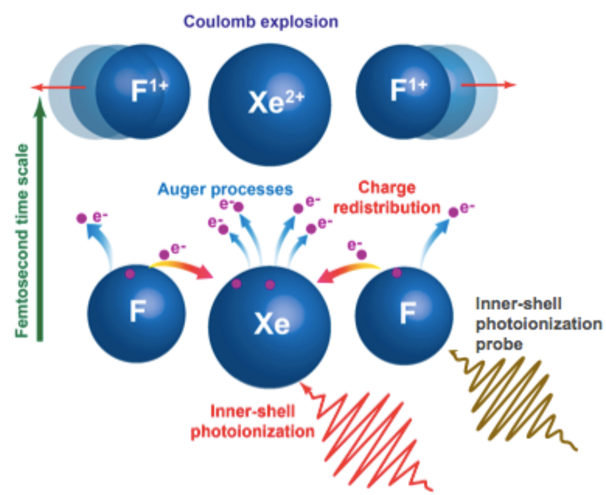
esteu ine of text (optional).

TART WITH YES.

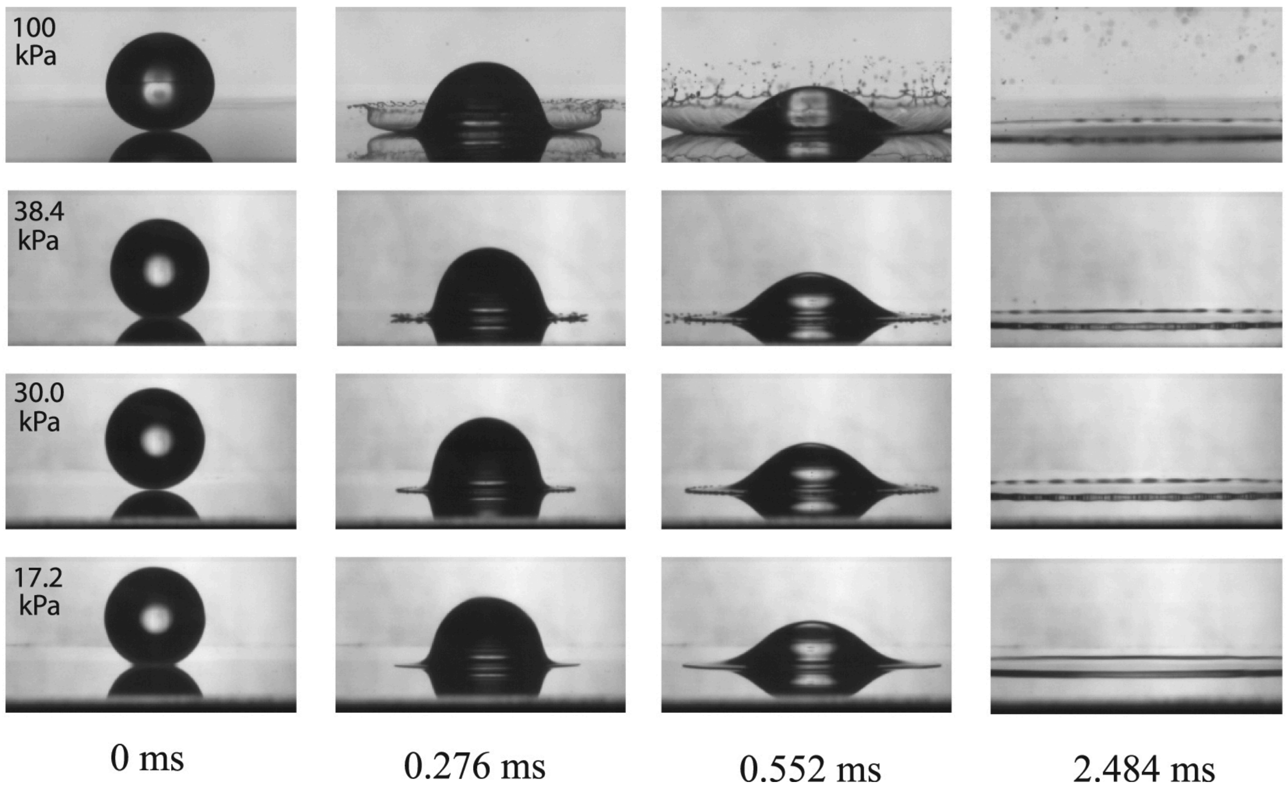
WATCHING THE ULTRAFAST – ULTRASMALL WORLD WITH PUMP-PROBE X-RAY EXPERIMENTS



LINDA YOUNG
Argonne National Laboratory
The University of Chicago

X-ray Neutron Summer School, Argonne National Laboratory, 26 July 2018

STOP-ACTION PHOTOS IN “DAILY” LIFE



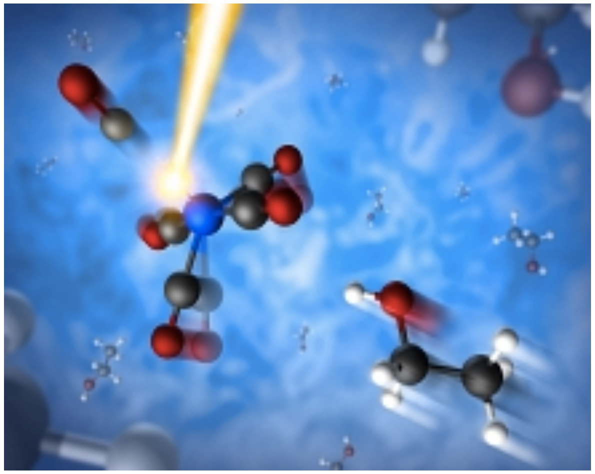
Xu, Zhang, Nagel, PRL 94, 184505 (2005)

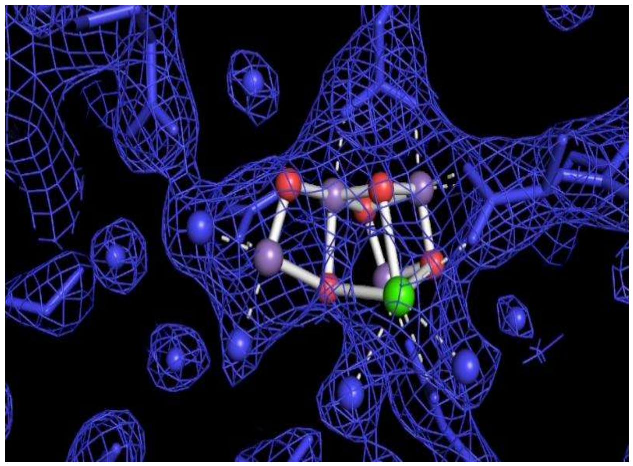
Splashing on Dry Smooth Surface

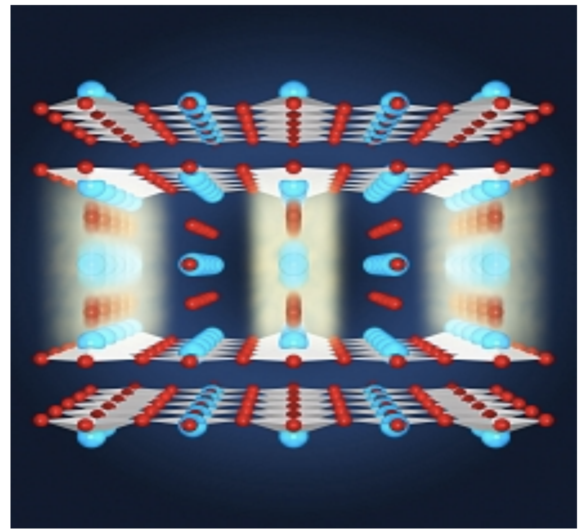
Lei Xu, Wendy W. Zhang, Sidney R. Nagel

University of Chicago

SEE THE ATOMS AND ELECTRONS MOVE


Chemical reactions in solution


Photosystem II


Light-induced superconductivity

NOBEL PRIZE CHEMISTRY 1967

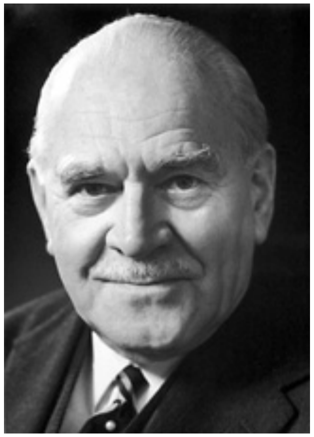
for their studies of extremely fast chemical reactions, effected by disturbing the equilibrium by means of very short pulses of energy

" Immeasurably fast reactions"

Manfred Eigen

Pressure
Electric field
Temperature

"Flash photolysis"



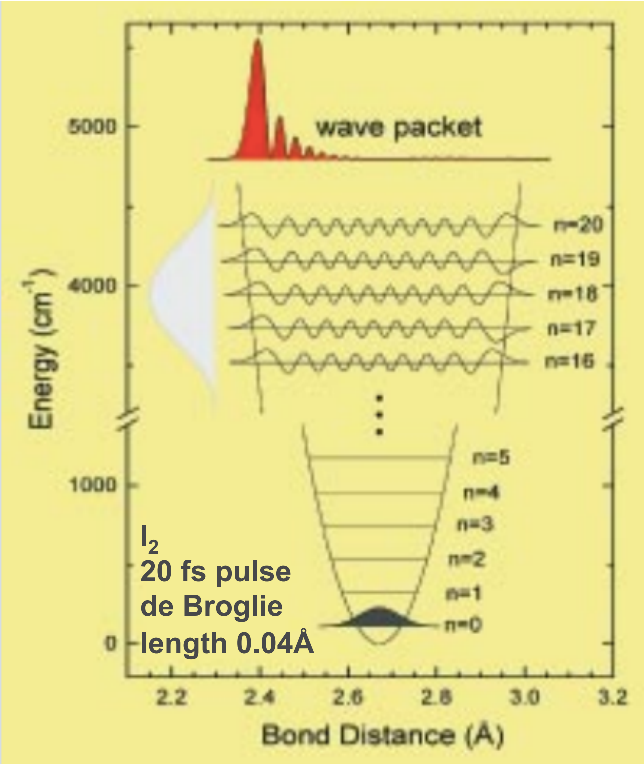
Ronald George Wreyford Norrish

George Porter

NOBEL PRIZE CHEMISTRY 1999

for his studies of the transition states of chemical reactions using femtoscond spectroscopy

Ahmed Zewail



Kinetics to Dynamics

- Coherent exitation
- Localized wavepacket formation
- ~"single molecule trajectory"

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

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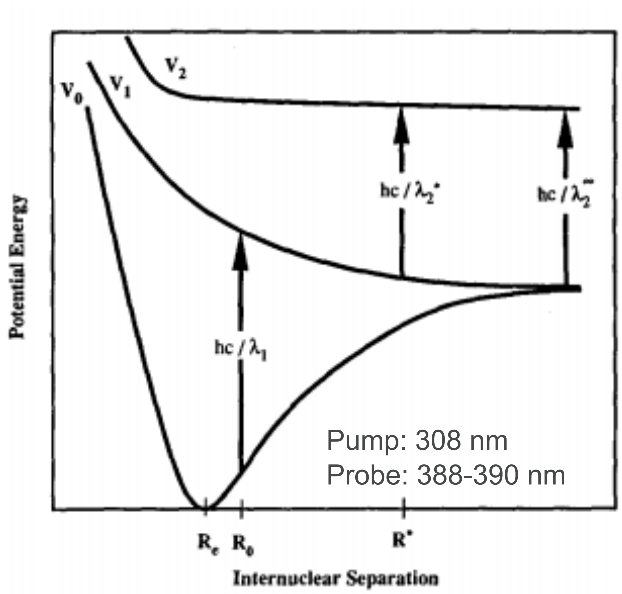
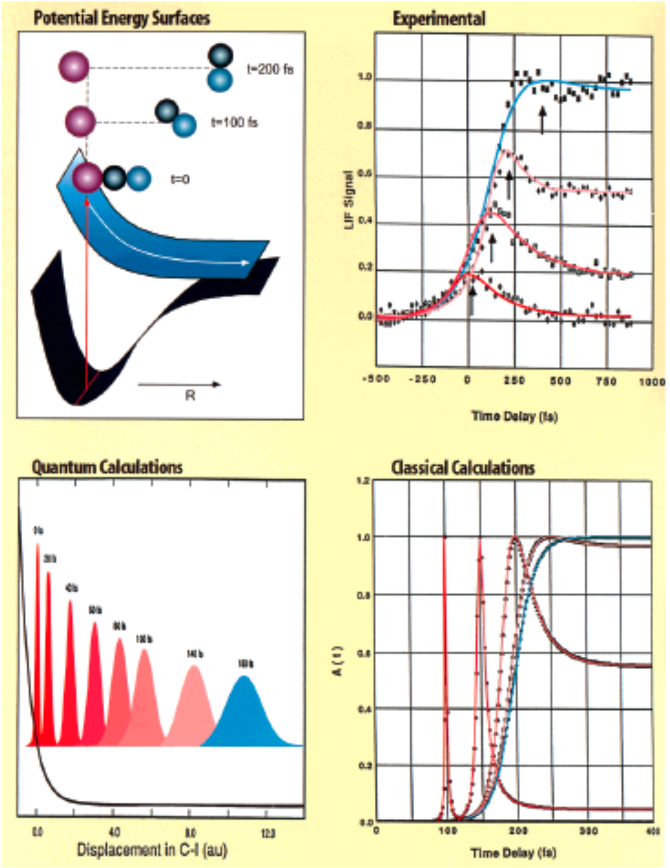
Femtosecond real-time probing of reactions

Demonstrate wavepacket formation in molecular systems!

