Perspectives for Time-Resolved UV to X-ray studies at Synchrotrons

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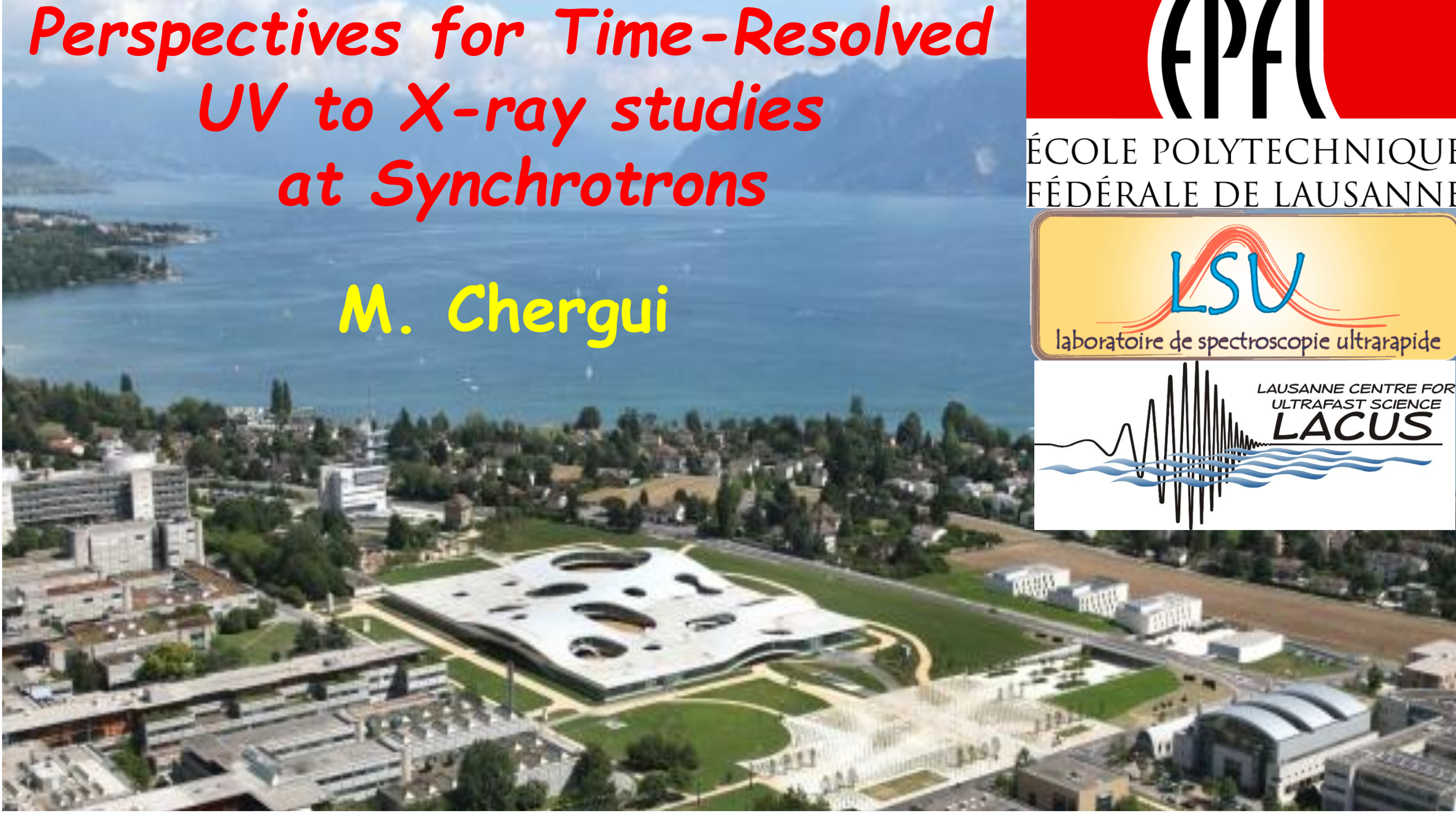
LACUS



TREES

Elettra Sincrotrone Trieste

XXVI Users' Meeting

Opportunities for Time-REsolved Experiments at new Synchrotron radiation facilities

Trieste, Italy / 4 - 5 December 2018

Wish list for (bio)chemical dynamics

- Element-selectivity
- Electronic structure
- Spin structure
- Geometric structure
- Time scales: ≥ 20 fs to 100s ps
- Condensed phase media (liquid, interfaces, amorphous, etc.)

The Science determines which tool to use!

Sources of short-wavelength pulses

Synchrotron Radiation (≥ 50 ps)

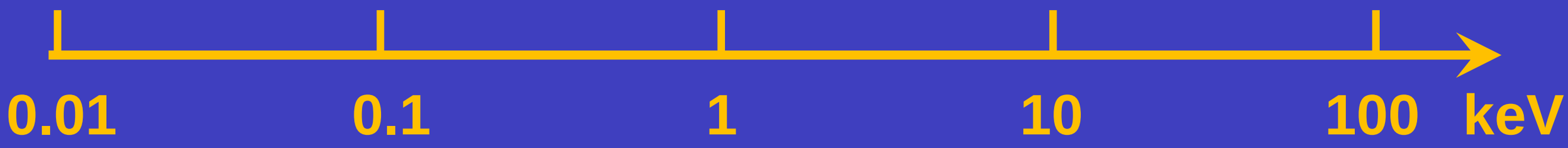
Stability
Tuneability
Average flux

Plasma-based sources (≥50 fs)

XUV Free electron Lasers (≥50 fs)

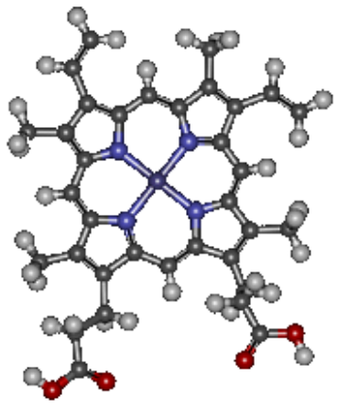
X-ray Free electron Lasers (≥50 fs)

High Harmonic Generation (≥As)

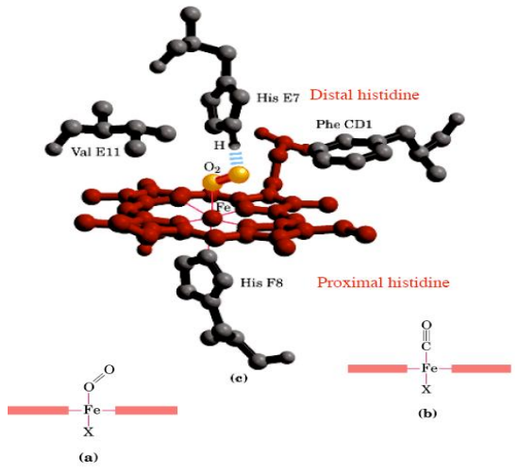


Protein Dynamics in Solution – From the Chromophore to the Scaffold

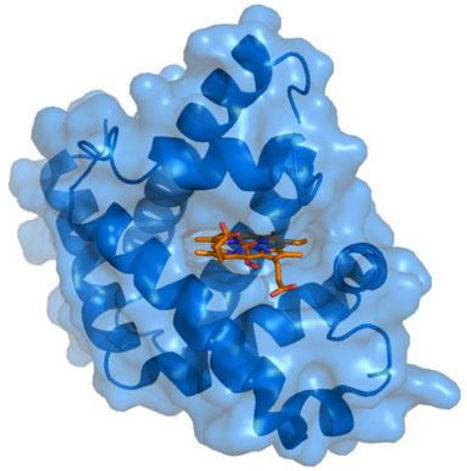
10 fs ... 10 ps | **1 ps ... 10 ps** | **10 ps … 100 ps** | **ps ... μs** | **> μs**



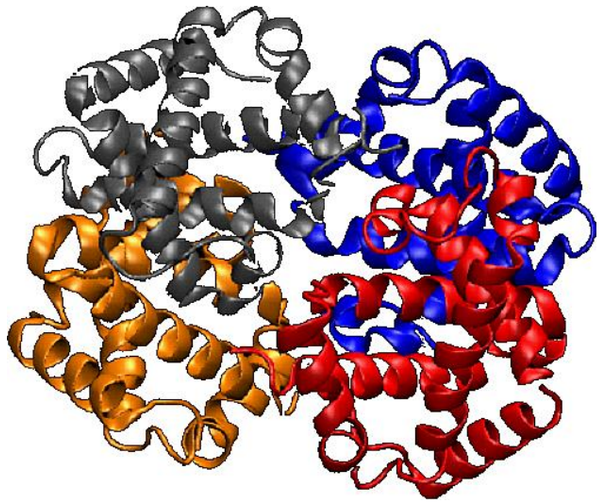
Spin dynamics (singlet to quintet)
• intramolecular ET (ring to metal, metal to ring)
• Intramolecular vibrational redistribution (IVR)
• Electronic relaxation: internal conversion



• Structural dynamics
• Ligand dissociation
• Doming
• Cooling



• Dielectric response of amino-acid residues
• Cooling and heat transfer
• Helix motion
• Conformational changes
• Correlated motions
• Role of biological water
• intermolecular ET



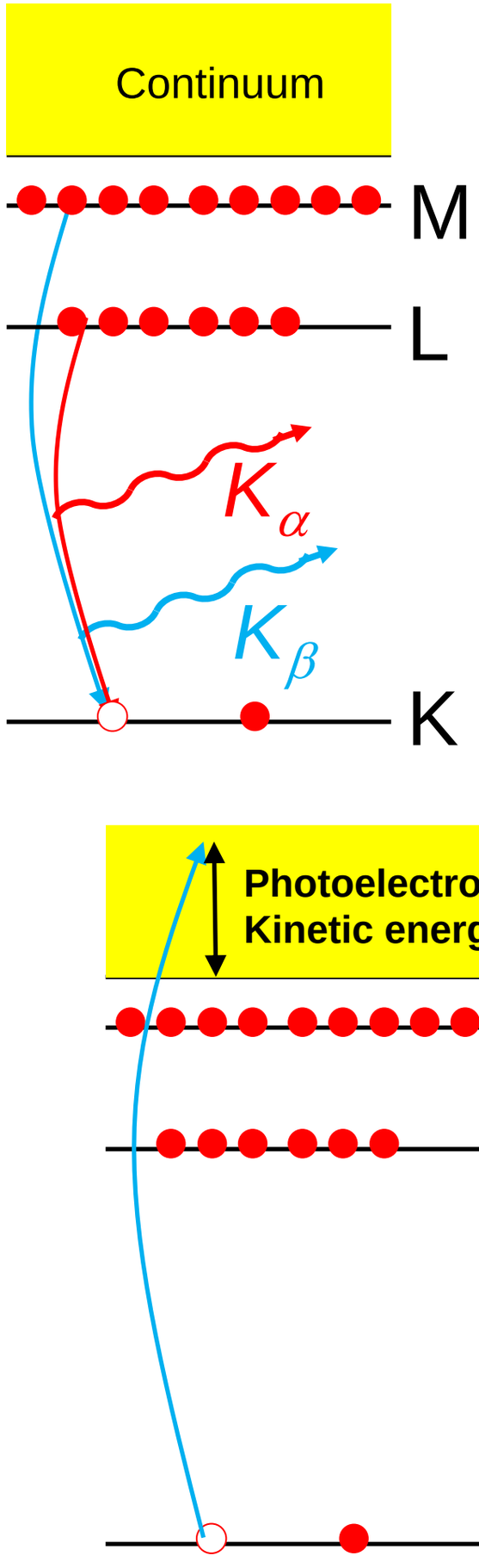
• Cooperativity
• Allostery
• Signaling
• Respiration

X-ray protein scattering

X-ray spectroscopy (XAS, XES)

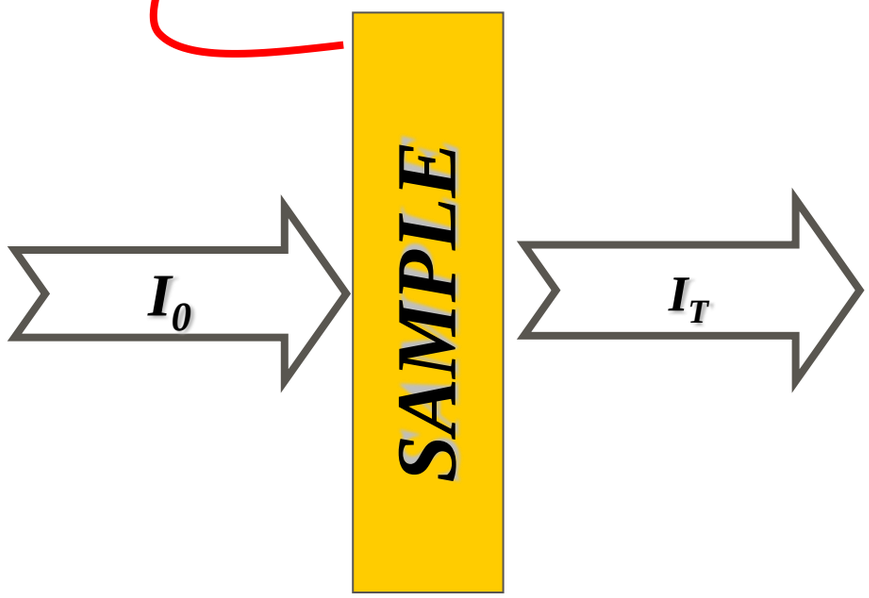
Deep-UV Circular Dichroism

Core-level spectroscopies



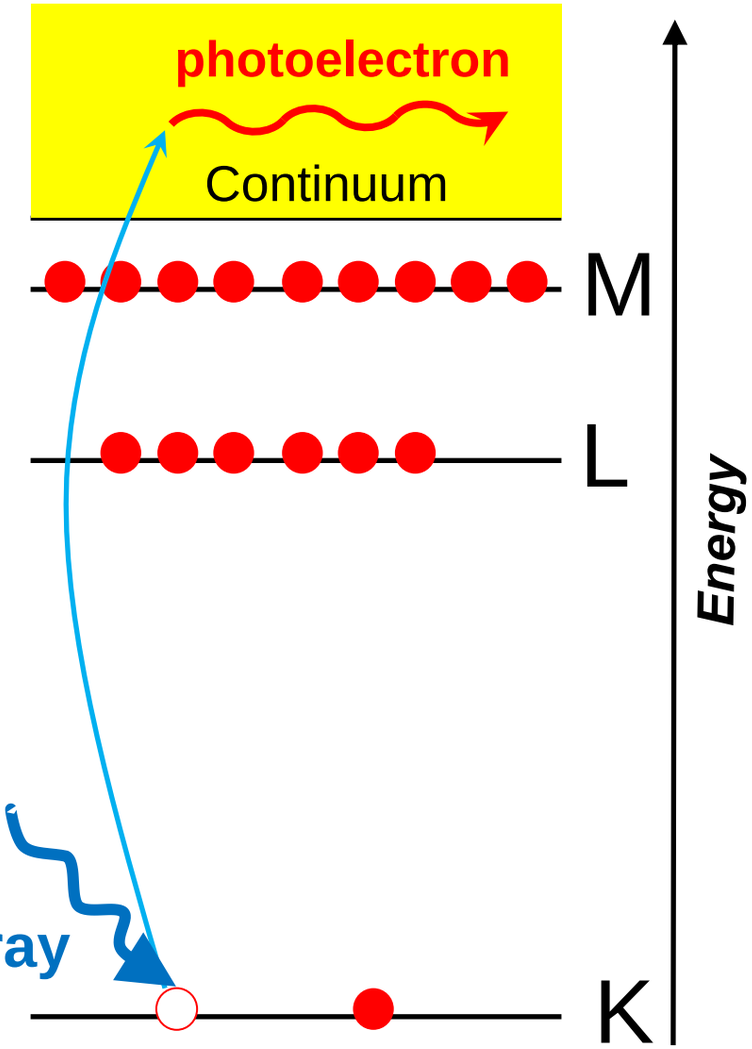
X-ray emission

Electronic structure
Spin state



X-ray absorption

Electronic structure
Local geometry

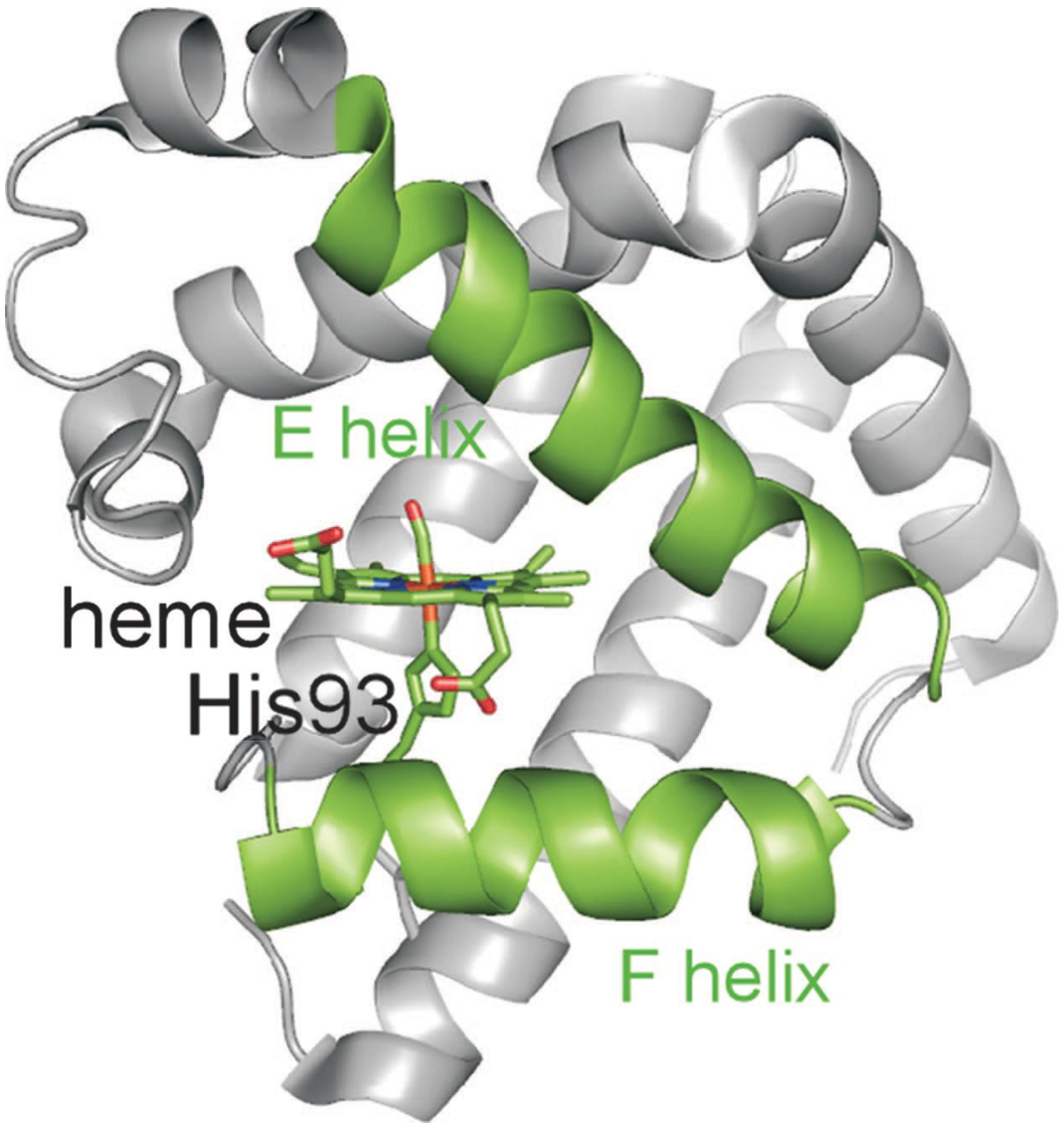


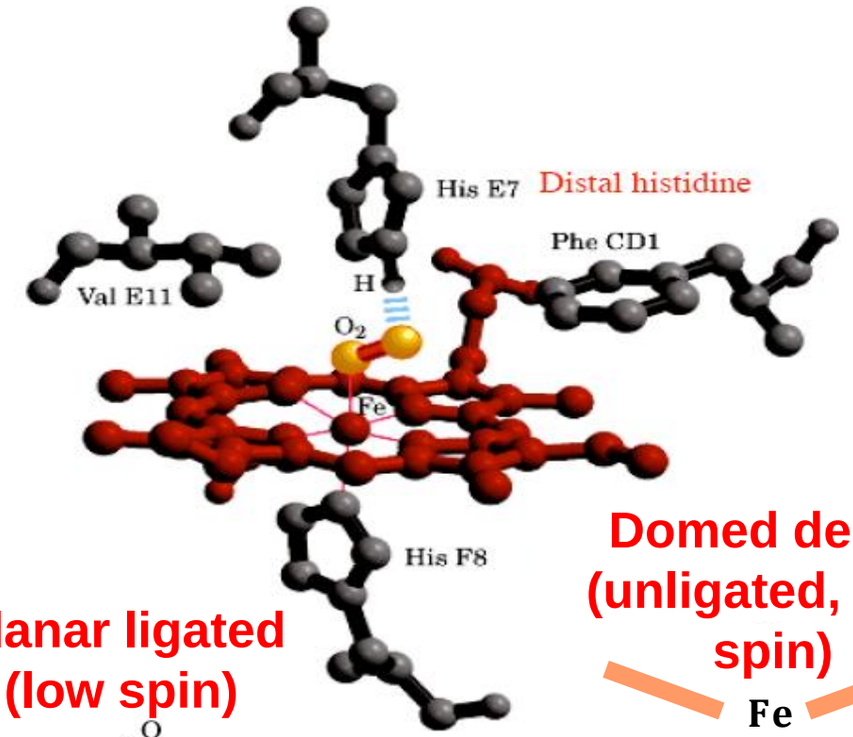
Photoelectrons

Binding energies
Chemical bond

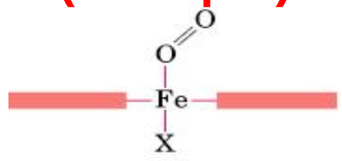
XANES, NEXAFS, EXAFS, SEXAFS,
XES, RIXS, ESCA, UPS, XPS, etc.

Fundamental processes in respiration

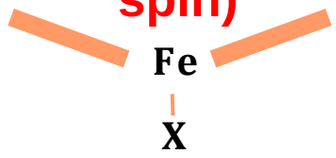


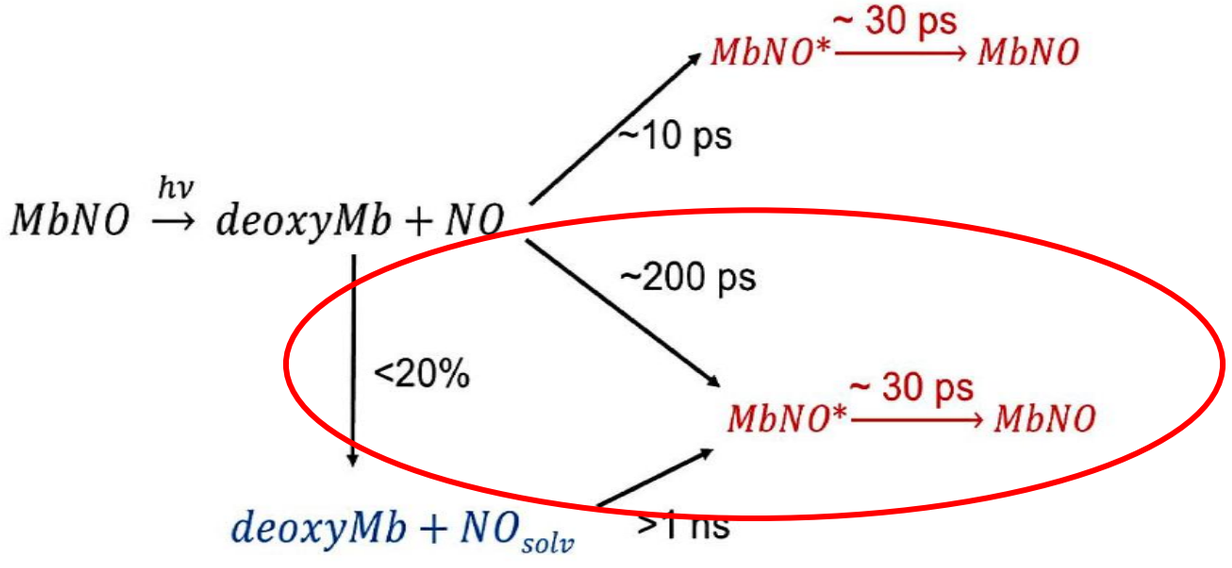


Planar ligated (low spin)

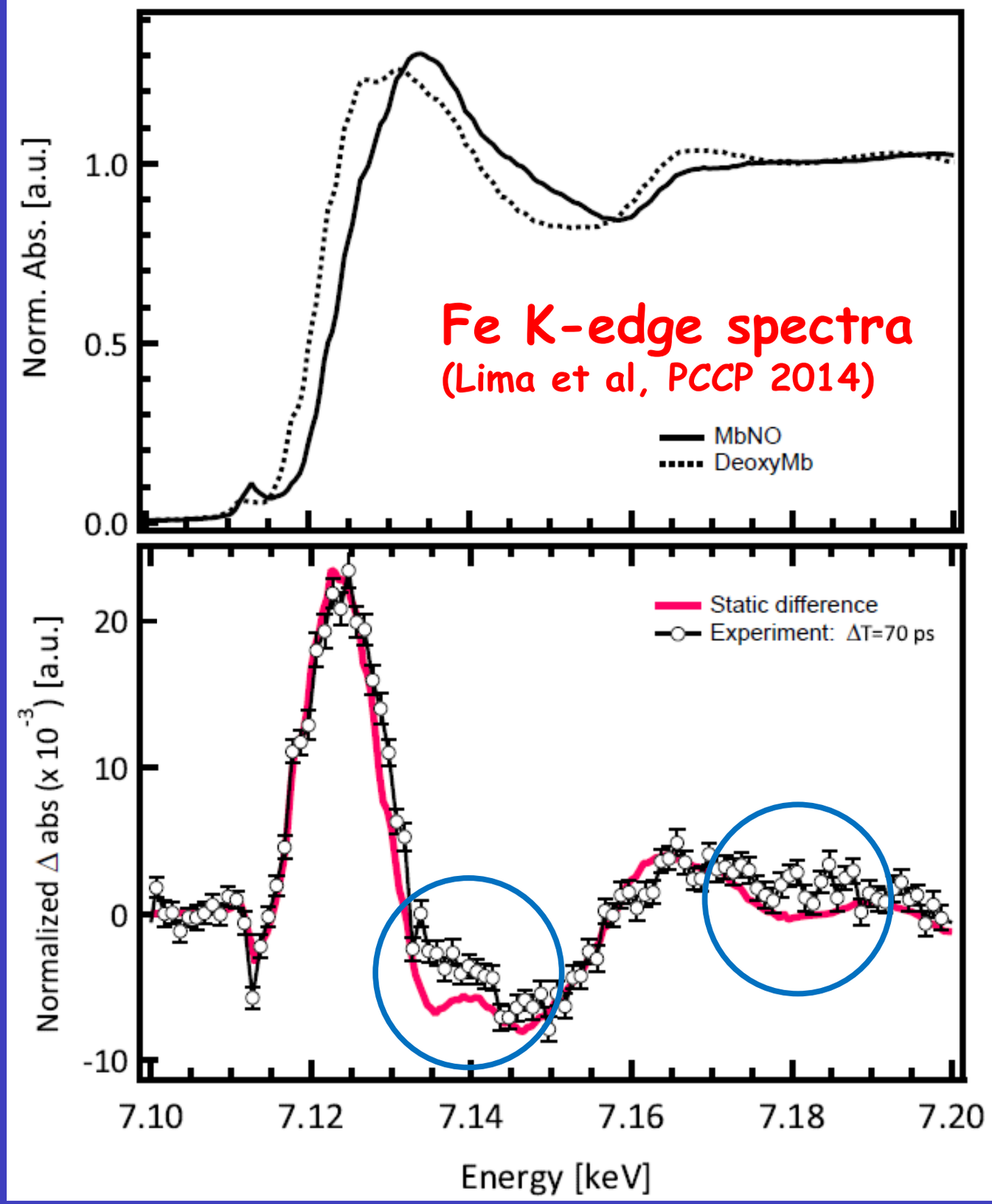


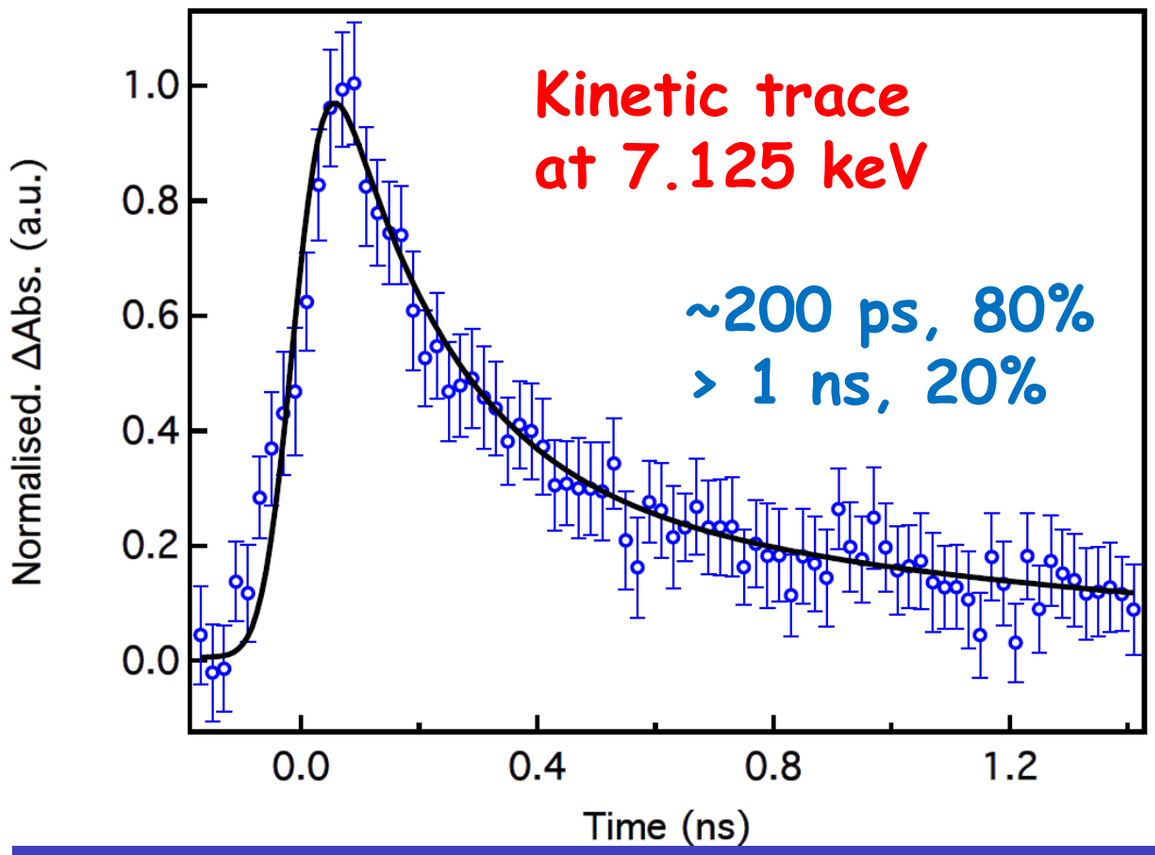
Domed deoxy (unligated, high spin)





