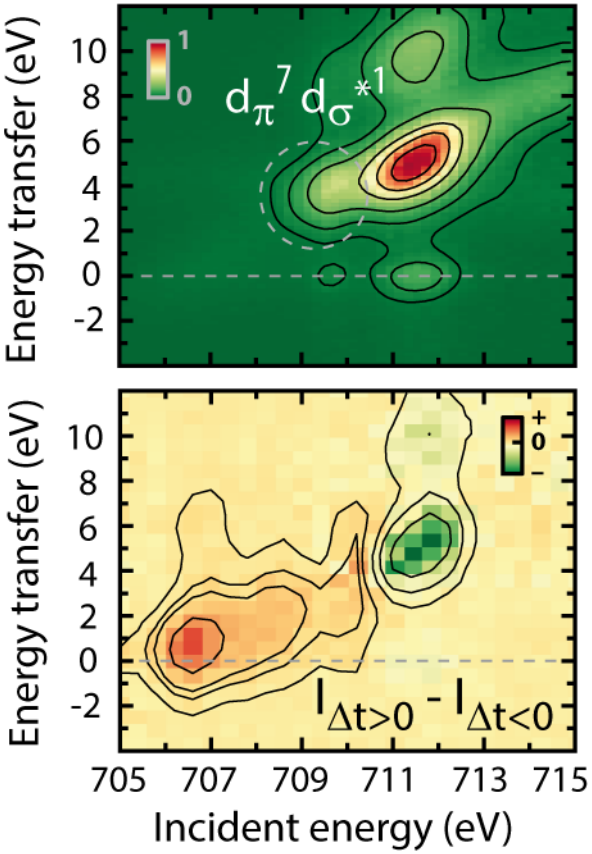
$Fe(CO)_5$ $Fe(CO)_4$ fragments



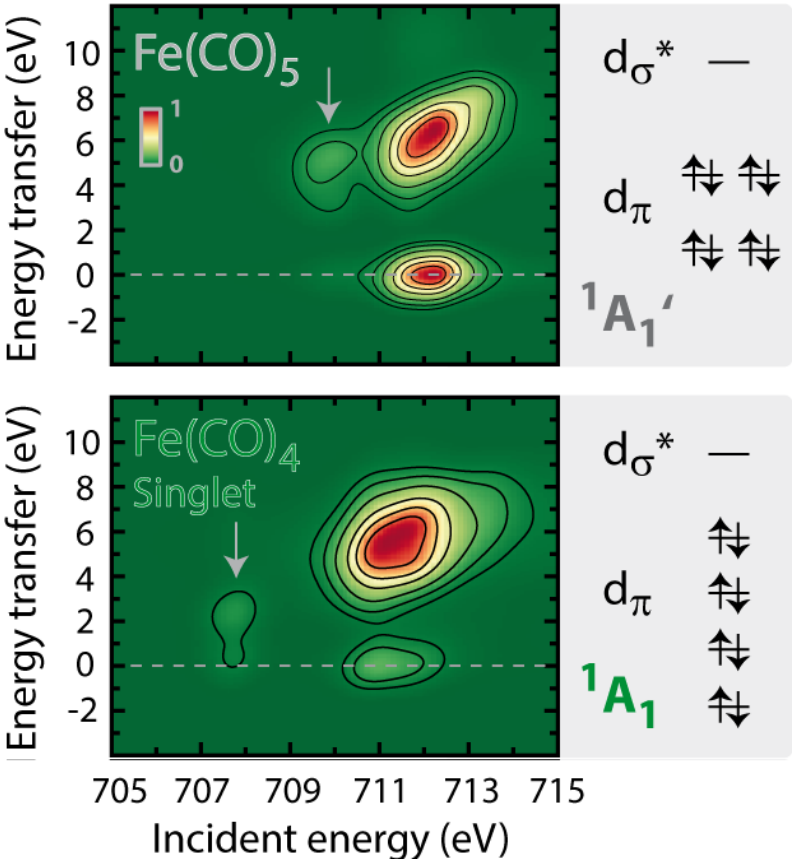
- Fe spin state and bonding of the $Fe(CO)_4$ photofragments?
- Reaction pathways?


Energy transfer (eV)
10
8
6
4
2
0
-2
1
0
$d_\pi{}^7 d_\sigma{}^{*1}$
Energy transfer (eV)
+
0
−
$I_{\Delta t>0} - I_{\Delta t<0}$
705
707
709
711
713
715
Incident energy (eV)