$ICN^* \rightarrow I\cdots CN^{*\ddagger} \rightarrow I\,(^2P_{3/2}) + CN\,(X\,^2\Sigma^+) + E_{tr}$





Review: A. Zewail, *J. Phys. Chem. A* ***104,*** 5660 (2000).
M. Dantos et al., JCP 84, 2395 (1987).
S.O. Williams & D. Imre, JPC 92, 6648 (1988)
M. Rosker, M. Dantos, Zewail JCP 89,6113 (1988)

Probing rxn dynamics on multiple surfaces

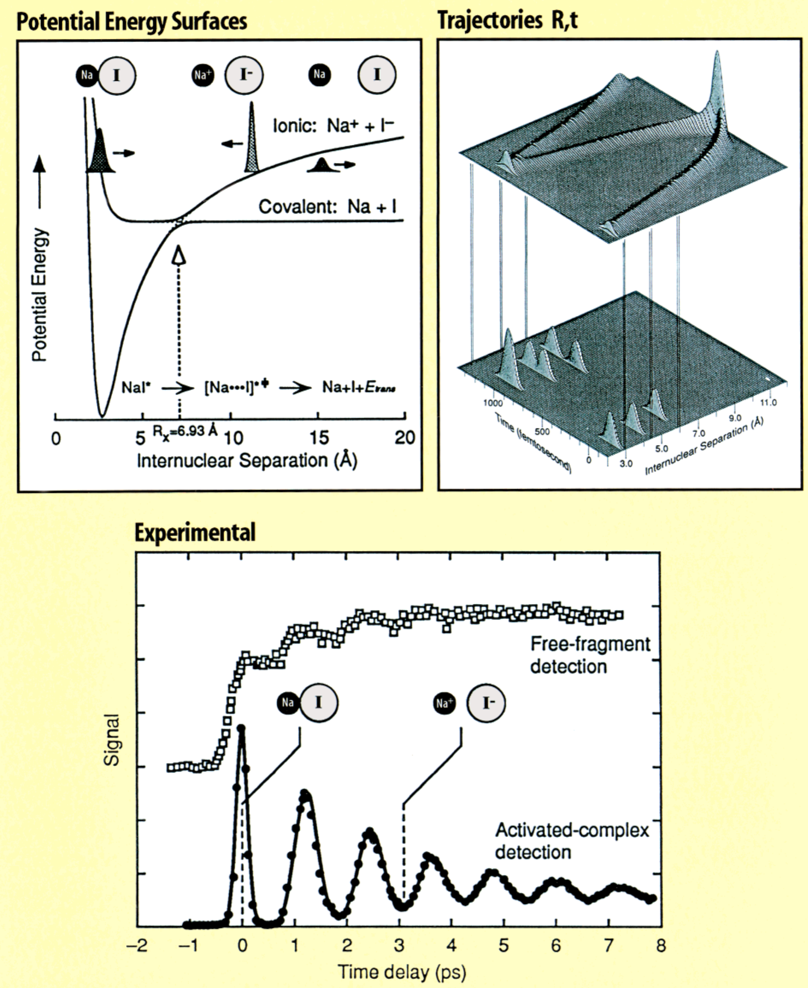
$NaI^* \rightarrow Na + I$
$\rightarrow Na^+ + I^-$

- Vary the probe wavelength to view dynamics of dissociation at different positions along the reaction coordinate (R).

- Detect resonance motion between ionic and covalent forms

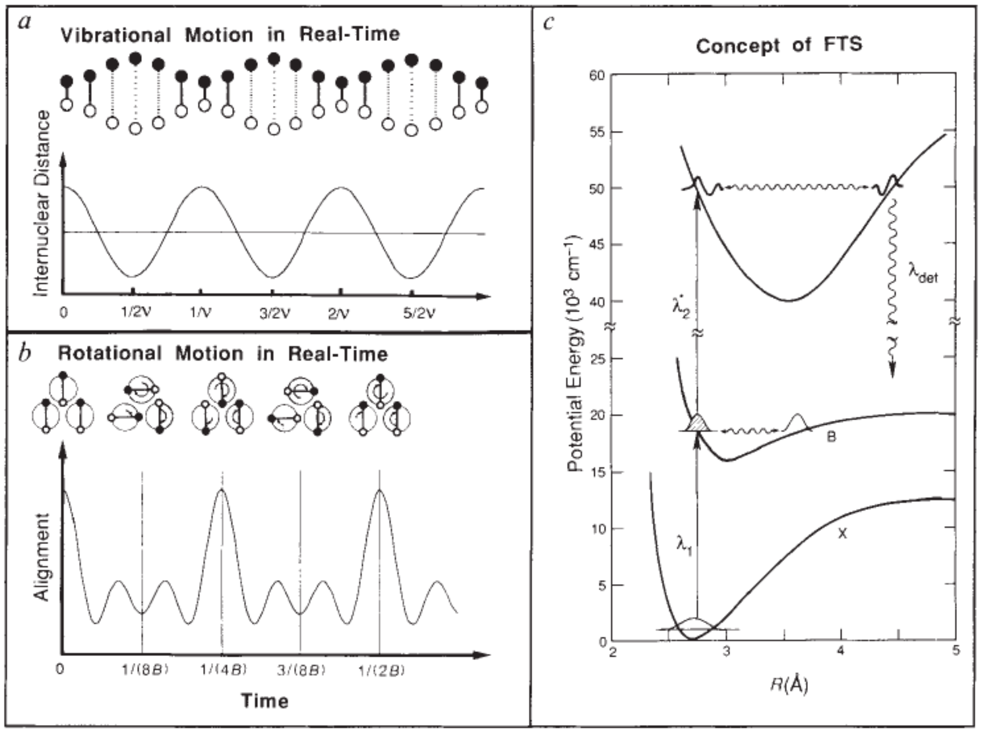
- Timescales for reaction and wavepacket spreading (initial localization to ~0.1Å)

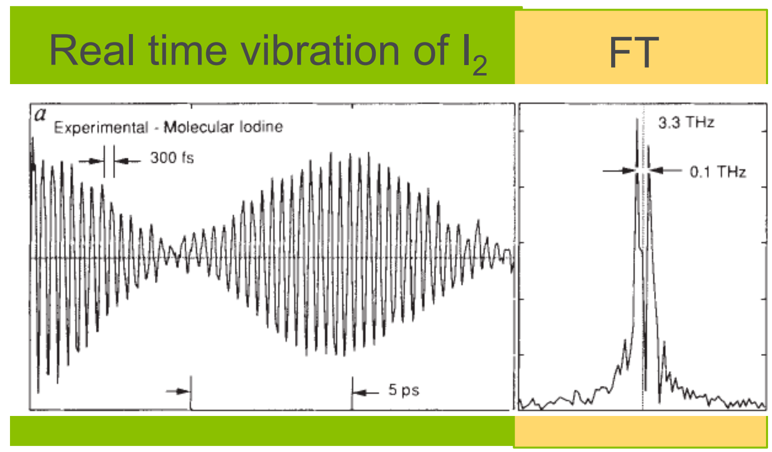
- Establish concept of *single molecule trajectories*



Pump-probe time-domain spectroscopy

Vibrational and rotational wavepacket recurrences yield molecular parameters through Fourier Transform of time domain data





- Wavepacket w/ two vibrational states
- Anharmonicity causes beating
- $\nu = 3.3$ THz, (13.5 meV)
  $\Delta\nu = 0.1$ THz, (0.41 meV)

Dantus et al Nature 343, 737 (2000)

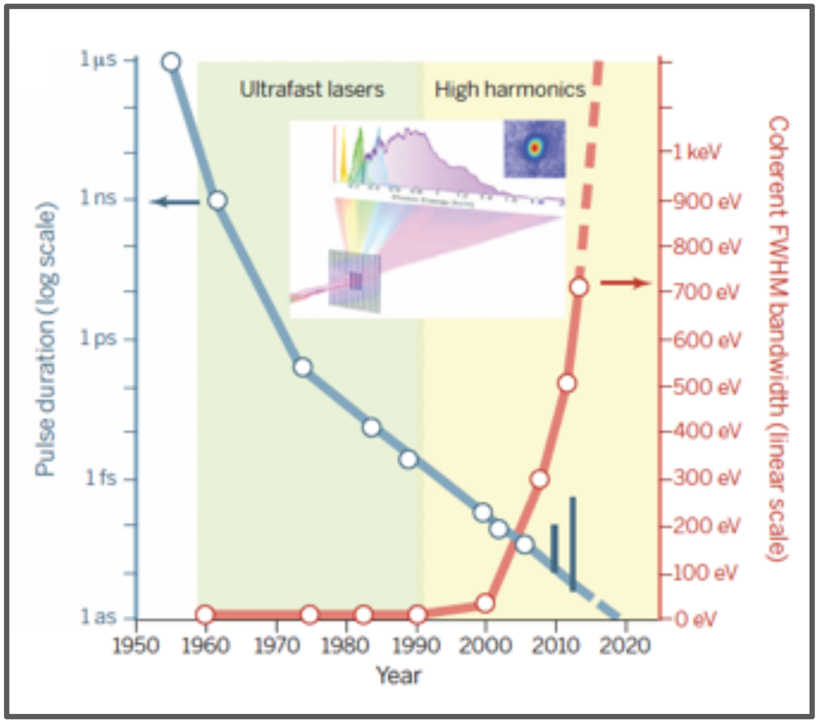
But ….

optical domain ultrafast pump/probe spectroscopies

do not provide direct structural information
do not reach the electronic timescale

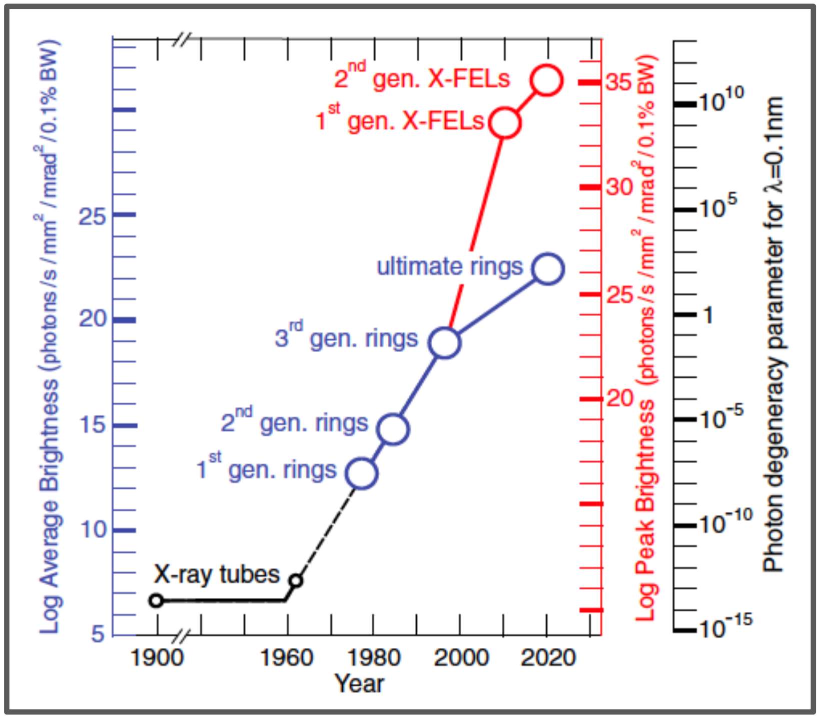
REVOLUTION IN ULTRASHORT X-RAY PULSES

High harmonic generation



10^5 x-rays/pulse/1% BW @ 1 keV
~1 fs
Current world record ~ 50 as

Accelerator-based sources



10^{13} x-rays/pulse/1% BW @ 1 keV
~100 fs
Current record ~ 200 as

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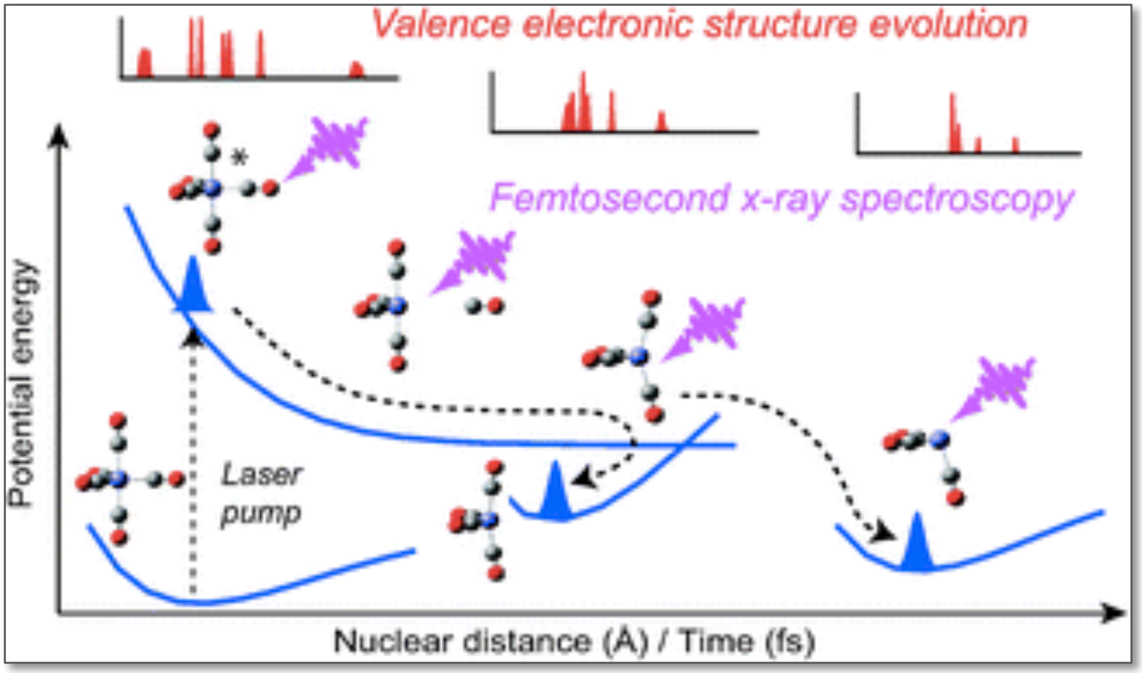
THE PUMP-PROBE CONCEPT – USING X-RAYS

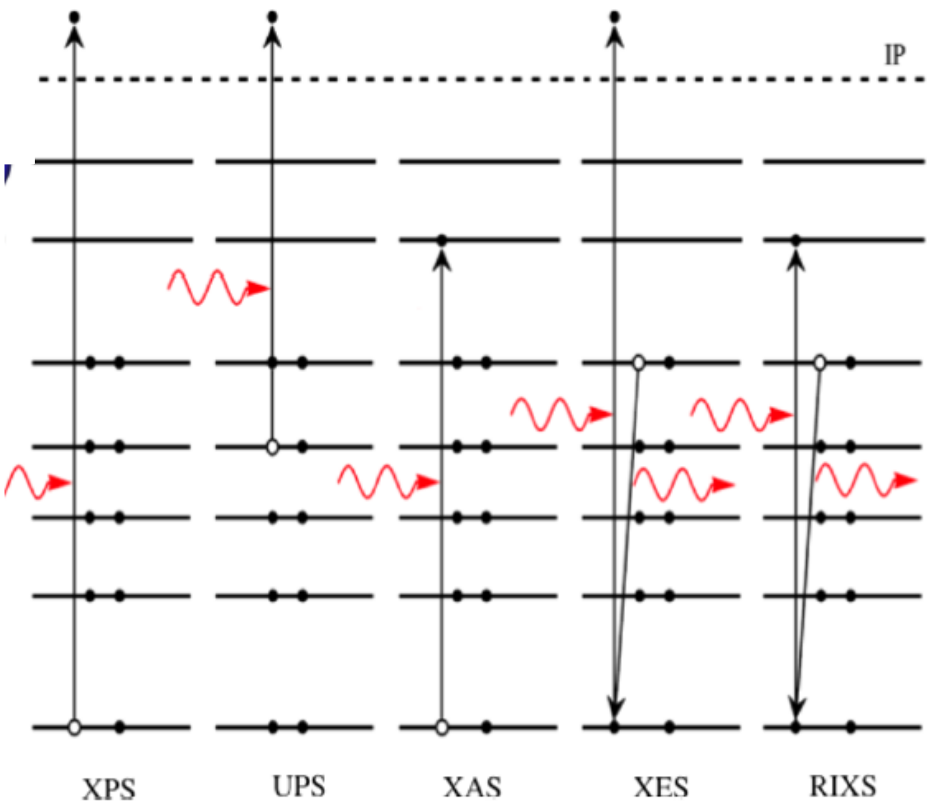
Mapping valence electron rearrangments during chemical rxns