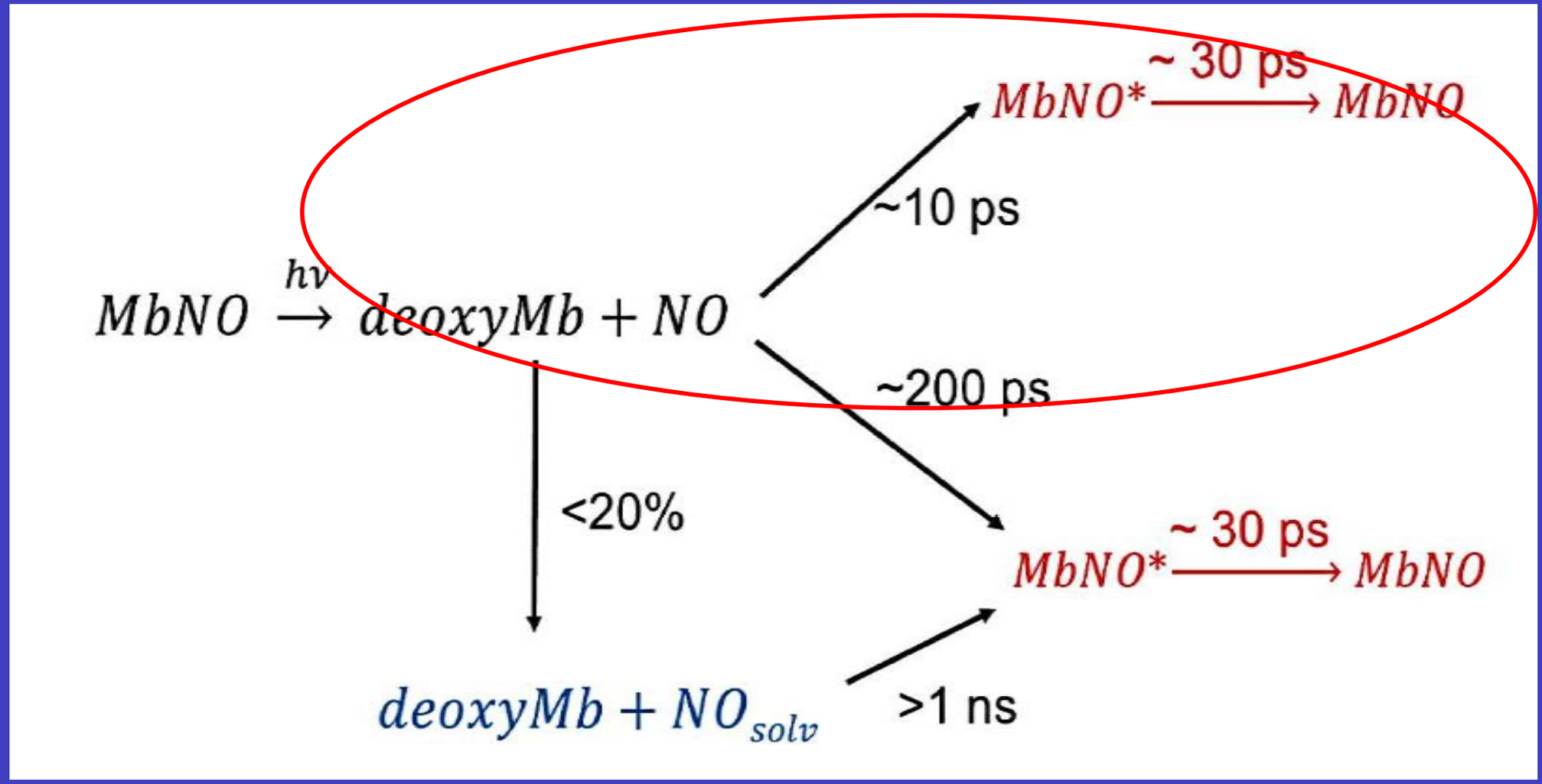
Local probing: XAS transients of Myoglobin-NO in a physiological solution with 70 ps resolution





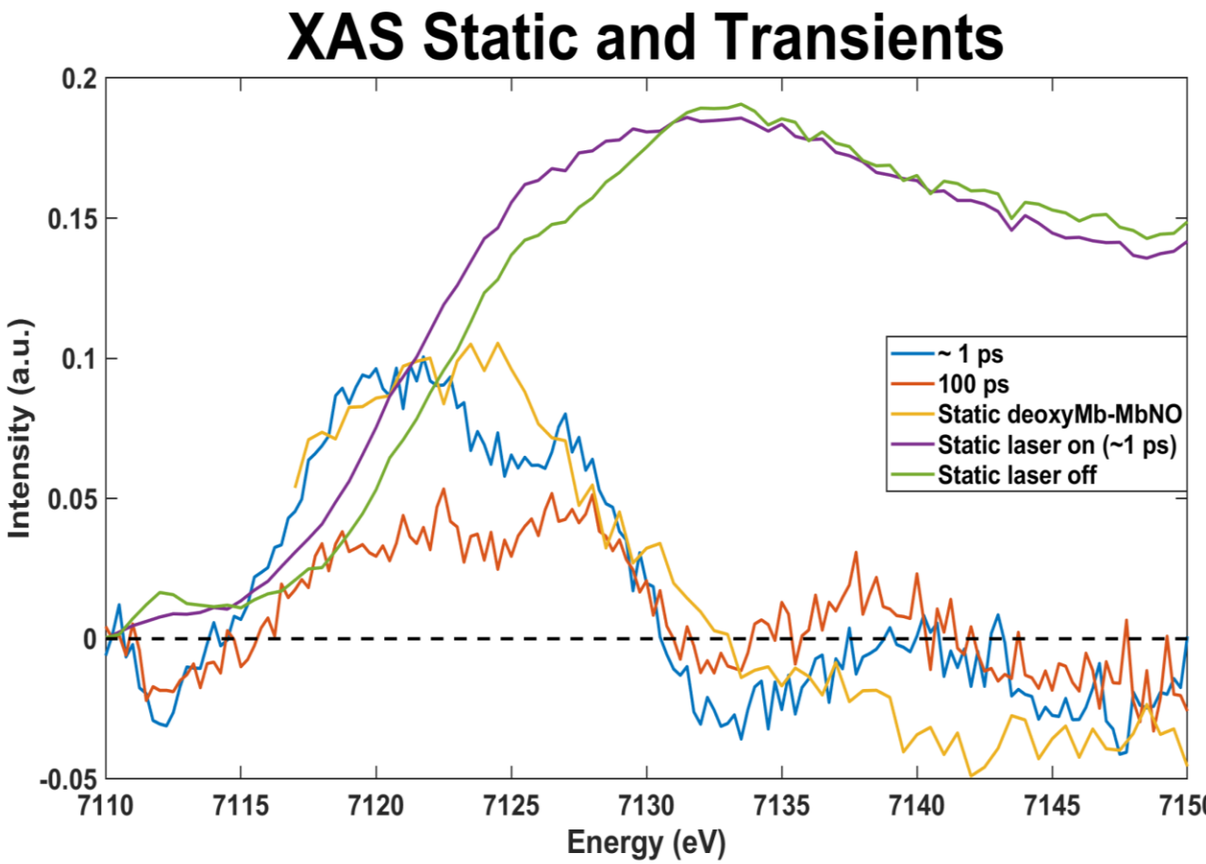
- Biosystems are robust !
- Opens opportunities for Fs/ps solution XRS, XES, RIXS, etc.

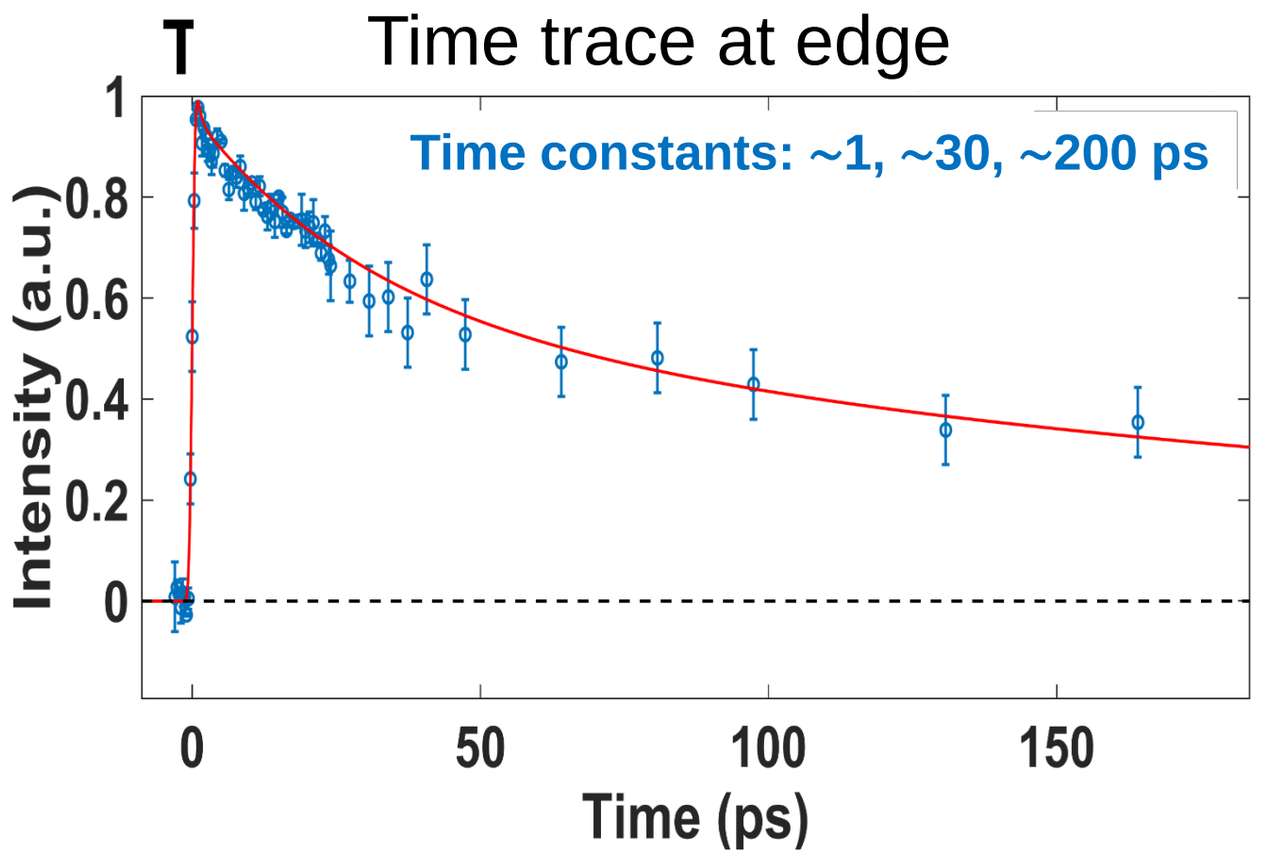
Silatani et al, PNAS (2015)

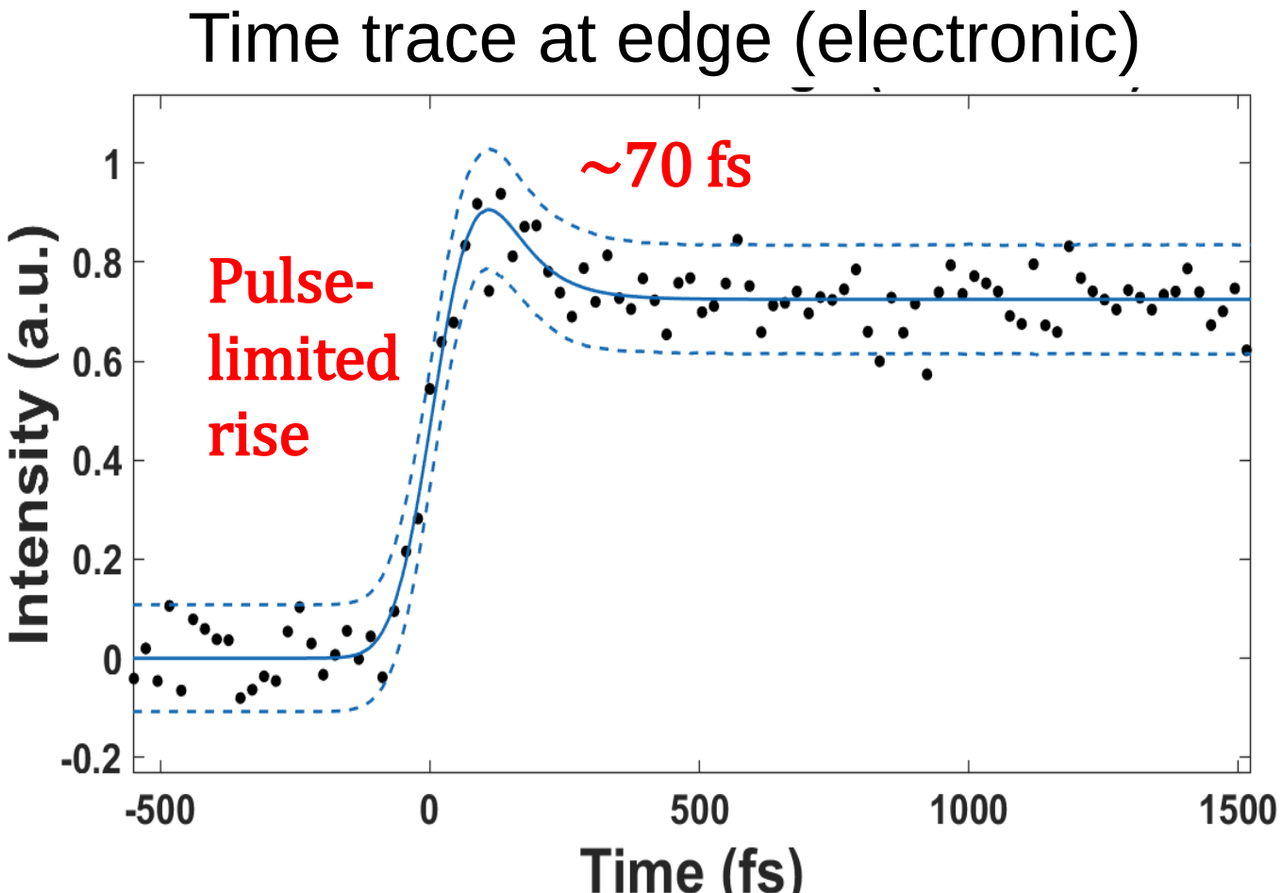


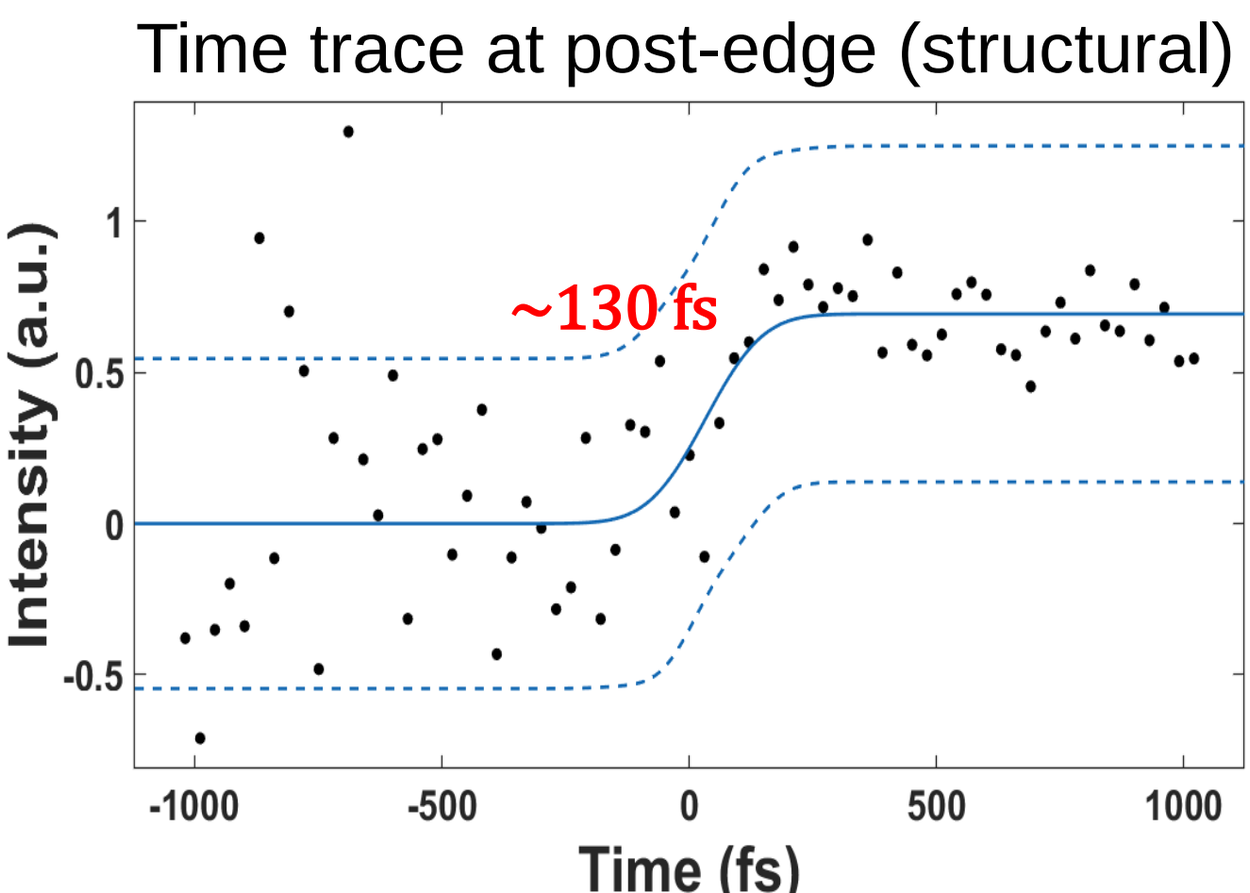
- Slow kinetics (ca. 200 ps) due to recombination from remote NO's
- Domed ligated form populated in ~200 ps and decays in ~ 30 ps.
- XFEL experiments to probe the short time components

Femtosecond X-ray absorption studies (Coll. SACLA)

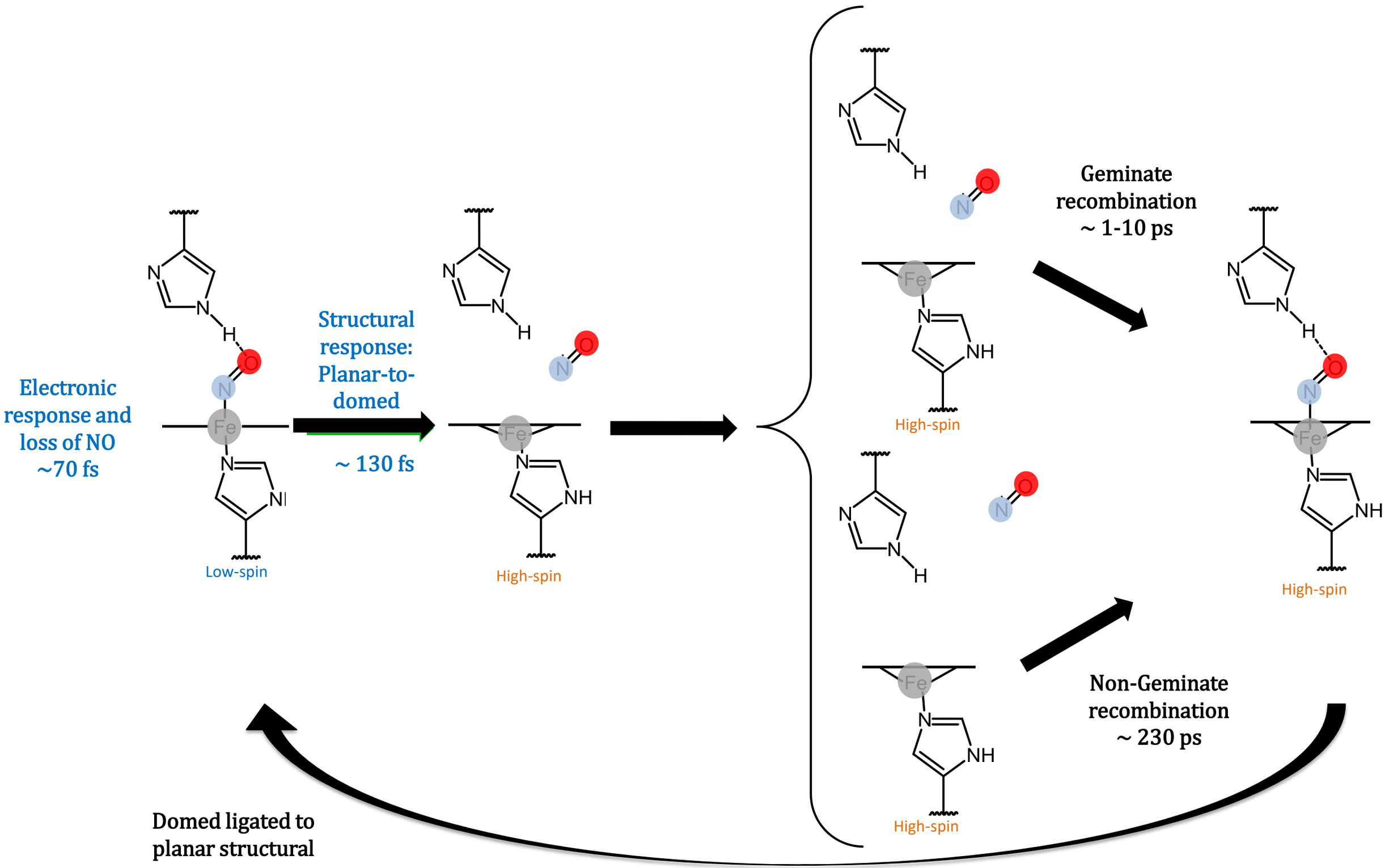








Proposed photocycle



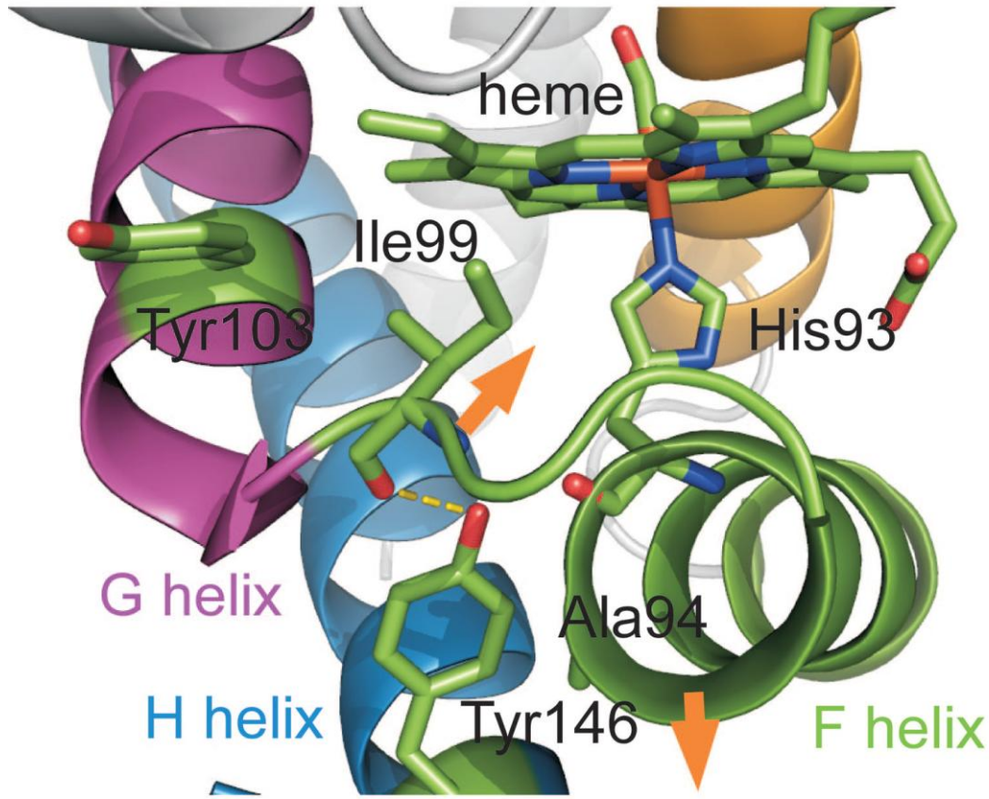
Environment response

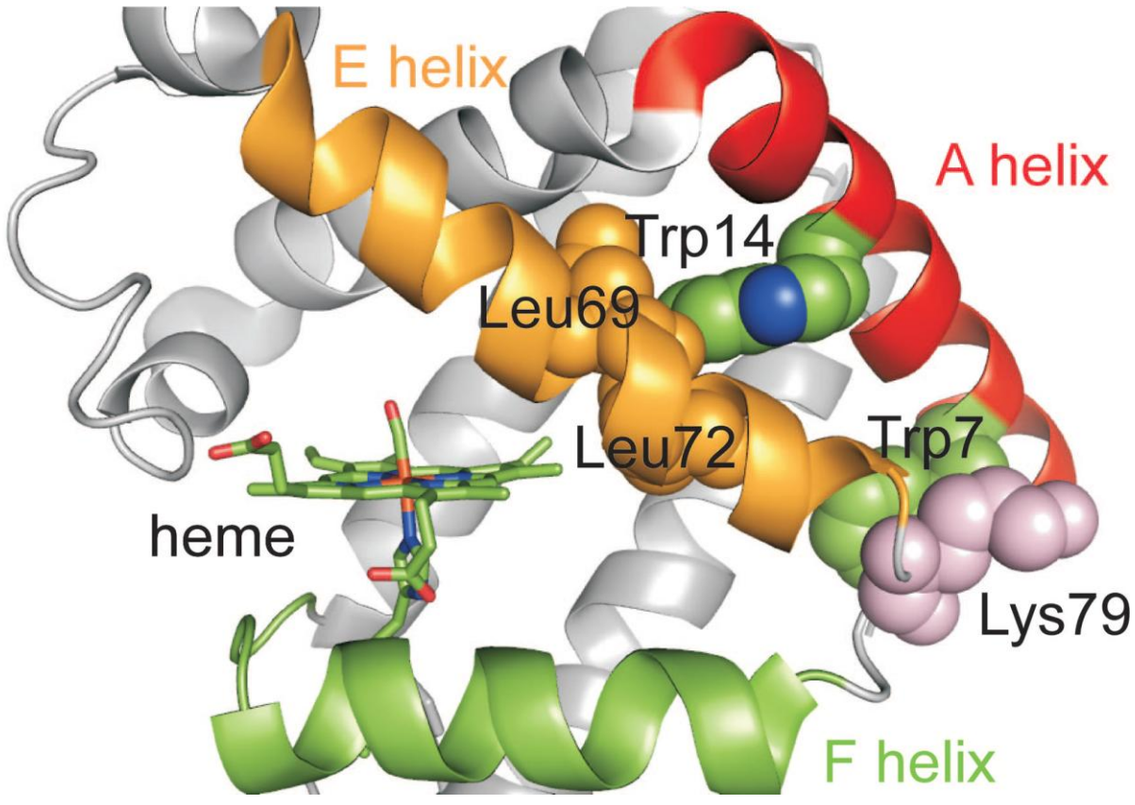
Side chain motion Probed by UV resonance Raman of amino-acid residues: 2-10 ps (Sato et al, PNAS 104 (2007) 9627–9632)