Experiment



Theory

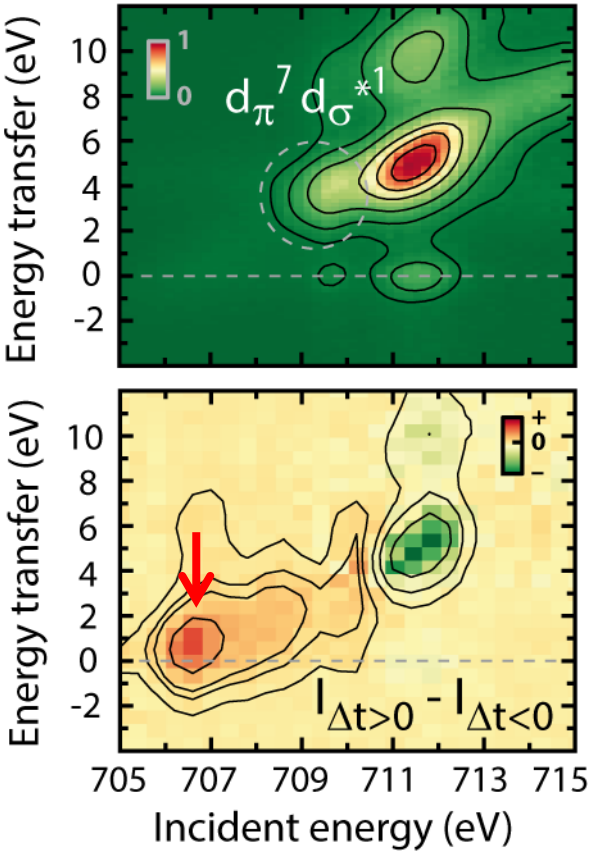


Novel ab initio quantum chemistry calculations of 3d TM x-ray spectra

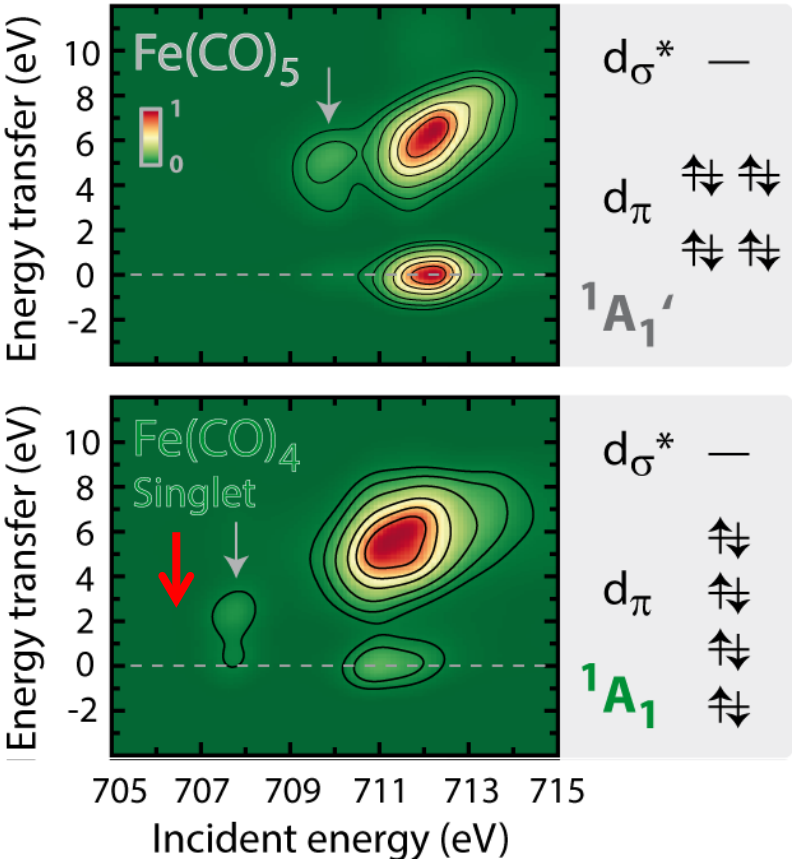
M. Odelius, Stockholm University

I. Josefsson et al., J. Phys. Chem. Lett. **3**, 3565 (2012).

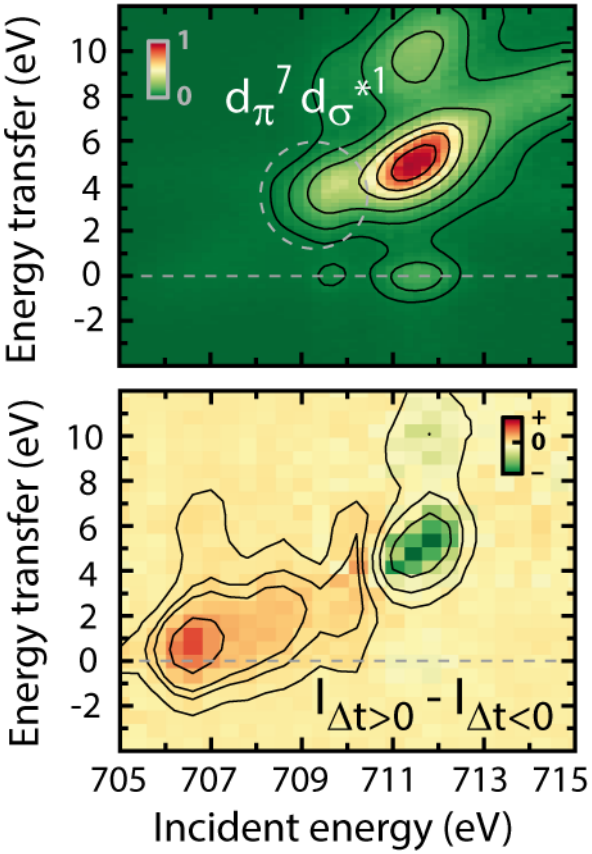
Experiment



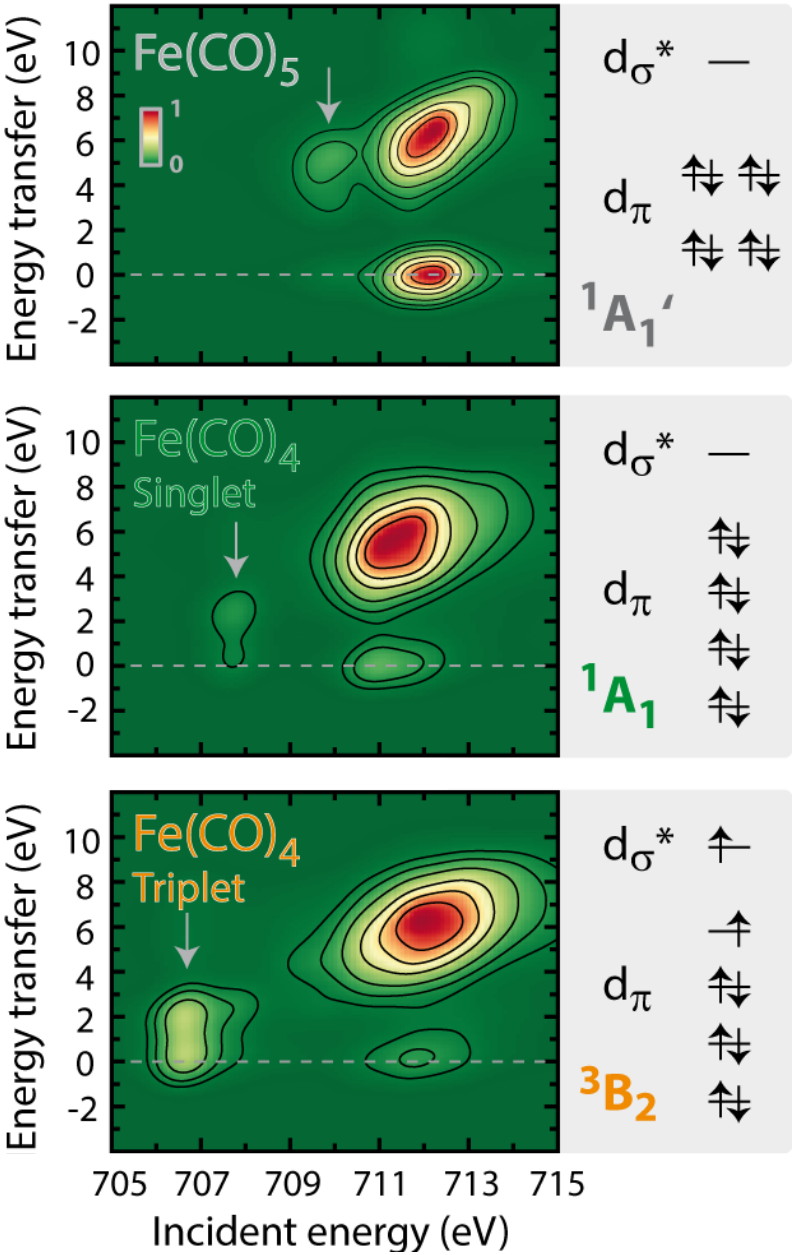
Theory



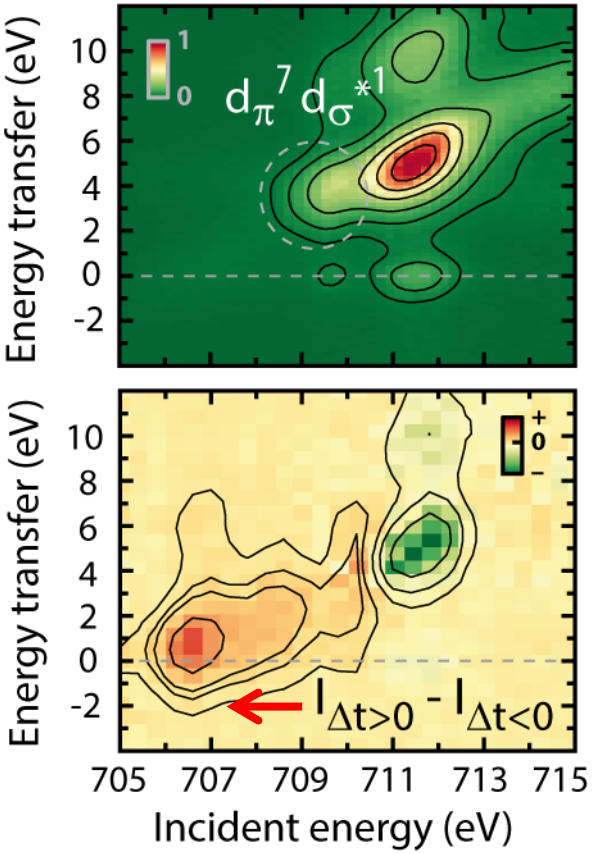
Experiment



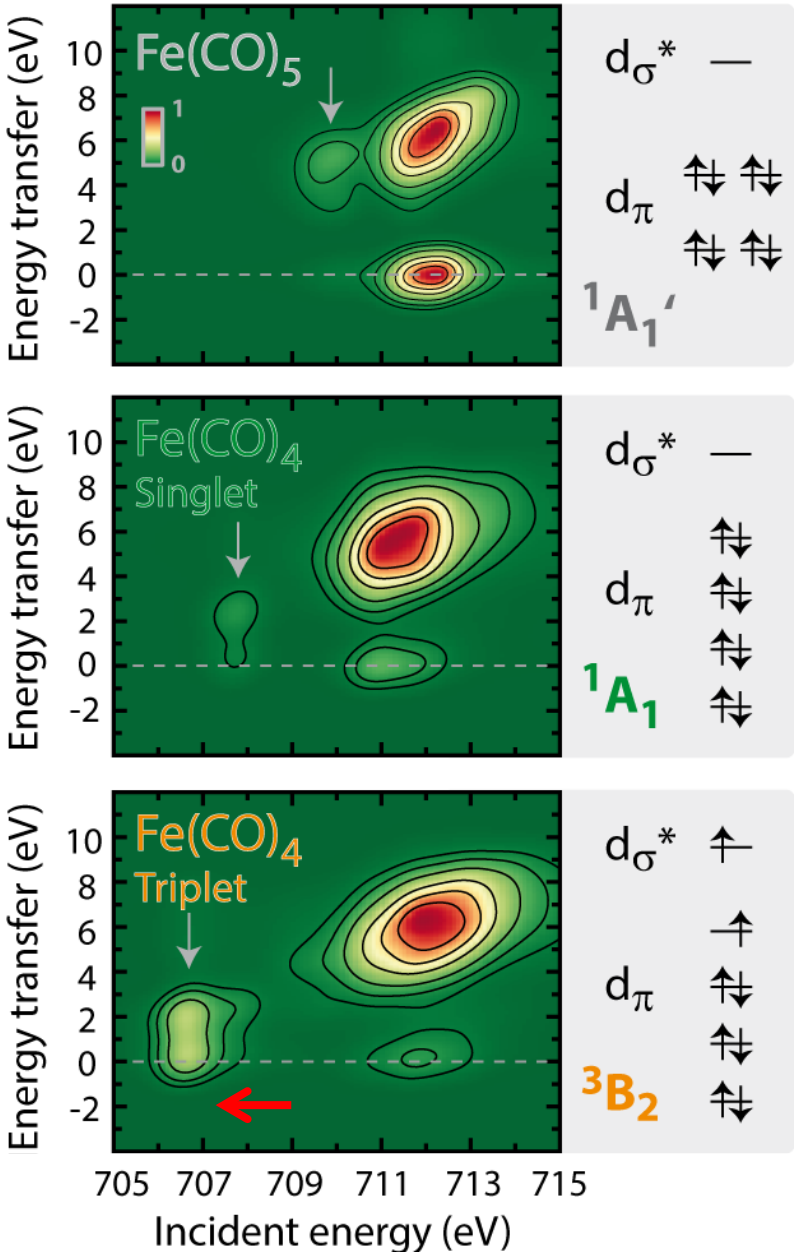
Theory