Ph. Wernet, PCCP (2011)

X-RAY SPECTROSCOPIC PROBES

All can be used in the time domain to track dynamics



- Photoelectron spectroscopy
  - binding energies (UPS,XPS)
  - prompt response
- Absorption spectroscopy
  - unoccupied orbitals (XANES)
  - local structure (EXAFS)
- Emission spectroscopy (XES)
  - occupied orbitals
  - spin-state sensitivity
- RIXS
  - spectroscopy w/o core-hole broadening

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FUNDAMENTAL TIMESCALES

Orbital time 1s electron in hydrogen atom: 150 as

$T_{orb} = 2\pi a_0/(\alpha c)\ [n^3/Z^2]$

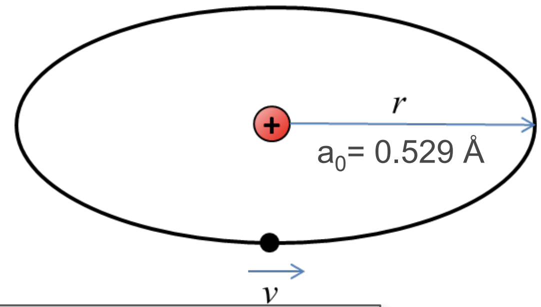
Vibrational period in H_2 : 4160 cm^{-1} ~ 8 fs

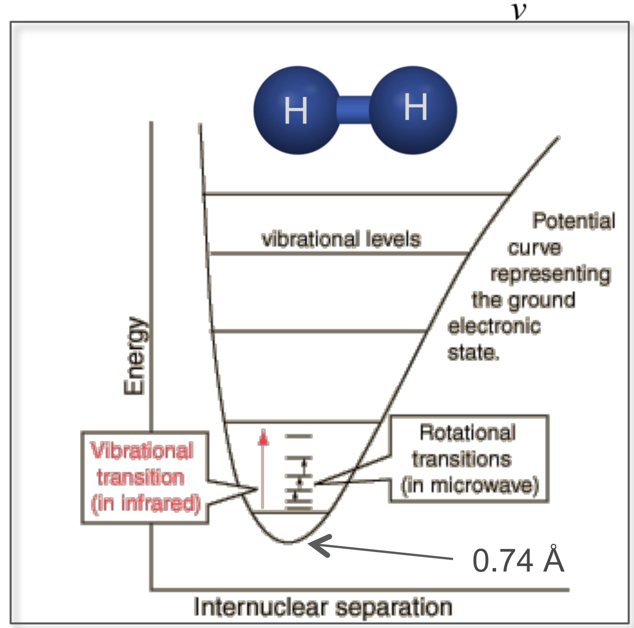
$T_{vib} = 2\pi(\mu/k)^{1/2}$

Rotational period in H_2 : 60 cm^{-1} ~ 0.55 ps

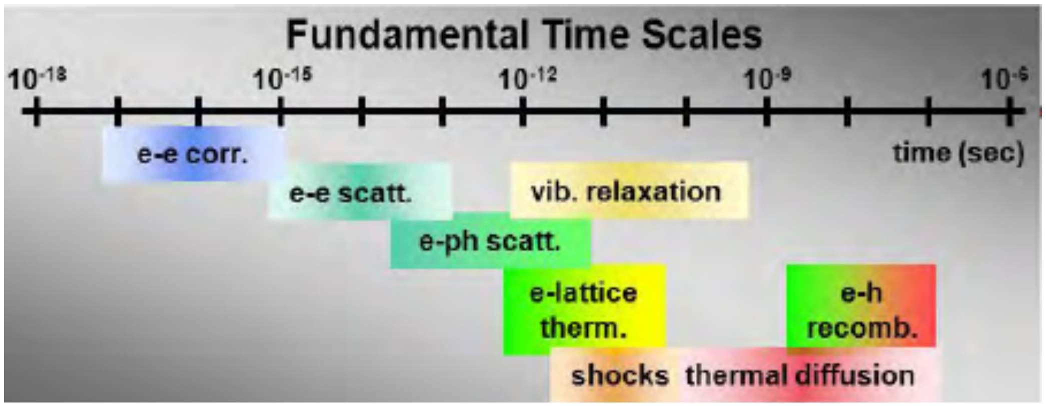
$T_{rot} = 2B_e = h/(2\pi)^2\mu R_e^2$

Hydrogen atom

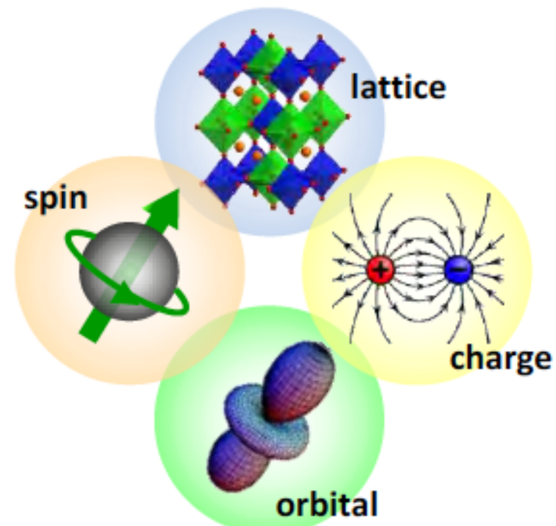




Fundamental timescales in condensed matter



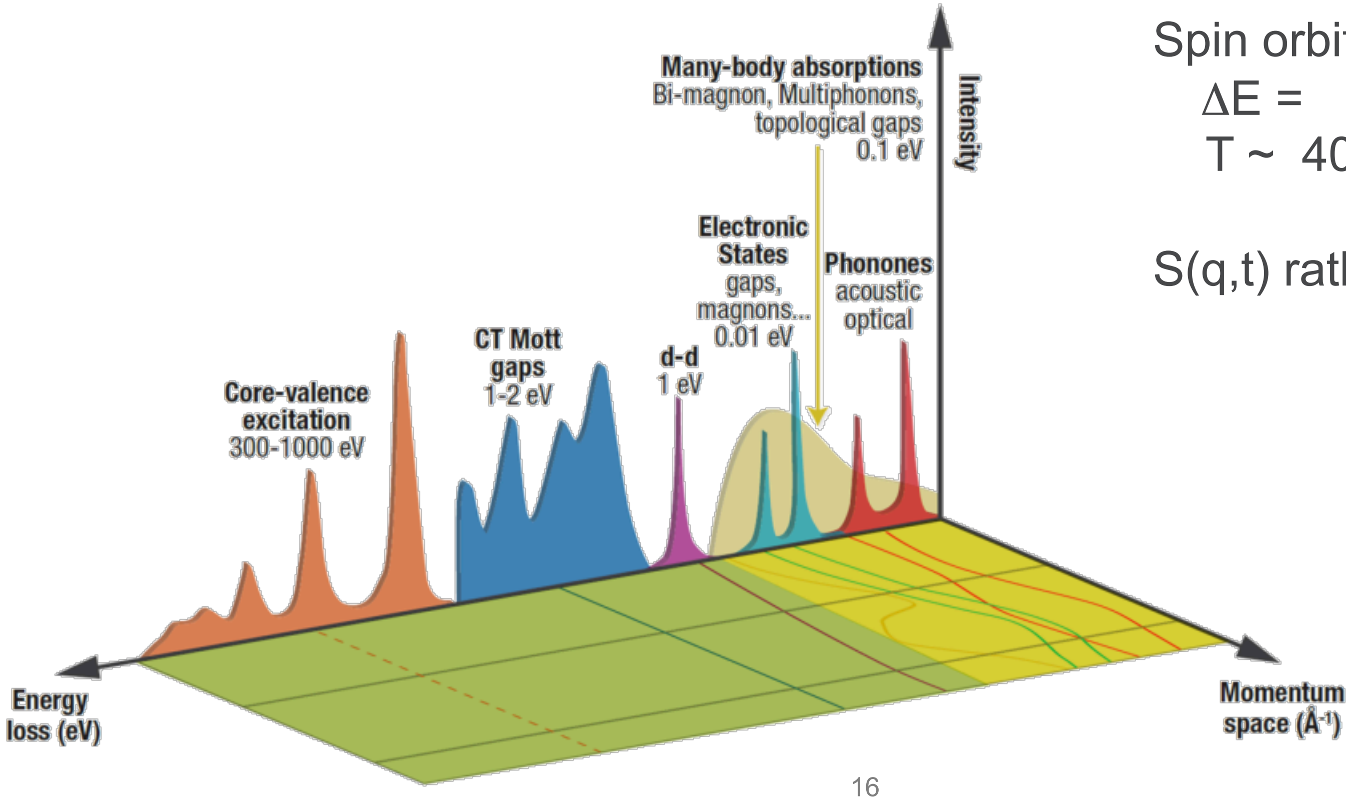
Coupled degrees of freedom



- Can we understand emergent phenomena (high Tc superconductivity, colossal magnetoresistance…) in systems with strongly interacting degrees of freedom?

- Can we control material properties in correlated systems
    - light, fields, pressure, composition…

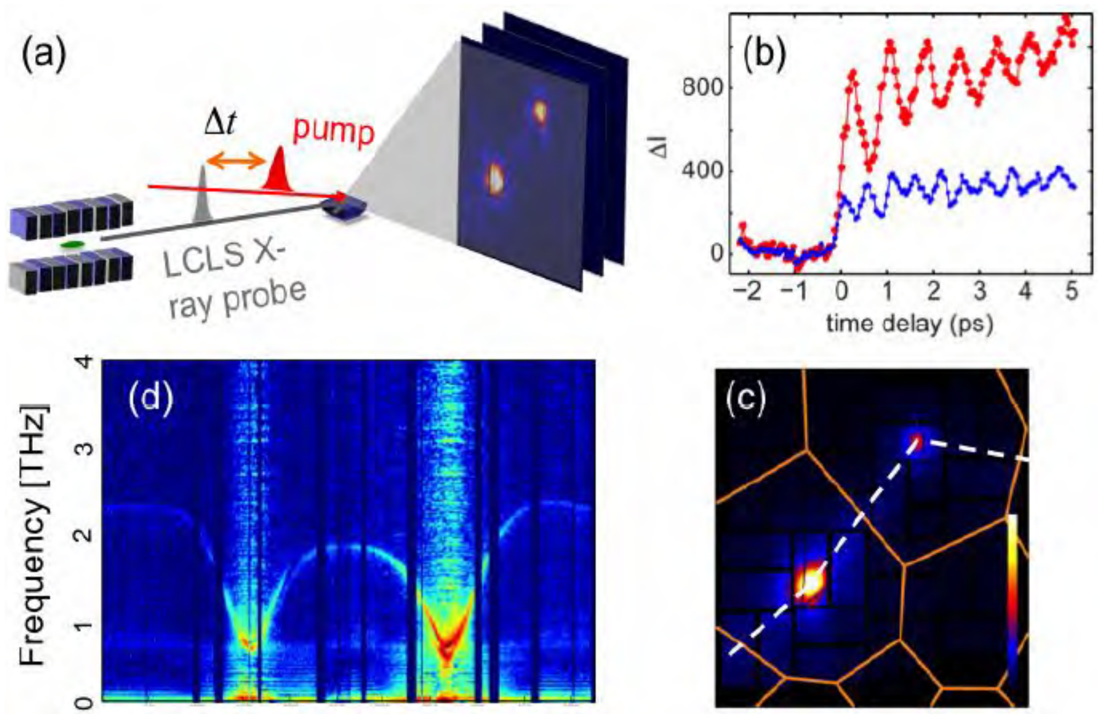
Time domain x-ray spectroscopies provide access to low energy collective excitations



Spin orbit, phonon, magnons…
ΔE = 1-100 meV
T ~ 4000 – 40 fs

S(q,t) rather than S(q,ω)

Time-domain phonon spectroscopy



X-ray diffuse scattering

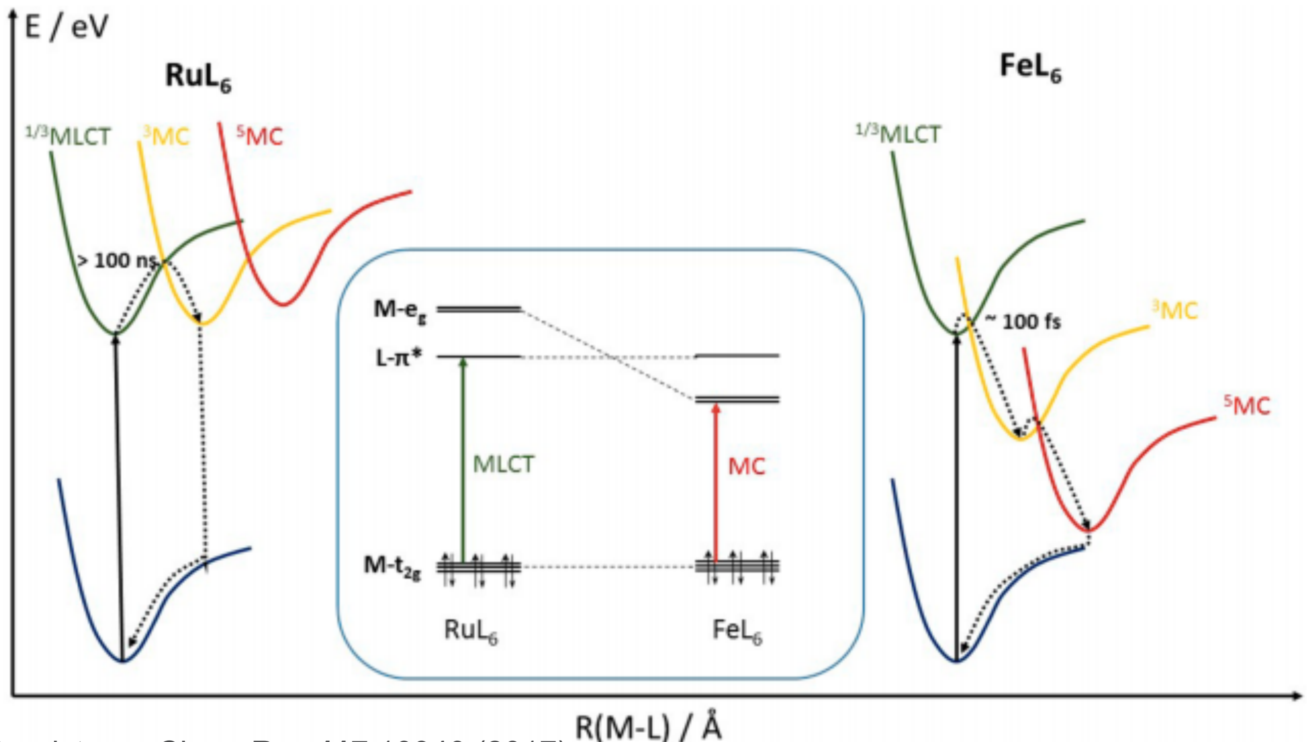
- ΔI(t) for different momentum xfers (pixels) oscillates with phonon frequency
- Phonon dispersion obtained from Fourier transform of ΔI(t)
- Access to very low energy modes w/ fs pulses