Levantino et al, Nat. Comm. 2015: solution small-angle scattering (SAXS) Poor spatial resolution

Baerends et al, Science 2015: Serial crystallography studies, non-physiological

Deep-UV Circular Dichroism





2D deep-UV set-up @

(Auböck et al, RSI 2012; Opt. Letters 2012)

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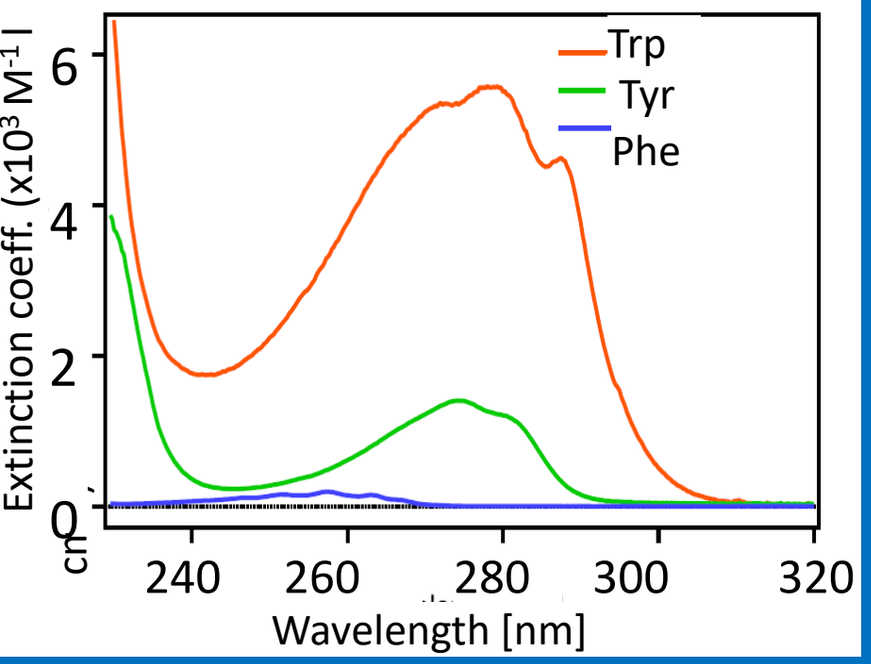
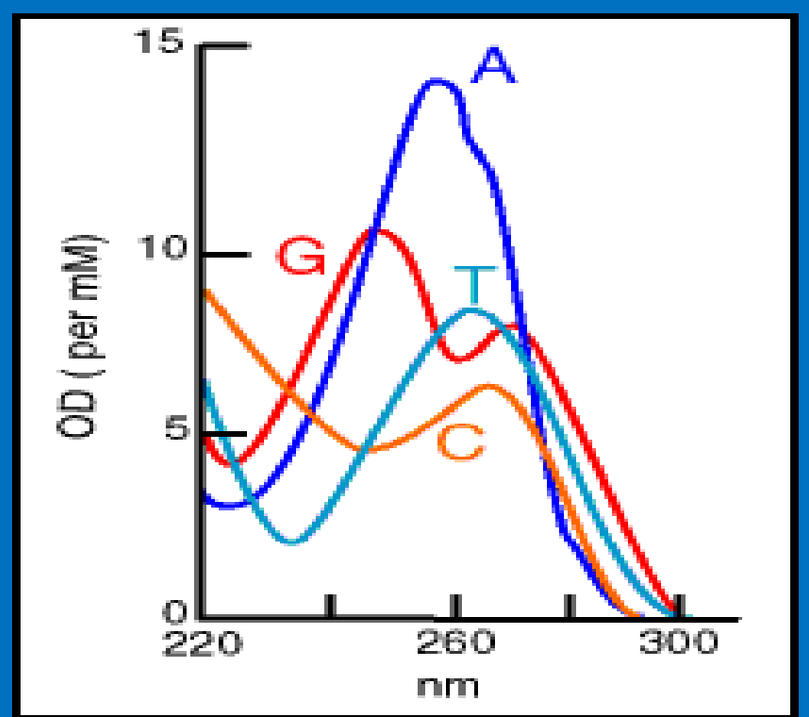
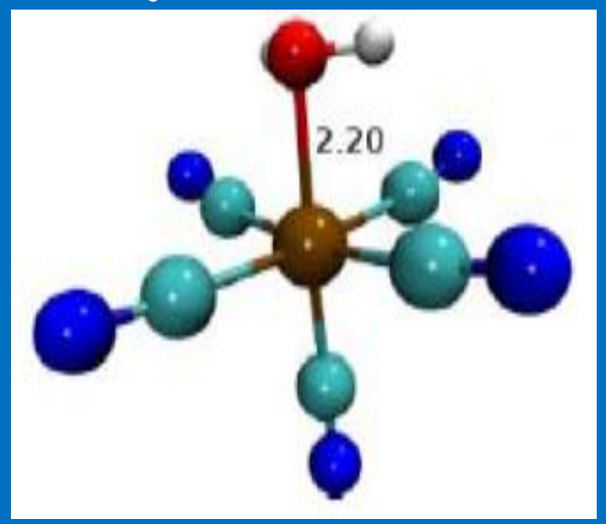
Biology: Amino acid residues and nucleotides



Consani et al, Science (2013)
Monni et al, PNAS (2015)

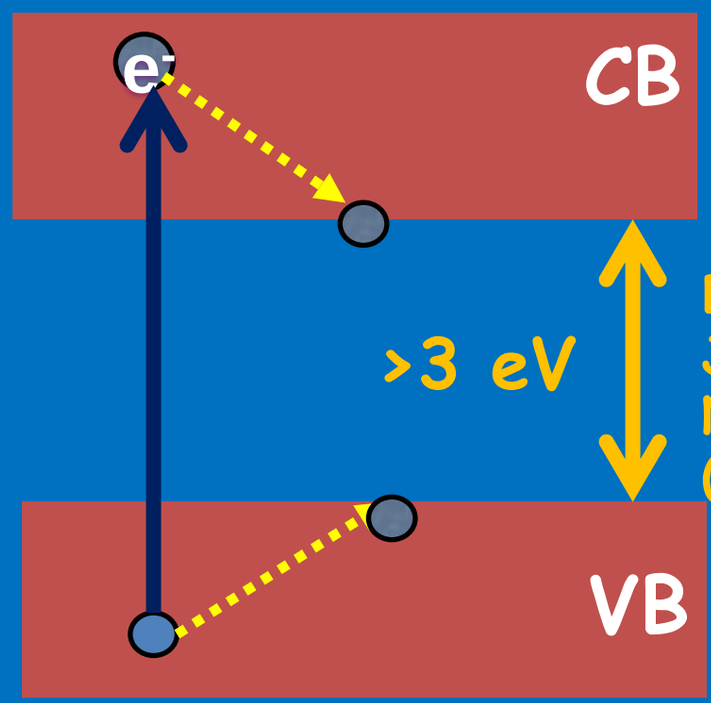


Chemistry: Small molecules



Auböck & Chergui, Nature Chem. (2015)
Reinhard et al, JACS (2017)
Monni et al, CPL (2017); PNAS (2018)

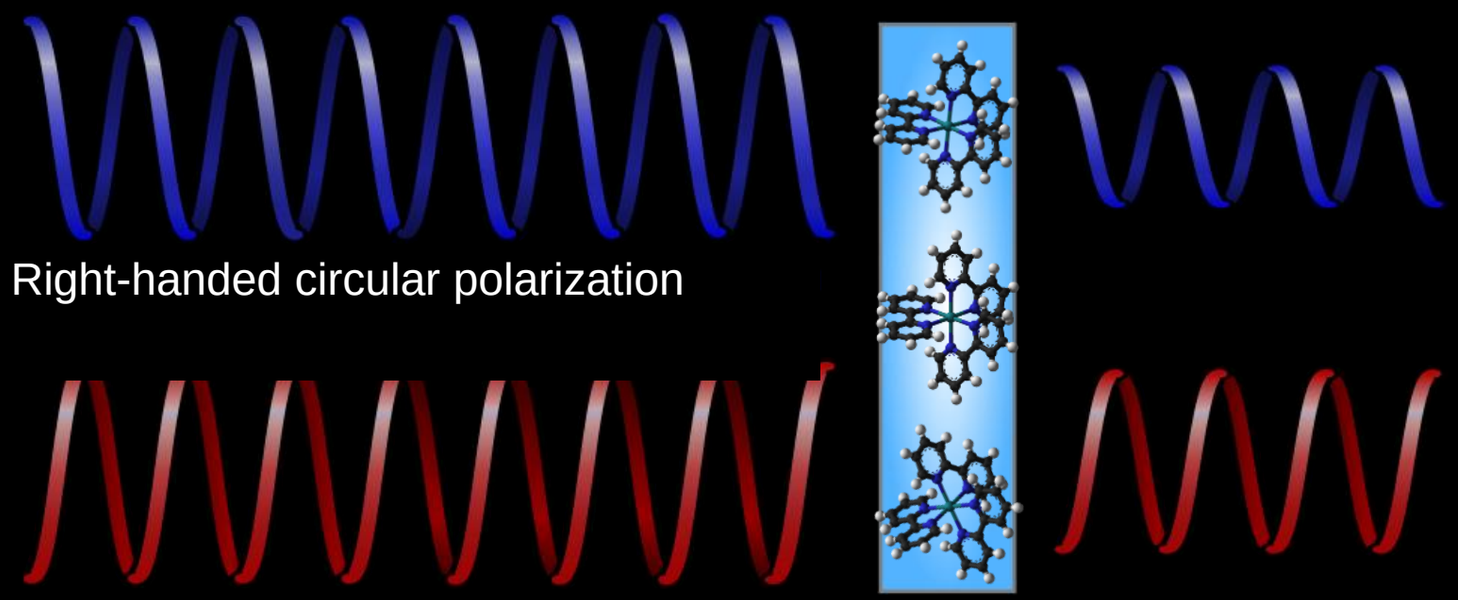
Materials science: Transition Metal oxides



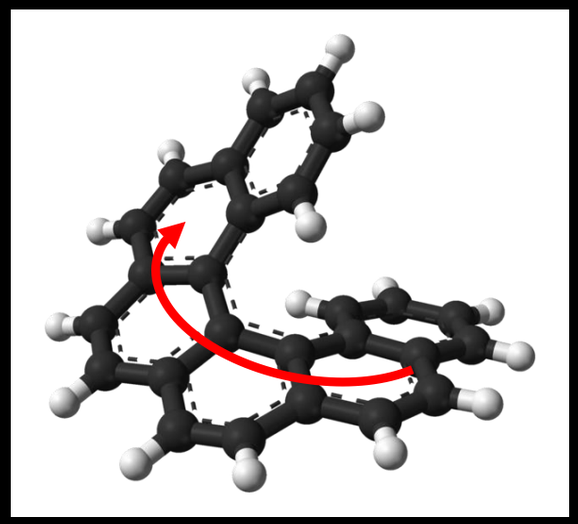
Baldini et al, Nature Comm. (2017); JACS (2017); ACS Photonics (2018), NanoLetters (2018);Nature Phys. (under review)

CIRCULAR DICHROISM

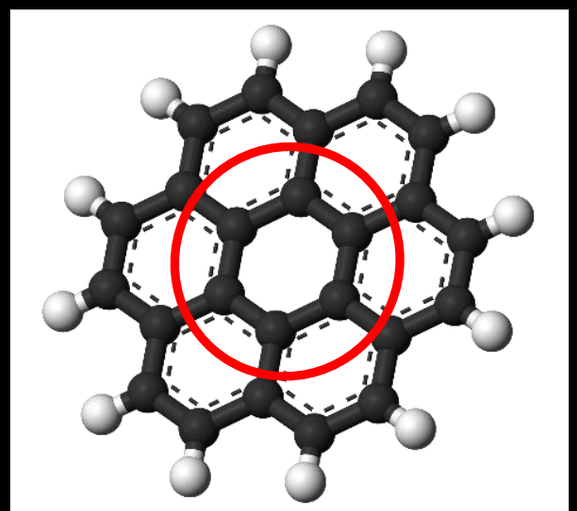
The absorption difference of left- and right-circularly polarized light:



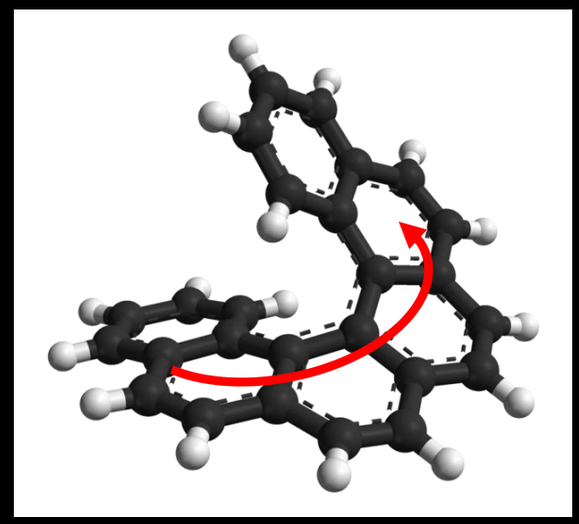
CD transitions are associated with helical charge displacements in chiral systems:



Chiral M-[6]helicene



Achiral coronene

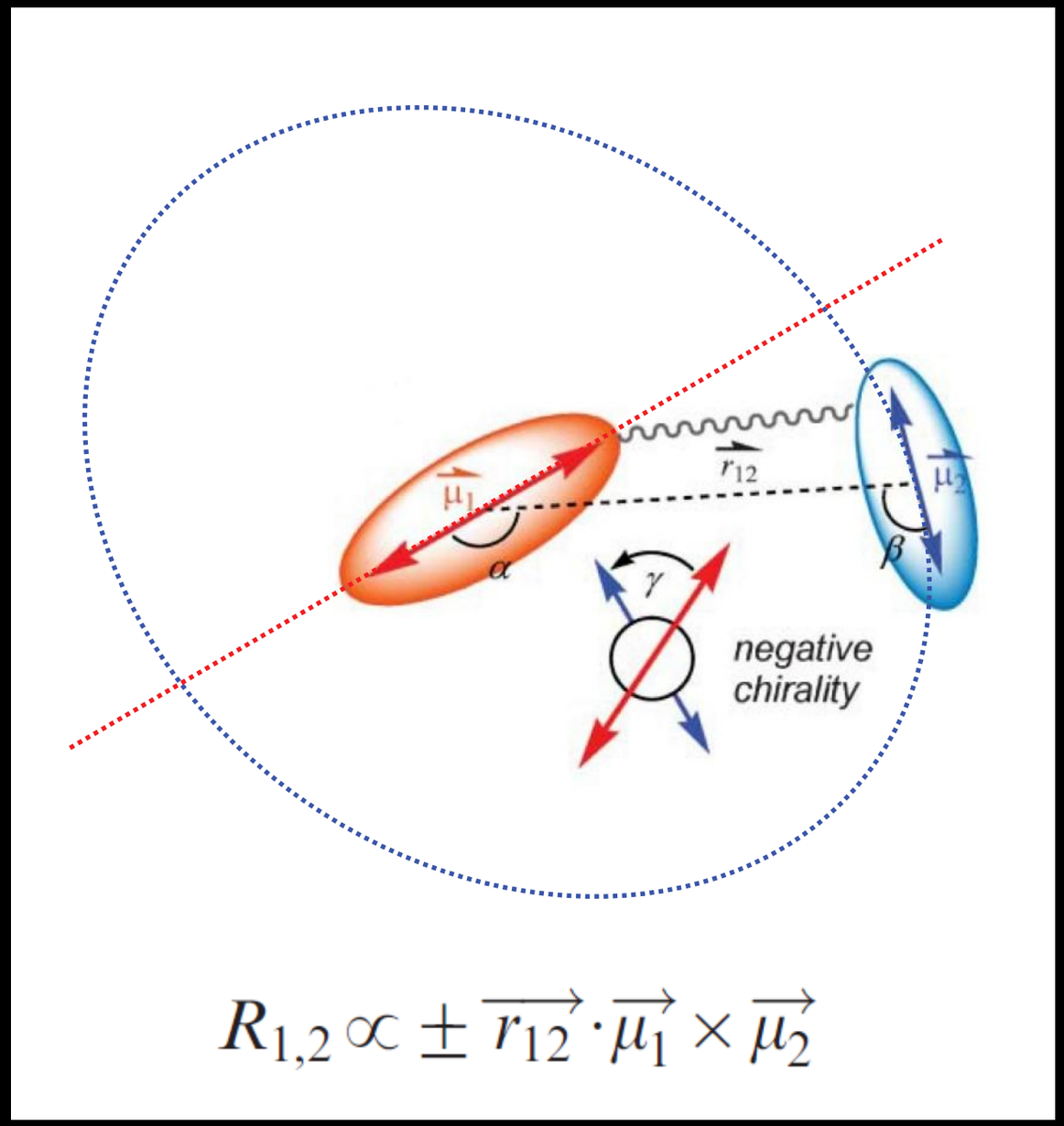


Chiral P-[6]helicene

Bottom figures: en.wikipedia.org

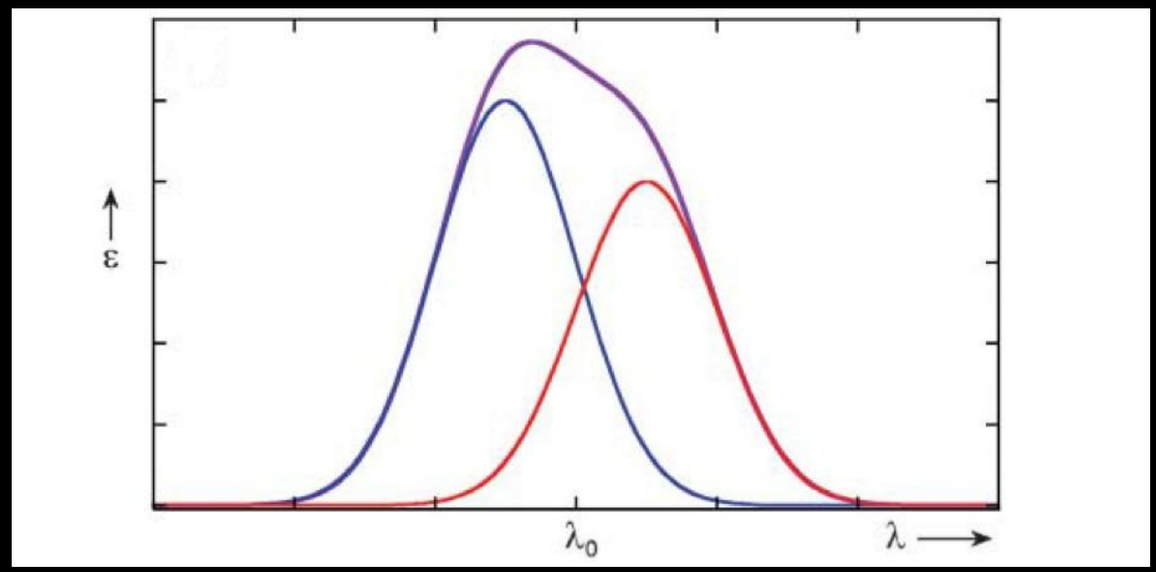
ELECTRONIC CD FROM COUPLED CHROMOPHORES

Excitonically coupled chromophores:

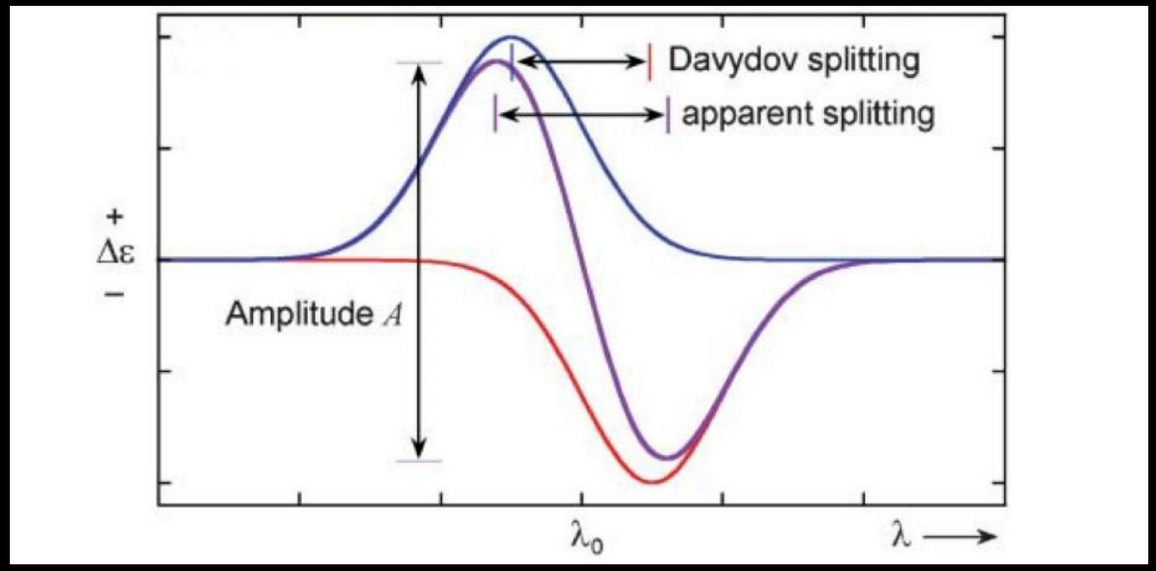


$$R_{1,2} \propto \pm \overrightarrow{r_{12}} \cdot \overrightarrow{\mu_1} \times \overrightarrow{\mu_2}$$

Linear absorption:



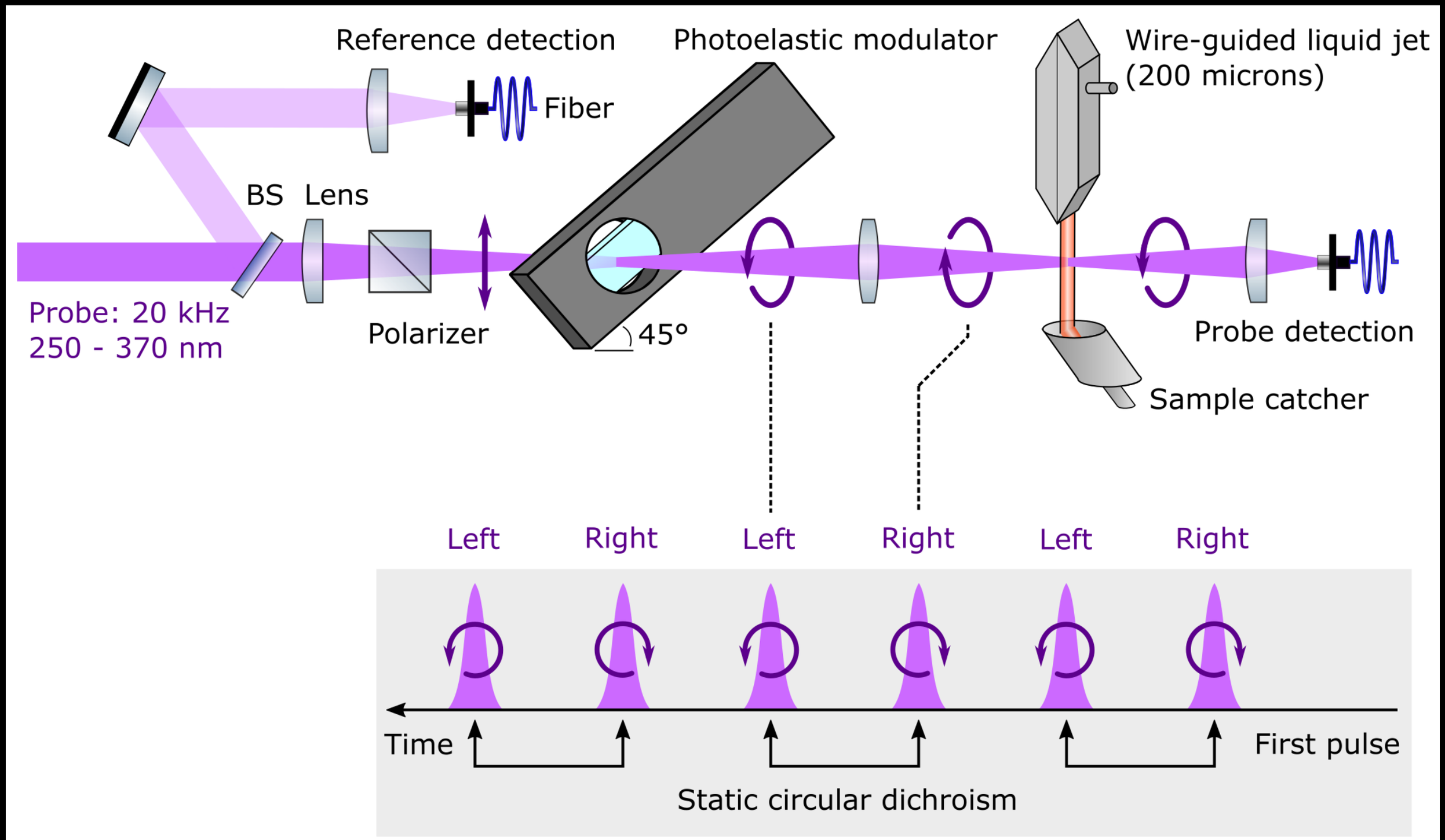
Circular Dichroism:



CD probes the geometry of chiral systems of excitonically coupled chromophores!