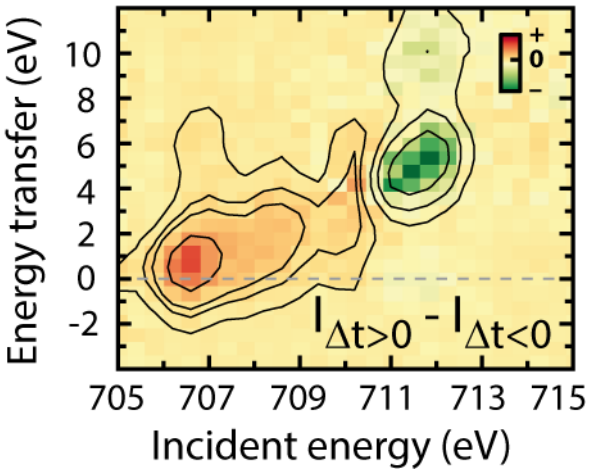
Experiment



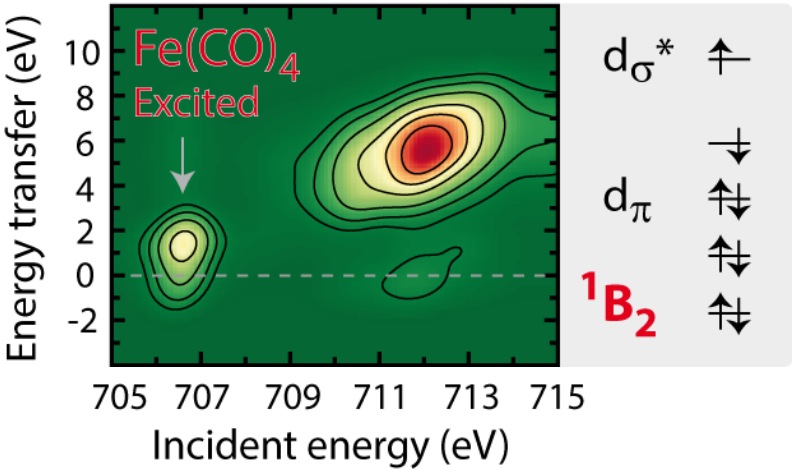
Theory



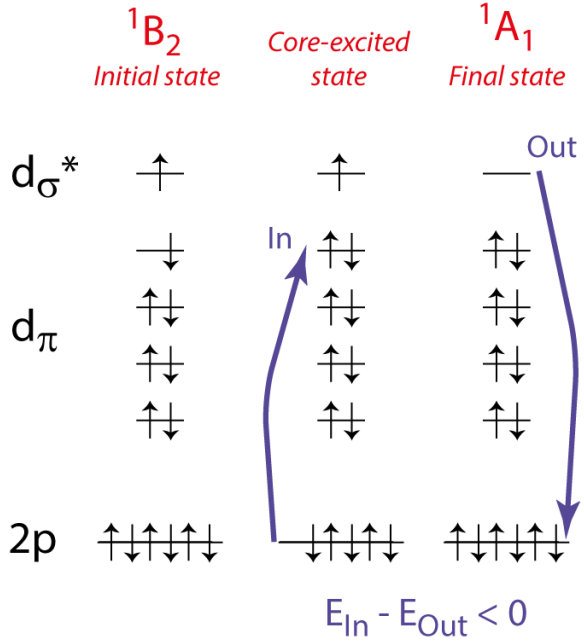
Experiment



Theory

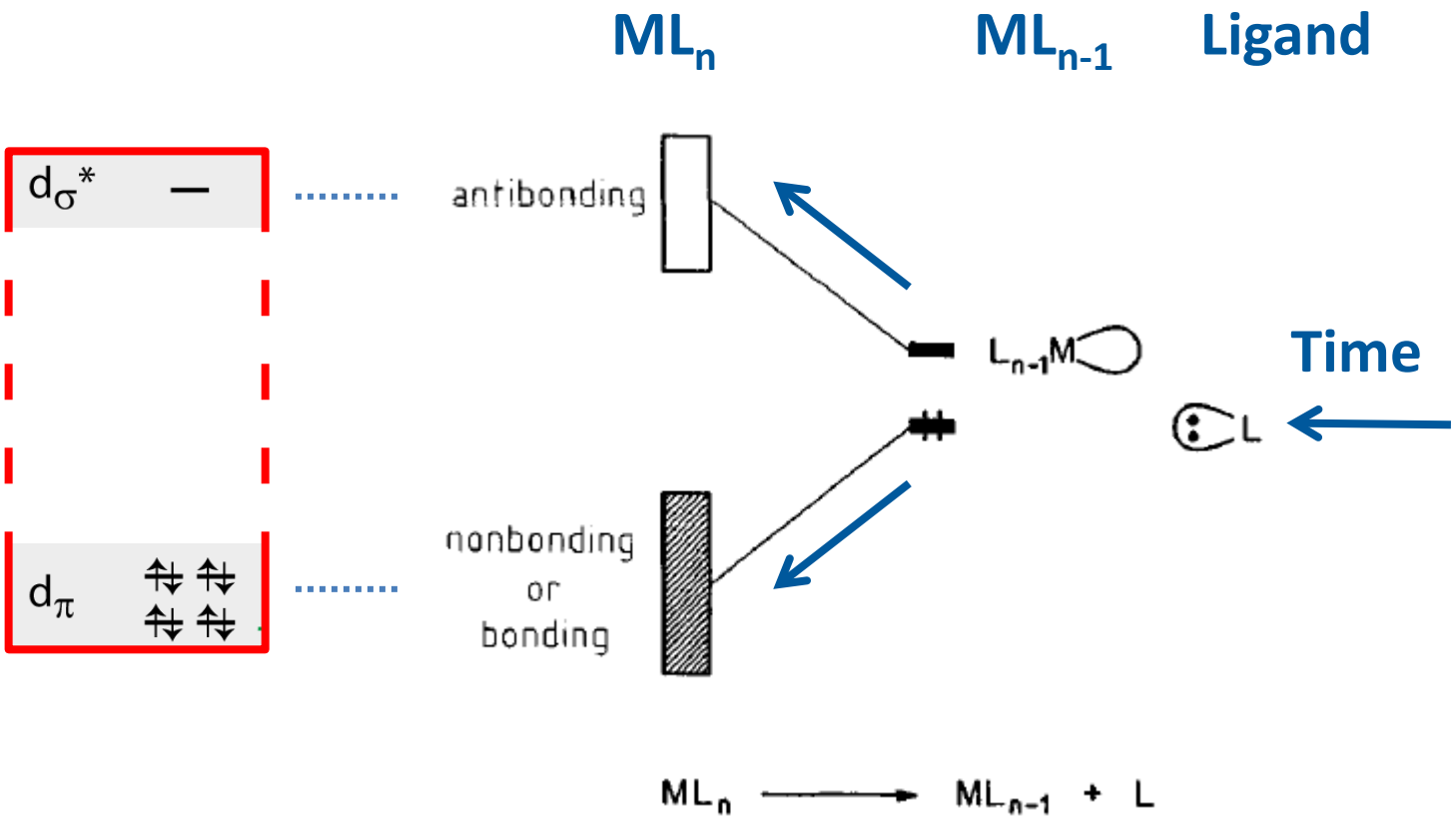


Energy transfer = $E_{In} - E_{out}$

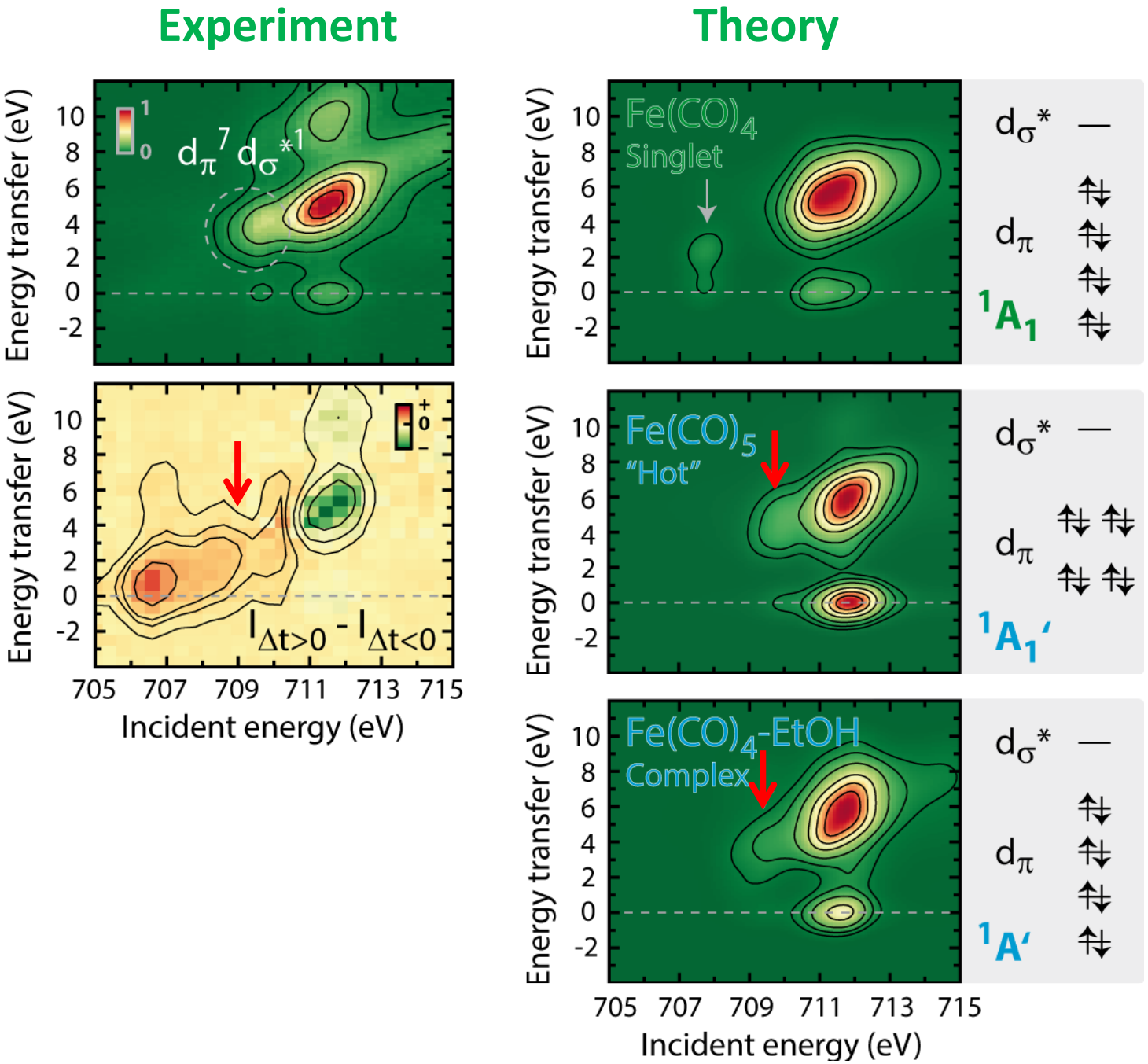


"Anti-Stokes RIXS" as a probe of electronic excited states

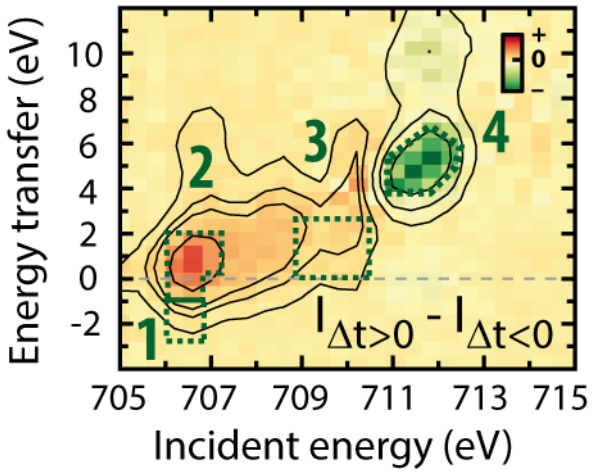
Ph. Wernet et al. Nature **520**, 78-81 (2015).
K. Kunnus et al., to be published