Transform-limited Gaussian pulse
ΔEΔT ~ 1.8 eV fs (FWHM)

M. Trigo et al., Nat. Phys. 9, 790 (2013)

Chemical systems exhibit complicated photoexcited state potential energy landscapes

4d, 5d vs 3d transition metals complexes of interest for solar energy



Ponseca … Sundstrom, Chem Rev **117**,10940 (2017)

OUTLINE – FOUR EXAMPLES

- Watching chemical reactions in solution
  – Laser-pump / x-ray probe spectroscopies (TR-RIXS)

- Elucidating the oxygen evolution mechanism in Photosystem II
  – Laser-pump / x-ray probe diffraction and spectroscopy

- Emergent superconductivity
  – Laser-pump / x-ray probe diffraction plus laser-pump / UV probe-photoemission

- Inner-shell electronic dynamics
  – X-ray pump / x-ray probe recoil ion spectroscopy

Example 1: watching chemical reactions in solution

LETTER

doi:10.1038/nature14296

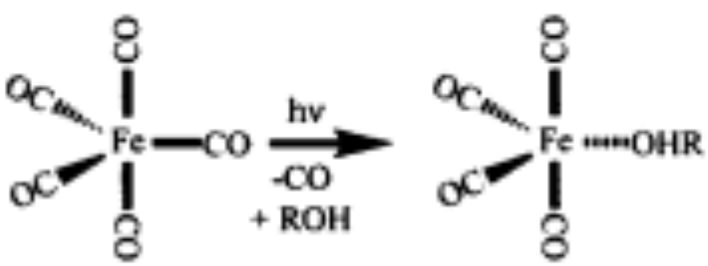
Orbital-specific mapping of the ligand exchange dynamics of $Fe(CO)_5$ in solution

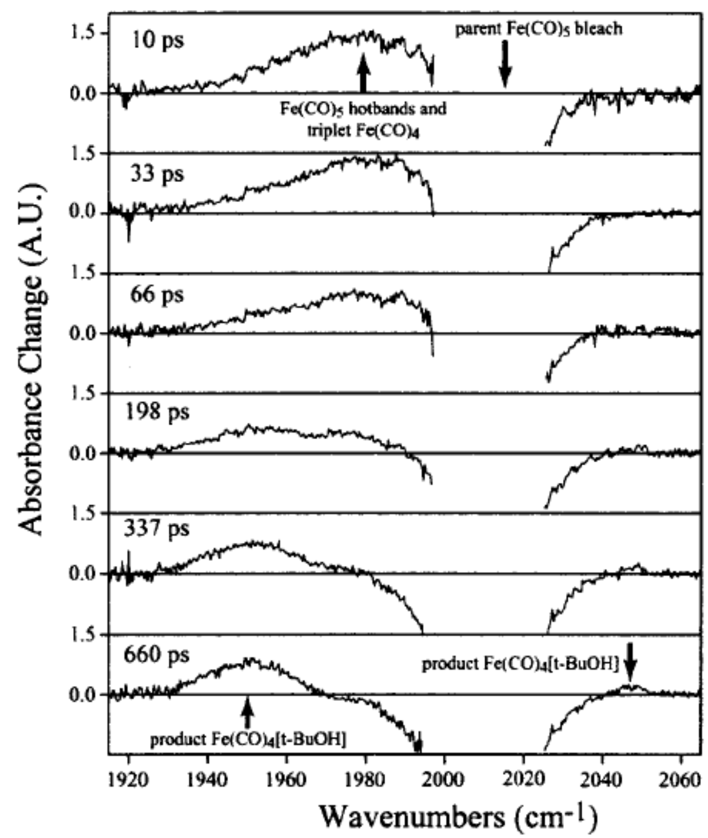
Ph. Wernet[1], K. Kunnus[1,2], I. Josefsson[3], I. Rajkovic[4]†, W. Quevedo[4]†, M. Beye[1], S. Schreck[1,2], S. Grübel[4]†, M. Scholz[4], D. Nordlund[5], W. Zhang[6]†, R. W. Hartsock[6], W. F. Schlotter[7], J. J. Turner[7], B. Kennedy[8]†, F. Hennies[8], F. M. F. de Groot[9], K. J. Gaffney[6], S. Techert[4,10,11], M. Odelius[3] & A. Föhlisch[1,2]

A classic light-induced chemical reaction in soln

Photoexcitation @ 295 nm: $Fe(CO)_5$ –› $Fe(CO)_4$ + CO

Study w/ UV pump/IR probe transient absorption
- singlet v triplet reactivity (spin barrier?)
- establish timescale for rxn (~40 ps MeOH)
- no evidence of singlet





P.T. Snee et al., JACS 123, 6909 (2001)
P.T. Snee et al., JACS 123, 2255 (2001)

A classic light-induced chemical reaction in soln

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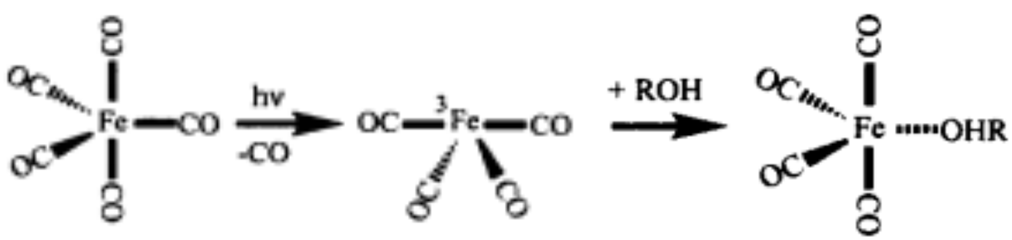
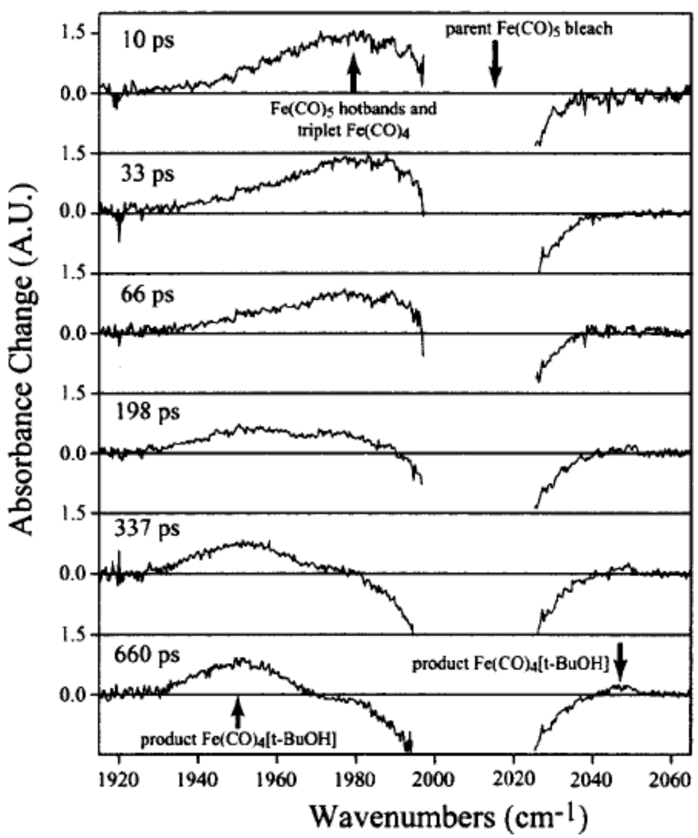
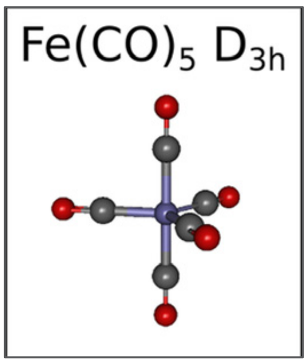




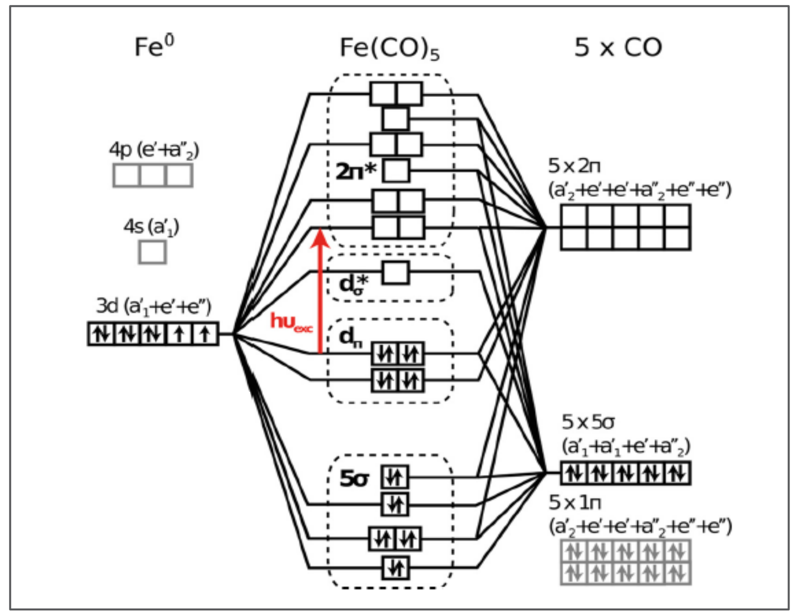
P.T. Snee et al., JACS 123, 6909 (2001)
P.T. Snee et al., JACS 123, 2255 (2001)

Revisit with x-rays focused on metal-ctr orbitals

Photoexcitation @ 266 nm: $Fe(CO)_5$ –› $Fe(CO)_4$ + CO



Valence molecular orbital diagram of $Fe(CO)_5$

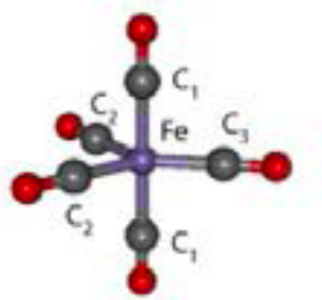


Ph. Wernet et al. Nature (2015)
K. Kunnus et al., Struct Dyn (2016)

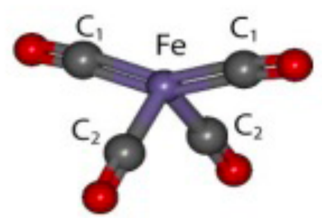
$FeCO_5$ photochemistry in solution - ethanol

The primary species involved

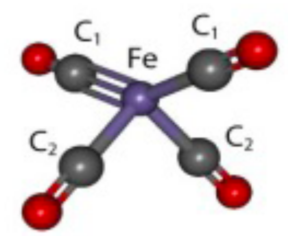
$Fe(CO)_5$ $^1A_1'$



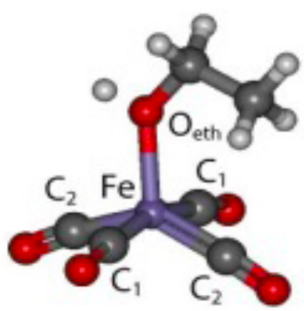
$Fe(CO)_4$ $^1B_2$



$Fe(CO)_4$ $^3B_2$

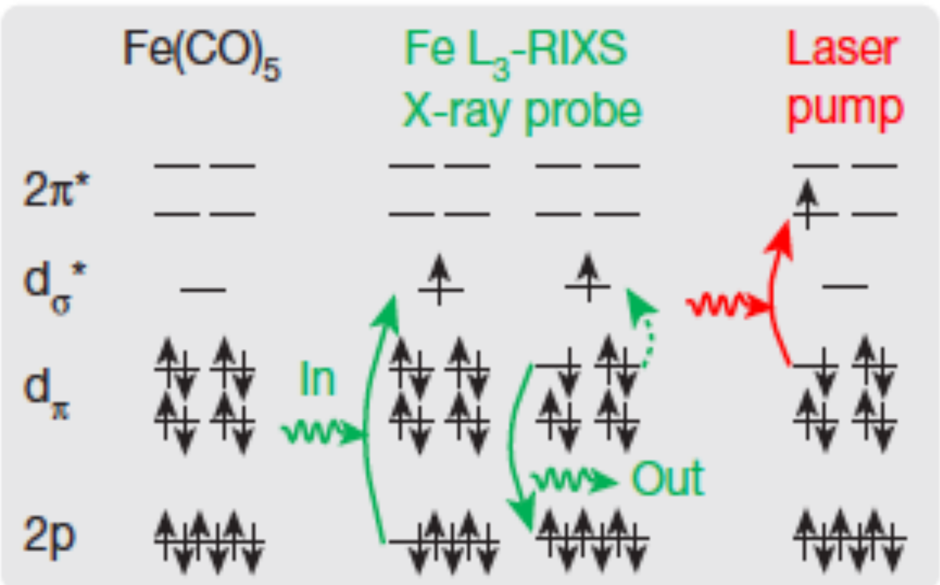


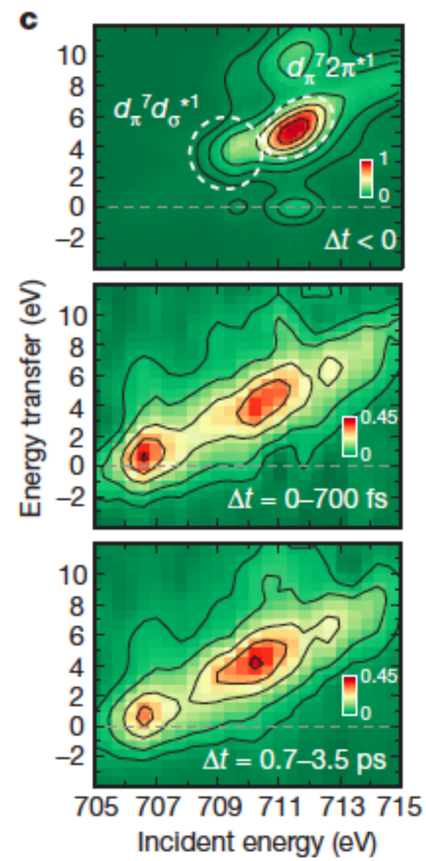
$Fe(CO)_4$-EtOH $^1A'$



RIXS probes orbital evolution during $Fe(CO)_5$ ligand exchange

Excite 2p –› LUMO and via IXS monitor the d_π –› $d\sigma^*$ Fe-centered frontier orbitals on fs timescale