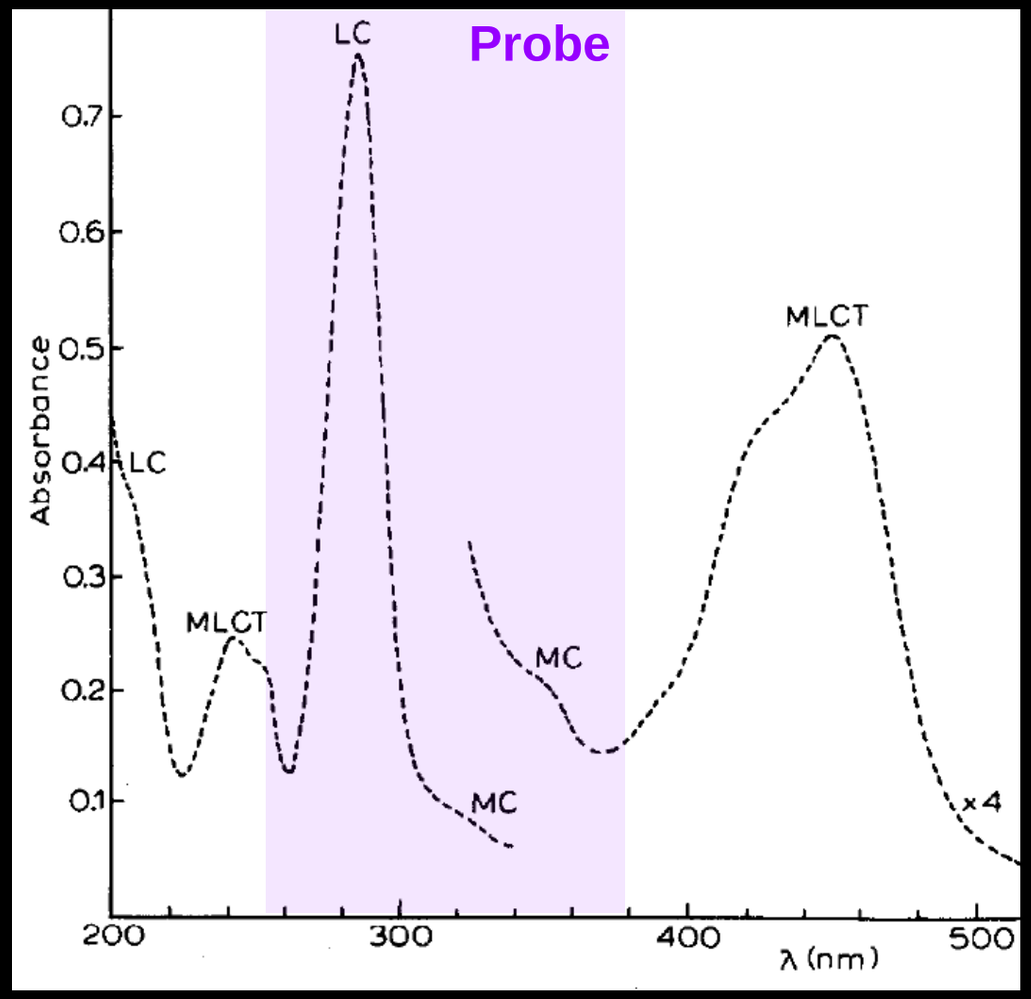
Figures adapted from: Berova et. al, Chem. Soc. Rev. 36, 914 (2007)

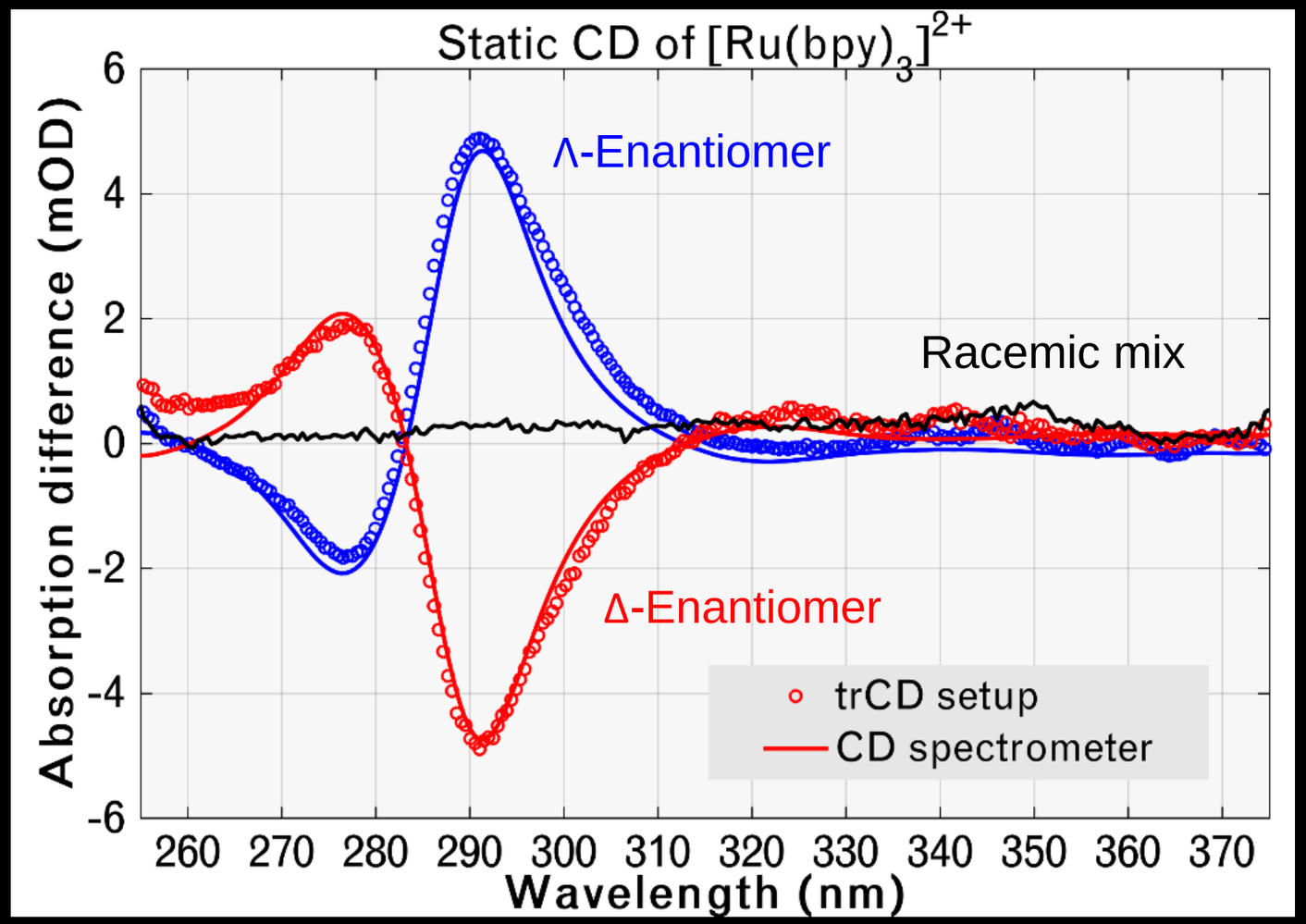
ULTRAFAST CD SETUP



Liquid jet design: Picchiotti et al., *Rev. Sci. Instruments* 86, 093105 (2015)

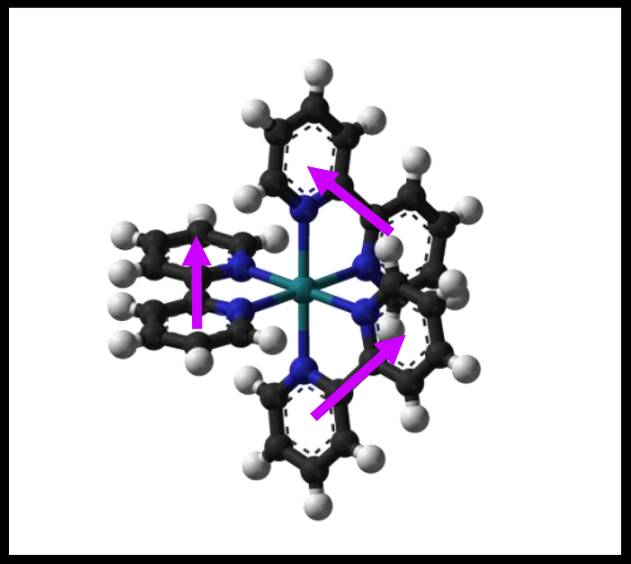
STATIC CD PERFORMANCE





1.0 mM aqueous solution

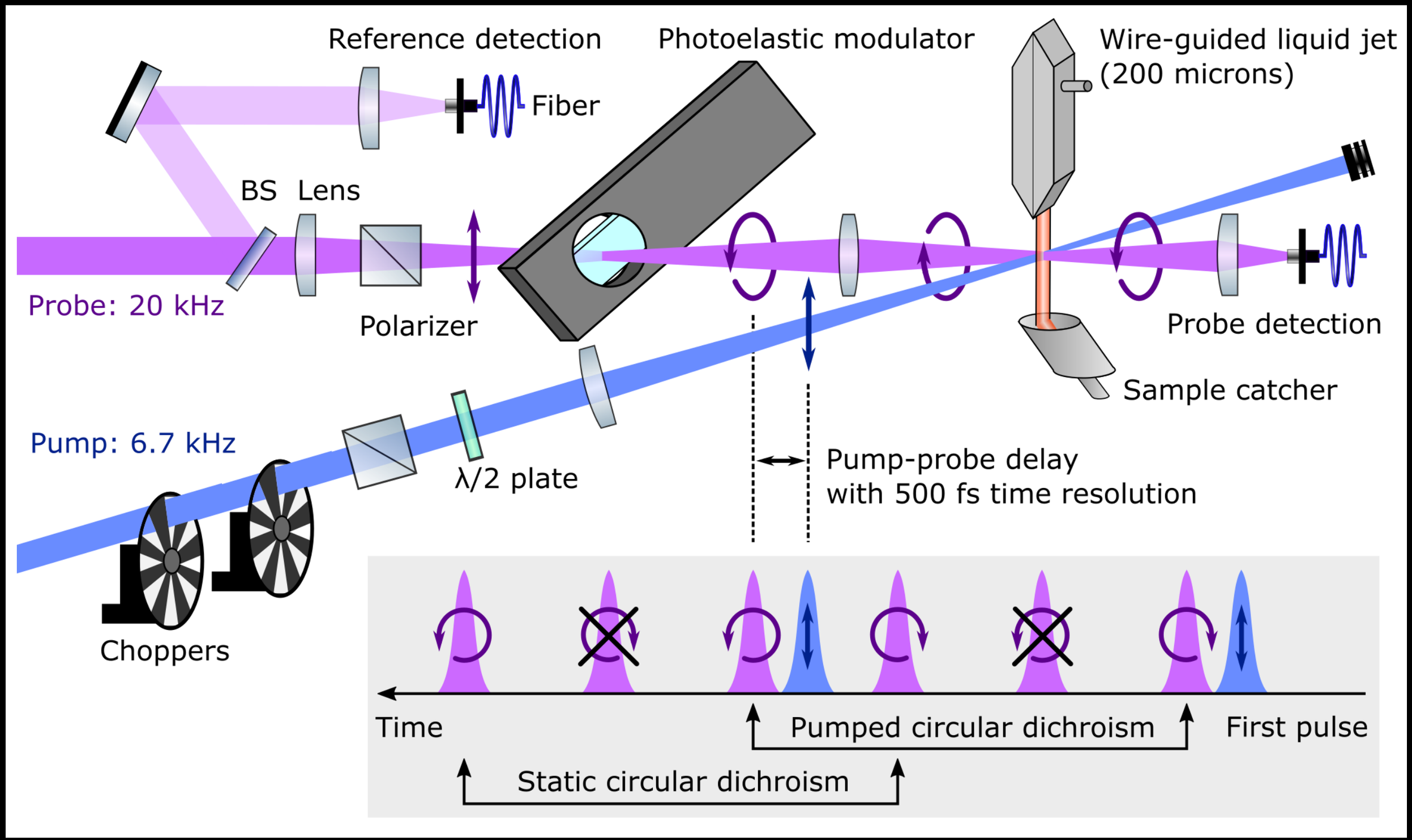
$[Ru(bpy)_3]^{2+}$



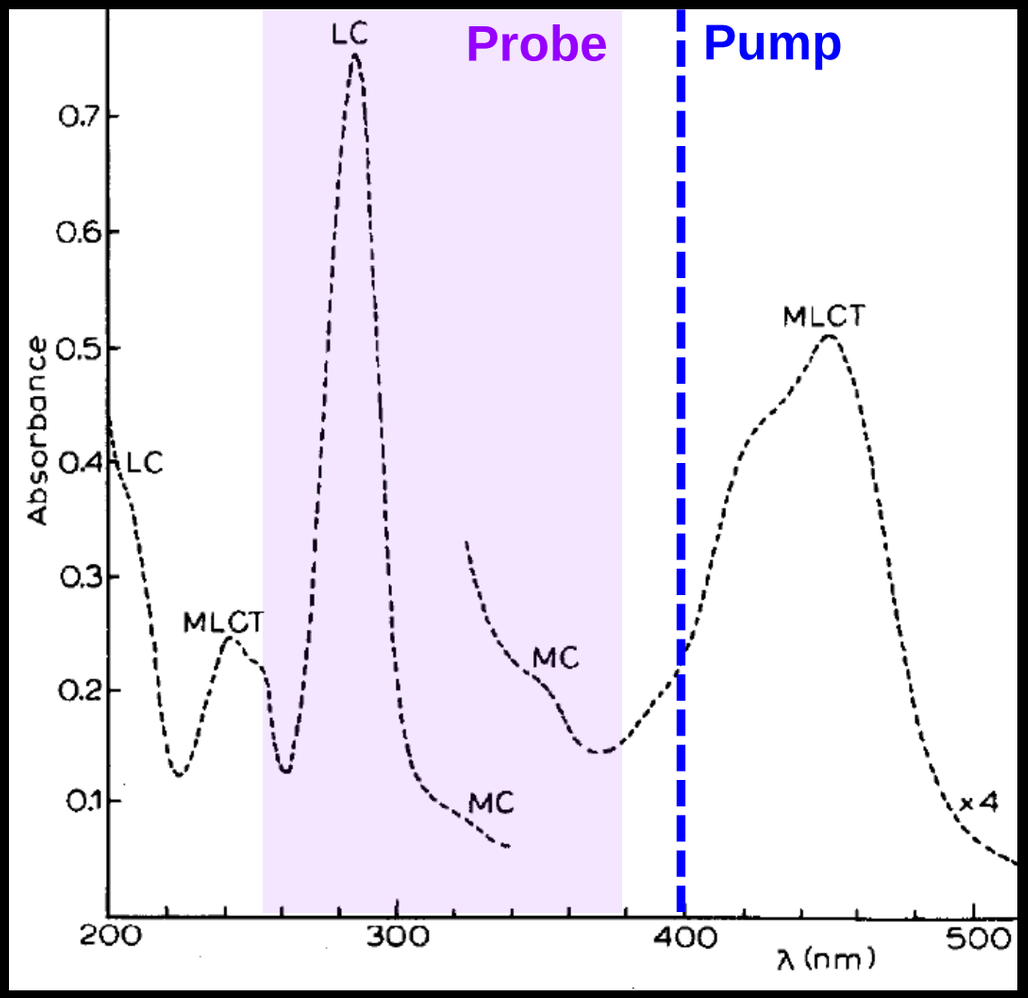
Performance of static CD acquisition:

- Good agreement with commercial spectrometer
- Baseline deviations < 0.5 mOD in racemic mix
- Minimization of polarization artefacts via polarization scrambling

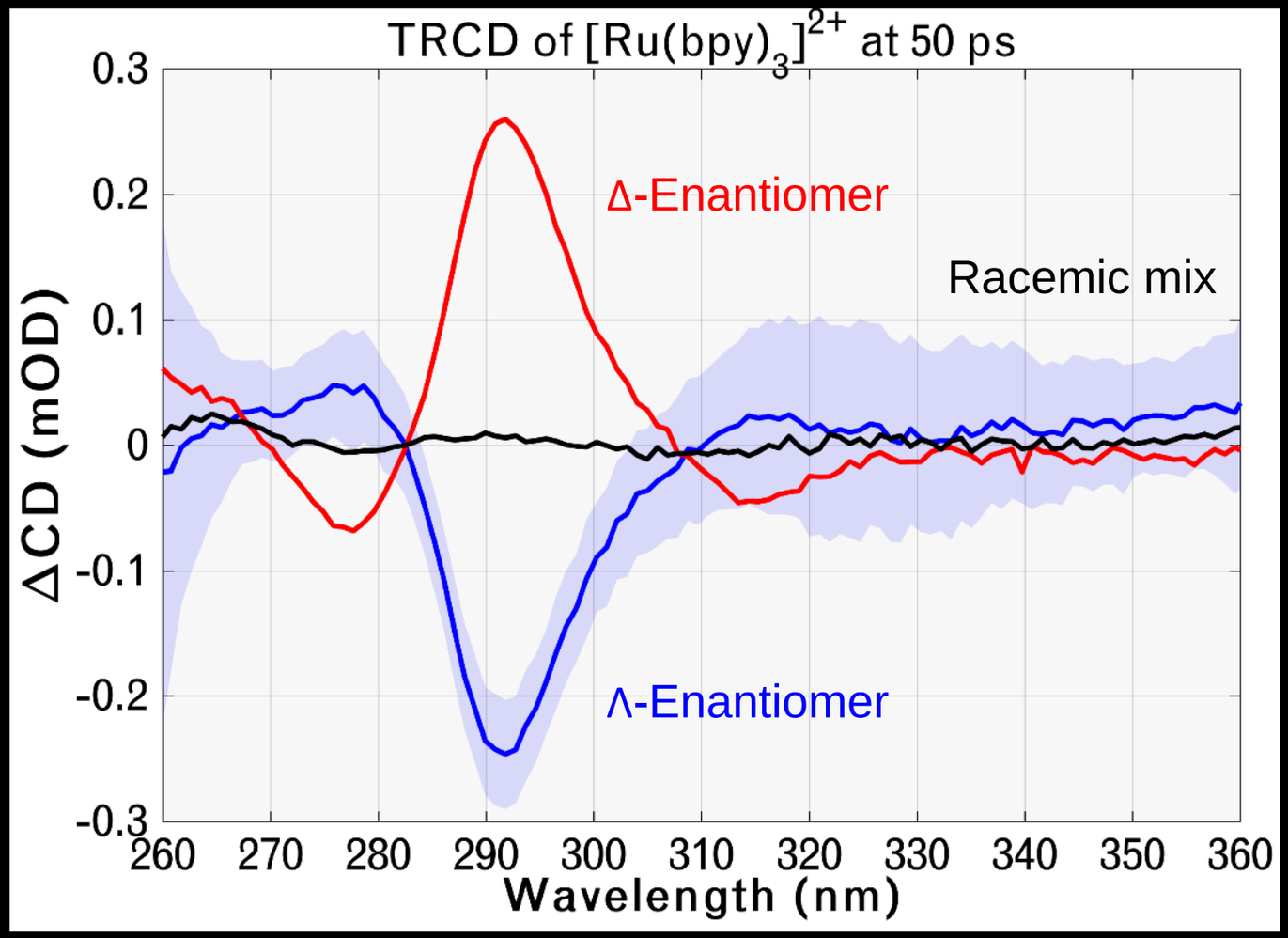
ULTRAFAST CD SETUP



TRANSIENT CD PERFORMANCE

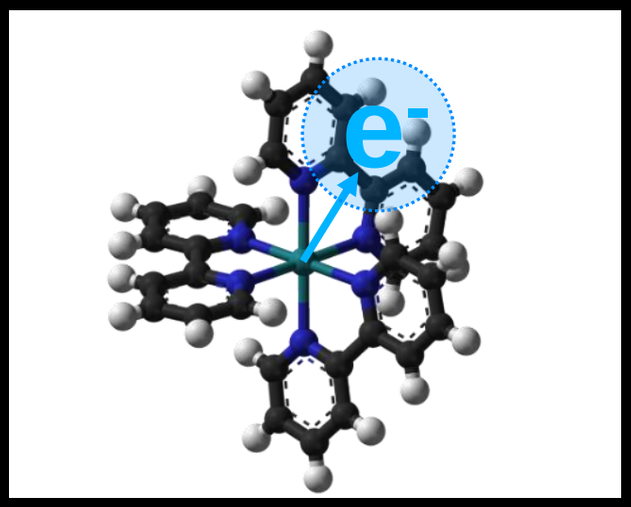


K. Kalyanasundaram, *Coord. Chem. Rev.* 46, 159 (1982)



0.3 mM aqueous solution, estimated peak fluence: 2 mJ cm^{-2}

$[Ru(bpy)_3]^{2+}$

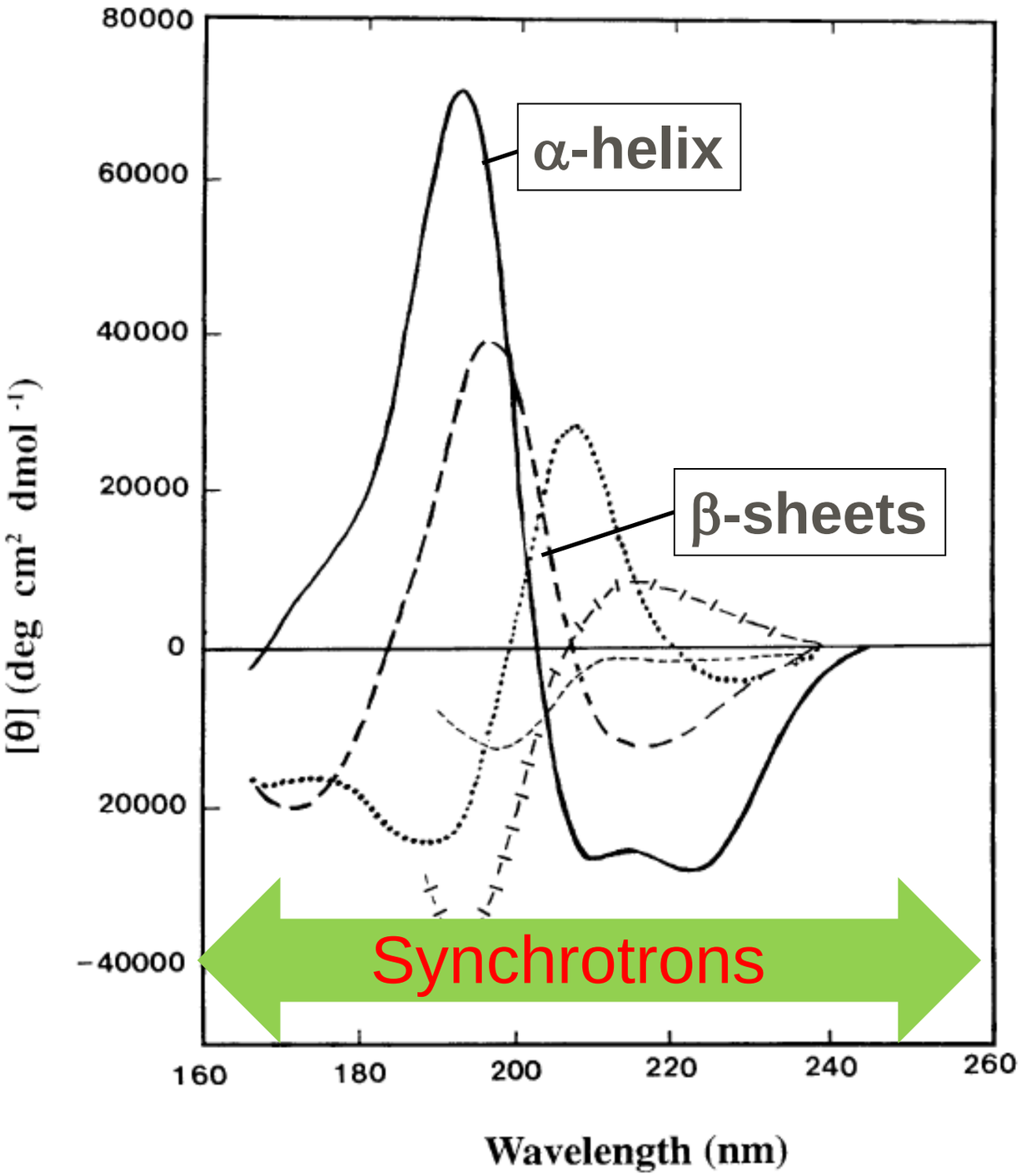


Performance of transient CD acquisition:

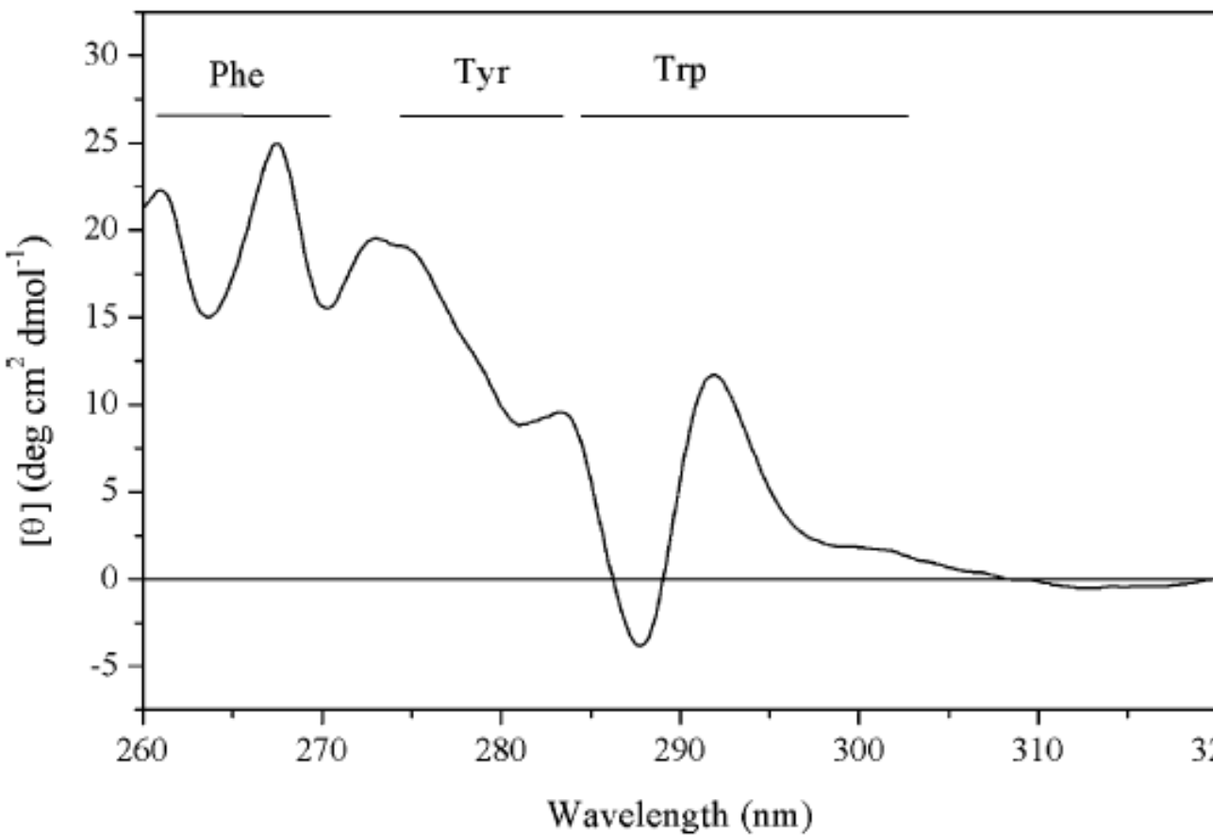
- Baseline deviations < 0.02 mOD in racemic mix
- Precision < 0.1 mOD can be reached routinely in < 15 min of DAQ time
- The TRCD spectra of the two enantiomers display an excellent symmetry

Oppermann et al, Optica (in press)

Deep-UV CD of amino-acid residues and helices



Deep-UV CD of secondary structures



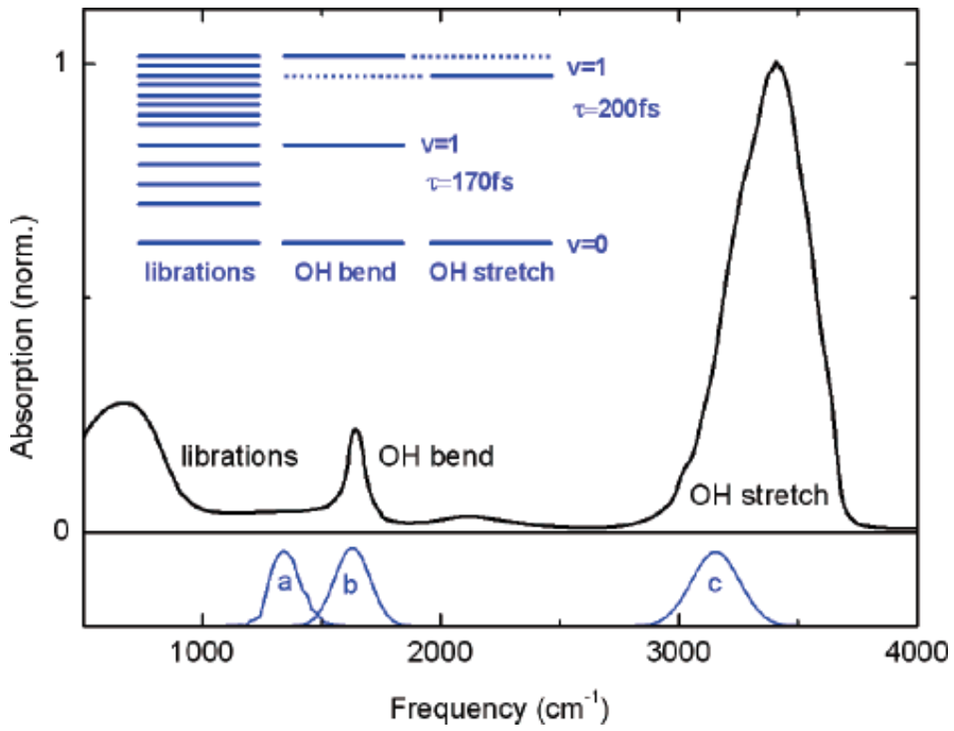
Near-UV CD of dehydroquinase

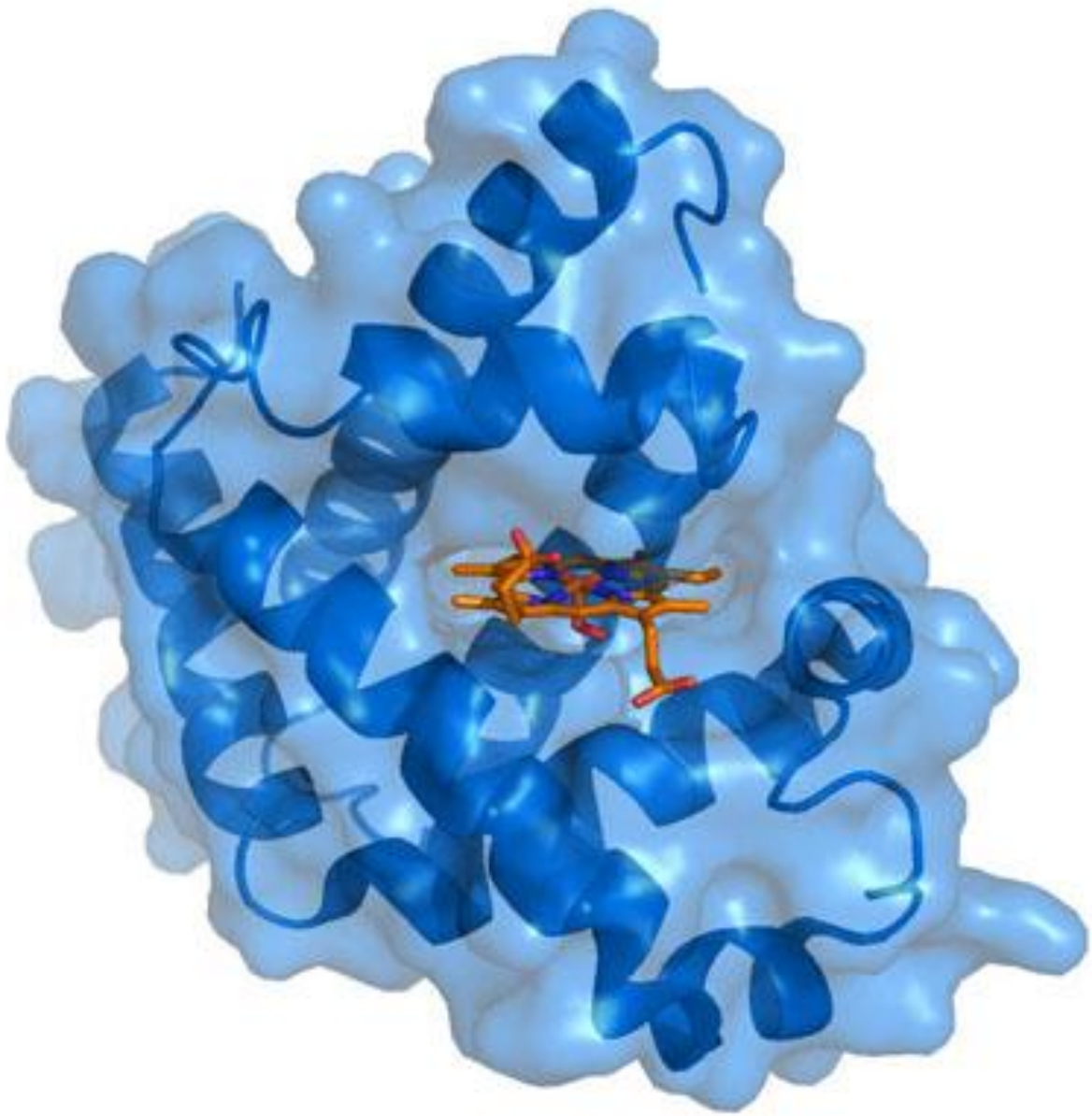
Stability
Tune-ability
Flux
Time-resolution
Compatible with UV res. Raman