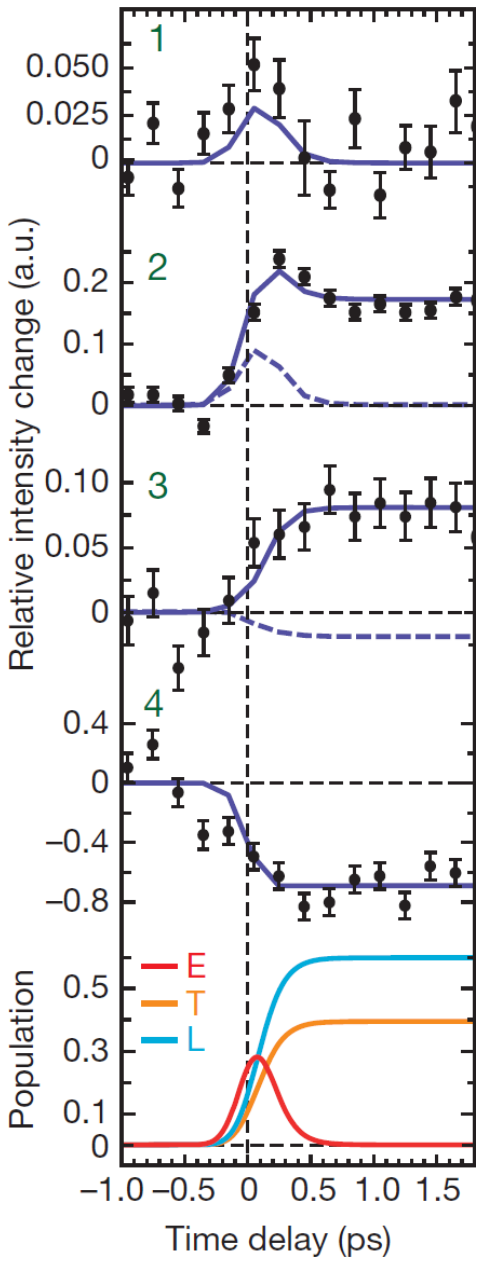


R. Hoffmann, Angew. Chem. Int. Ed. Engl. **21**, 711-724 (1982).


Experiment
Theory
Energy transfer (eV)
Incident energy (eV)
$d_\pi^7 d_\sigma^{*1}$
$I_{\Delta t>0} - I_{\Delta t<0}$
Fe(CO)$_4$
Singlet
$^1A_1$
Fe(CO)$_5$
"Hot"
$^1A_1'$
Fe(CO)$_4$-EtOH
Complex
$^1A'$
d_σ^*
d_π

$Fe(CO)_4$





Fit $I(exp)_{i=1,\ldots,4}$ with $I(calc)_{i=1,\ldots,4}$

I. Triplet (T): 300±100 fs

II. Excited (E): Within resolution

III. Ligated (L): 200±100 fs

→ Reaction pathways

Excited (E)

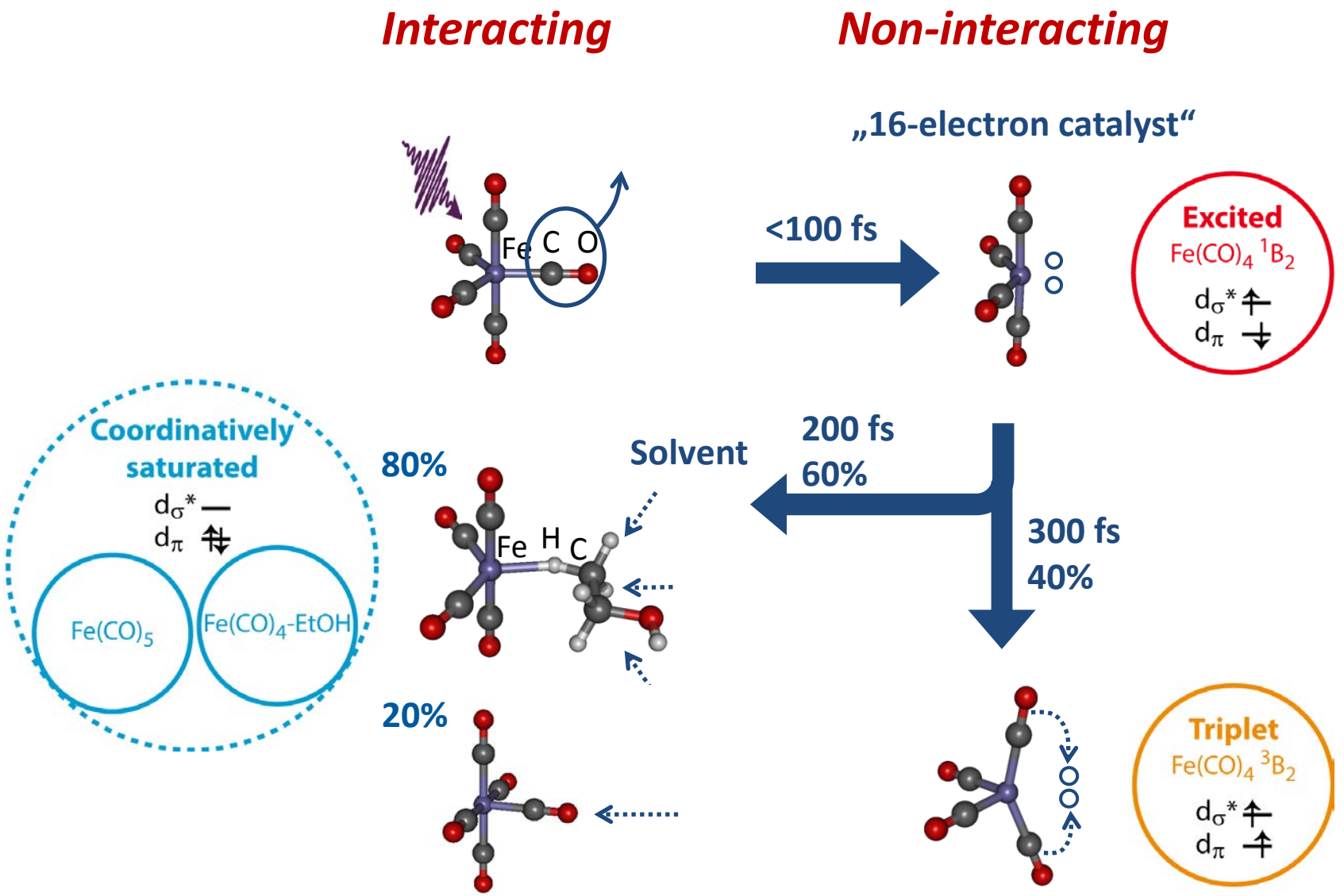
Excited + Triplet (T)

Ligated (L)

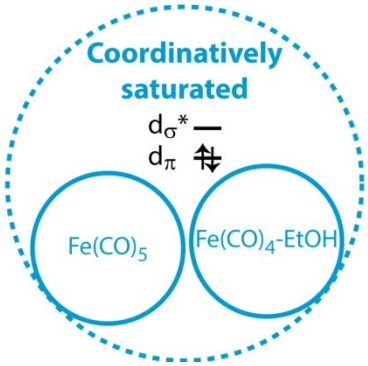
Ground state (bleach)

The reaction pathways of $Fe(CO)_5$ in solution

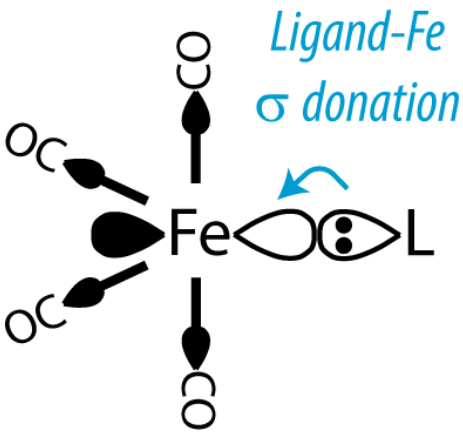
Ph. Wernet et al., *Nature* **520**, 78-81 (2015)