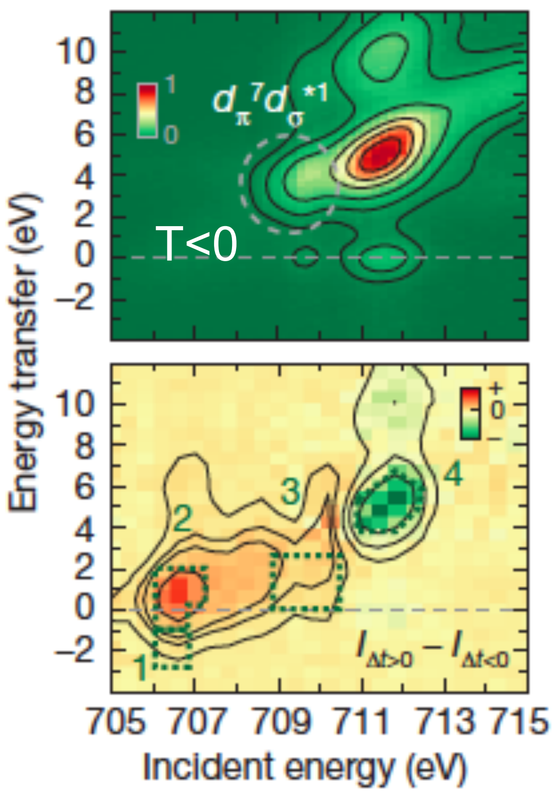




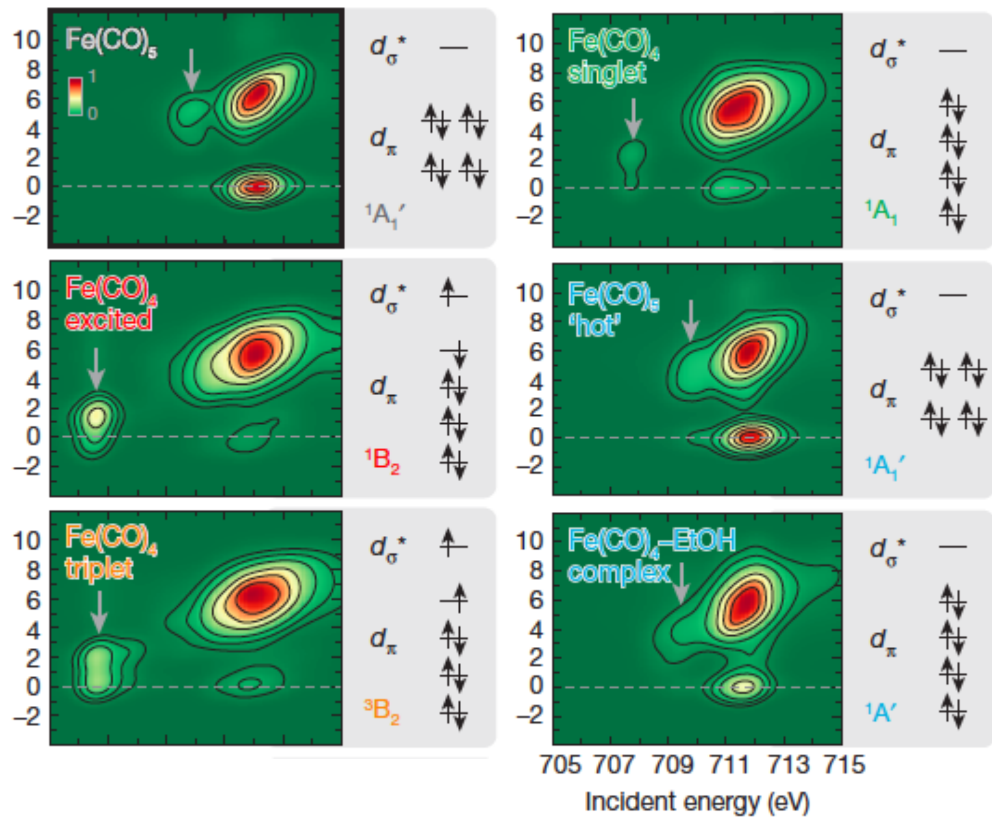
Ph. Wernet et al. Nature (2015)

More quantitative analysis of TR-RIXS data

Experimental data



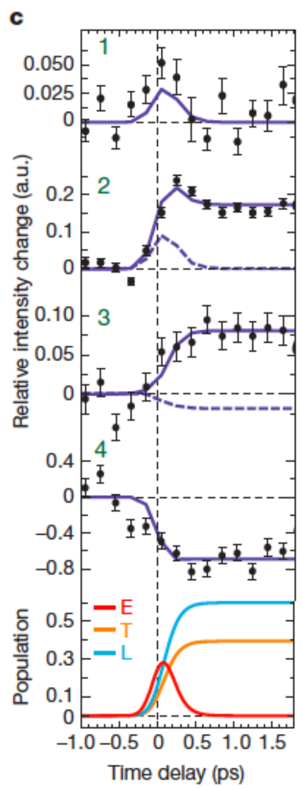
Ab initio Fe L_3 RIXS for relevant species

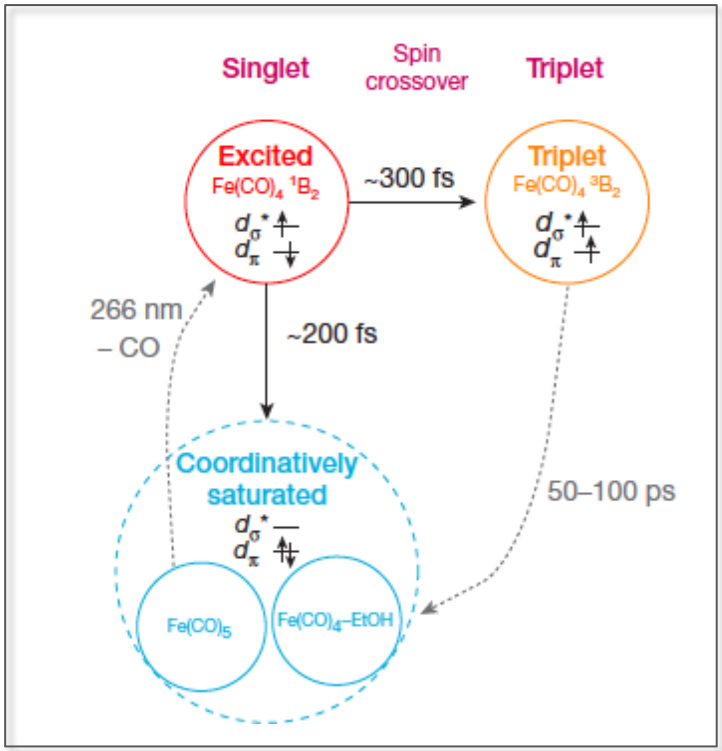


Ph. Wernet et al. Nature (2015)

Deduced kinetic model for ligand exchange

Three component model: Excited Singlet, Triplet and Ligated $Fe(CO)_4$





Summary

- Primary rxn steps involve singlet in soln as in gas phase
- Sub-ps ISC to triplet
- Triplet persistent to 3 ps –
- Competing channels of spin-crossover and ligation

TR-RIXS provides capability to correlate orbital symmetry with spin multiplicity and reactivity

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

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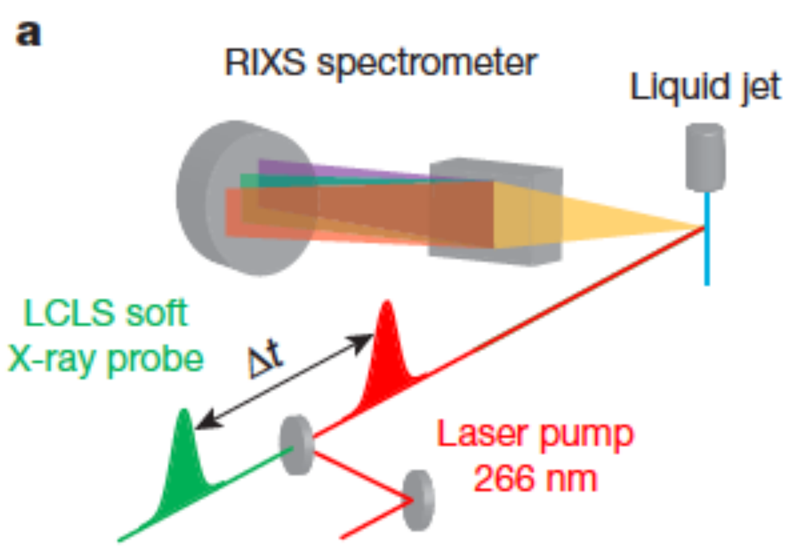
Expt'l details: RIXS orbital specific mapping of ligand exchange

$Fe(CO)_5$ in ethanol solution, 1 M, 20 μm jet



Laser pump:
- 4.66 eV (266 nm)
- 5 μJ, 100 fs, 100x400 μm^2

X-ray probe:
- 703-715 eV, dE = 0.5 eV
- 1.6×10^{10} photons/pulse
- 20 x 300 μm^2

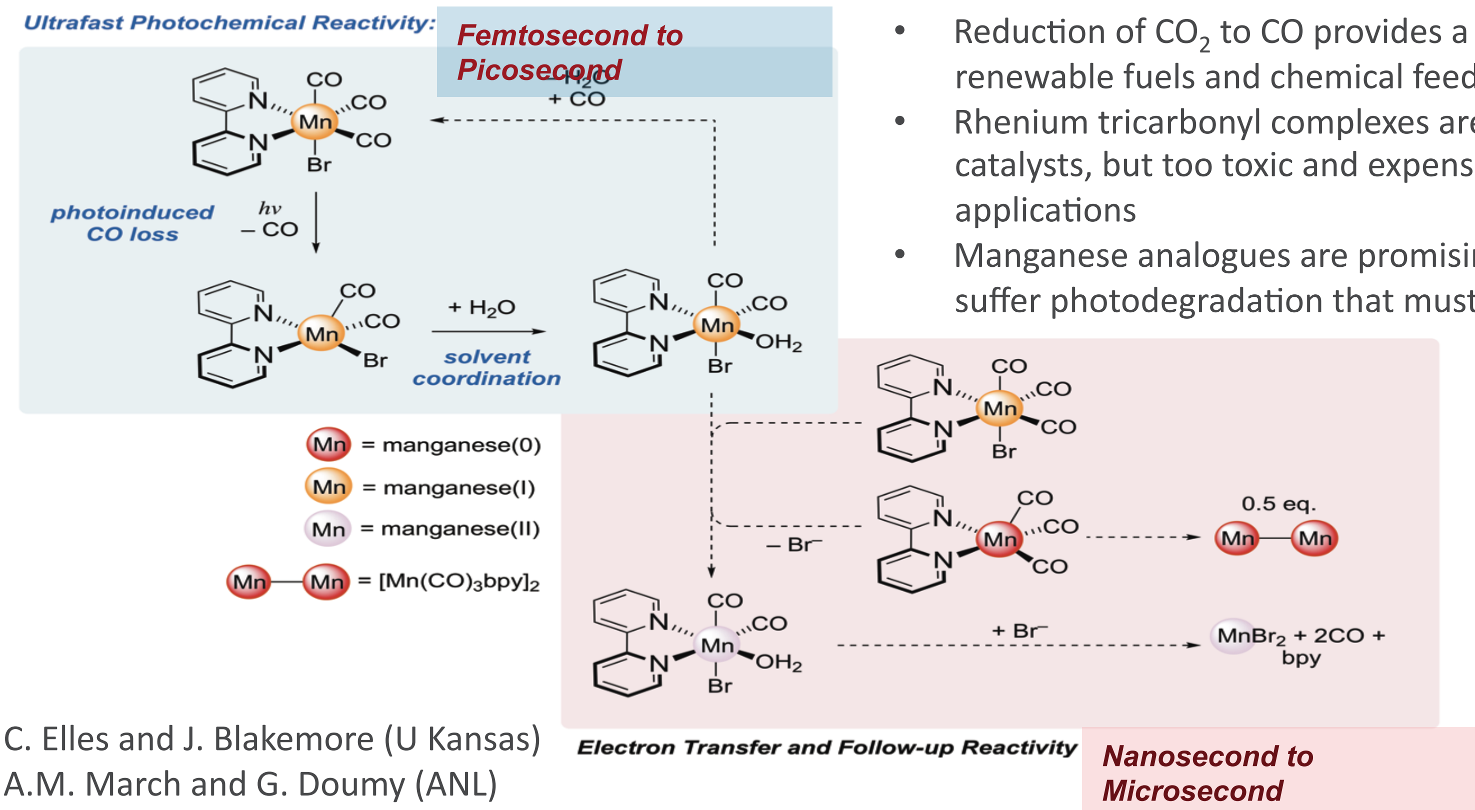
RIXS resolution
- 0.7 eV incident
- 1.2 eV energy transfer

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

Mn-based catalysts for CO_2 reduction

Understanding photodegradation mechanisms in order to make inexpensive and earth-abundant catalysts – x-ray spectroscopy probes mechanism over wide timescales

- Reduction of CO_2 to CO provides a promising source of renewable fuels and chemical feedstock
- Rhenium tricarbonyl complexes are efficient and stable catalysts, but too toxic and expensive for large-scale applications
- Manganese analogues are promising alternatives but suffer photodegradation that must be overcome



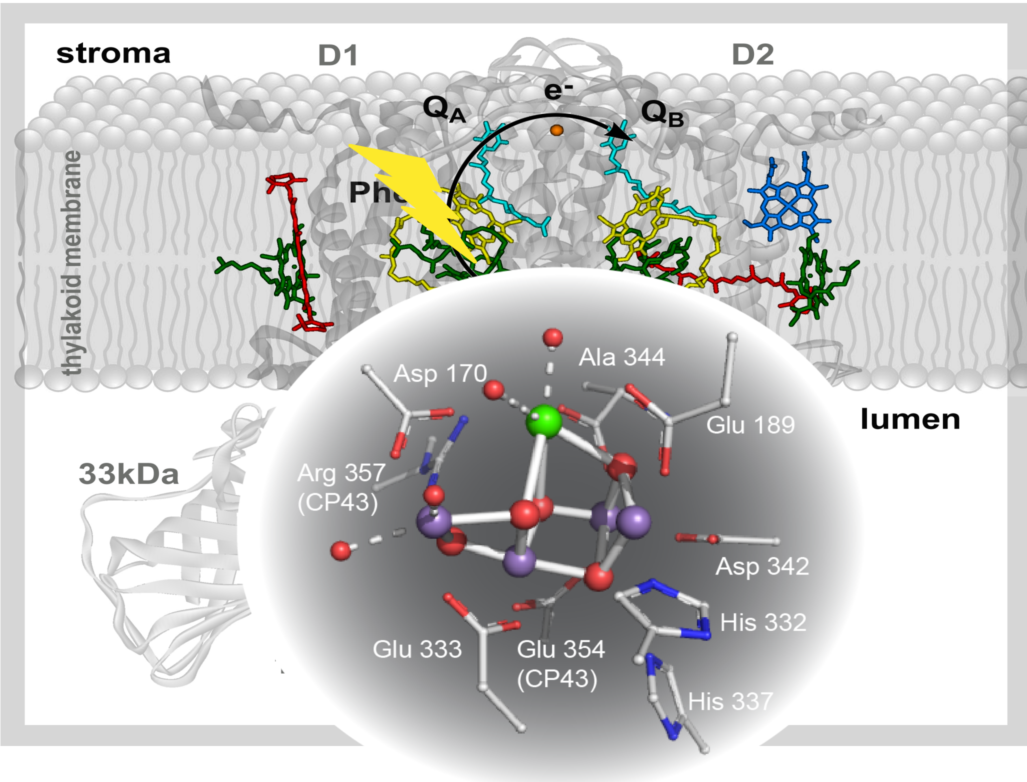
C. Elles and J. Blakemore (U Kansas)
A.M. March and G. Doumy (ANL)

M. Bourrez, *et al.*, Angew. Chem. Int. Ed., **50**, 9903-9906 (2011), J. M. Smieja, *et al.*, Inorg. Chem. **52**, 2484-2491 (2013).