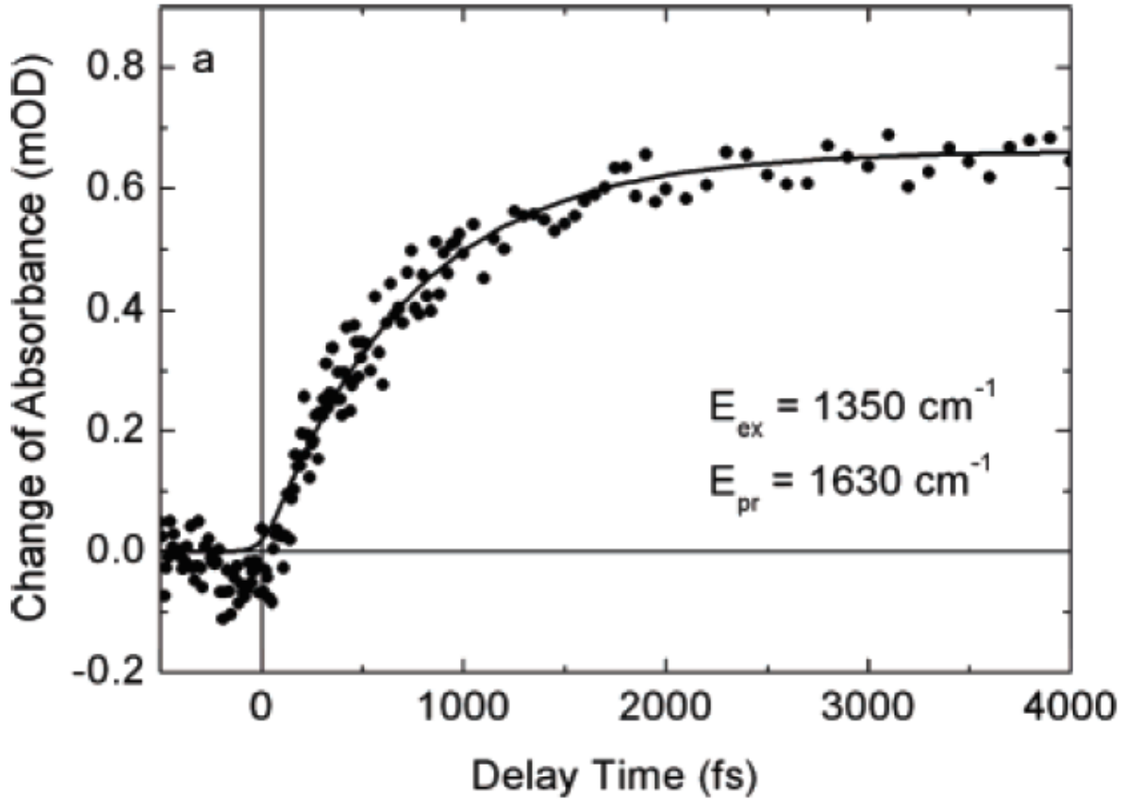
Extension to the X-ray domain

S.M. Kelly et al. / Biochimica et Biophysica Acta 1751 (2005) 119– 139

Non-photoinduced biological functions: Laser T-jump

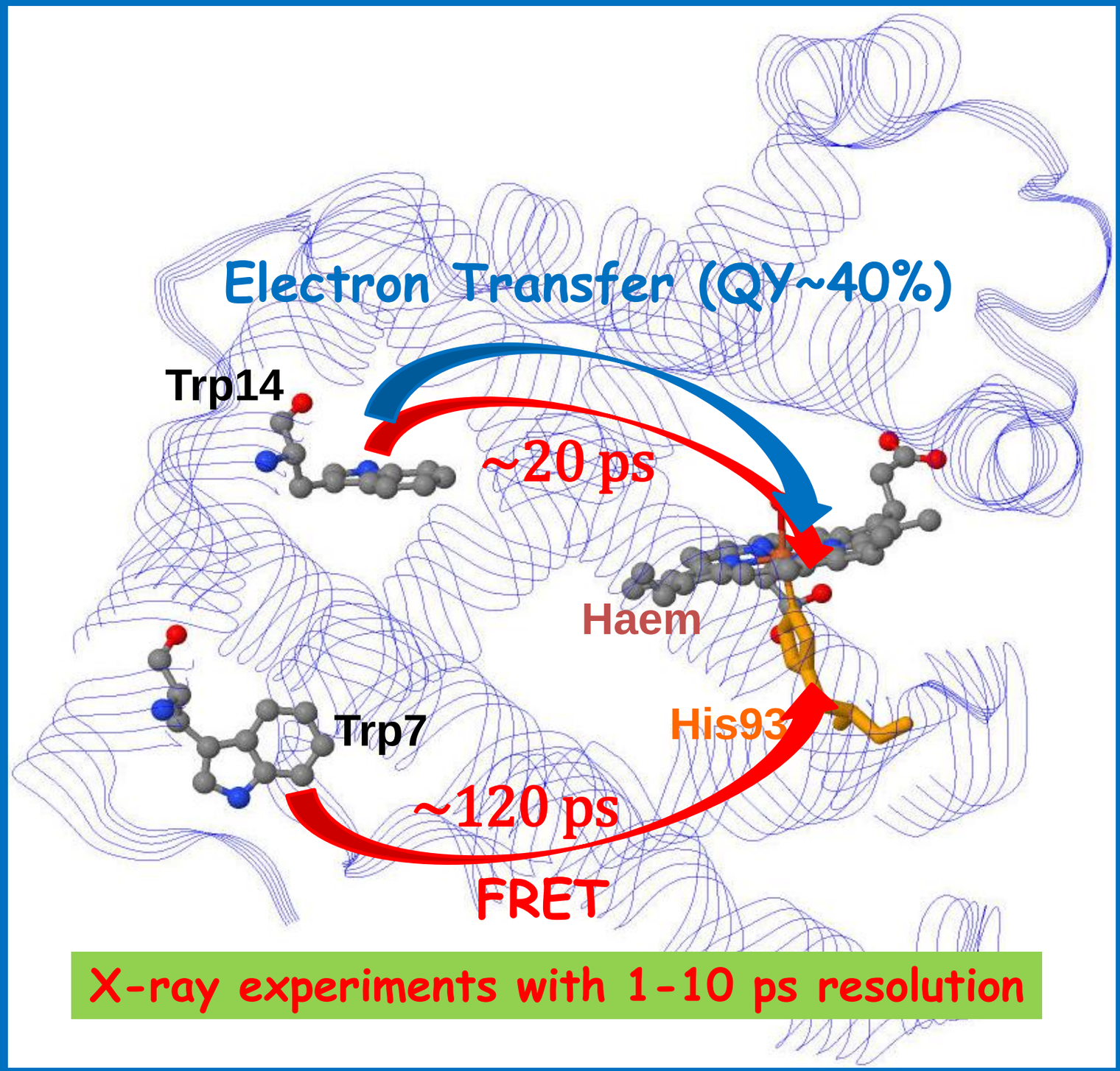






Ashihara et al, JPCA 2007 *Ma et al, PNAS 2008*

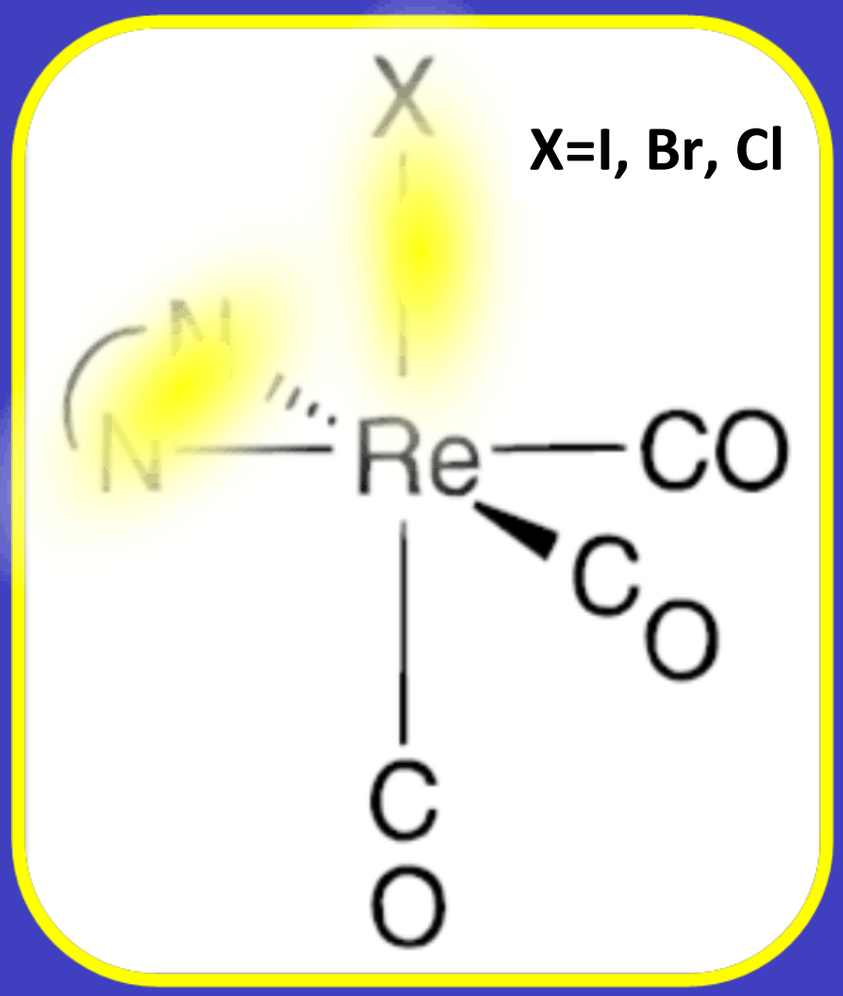
Open scientific questions: electron transfer in heme Proteins (hemoglobin, myoglobin, cytochromes, etc.)



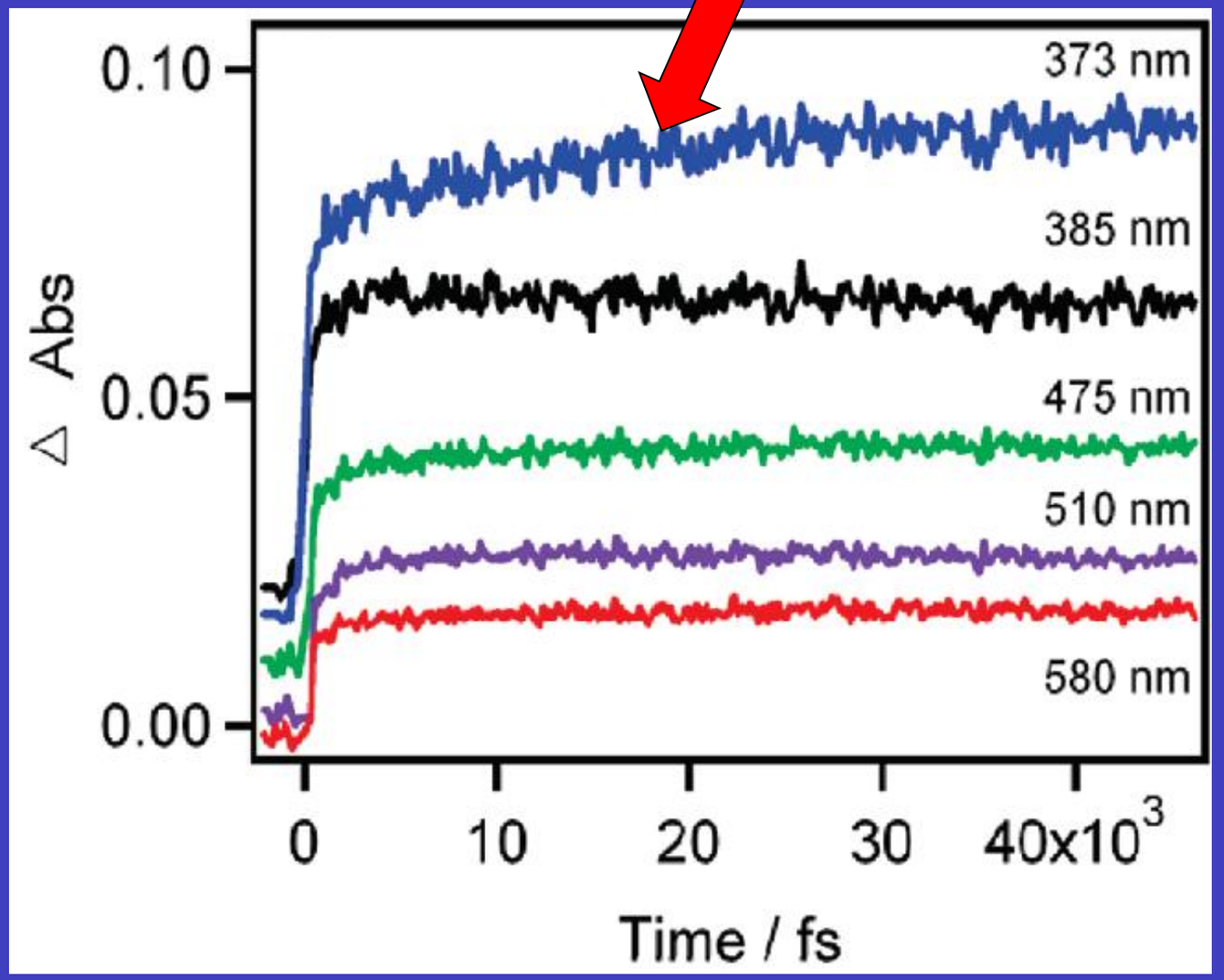
X-ray experiments with 1-10 ps resolution

Deep-UV to visible transient absorption: Consani et al, Science (2013)
Monni et al, PNAS (2015); JACS (submitted)

Open scientific questions: intramolecular electron transfer and solvation dynamics



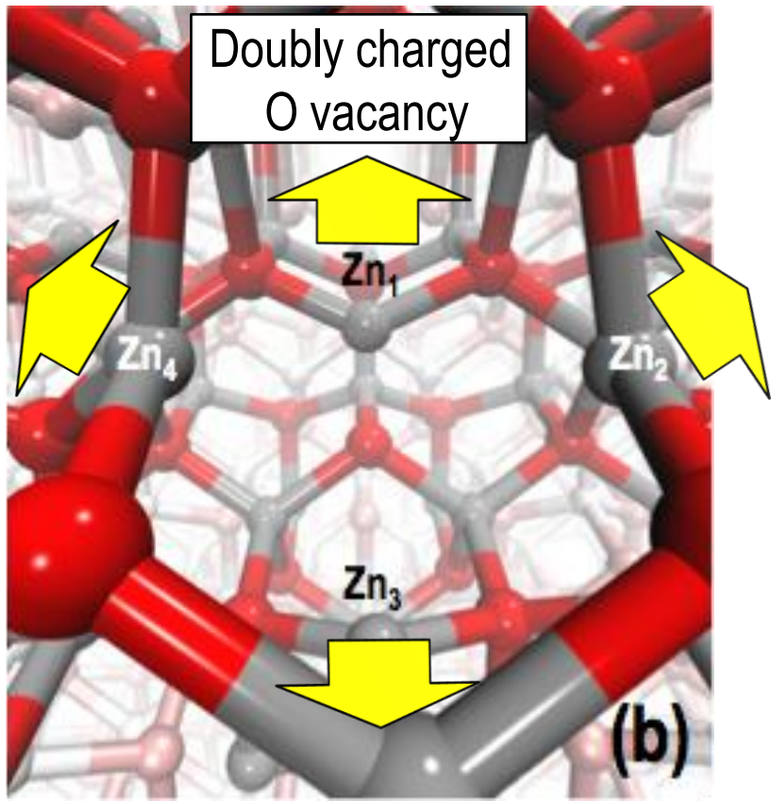
Cannizzo et al, JACS 2008
El Nahhas et al, JPCA 2010
El Nahhas et al, Inorg. Chem. 2011
El Nahhas et al, JPCA 2013



Delayed electron transfer, two-centre electron transfer?
Change of transition dipole due to solvation?

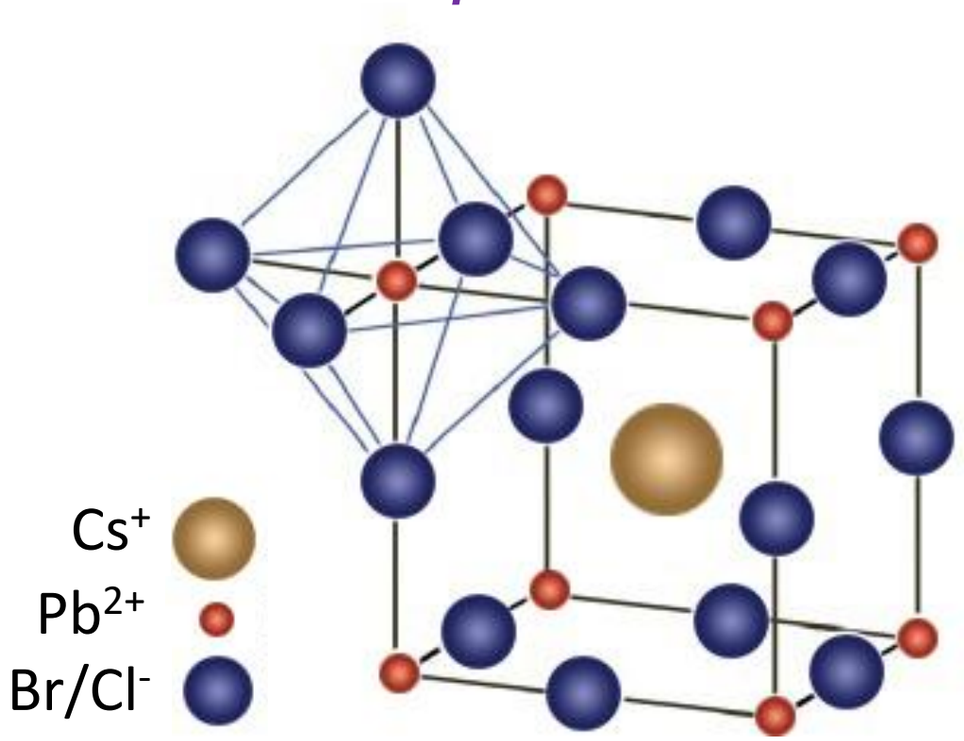
X-ray experiments with 1-10 ps resolution

Charge carrier trapping in transition metal oxides



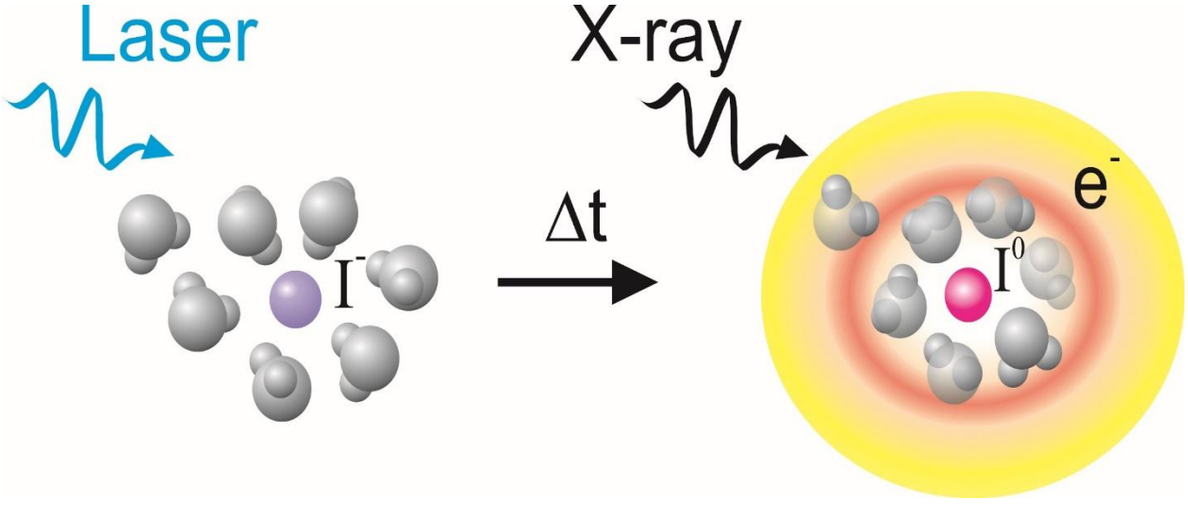
Penfold *et al*, Nature Comm. (2018)

Charge carrier dynamics in perovskites



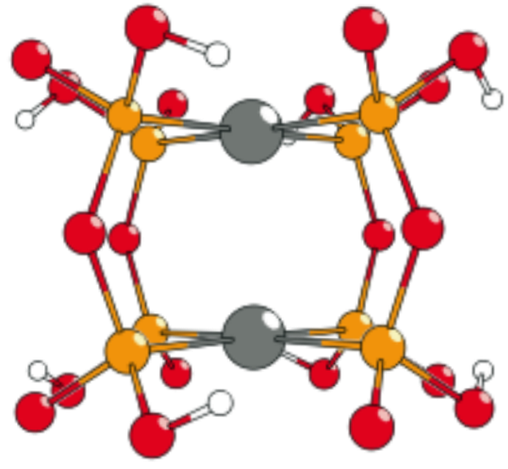
Santomauro *et al*, Struct. Dyn. (2017)

Electronic solvation dynamics



Pham *et al*, JACS (2007); JACS (2011)

"Dark" states in chemical dynamics



Monni *et al*, PNAS (2018)

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

LAUSANNE CENTRE FOR ULTRAFAST SCIENCE LACUS

LSU laboratoire de spectroscopie ultrarapide

G. Auböck, E. Baldini,
C. Bacelar, Th. Barillot,
B. Bauer, J. Budarz,
O. Cannelli, G. Capano,
R. Ingle, A. Lübcke, D. Kinschel, G. Mancini,
F. van Mourik, M. Oppermann,
Th. Penfold, S. Polishchuk, M. Puppin,
H. Rittmann-Frank, J. Rittmann,
Th. Rossi, F. Santomauro,
B. Sorokin, L. Wang, Y. Zhao

Universität Zürich[UZH]

Jan Helbing

erc European Research Council

70 NRP Energy Turnaround
National Research Programme

must | Molecular Ultrafast Science and Technology
National Center of Competence in Research

PAUL SCHERRER INSTITUT PSI

P. Beaud, C. Borca,
D. Grolimund, G. Ingold,
J. A. Johnson, C. J. Milne

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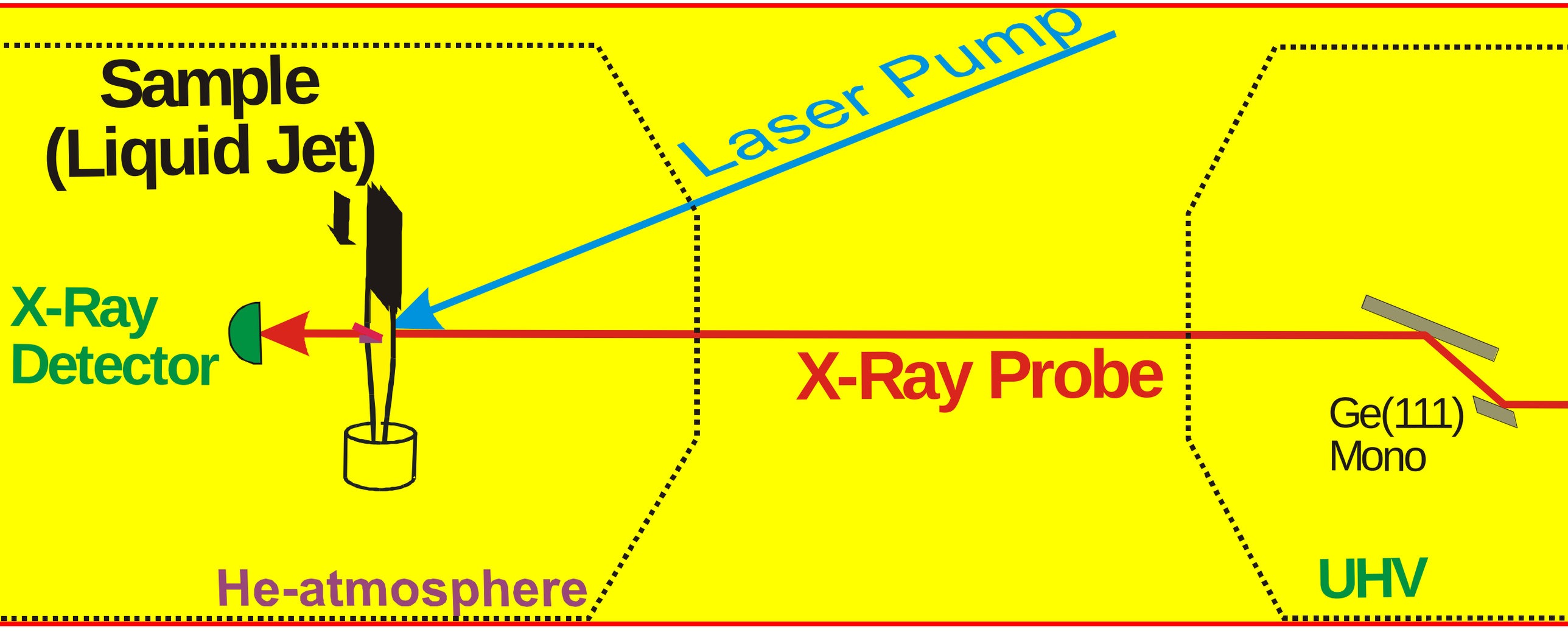
SACLA

T. Katayama
M. Yabashi

European XFEL

F. Lima, D. Khakhulin, W. Gawelda,
P. Zalden, S. Schulz, Ch. Bressler

Optical Pump/X-ray probe experiments



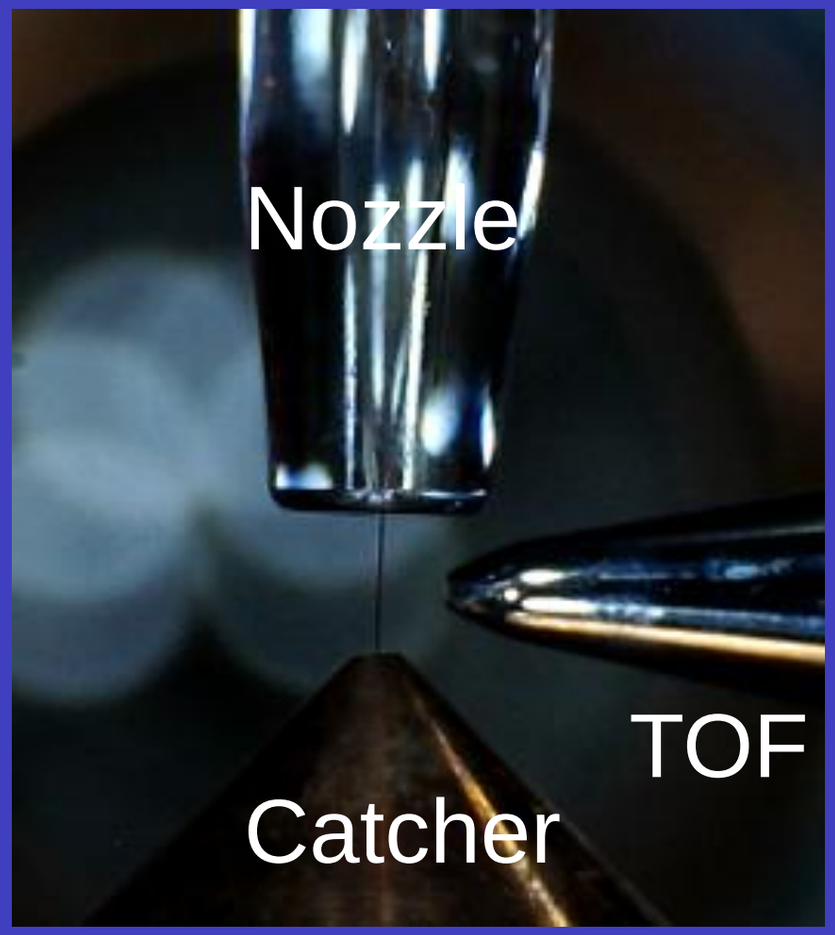
Measured signal = excited minus unexcited sample transmission at MHz rep rates