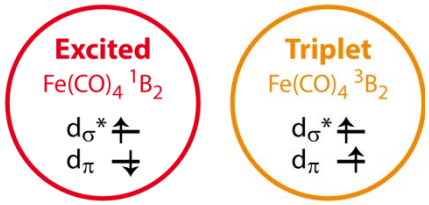
Interacting



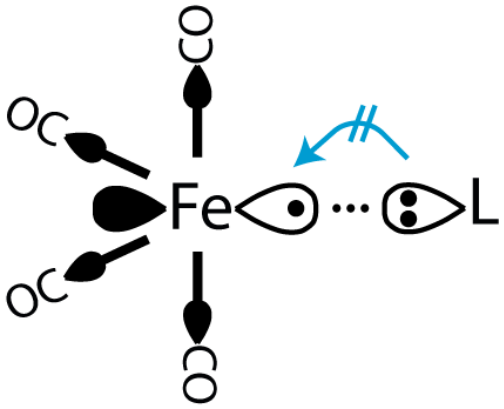
LUMO d_{σ}^* *Ligand* σ



Non-interacting

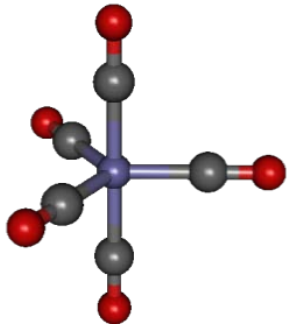


LUMO d_{σ}^* *Ligand* σ



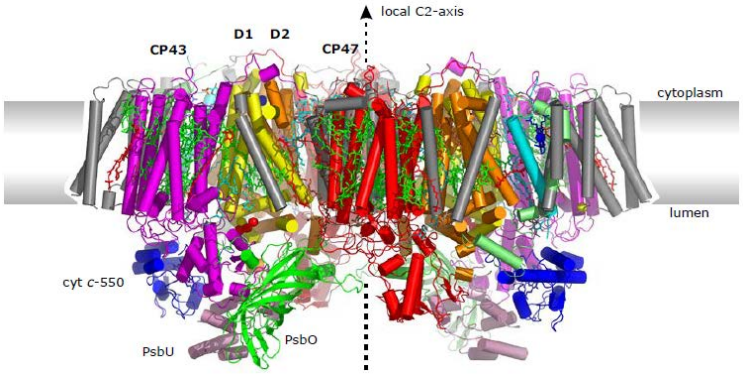
$Fe(CO)_5$

0.1-1 mol/l



Photosystem II

0.001 mol/l

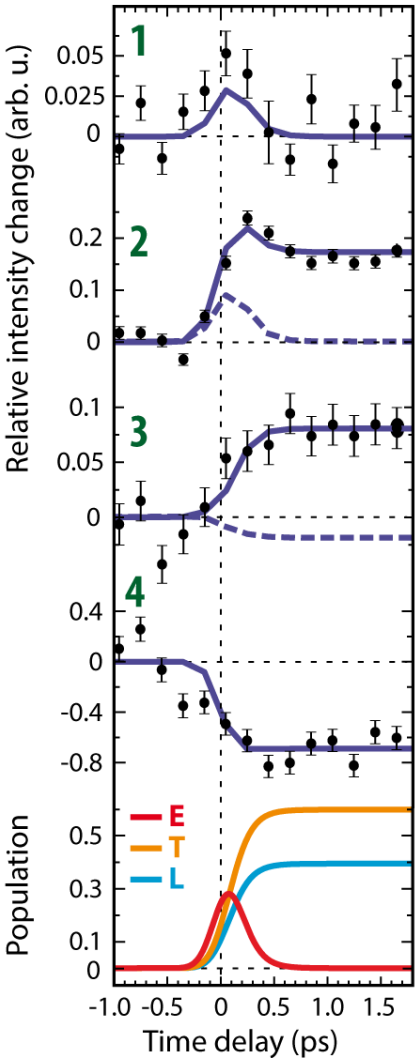


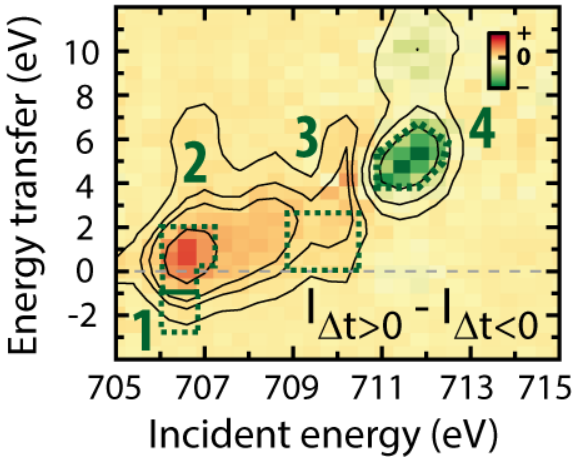
The challenges

Time-resolved soft x-ray spectroscopy

- 30 fs resolution
- mM concentrations
- Sensitivity << 1%
- Large turnover
- Interpretable observables (theory)

The count rate is always a challenge



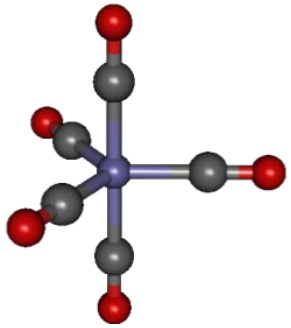


Region	Cts/pulse*
1	0.001
2	0.007
3	0.003

*Per inc. energy, energy transfer and delay bin, ave. over all pos. delays

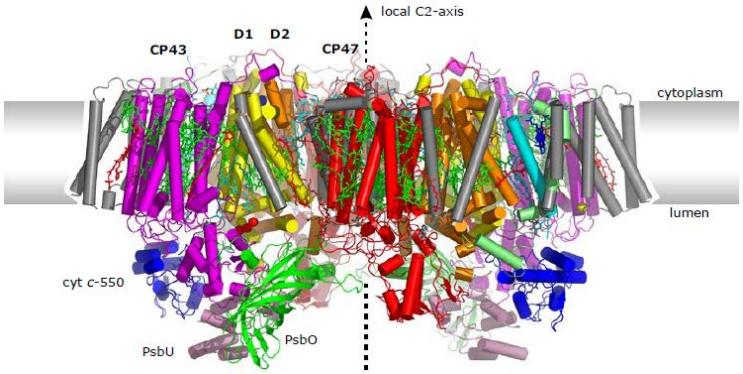
$Fe(CO)_5$

0.1-1 mol/l



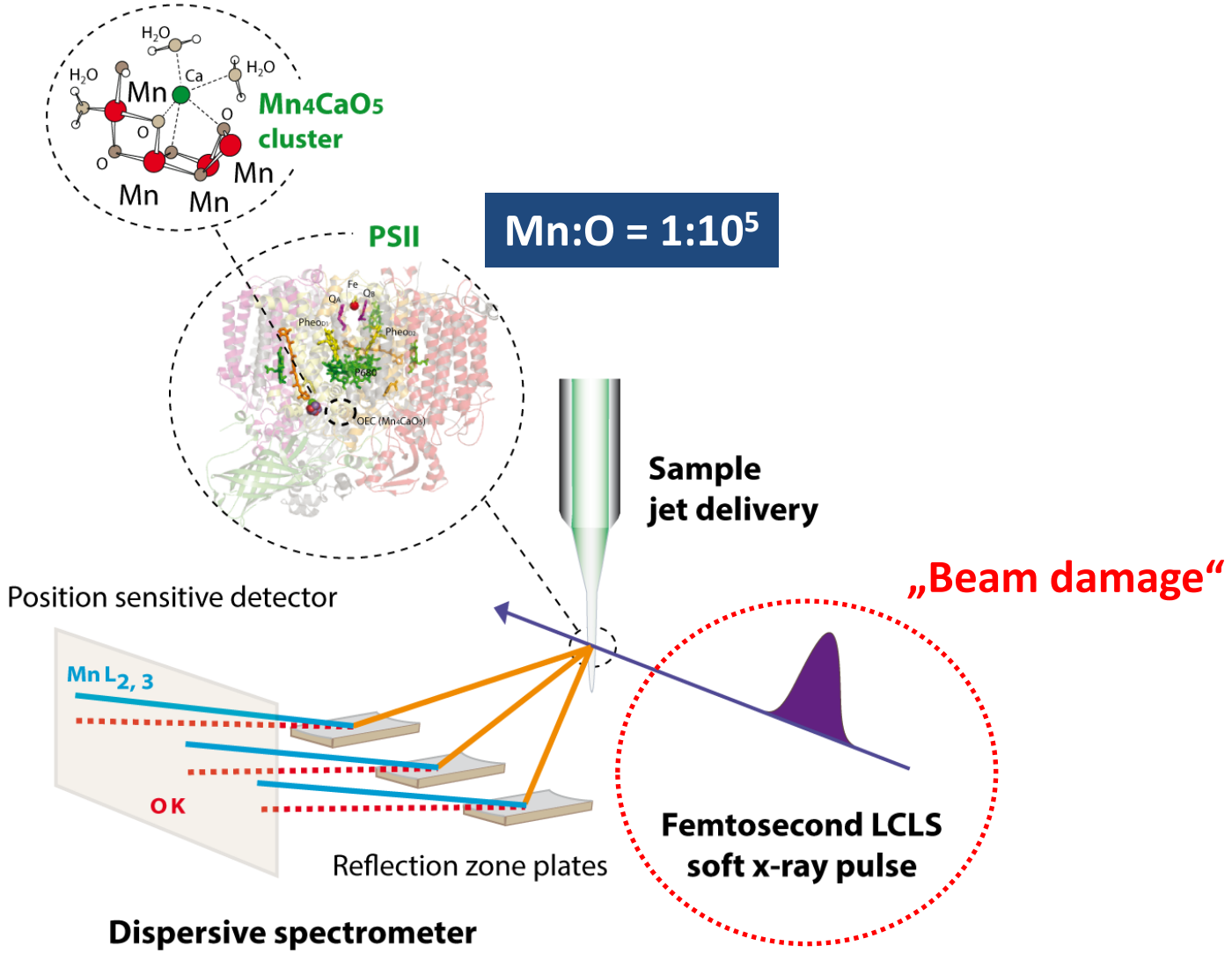
Photosystem II

0.001 mol/l



Application 2

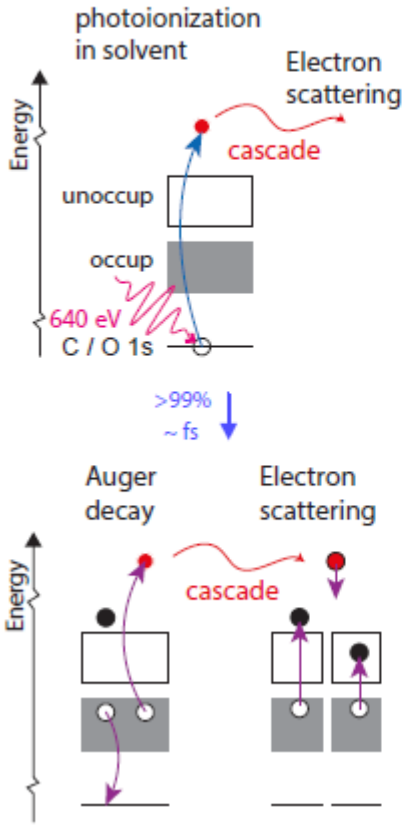
Mn L-edge absorption spectroscopy of photosystem II



Mitzner et al. J. Phys. Chem. Lett. **4**, 3641 (2013).
Braig et al. Optics Express **22**, 12583 (2014).
Kern et al. Phil. Trans. R. Soc. B **369**, 20130590 (2014).

Why an x-ray FEL?