Photosystem II – structure and mechanism

Slides courtesy Junko Yano

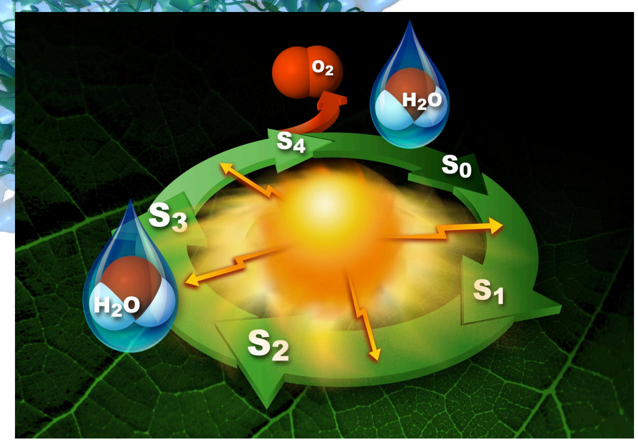
Water oxidation reaction in photosystem II



4 photons

$$2\ H_2\mathbf{O} \rightarrow \mathbf{O}_2 + 4\ H^+ + 4\ e^-$$

- Where and how the O-O bond formation occurs?
- How substrate water comes in?
- How the protein environment modulates the catalytic reaction?



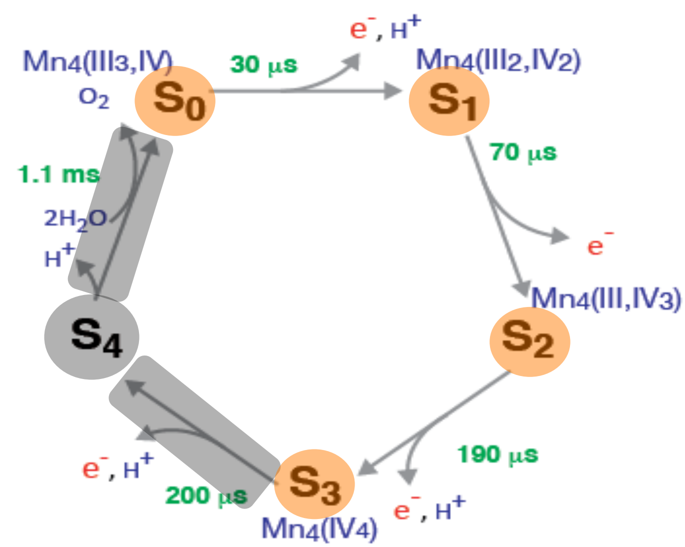
Understanding the mechanism of the water oxidation reaction in Photosystem II

Status prior to XFEL experiments:

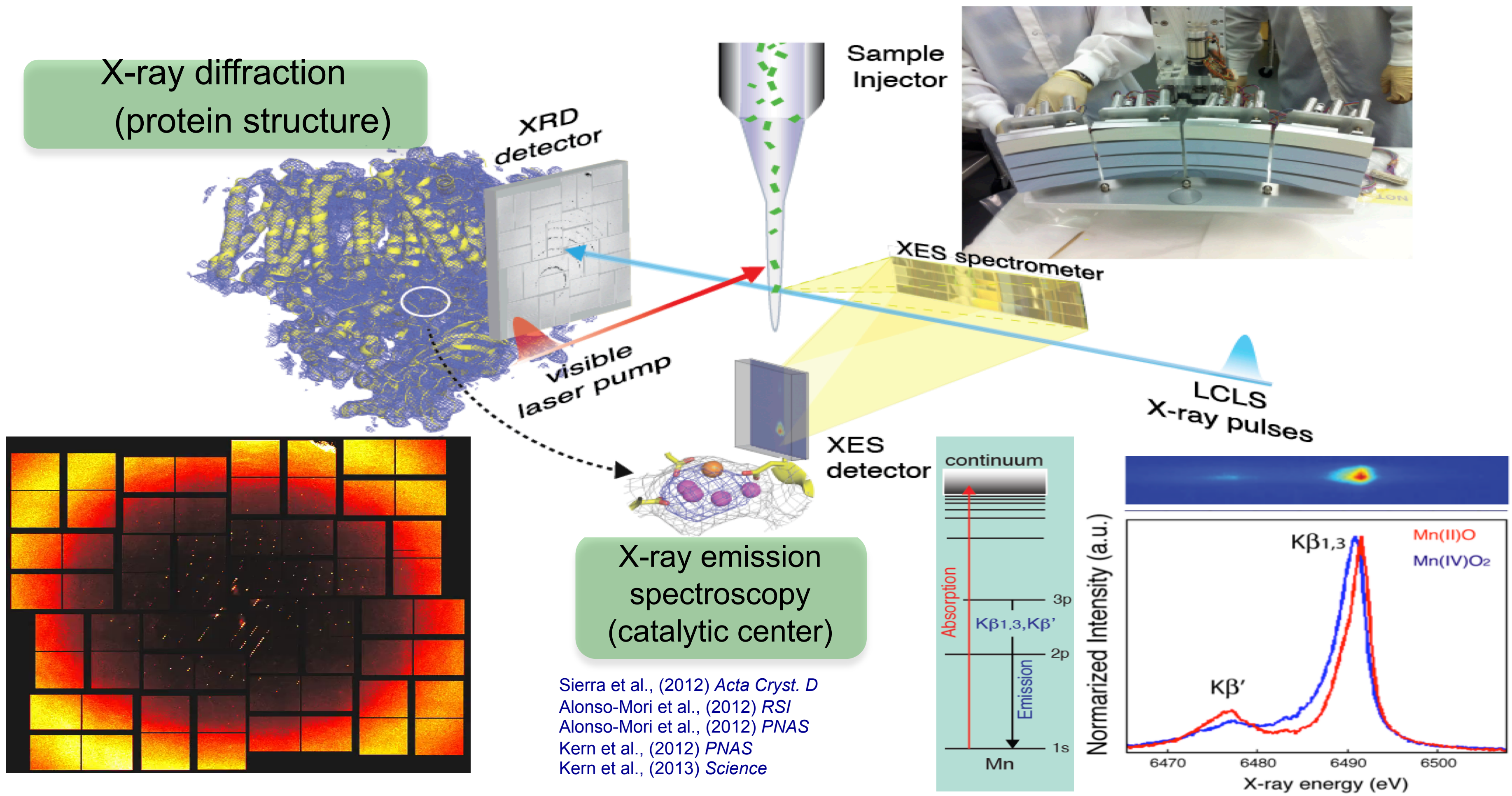
- High-resolution crystal structure of **the dark (S_1) state**.
- Information from **various advanced spectroscopies** (EPR, IR, Optical, and X-ray) of the stable S (S_1, S_2, S_3, and S_0)-states at cryo. temp. that predict possible structure and electronic structure of those states.
- Proposed water oxidation mechanisms from theoretical studies.

Gaps:

- Requires high-resolution **room temperature structure** of **each S-state** as well as **time-points** during the transitions.
- Capability (methods) for interpreting structural information together with spectroscopic data.
- **Charge/spin localization/delocalization** between metals and ligands during the catalytic cycle.
- **Theoretical capabilities** to simulate detailed electronic structures, in particular, for multinuclear complexes, and at *room temperature*.



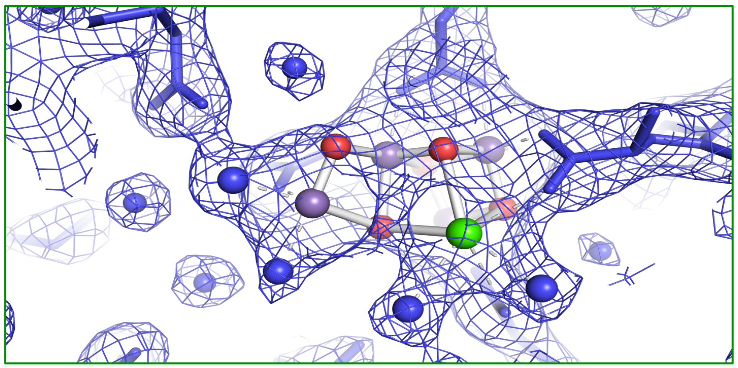
Simultaneous x-ray crystallography and spectroscopy at RT



Sierra et al., (2012) *Acta Cryst. D*
Alonso-Mori et al., (2012) *RSI*
Alonso-Mori et al., (2012) *PNAS*
Kern et al., (2012) *PNAS*
Kern et al., (2013) *Science*

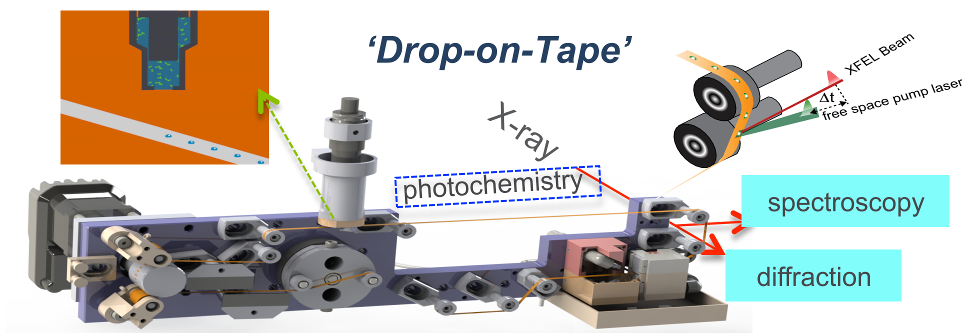
High resolution structure of OEC in light activated state!

Enabled by improved sample delivery and data collection efficiency



Structure of the oxygen evolving Mn_4Ca complex in photosystem II in the S1 and S3 state at RT to 2.25 Å.

Kern et al., (2014) Nature Comm.
Young, I. D., *et al.* (2016) *Nature*
Fuller, F.D., *et al.* (2017) *Nature Methods*

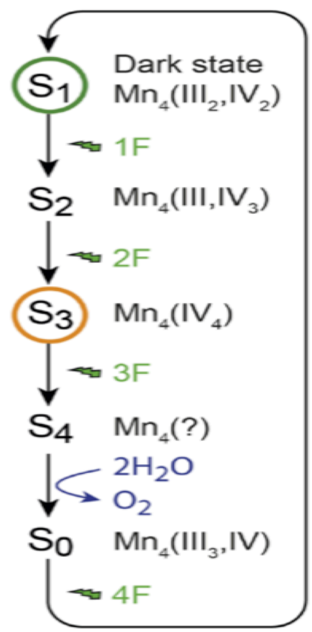


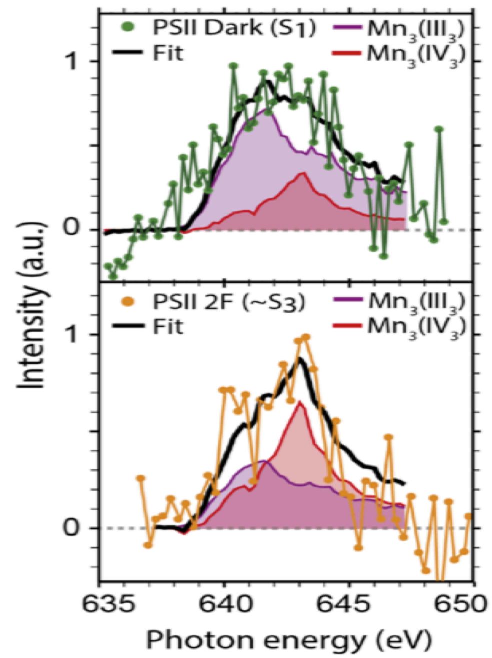
Future Outlook

- High-resolution data collection of the **transient states** to understand the **sequence of events** and the role of **protein dynamics** that enable the multielectron catalysis.

- Application of metal L-edge XAS and RIXS to understand the evolution of the Mn electronic structure at room temperature.

- High rep. rate of LCLS-II realizes some of the photon-hungry spectroscopy of dilute protein samples.