M. Chergui, Acta Crystal. (2010); ARPC (2010); Comprehensive Biophysics (2012)

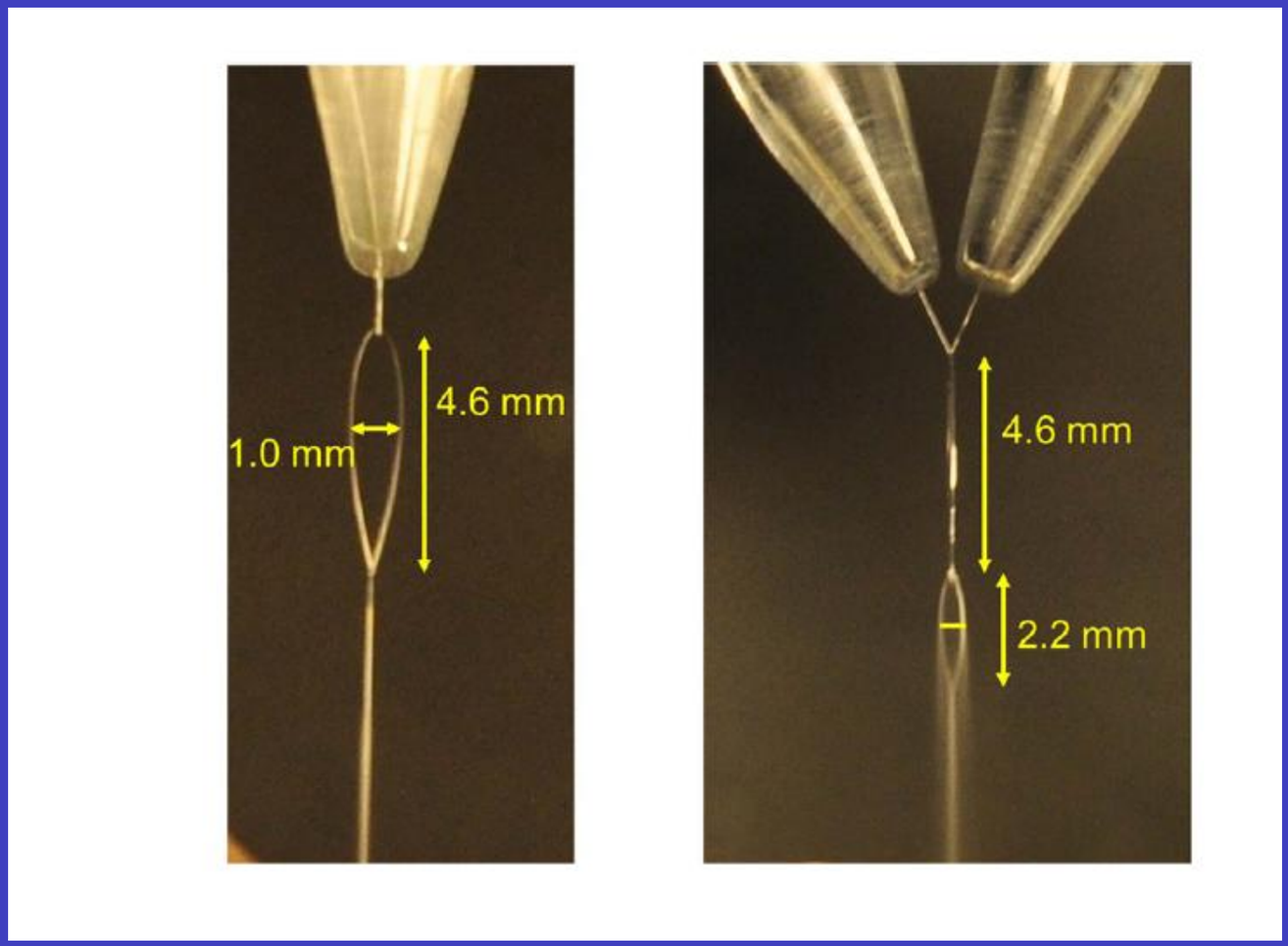
Methods available with table-top systems

Soft X-ray absorption spectroscopy

Photoelectron spectroscopy



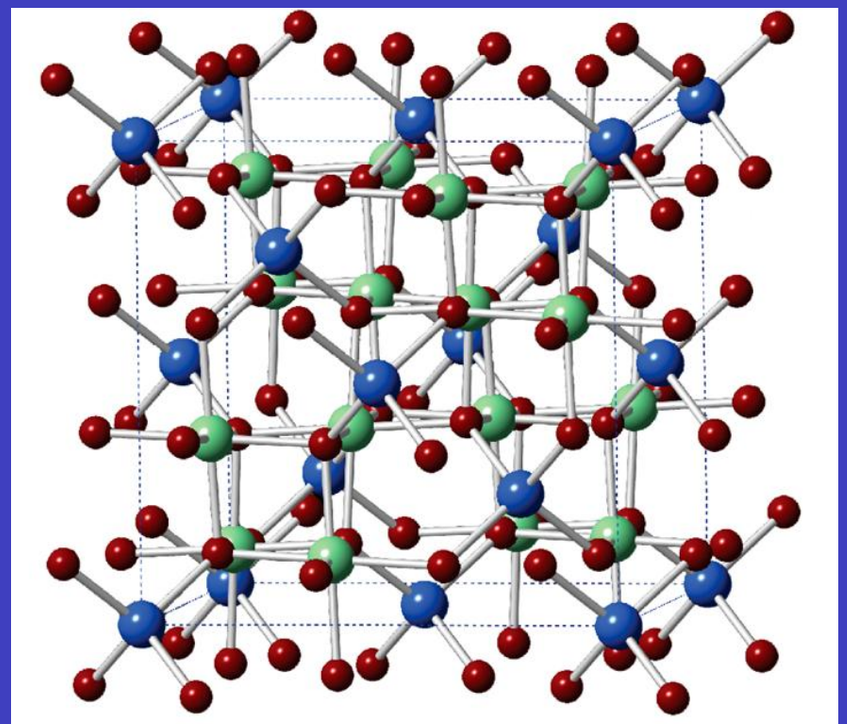
Faubel and Winter, Chem. Rev. 2006
Abel, Faubel et al, Appl Phys A 2009
Ojeda et al, PCCP 2017

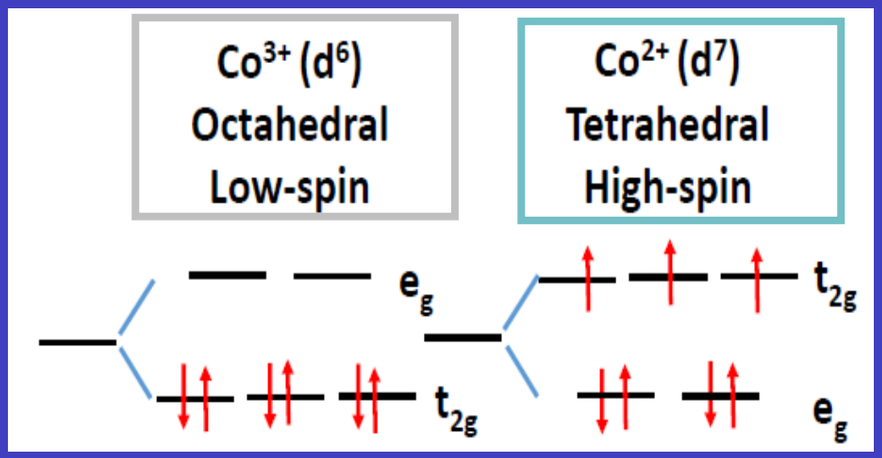


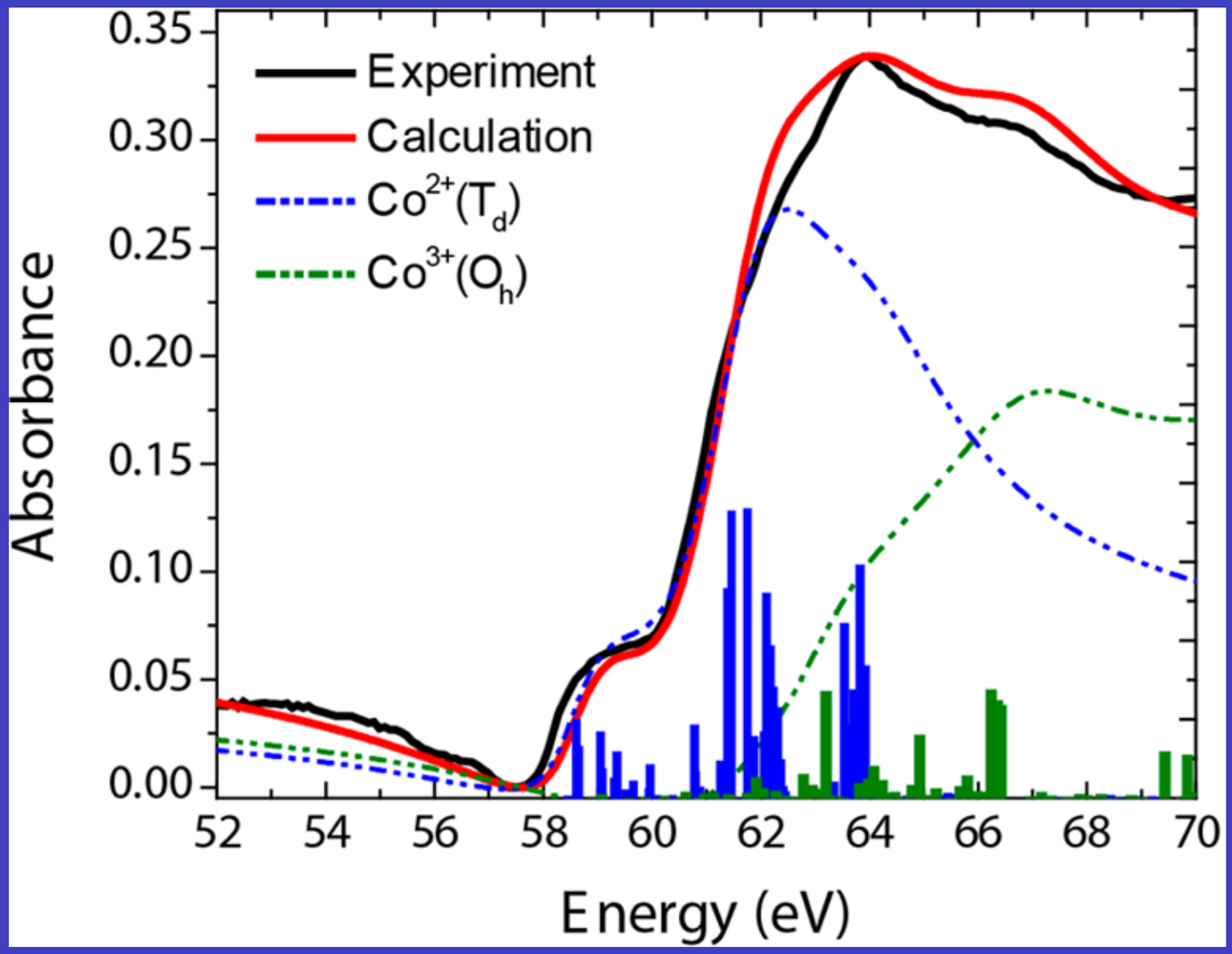
Ekimova et al, Struct. Dyn. 2015
Galinis et al, Rev. Scient. Instr. 2017
Koralek et al, Nature Comm. 2018

Issue with neighbour absorption edges

Charge carrier dynamics in Spinel Cobalt oxide (Co_3O_4)







Jiang et al, JPCC 2014

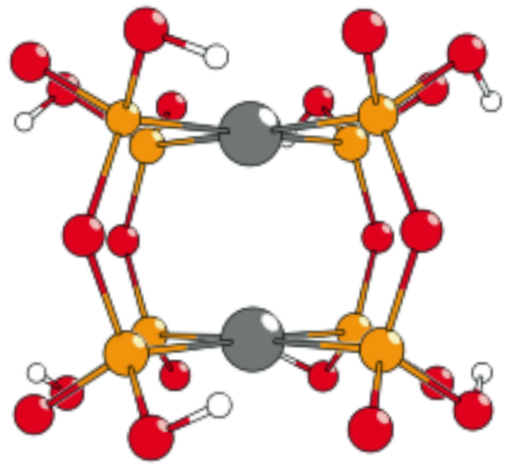
Fs non-resonant XES with hard X-rays

What can we do "only" at X-ray Free Electron Lasers?

- Ultrafast photon-in/photon-out experiments:
Non-res. XES, RIXS, X-ray Raman, etc.

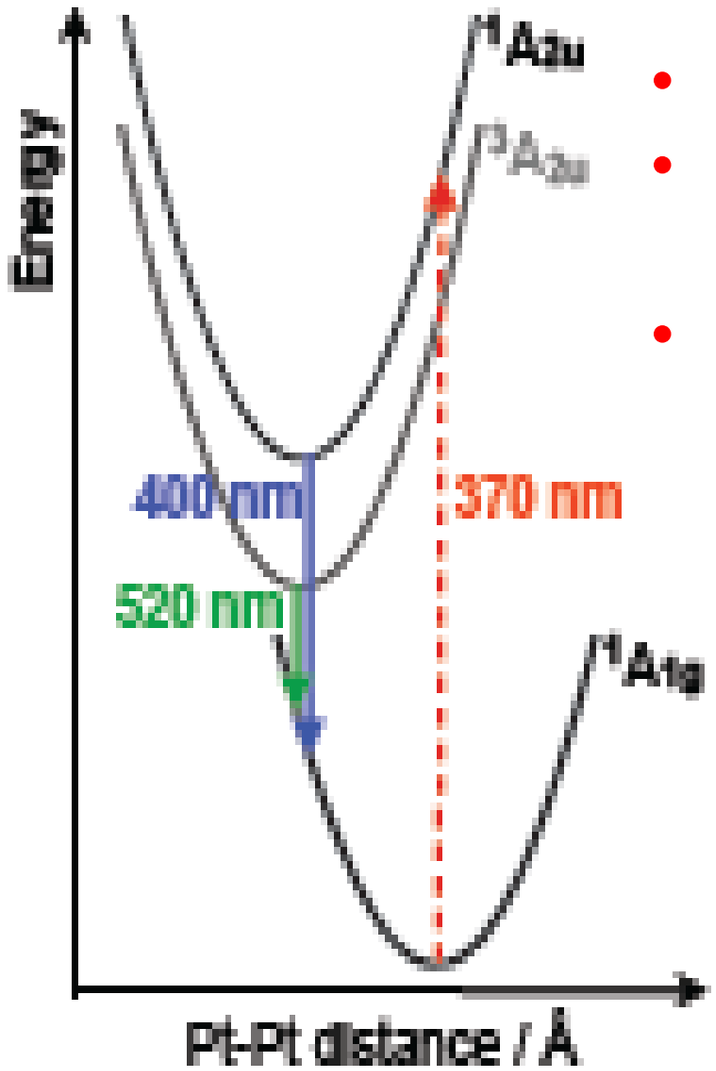
- Non-linear X-ray optics:
Multiphoton absorption, SHG, 4W-mixing, Transient Gratings, 2D X-ray spectroscopy

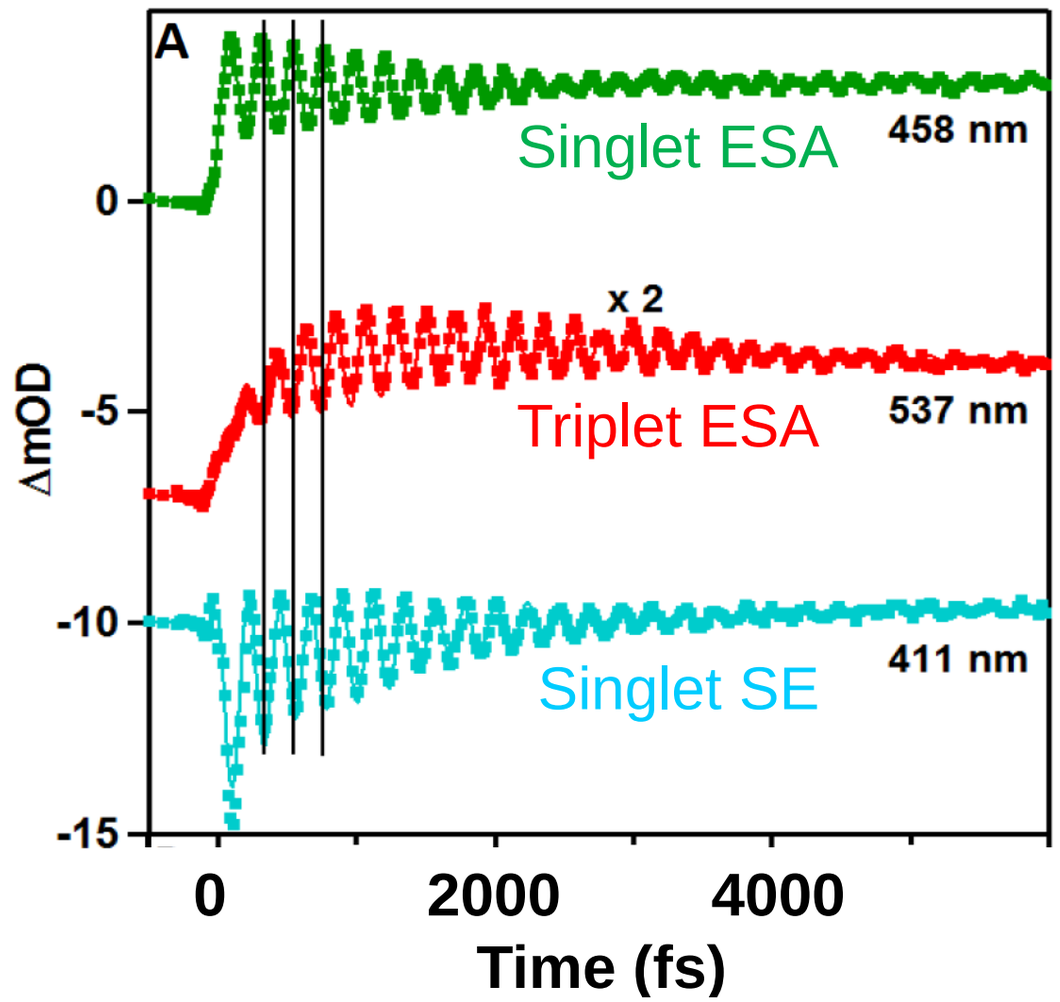
d^8-d^8 complexes: PtPOP



PtPOP = Tetrakis(μ-diphosphito(2-)-P,P')diplatinate(II)

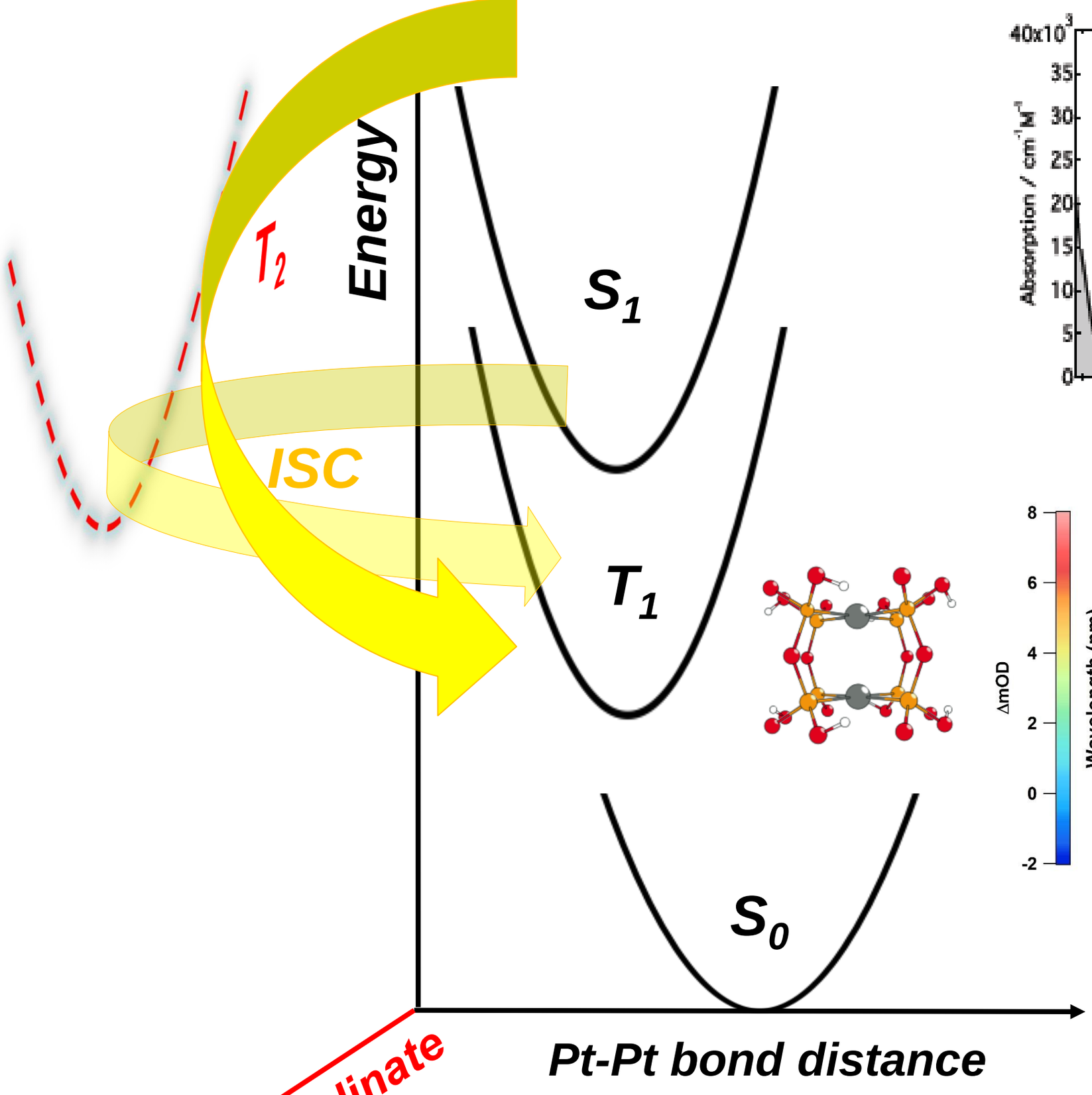
- **Coherence transfer from S to T**
- **ISC time is 0.7 ps**
- **Pure Dephasing Time= 2 ps**
- **Solvent dependent ISC**

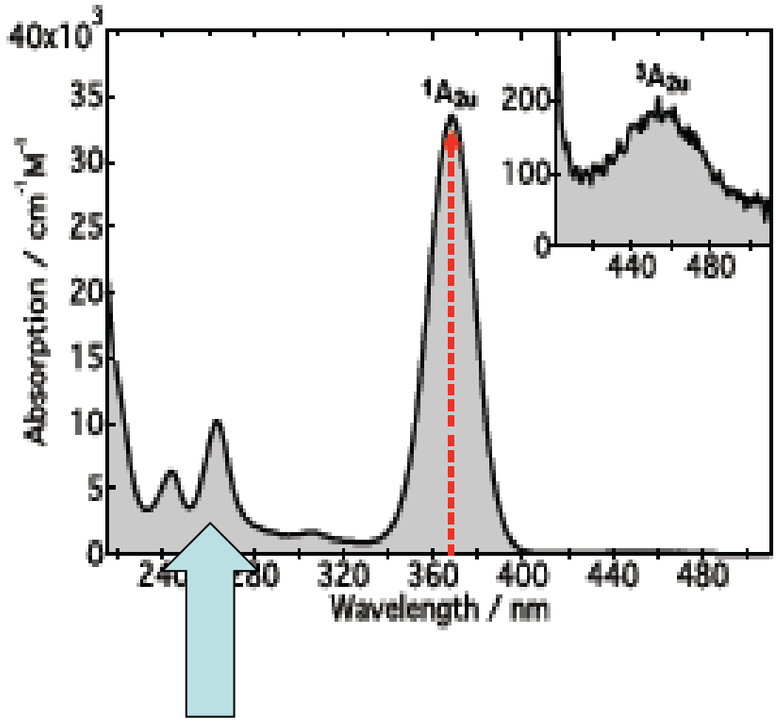


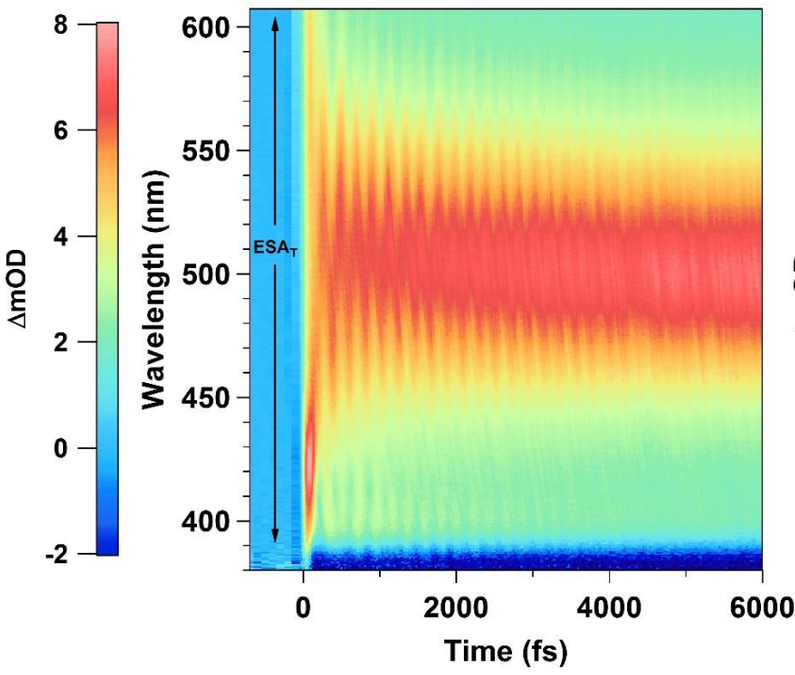


Crosby et al, Gray et al, etc.

R.M. van der Veen et al., Ang. Chem. IE (2009); PCCP (2010); J. Am. Chem. Soc. (2011)



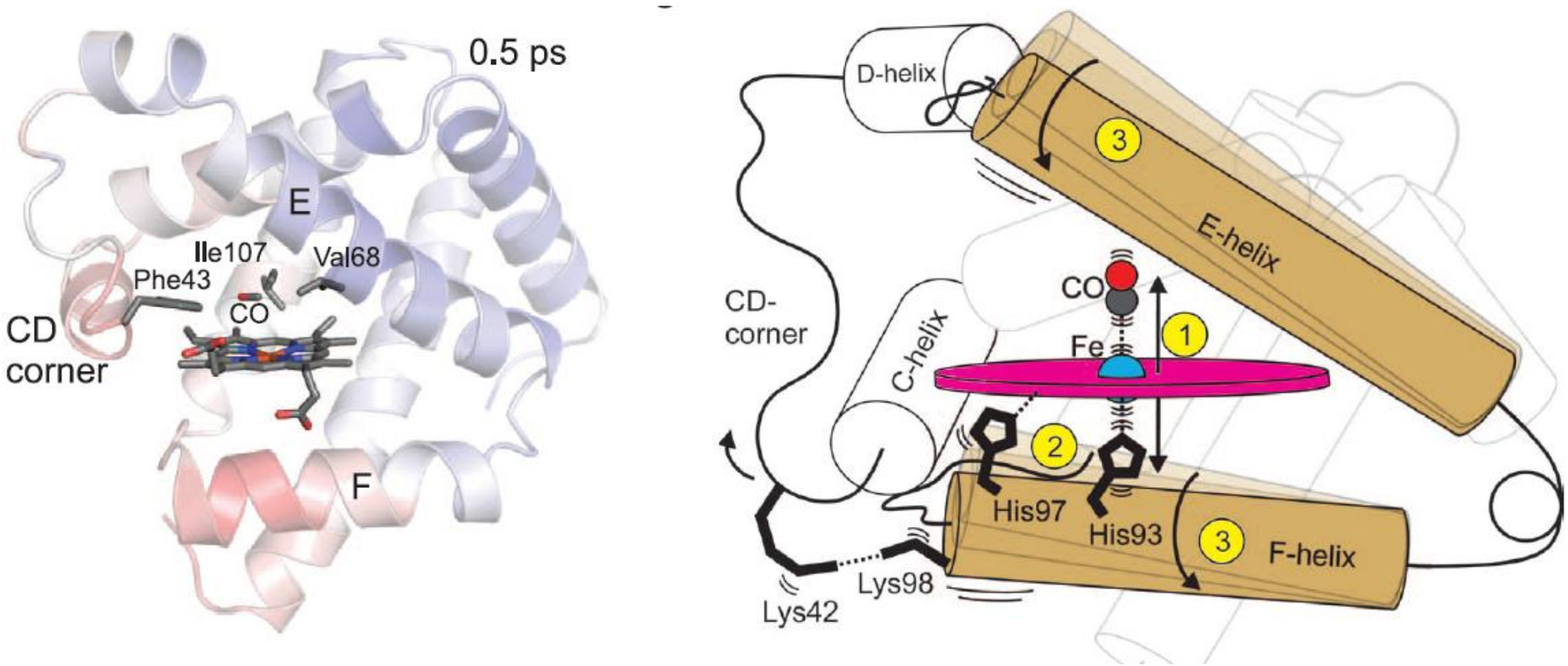




QM/MM simulations (Coll. I. Tavernelli) *Monni et al., PNAS (2018)*

Protein dynamics: Myoglobin-CO

Levantino et al, Nat. Comm. 2015: solution small-angle scattering (SAXS)



Baerends et al, Science 2015: SFX studies

Levantino et al, Struct. Dyn. 2015: fixed energy fs XAS

Sension et al, in progress: polarized fs-XANES on Vitamin B12

Time-resolved core-level spectroscopies

Resonant inelastic X-ray scattering

X-ray absorption

Non-resonant X-ray emission

Resonant X-ray emission

UPS-XPS of liquids

ARPES

ESCA

XPS

Non-linear X-ray optics

Multidimensional X-ray spectr.