Mechanisms of x-ray damage



Direct photodamage
by x-ray interaction

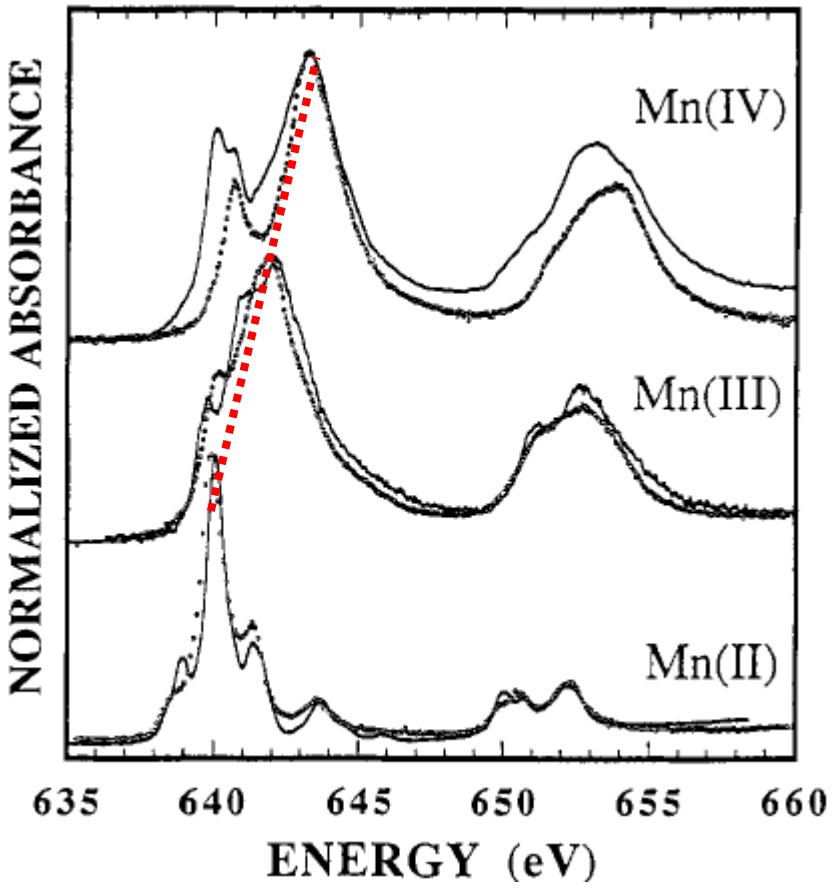
- ionization 'spurs' / 'blobs' [Nave 1995]
- electron scattering ~fs [Schreck 2014]
- Coulomb explosion ~100 fs [Neutze 2000]

Indirect damage
by radicals

- radicals modify protein
- radicals reduce Mn cluster
- radical diffusion ~µs..ms
- dose dependence

Probe before destroy (fs pulses)

Probing the oxidation state of 3d TM atoms with L-edge absorption spectroscopy

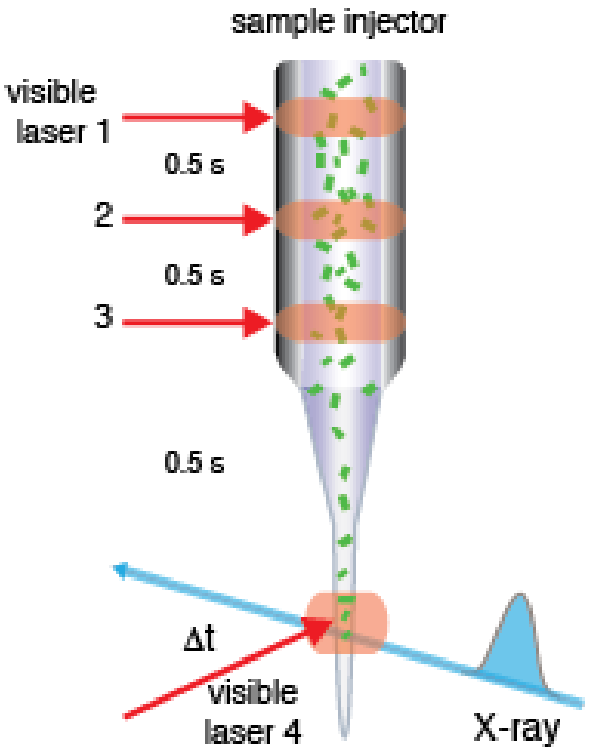


Crystal-field model calculations

Experiment

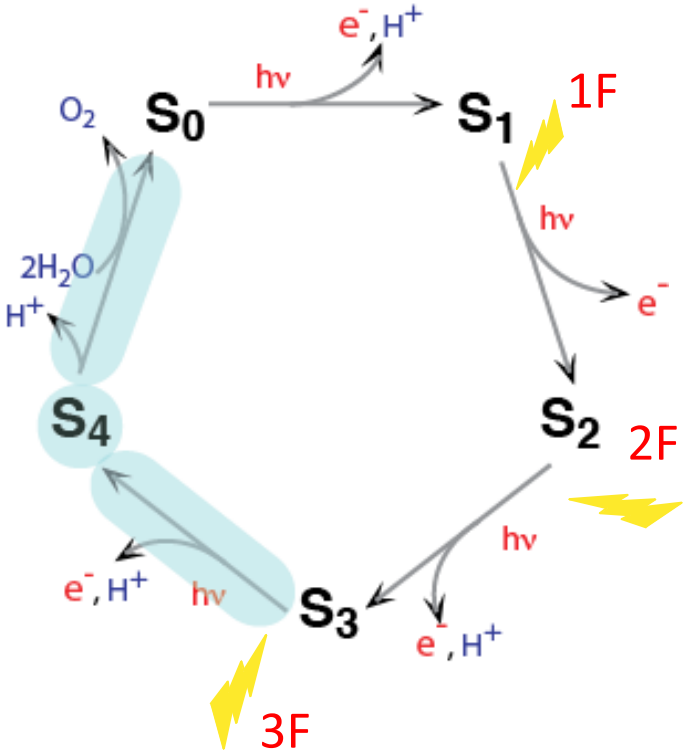
Cramer, de Groot, Chen, Sette, Fuggle et al. JACS **113**, 7937 (1991).

Bonding, spin and oxidation states of PSII



Visible pump laser

- multiple flashes (1F, 2F, 3F)
- flash spacing
- flash saturation



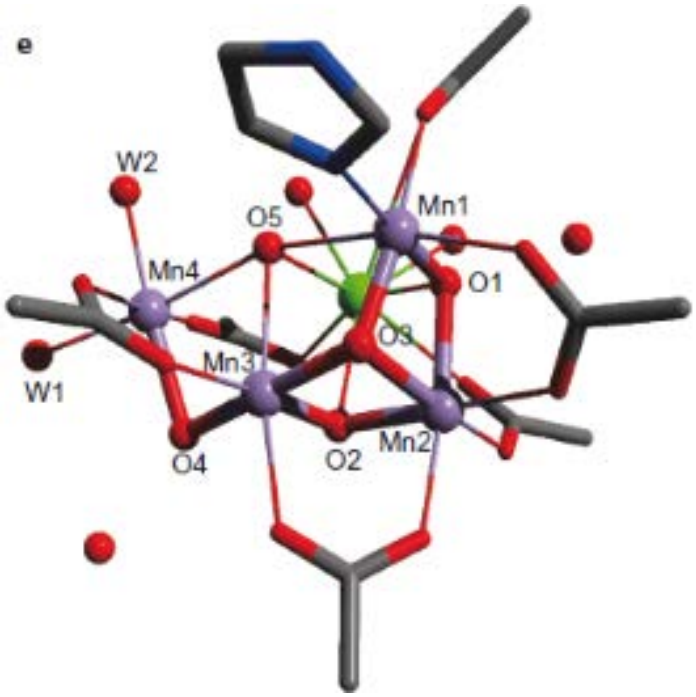
Kern, Yano, Yachandra et al., Nat. Communications **5**, 437 (2014).