Mitzner et al. (2013) J. *Phys. Chem. Letts.*, Kubin et al. (2017) *Structural Dynamics*

Courtesy J. Yano

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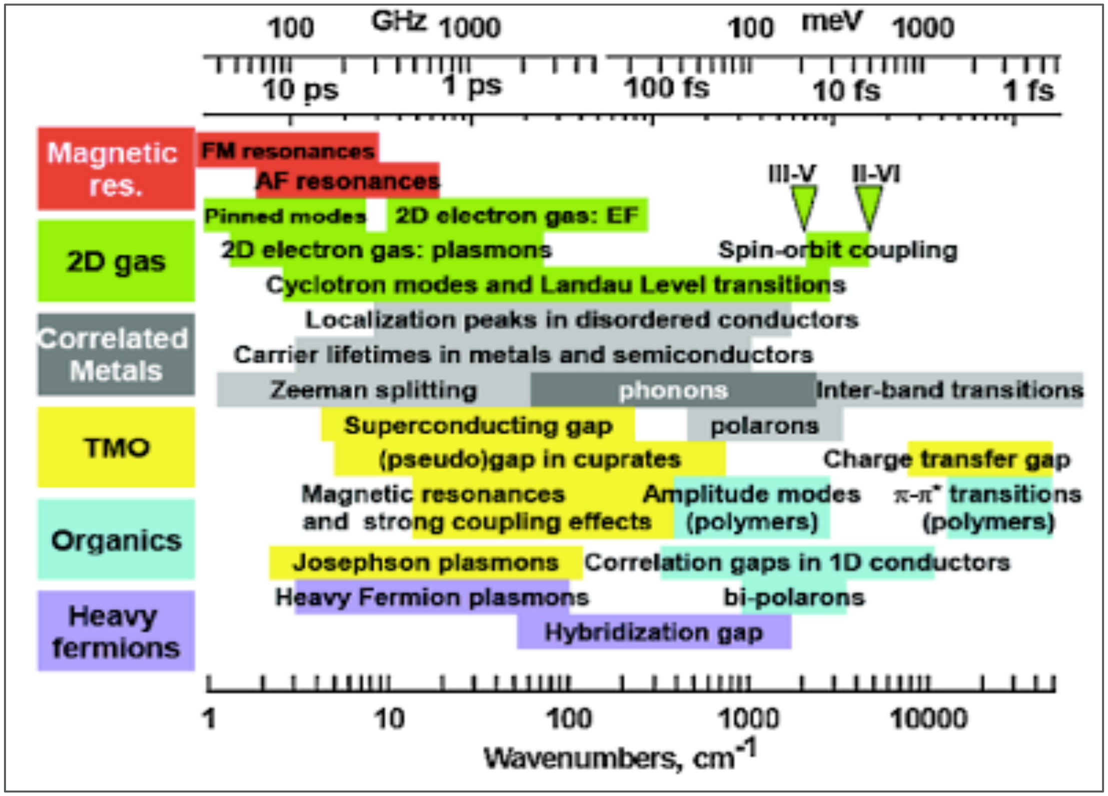
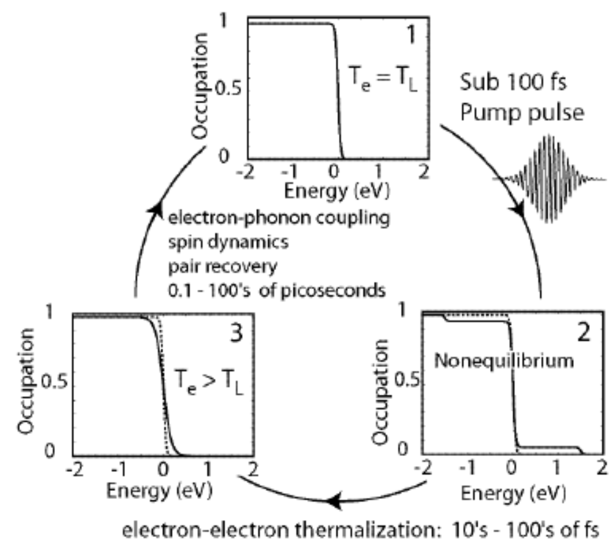
Condensed matter and materials

Excitations in strongly correlated materials





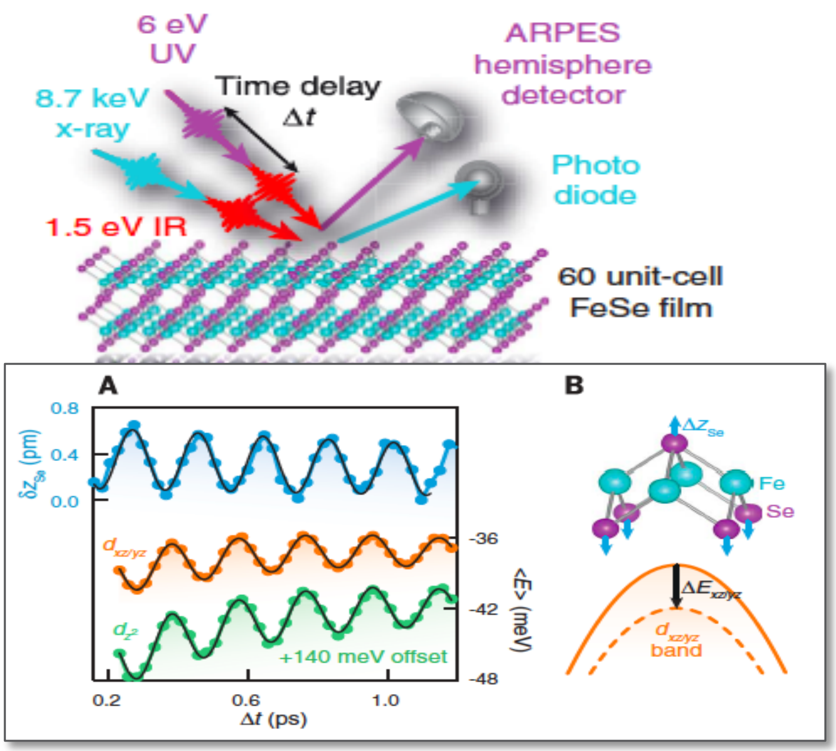
a la Eigen

D. Basov et al, RMP 83, 471 (2011)

Combining TR-XRD + TR-ARPES yields orbitally-resolved electron-phonon coupling

Provides quantitative guidance for many-body theory

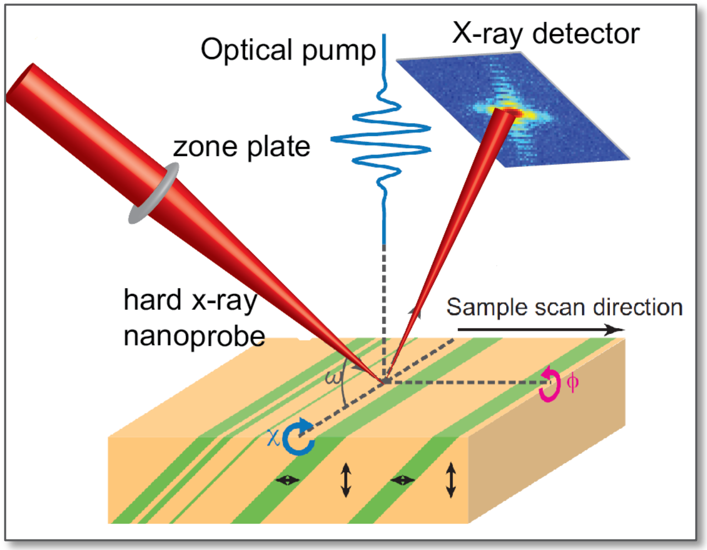
- Single mode response of A_{1g} optical phonon allows “lock-in” of two separate time-resolved measurements
- Diffraction –› atomic displacement
  ARPES –› band structure $d_{xz/yz}$ and d_{z^2}
- Determination of potential seen by Fe electrons due to Se anion movement
- Meaured value is an order of magnitude larger than DFT result –› theory guidance



Gerber et al., Science 357, 71 (2017)

Light activated domain dynamics in ferroelectrics

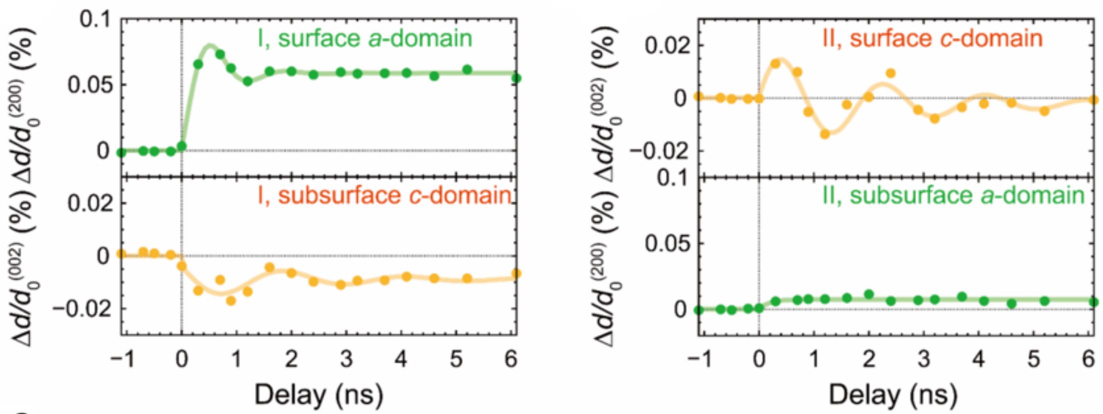
APS: Nanofocused x-ray beam circumvents spatial averaging to reveal emergent phenomena on the mesoscale



7ID-C@APS

X-ray beam size: 400 nm
X-ray pulse duration: 100 ps

- Domain-dependent gigahertz acoustic wave
- Photoinduced large surface electric field
- Derived domain wall speed of 2.5 m /s



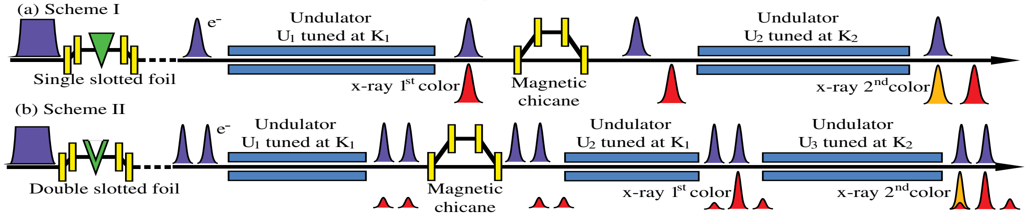
H. Akamatsu et al, Phys. Rev. Lett. **120**, 096101 (2018)

X-ray pump / x-ray probe studies

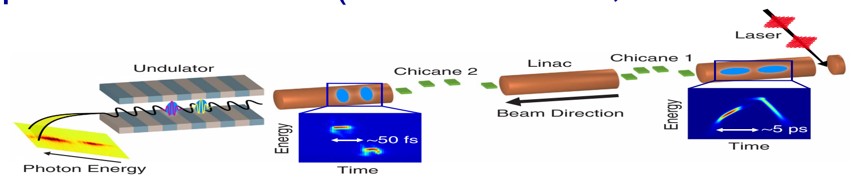
watching & controlling inner-shell electron motion
understanding radiation damage

X-ray pump/x-ray probe capabilities at LCLS

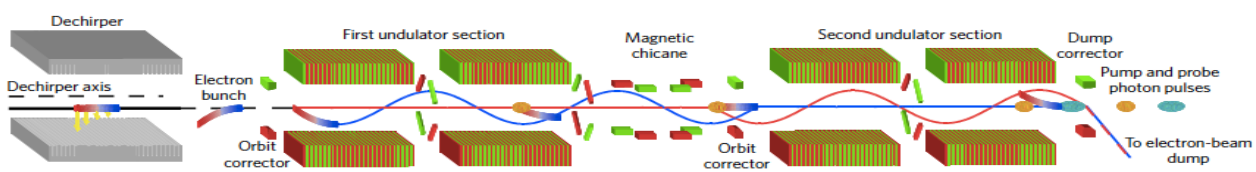
One e-bunch – two x-pulse – two color (Lutman *et al.*, PRL **110**, 134801 (2013))



Two e-bunch – two x-pulse – two color (Marinelli *et al.*, Nat. Comm. **6**, 6369 (2015))

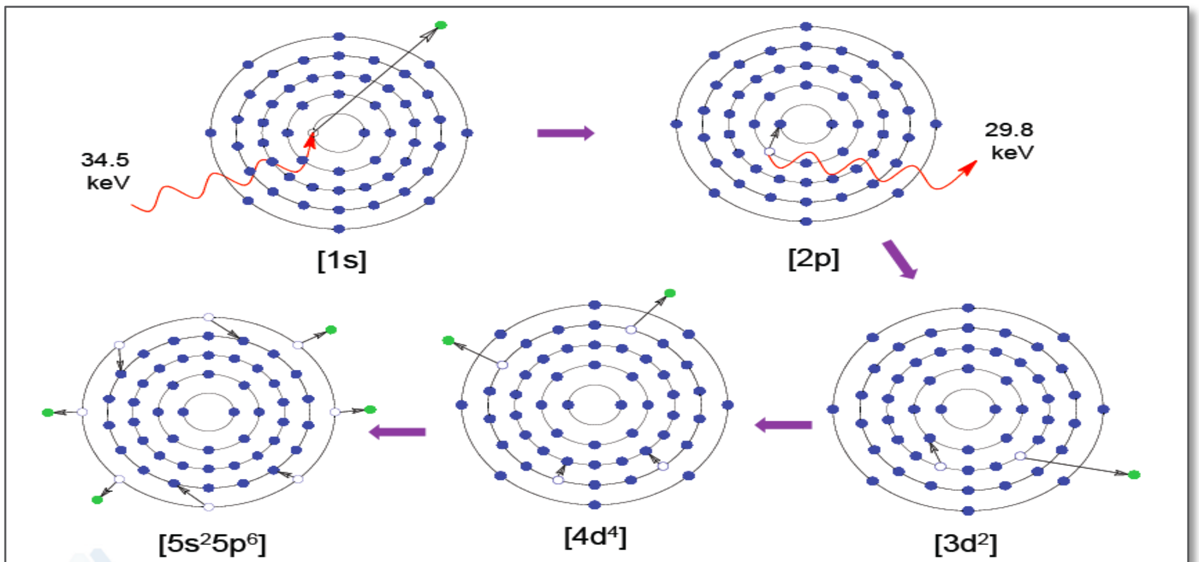


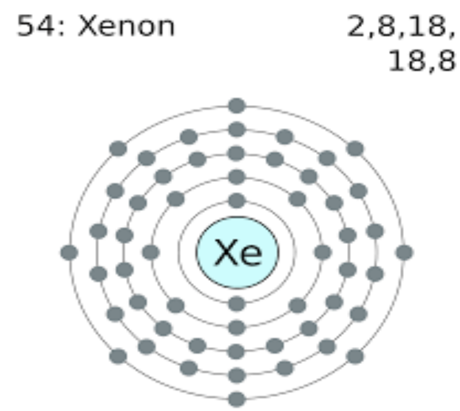
Fresh-slice multicolor (Lutman *et al.*, Nat. Photon. **10**, 745 (2016))



Motivation: inner-shell vacancies initiate radiation damage

Radiation damage limits resolution in x-ray imaging applications
Localized damage can be used for therapies [Gohkberg..Cederbaum Nature (2015)]





Single K-shell vacancy in Xe can create Xe^{8+}
Cascade happens on tens of fs timescale

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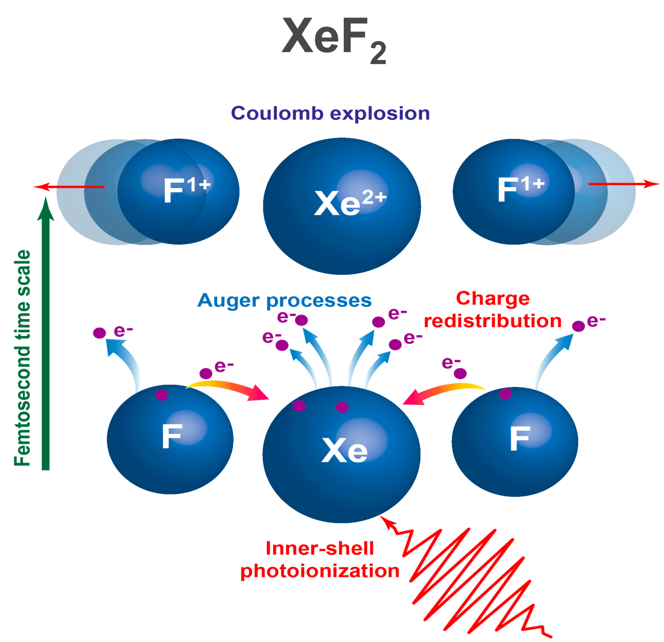
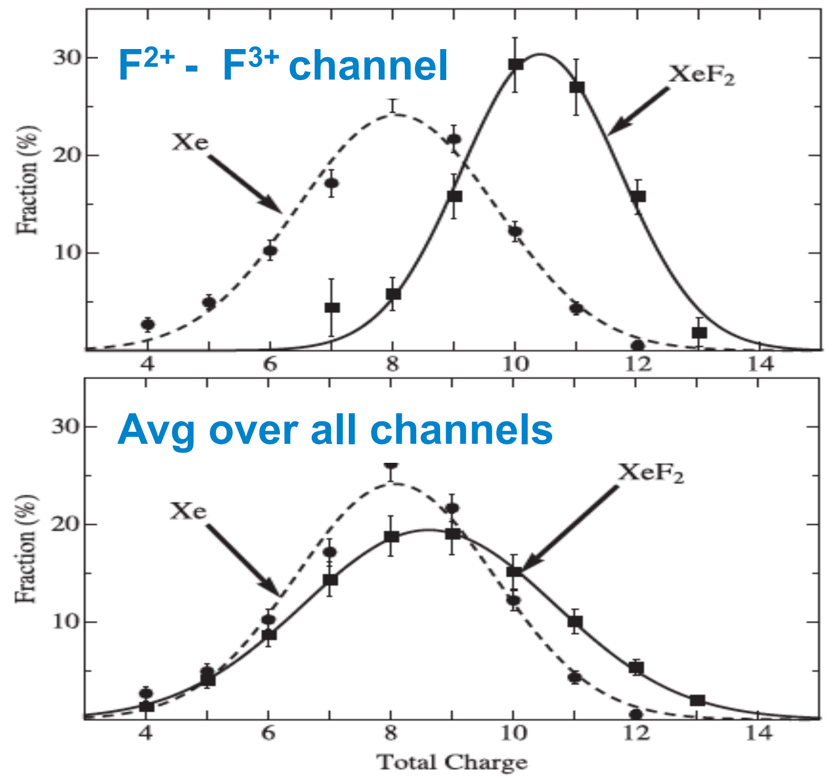
What happens in “complex” environment?