UPS

Electron transfer

Nanoparticles

Solar energy conversion

Spin cross-over

Strongly correlated materials

Solvation dynamics

Charge carrier dynamics

Molecular Magnetism

Photocatalysis

Superconductivity

Bond forming and breaking

Photosynthesis

Electrochemistry

Surface dynamics

Defects

Charge carrier dynamics

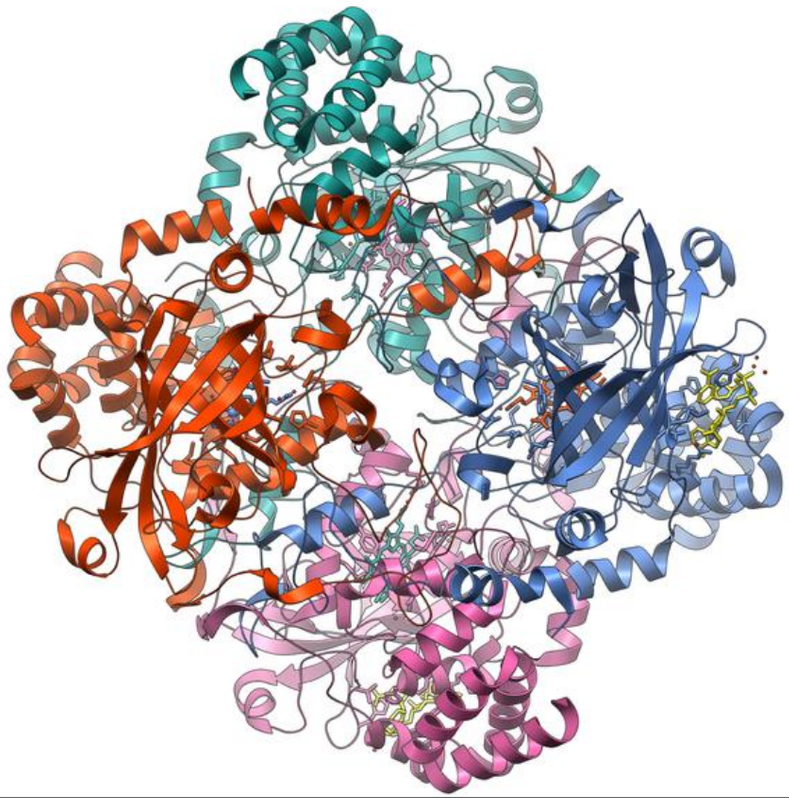
Interface dynamics

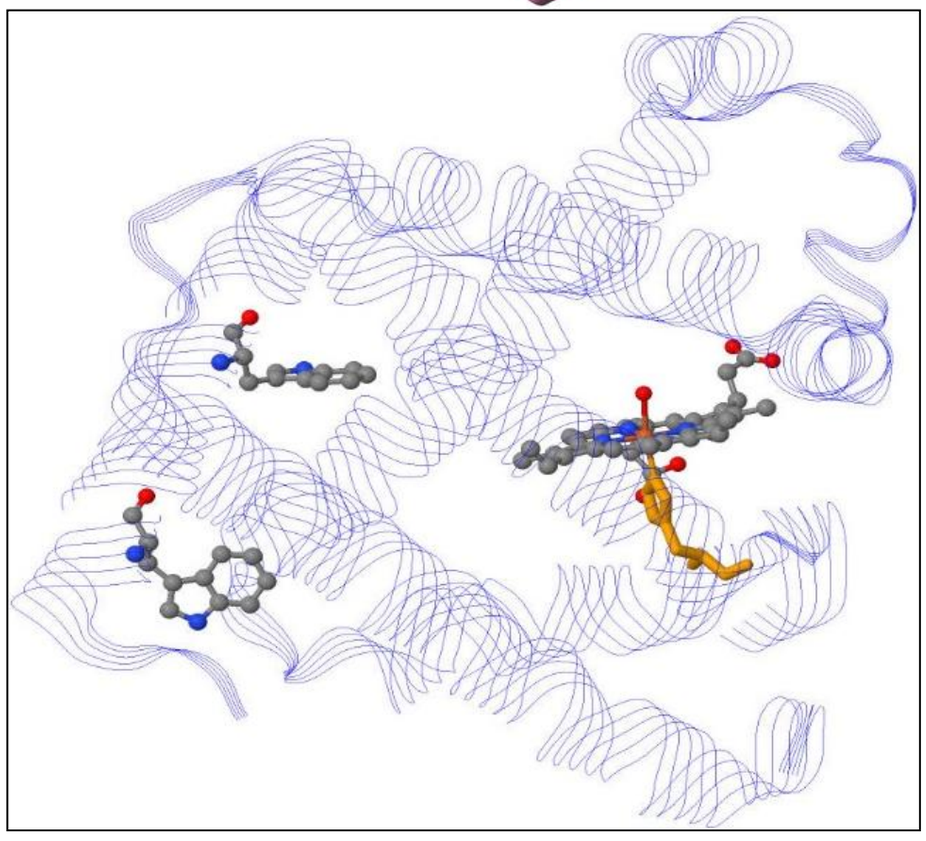
Protein Dynamics

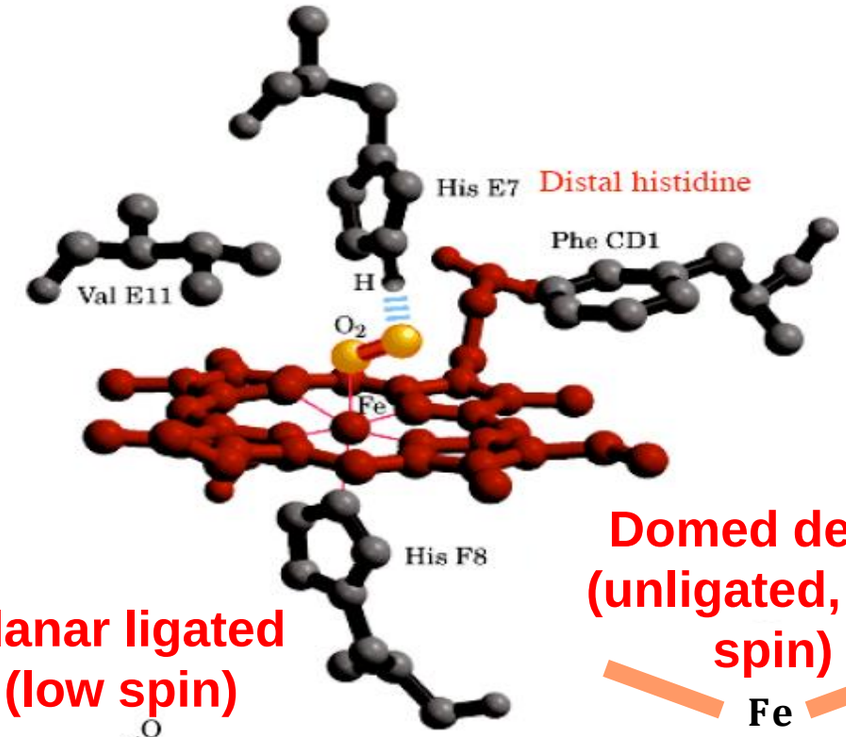
Lattice dynamics

Chirality

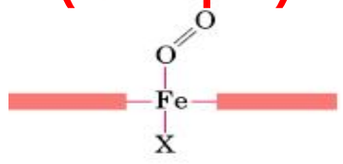
3. Biology: Fundamental processes in respiration



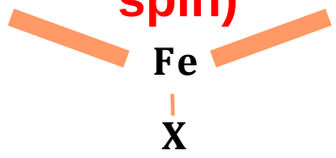


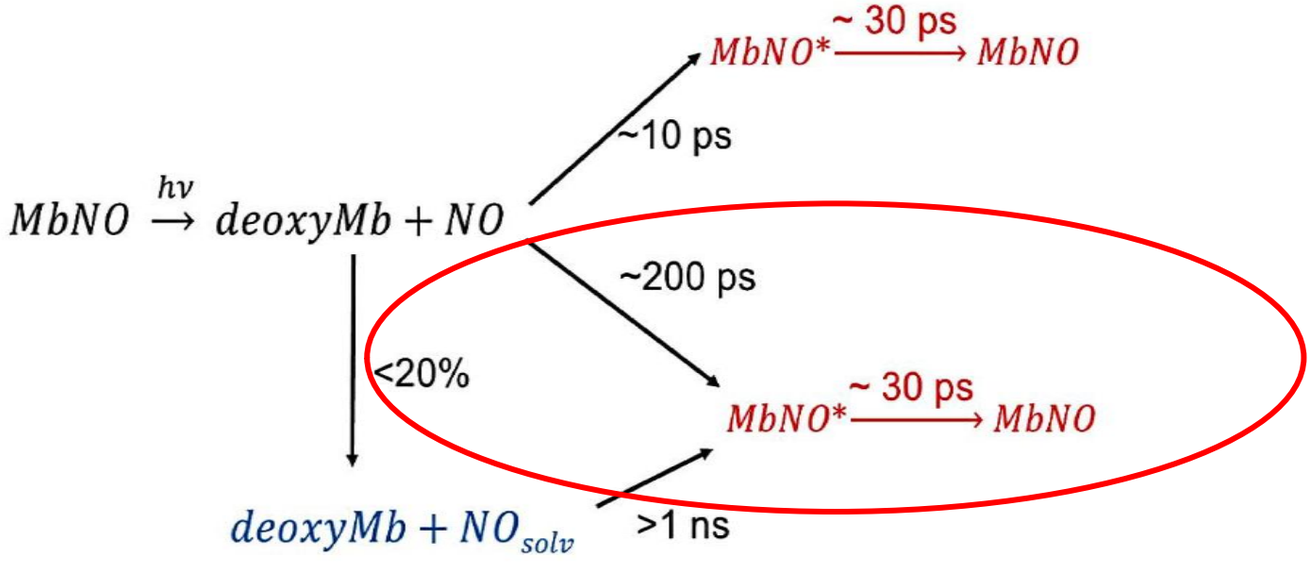


Planar ligated (low spin)



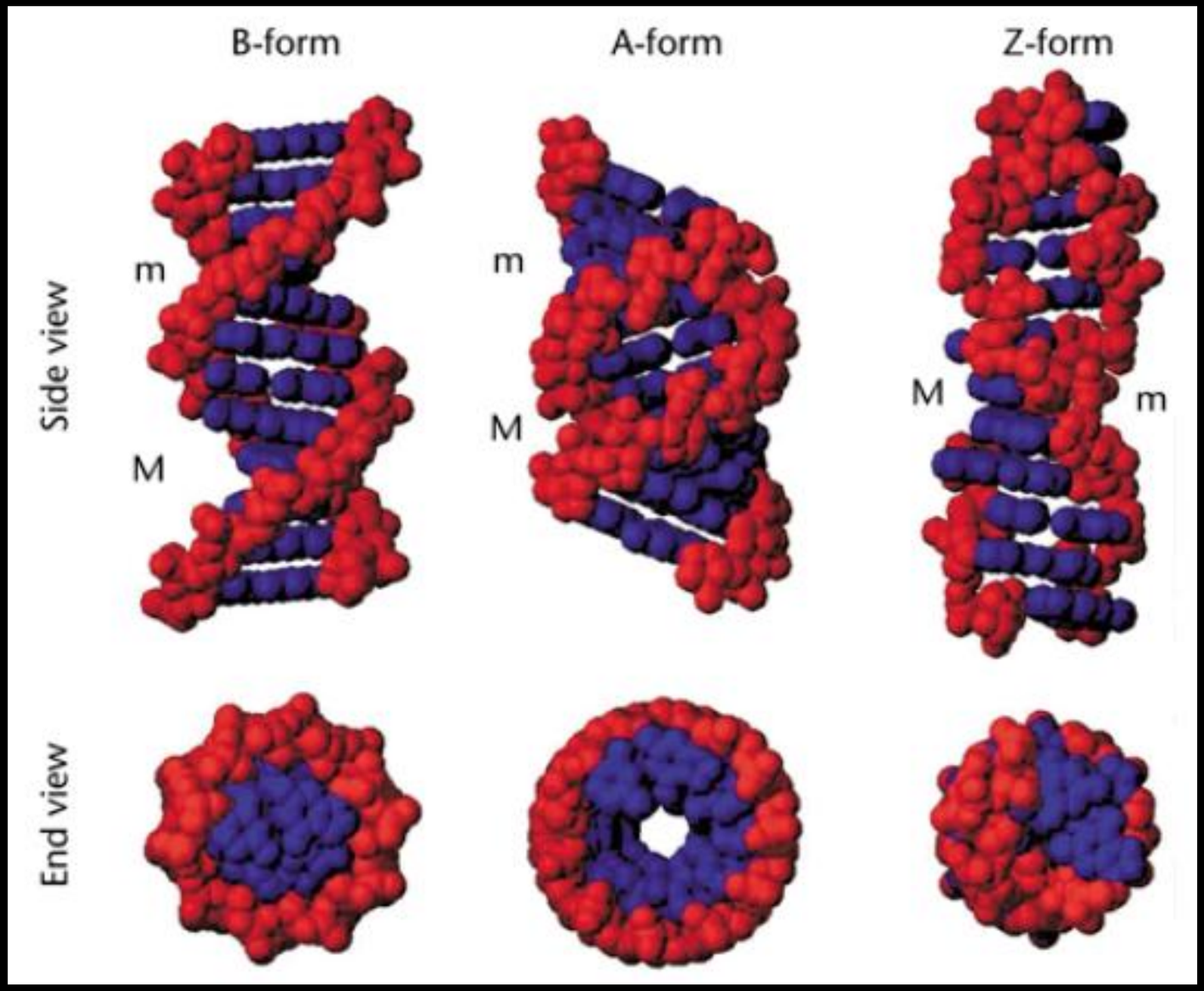
Domed deoxy (unligated, high spin)

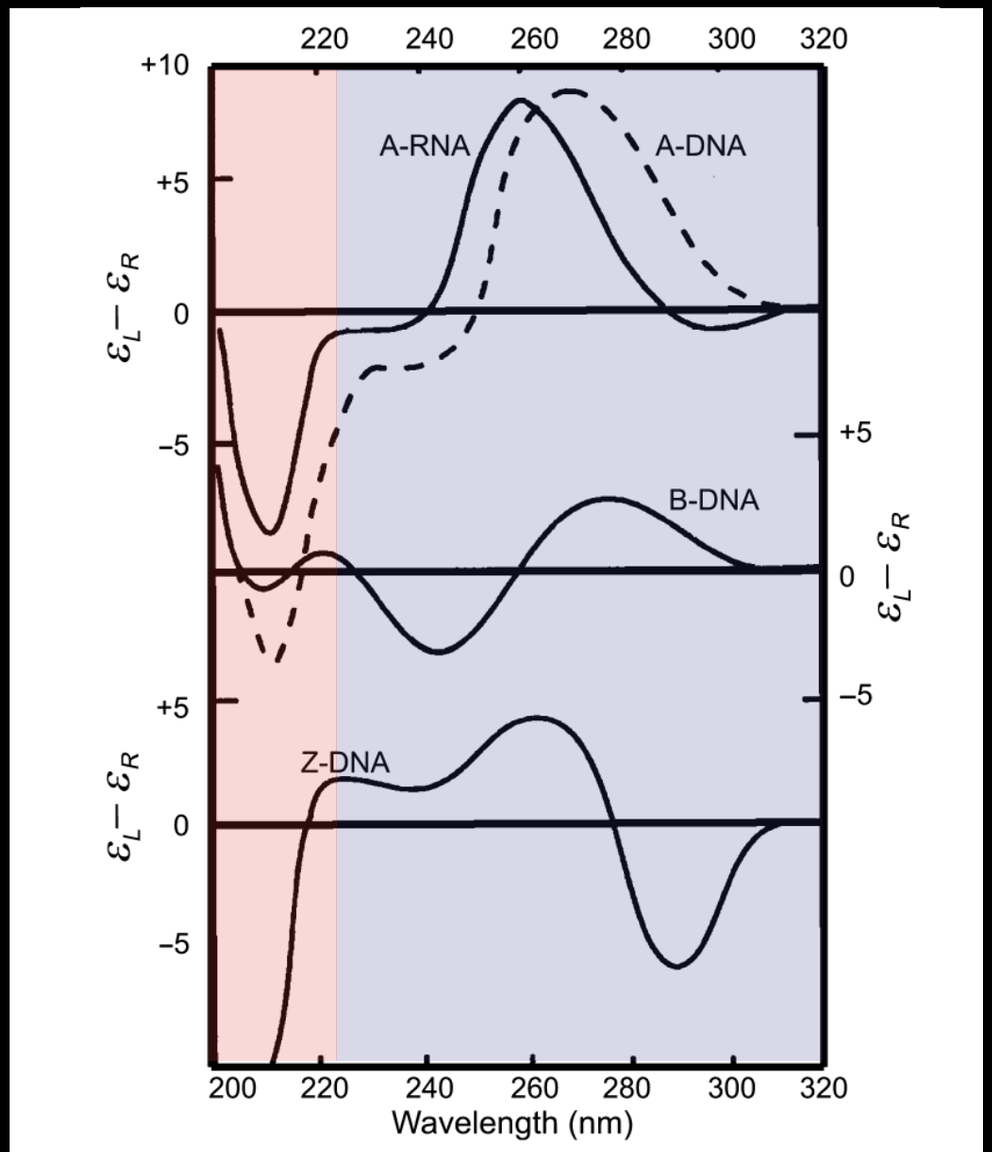




Mills et al, Science 1984

ELECTRONIC CD SPECTROSCOPY





Key features:

- Non-empirical structural probe
- Requires chiral, coupled chromophore assemblies
- Applicable to liquid-phase samples
- All-optical technique: ideal for femtosecond pulses

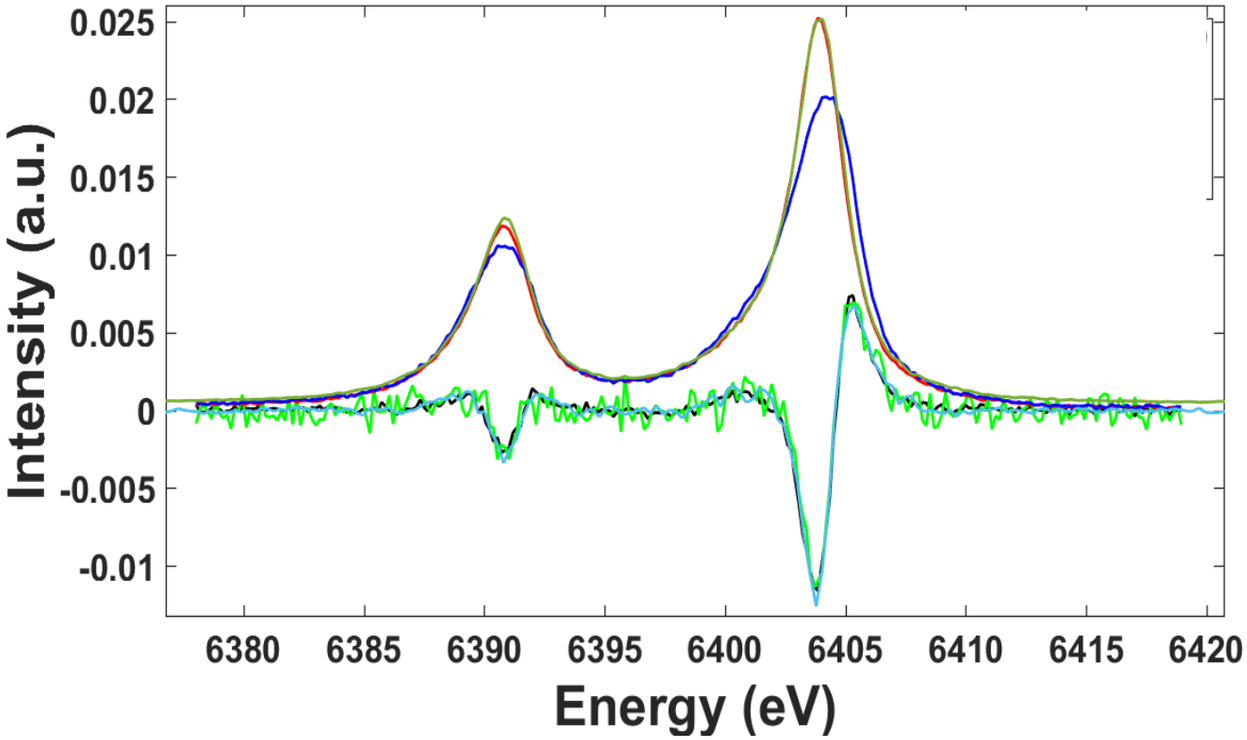
Applications:

- Global structure determination
- Stability via melting curves
- Ligand binding via induced CD
- Local chromophore interactions

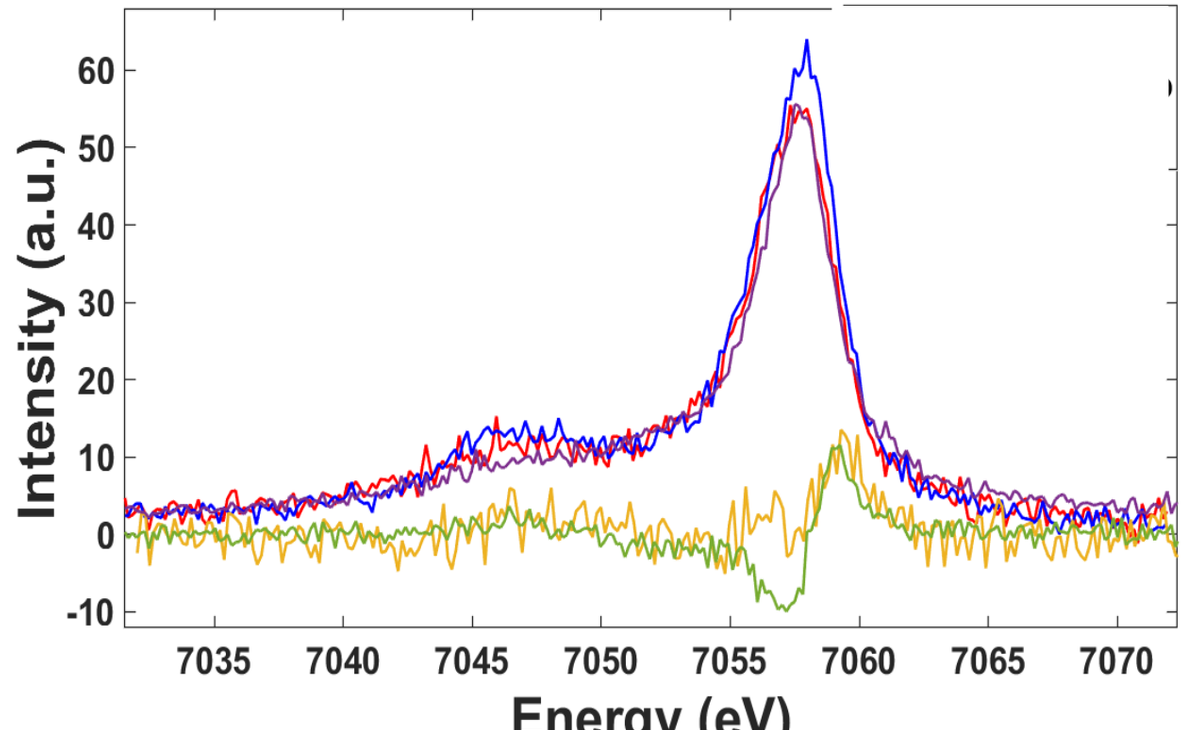
Figures: Ranjbar and Gill, Chem. Biol. Drug Des. 74, 101 (2009)

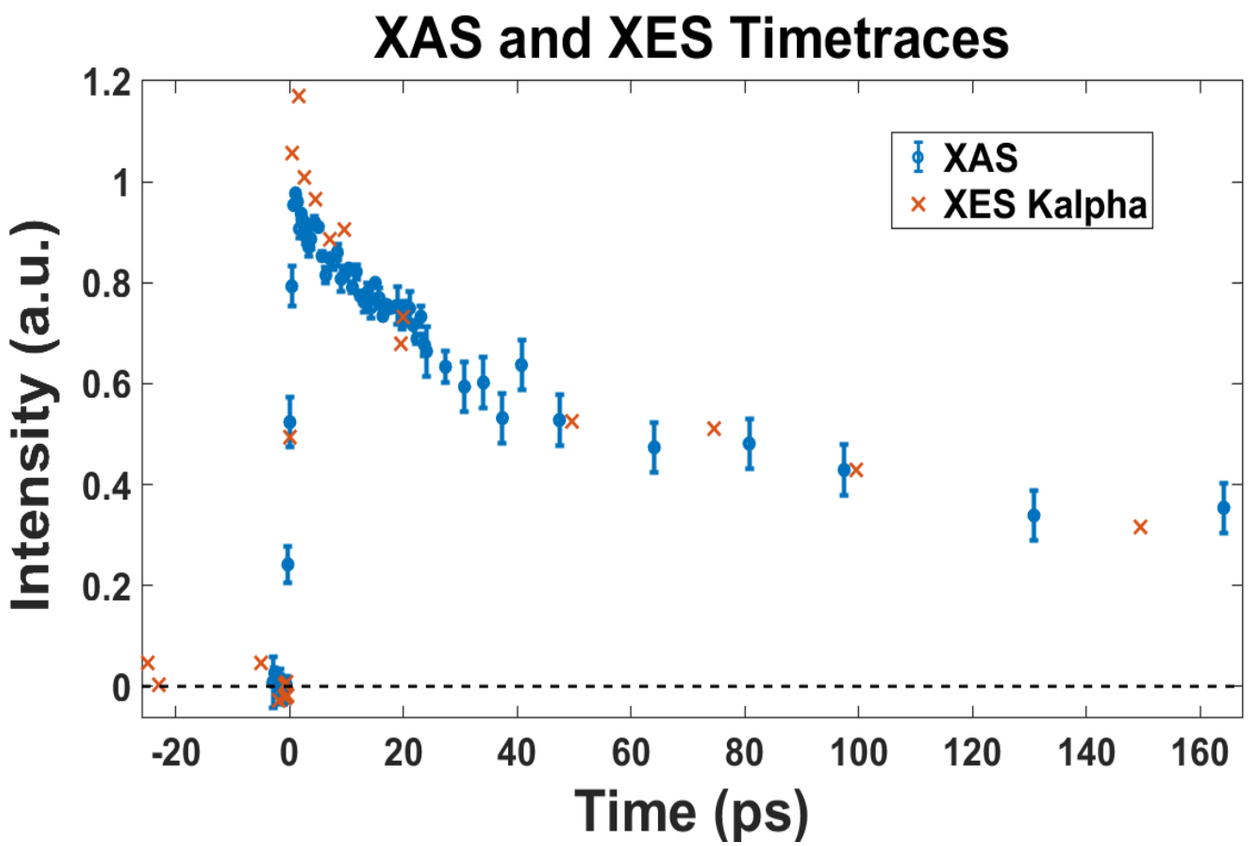
Femtosecond X-ray emission studies

Steady state and transient K_α XES



Steady state and transient K_β XES





K_β: sensitive to spin state

XES K_α and XAS edge time traces match, but ~1 ps component is stronger in XES K_α

Significant time scales

attoseconds 10^{-18} s — femtoseconds 10^{-15} s — picoseconds 10^{-12} s — nanoseconds 10^{-9} s — microseconds 10^{-6} s — milliseconds 10^{-3} s

electron motion
core-hole lifetimes

motion of nuclei
molecular vibrations
optical phonons
molecular bond formation

rotation of molecules
molecular librations
Acoustic phonons
vibrational dephasing

electronic relaxation
fluorescence
thermal effects

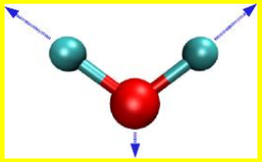
large-scale protein motion
phosphorescence

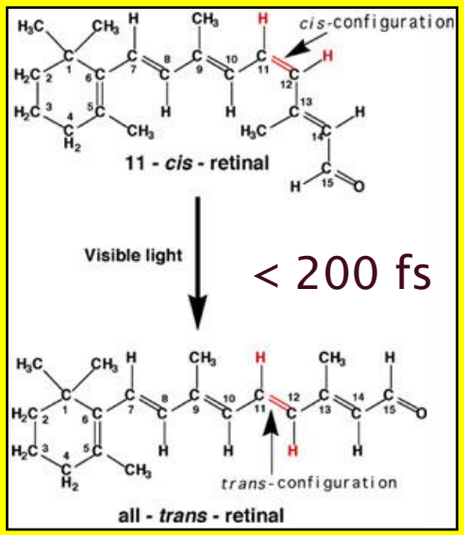
protein folding
chemical kinetics

110 as delay between electron emission from conduction band and lower-lying states in Tungsten upon irradiation