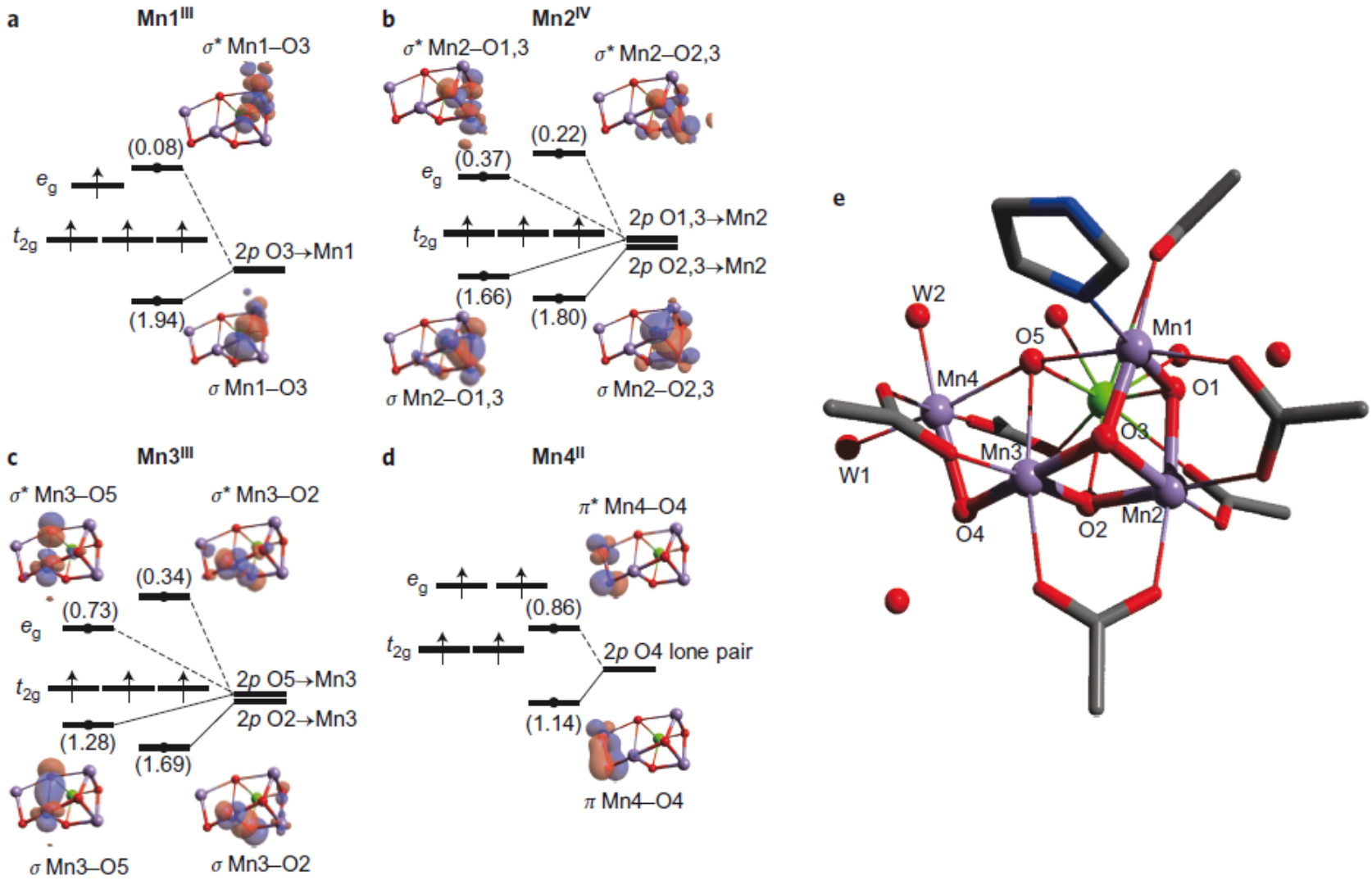
An outlook

ARTICLES
PUBLISHED ONLINE: 9 JUNE 2013 | DOI: 10.1038/NCHEM.1677
nature chemistry

Entangled quantum electronic wavefunctions of the Mn_4CaO_5 cluster in photosystem II

Yuki Kurashige[1]*, Garnet Kin-Lic Chan[2] and Takeshi Yanai[1]

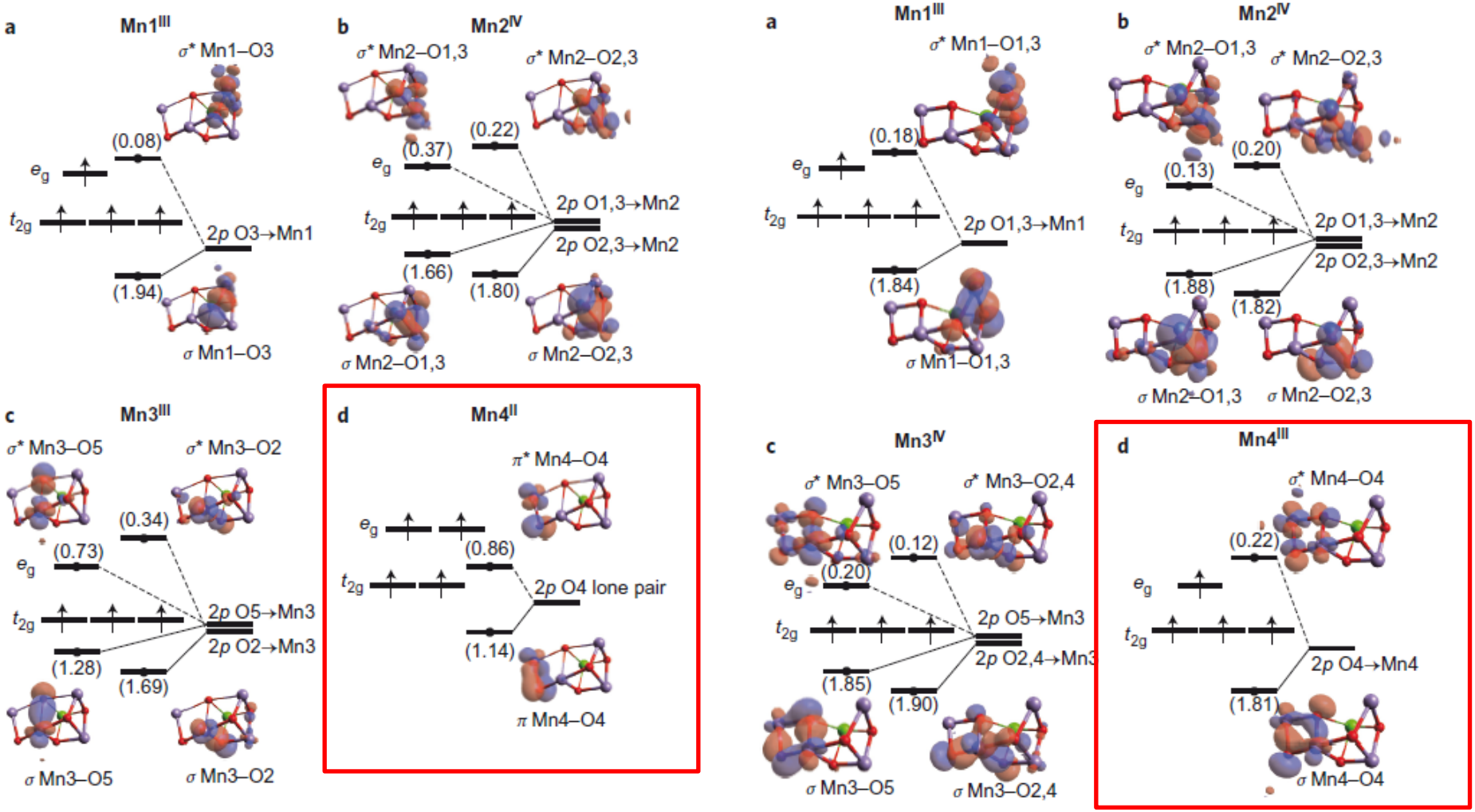




Kurashige, Chan, Yanai, Nat. Chemistry **5**, 660 (2013).

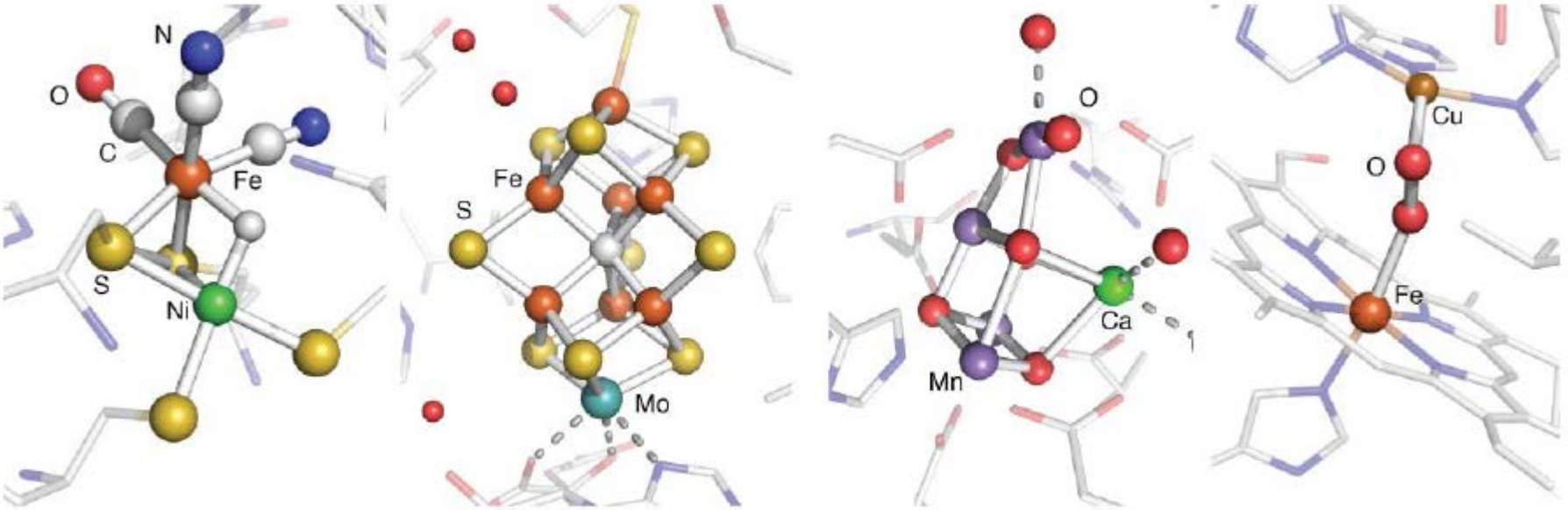
X-ray diffraction structure

Refined structure



Kurashige, Chan, Yanai, Nat. Chemistry **5**, 660 (2013).

Hydrogenase | Nitrogenase | Photosystem II | Cytochrome C oxidase



NiFe H_2ase

$2H^+ \rightarrow H_2$

FeMoS Nitrogenase

$N_2 \rightarrow NH_3$

Mn_4Ca Water oxidase

$2H_2O \rightarrow O_2 + 4H^+$

FeCu Cyt c oxidase

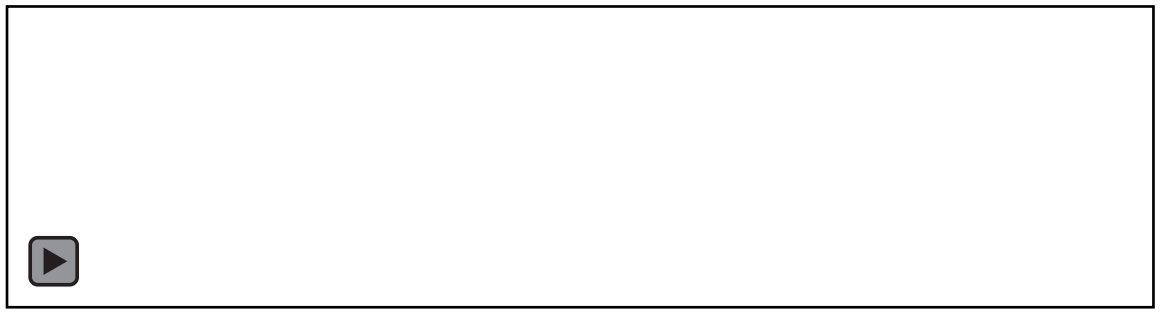
$O_2 + 4H^+ \rightarrow 2H_2O$

Let‘s leave the ball-and-stick picture behind and have a look at the orbitals!