- Higher charge in molecule vs atom
- Evidence for “Interatomic Coulombic Decay”

R.W. Dunford et al., PRA **86,** 033401 (2012)

TIME-RESOLVED X-RAY SPECTROSCOPY OF XeF_2

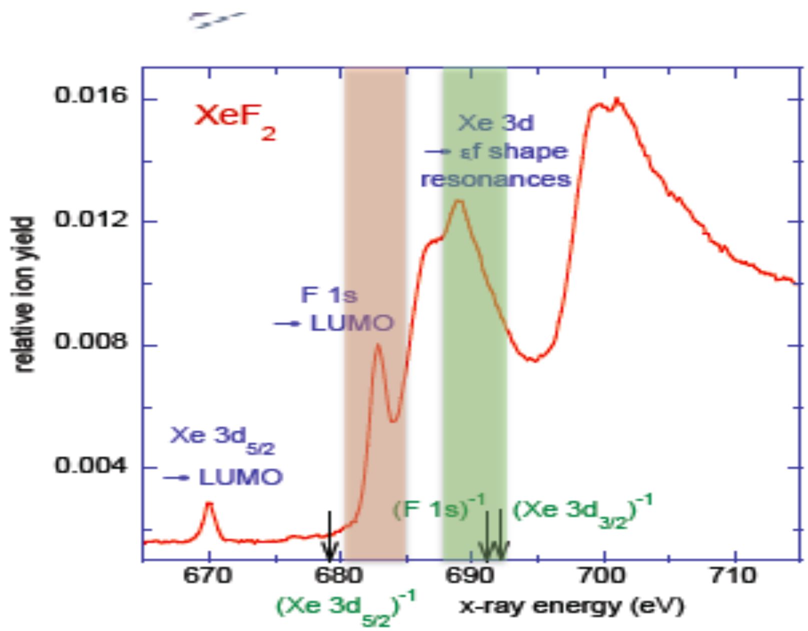
Early two-color SASE x-ray pump/probe: Lutman PRL (2013) scheme

Monitor competition

Auger decay
Charge redistribution
Coulomb Explosion

Pump: 690 eV
Xe 3d → εf shape resonance
Probe: 683 eV
F^+, F^{2+} 1s → 2p
10-fs pulses
Δt = 4, 29, 54 fs

33 μJ combined pulse energy
20% optics efficiency
5 μm^2 focal spot
1.3 x 10^{16} W/cm^2 peak intensity

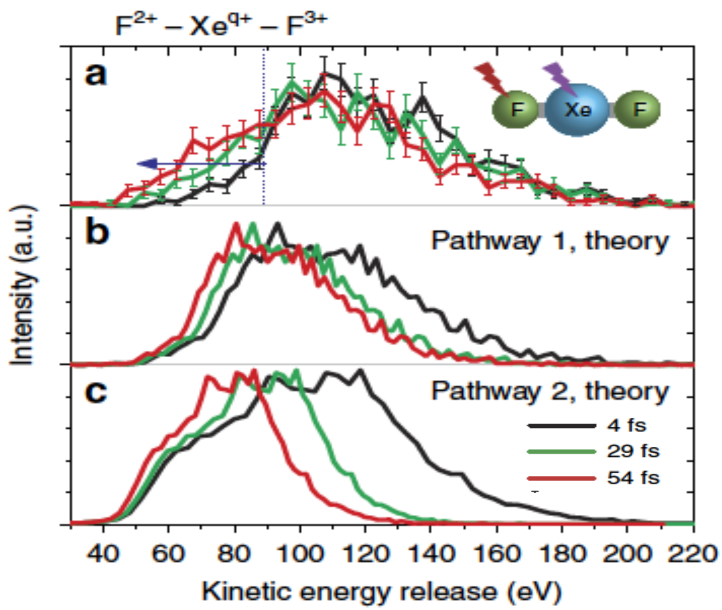


Southworth *et al.*, JCP **142,** 224302 (2015)

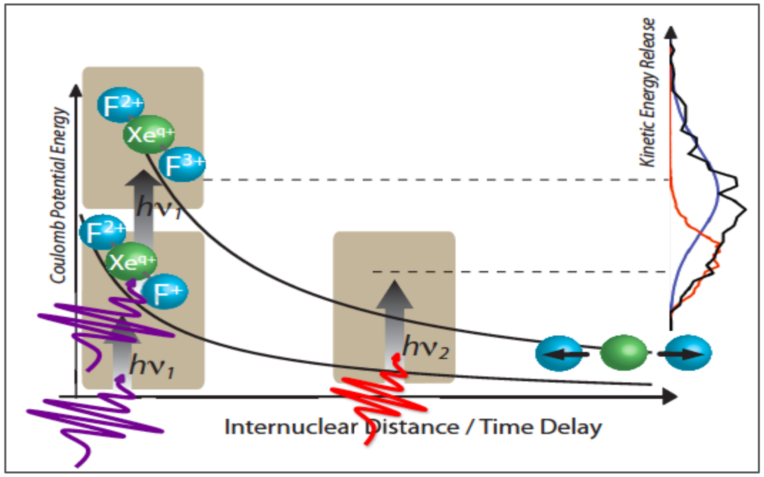
Picon…Southworth, Nat. Commun. **7,** 11652 (2016)

THE F^{2+} Xe^{q+} F^{3+} BREAKUP CHANNEL

Time-dependent dynamics manifest in recoil ion energies



Static + pump/probe KER observed



- KERs modeled w/classical eqns of motion & Coulomb forces consistent w/observations
- KER is a ruler for internuclear distance
- 600,000 x-ray shots …. 800 F^{2+}- Xe^{q+}-F^{3+} coincidences

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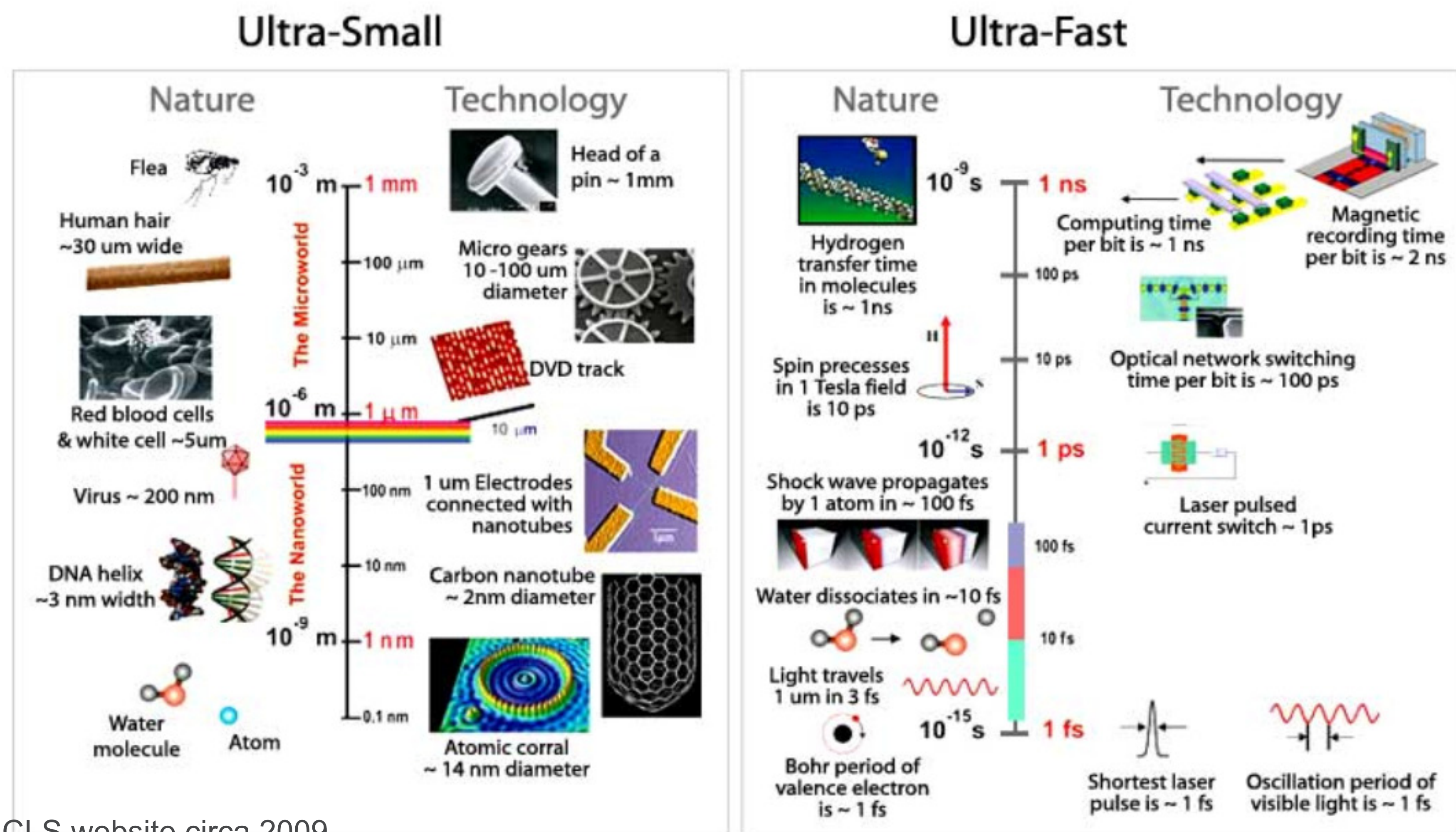
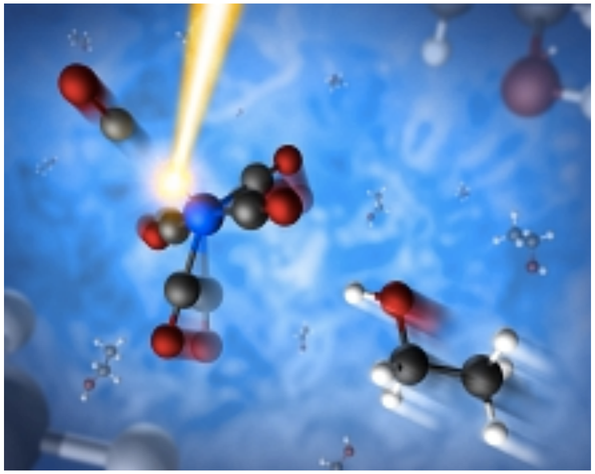
Outlook is bright for molecular movies

- Multiple timescales contain interesting scientific problems in chemistry, biology, materials science.
- For the nanoscale, mesoscale phenomena the picosecond - microsecond timescale and nanofocusing available at synchrotrons is ideal
- For atomic-scale phenomena the attosecond – femtosecond timescales available at XFELs is becoming more readily available with multiple XFELs just coming online.

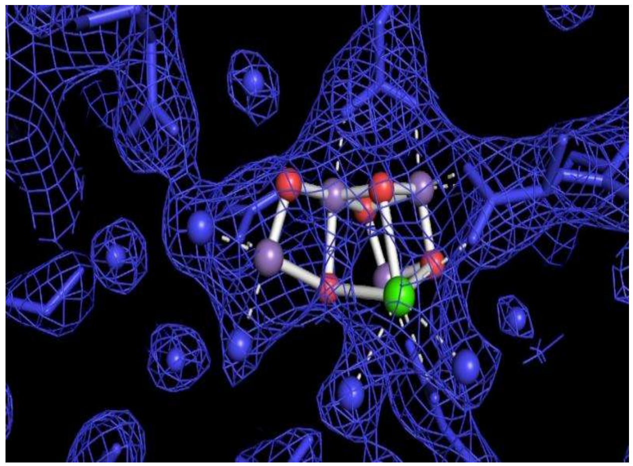


LCLS website circa 2009

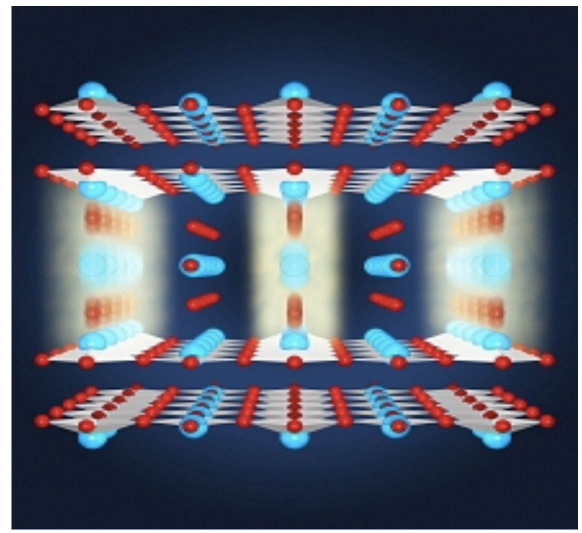
SEE THE ATOMS AND ELECTRONS MOVE



Chemical reactions
in solution



Photosystem II



Light-induced
superconductivity