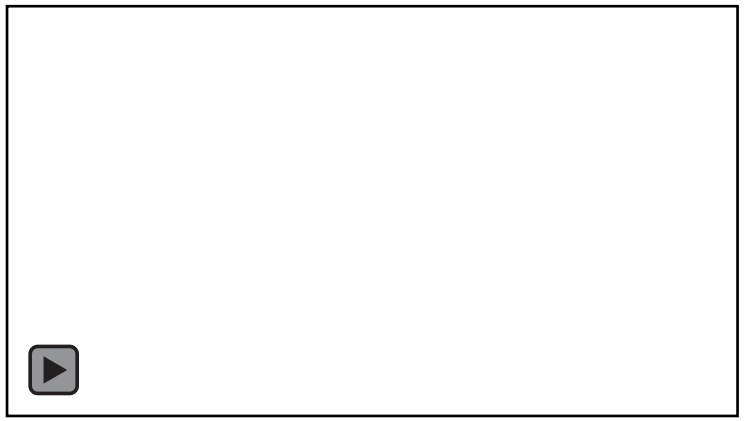
“New Science Opportunities Enabled by LCLS-II X-ray Lasers”, SLAC-R-1053

Liquid jets

„Rayleigh“ jet



GDVN



Animations by Chris Smith, SLAC National Accelerator Laboratory

Jet	Flow rate (min^{-1})	Sample consumption (12 h)
„Rayleigh“ jet	1 ml	1 l
GDVN	10 µl	10 ml
Eletrospinning	< 1 µl	< 1 ml

Nozzle

X-rays on jet

SXR-LCLS
09/2010

Jet

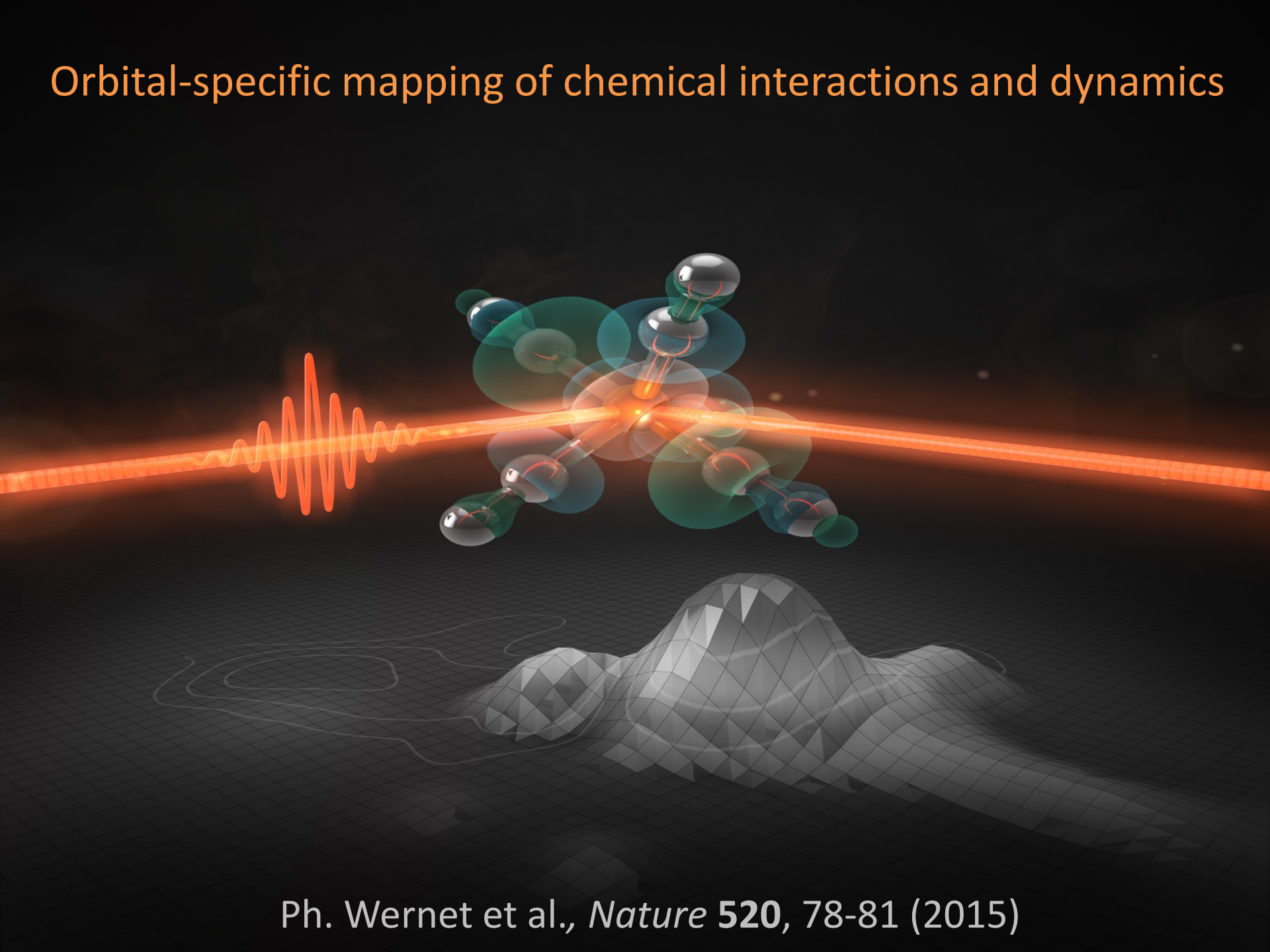
- Flow rate: 1-2 ml/min
- Diameter 20 µm
- Replenishment rate of sample: 0.5-1 MHz for 100 µm high cyliner between x-ray shots

This and the available optical laser densities for sample excitation limits the ideal repetition rate to 100-300 kHz!

Soft x-ray spectroscopy of 3d TM atoms

- Mechanistic explanation of molecular photocatalysis
- The local chemistry in metalloproteins

Orbital-specific mapping of chemical interactions and dynamics



Ph. Wernet et al., *Nature* **520**, 78-81 (2015)

Ultrafast support at LCLS

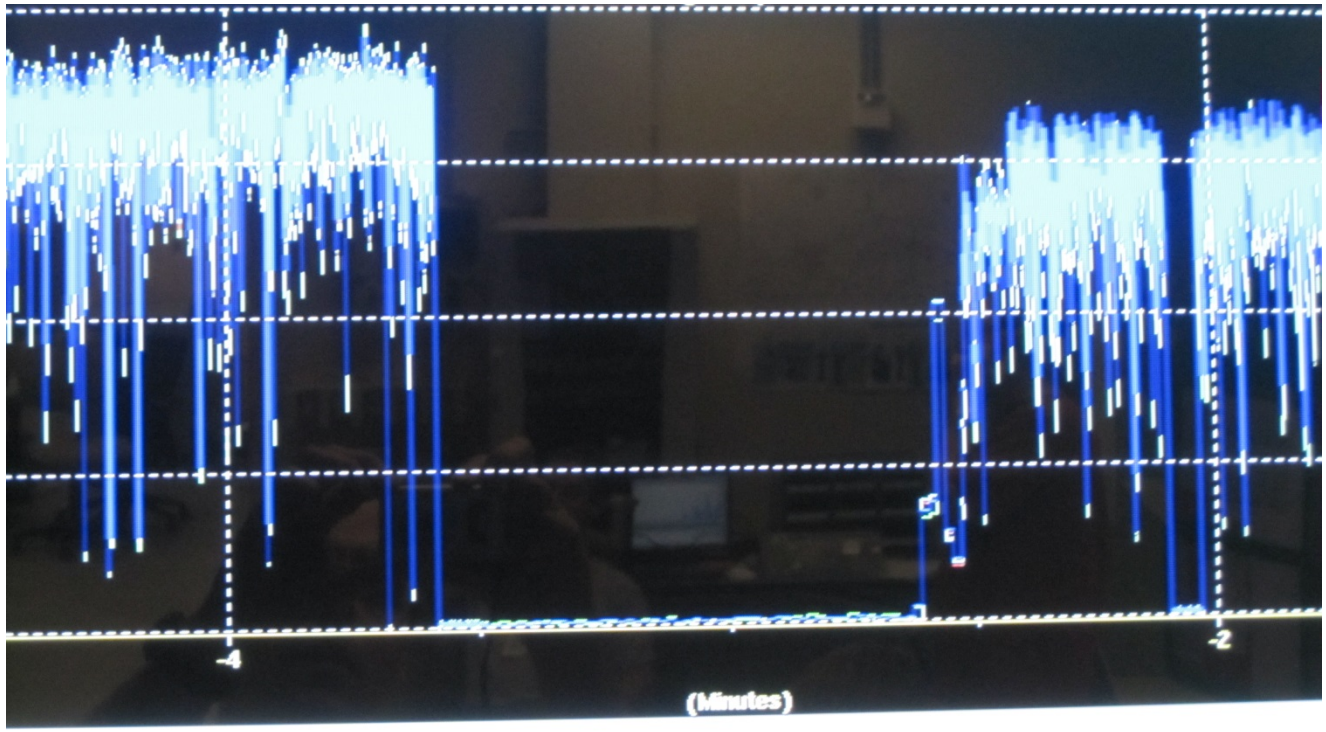
Saturday, September 4, 2010

Beamloss

We realize the beamloss

The red phone (MCC) rings
Bill Schlotter picks up „Uhum, aha“, hangs up and informs us „They lost a Klystron, maintenance is on its way.“

Beam is back, we are confused, that was too fast…



Pulse energy

0 **30** **60 seconds**

Thank you

Kristjan Kunnus, Wilson Quevedo, Alexander Föhlisch
HZB

Simone Techert
DESY

Kelly Gaffney, Uwe Bergmann, Bill Schlotter, Josh Turner
SLAC, Stanford

Michael Odelius
Stockholm University

Franz Hennies
MAX-Lab, Lund

Frank De Groot
Utrecht University

Junko Yano, Jan Kern, Vittal Yachandra
LBNL, Berkeley

Athina Zouni
HU Berlin

Marcus Lundberg
Uppsala University

Helmholtz Virtual Institute

Dynamic Pathways in Multidimensional Landscapes