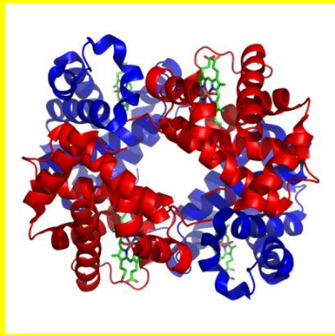
The Fe K-edge core-hole lifetime is 4 fs

period of the symmetric stretch in H_2O is 10 fs





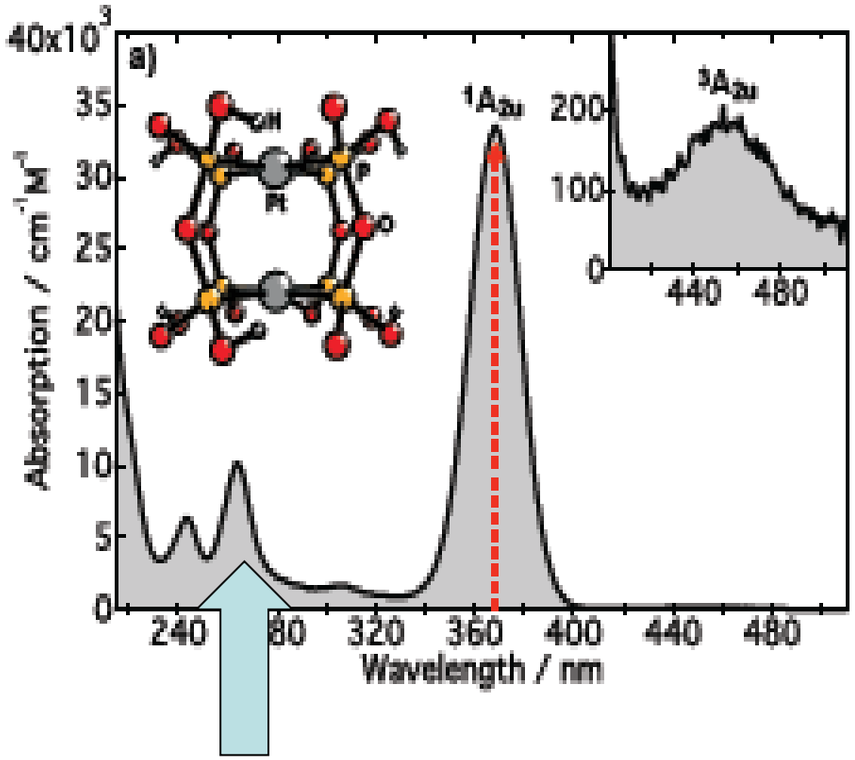
Hemoglobin R->T transition takes microseconds

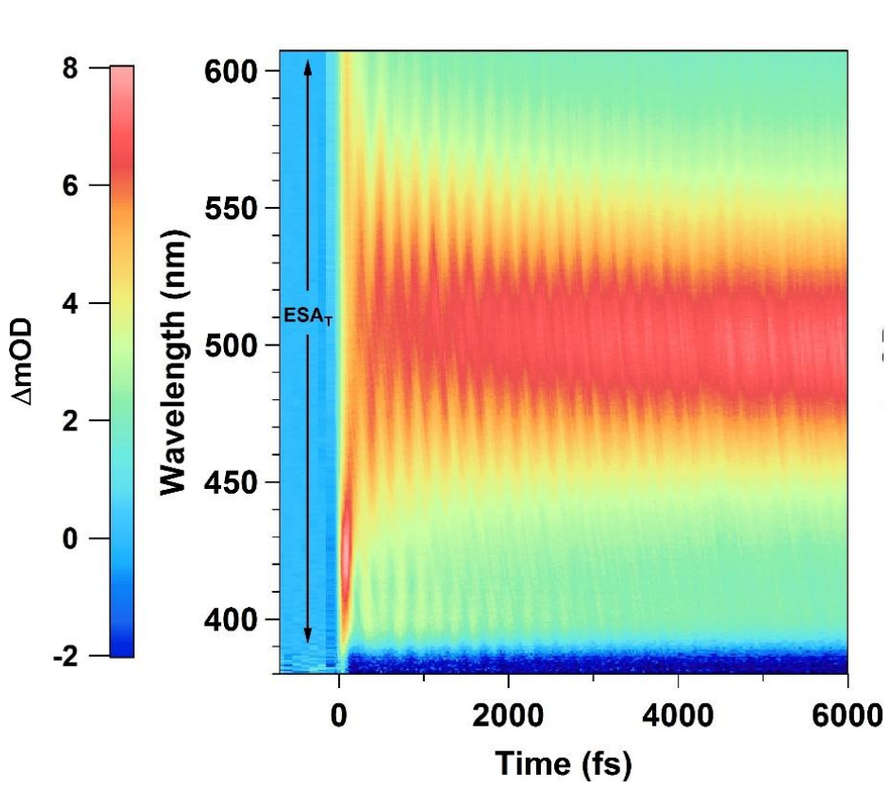


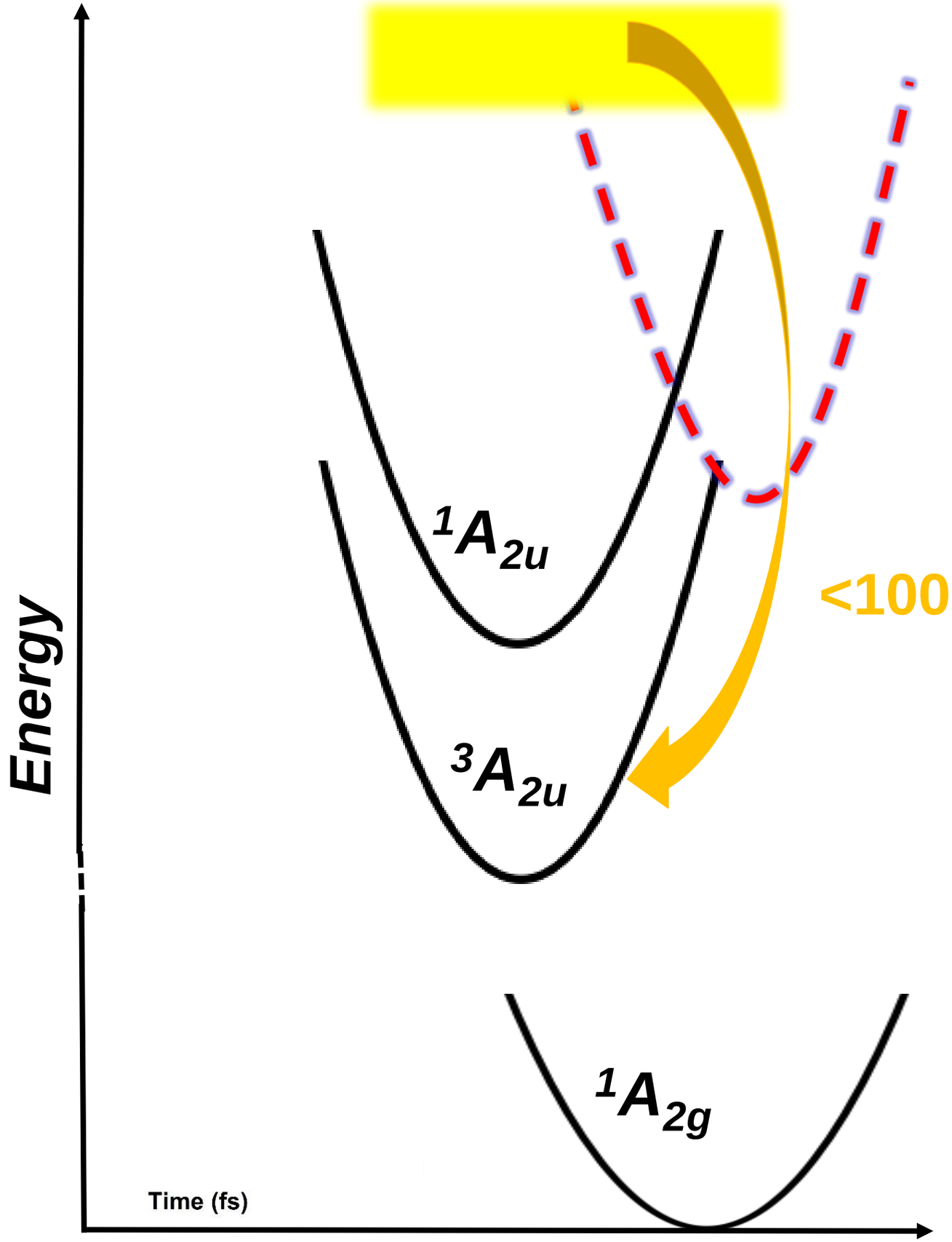
Electronics (Flash Photolysis) *Eigen-Porter-Norrish 1967*

Lasers *Zewail 1999*

high-harmonic generation



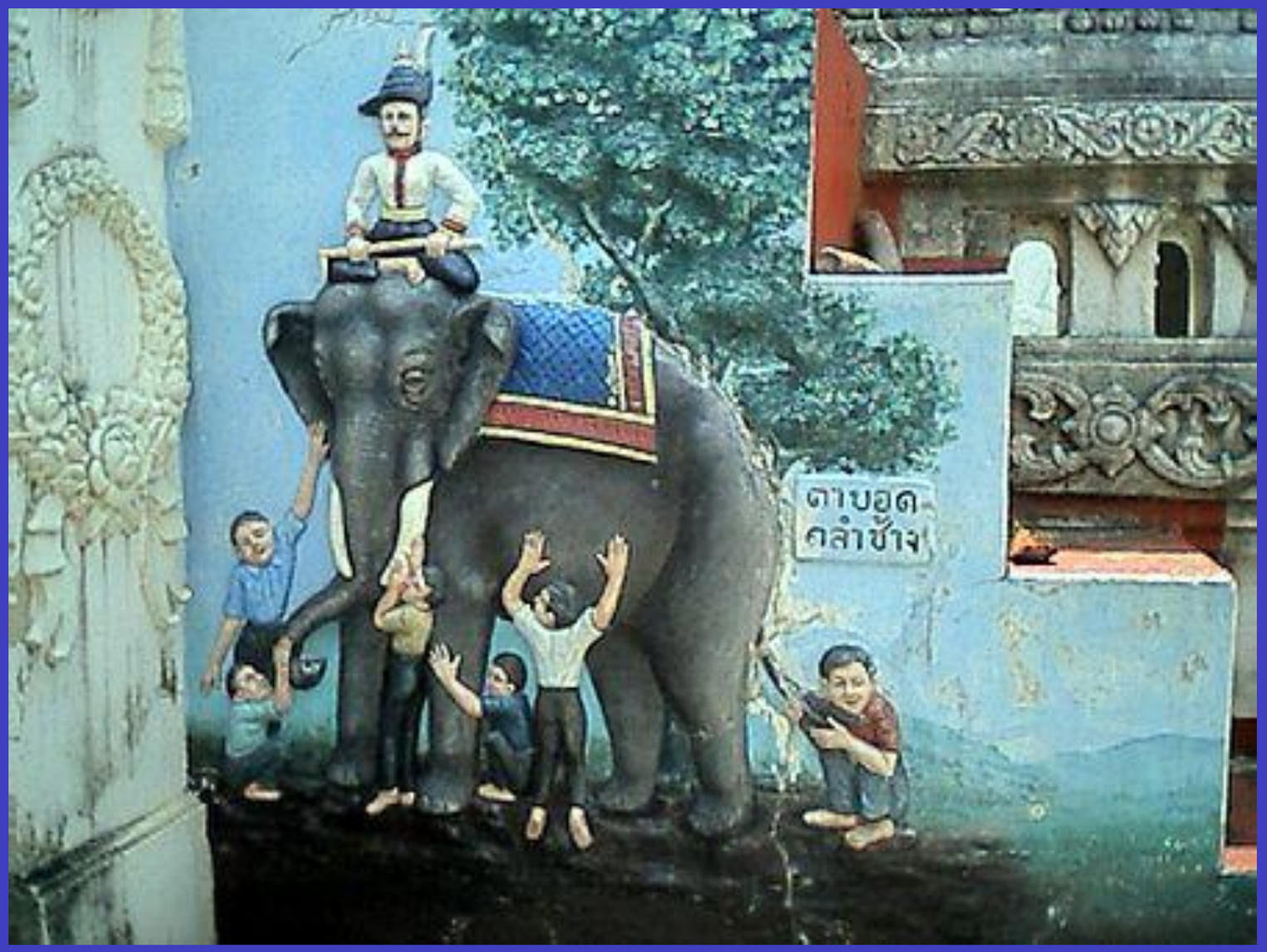




Violation of the Kasha-Vavilov rule!

Monni et al., Chem. Phys. Lett. (2017)

The blind men and the elephant
(Jain, Buddhist, Sufi and Hindu lore)

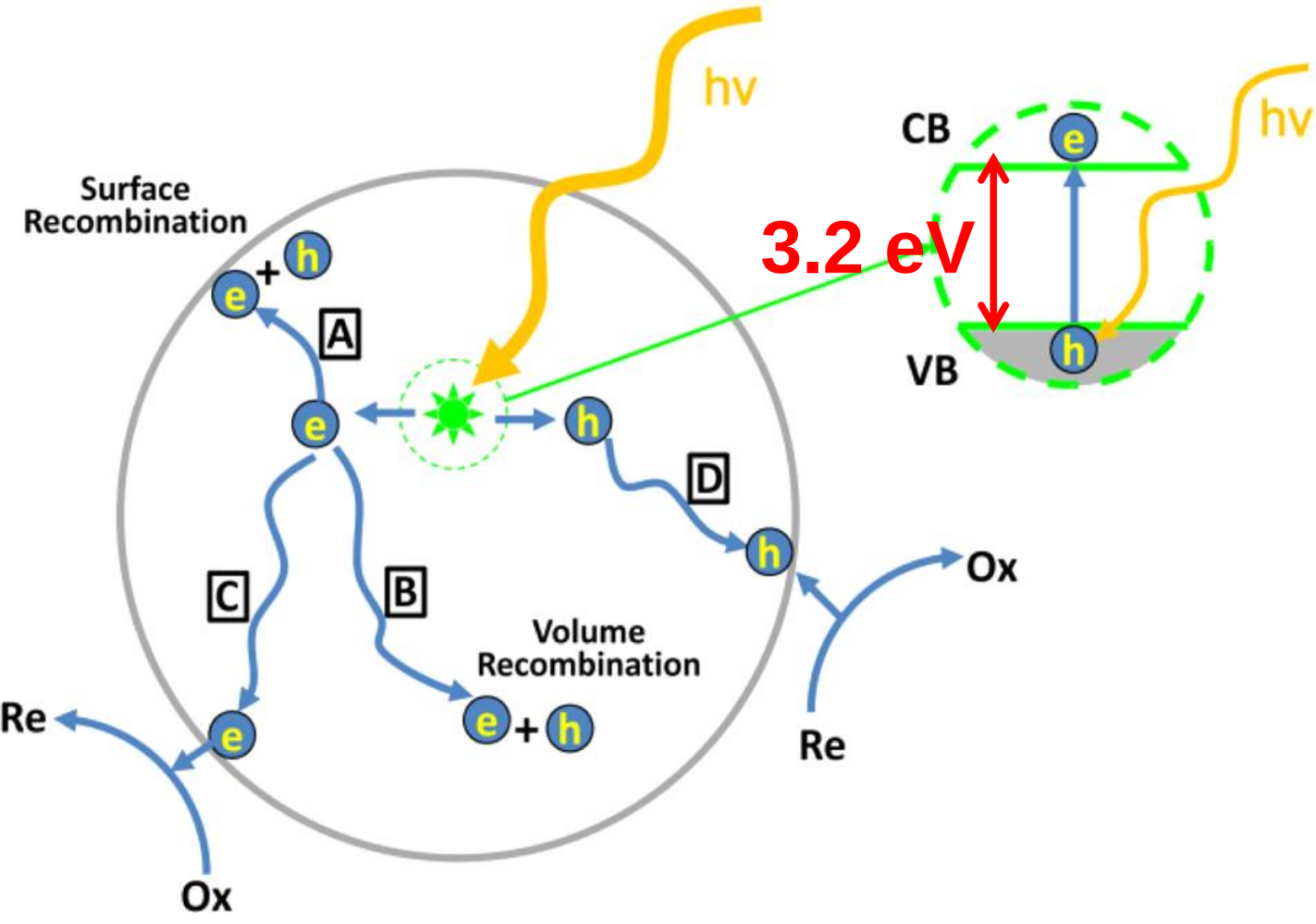


One single experience can be true, but it is inherently limited by its failure to account for other truths or a totality of truth

Catalysis and solar energy conversion with Metal Oxides

Photocatalysis

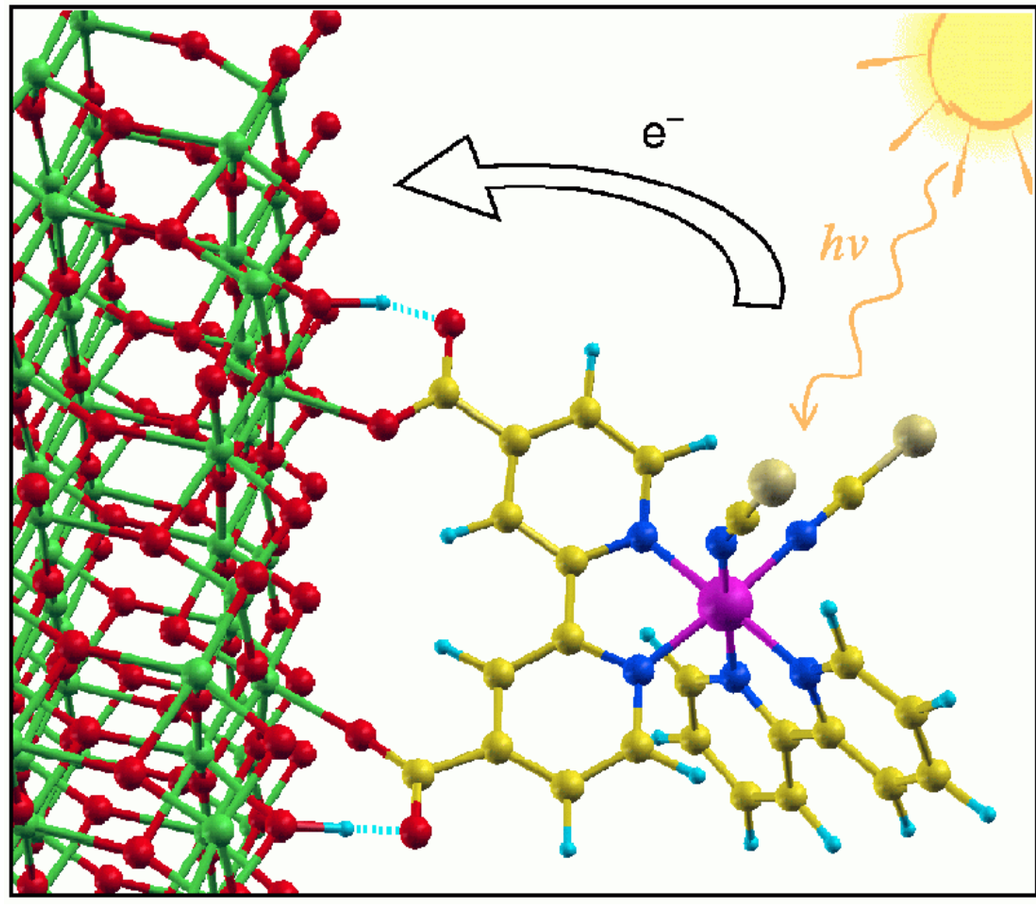
Fujishima, Honda (1972)



- Charges at surfaces
- Long time trapping

Solar energy

Grätzel, O'Regan (1991)



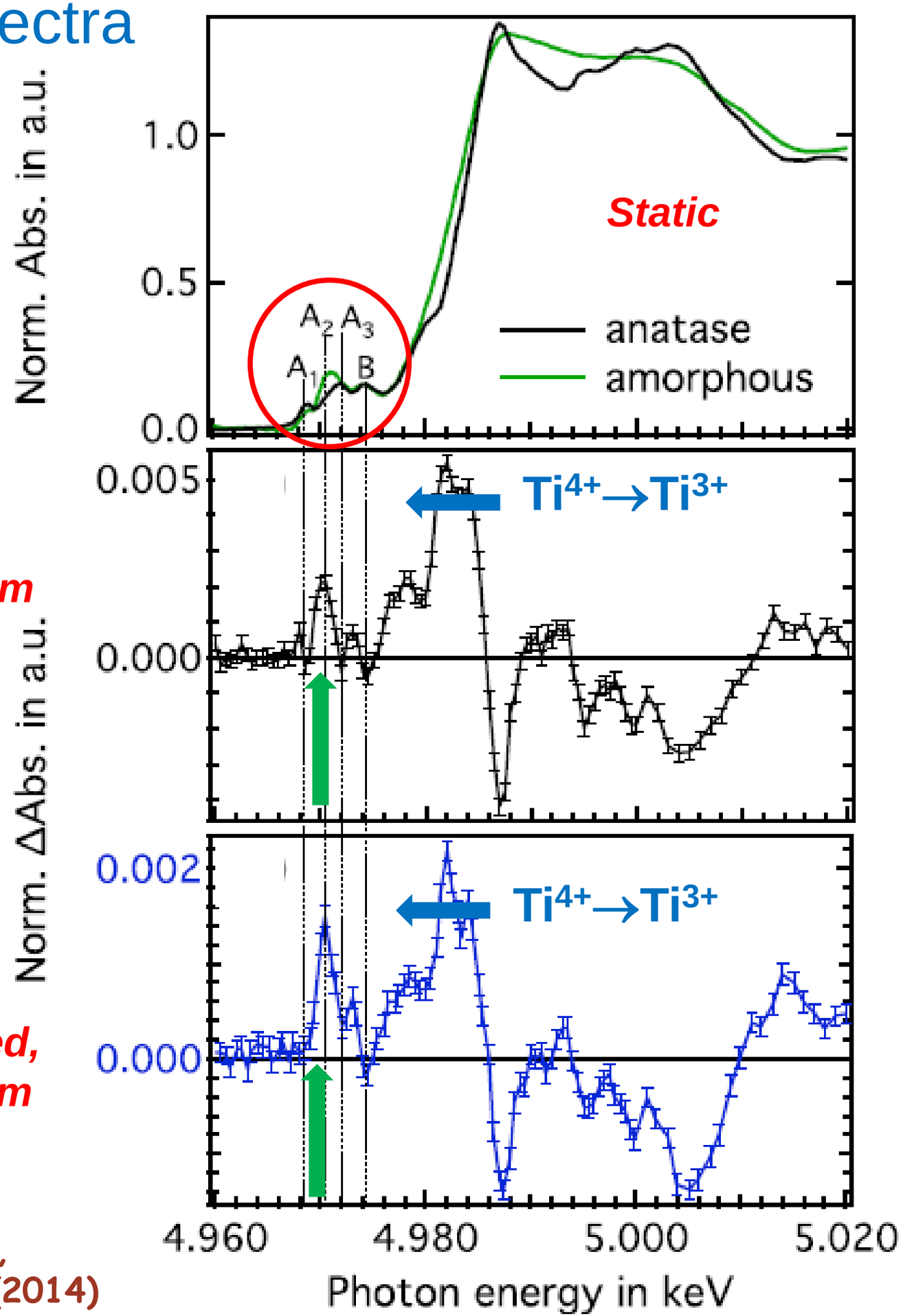
- Long range transport
- High mobility: no trapping

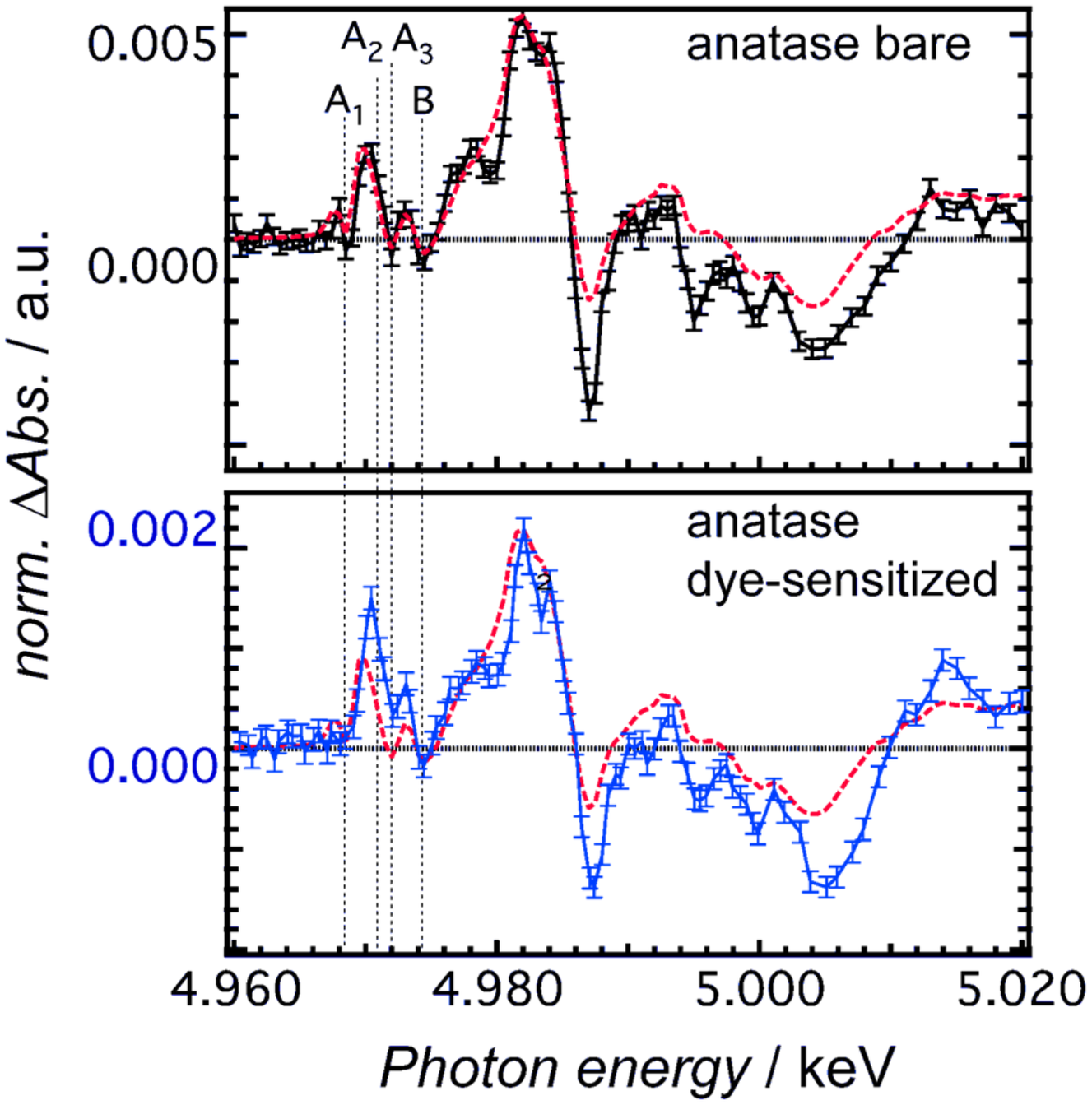
Ti K edge spectra

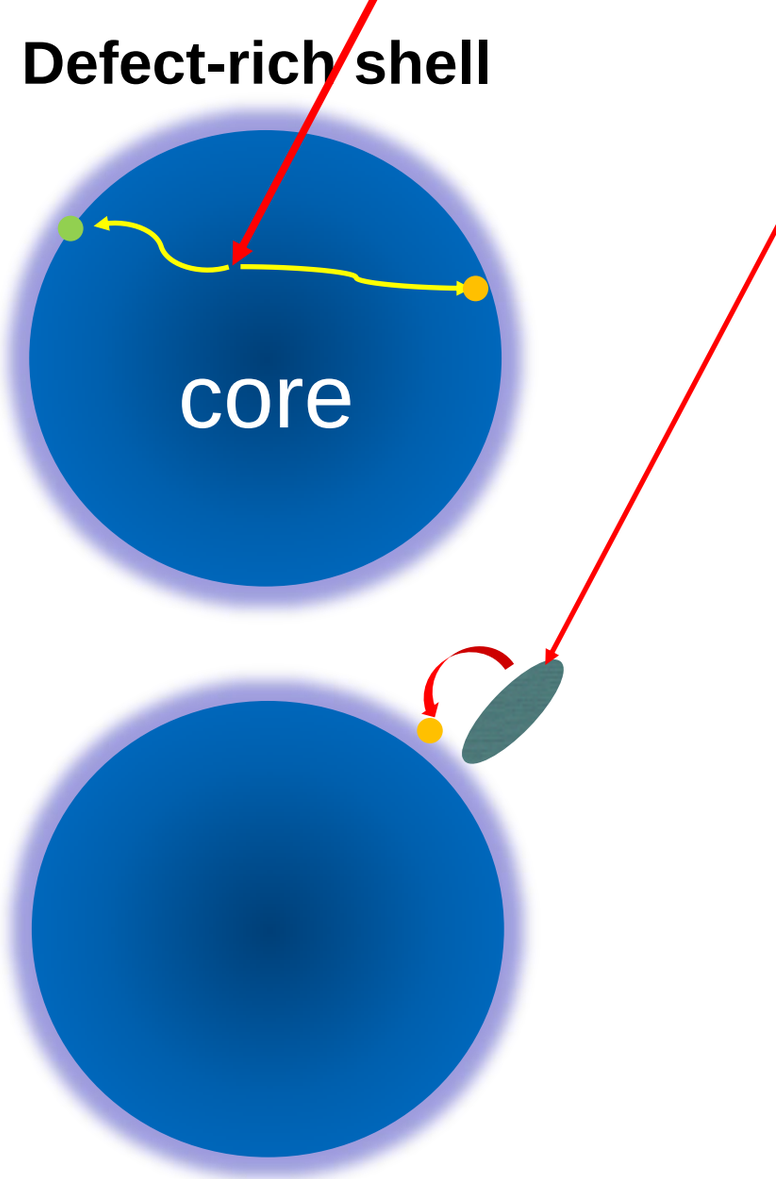
Bare,
100 ps, Exc. 355 nm

N719 dye-sensitized,
100 ps, Exc. 532 nm

Ps-studies:
Rittmann-Frank et al,
Ang. Chem. Int. Ed (2014)





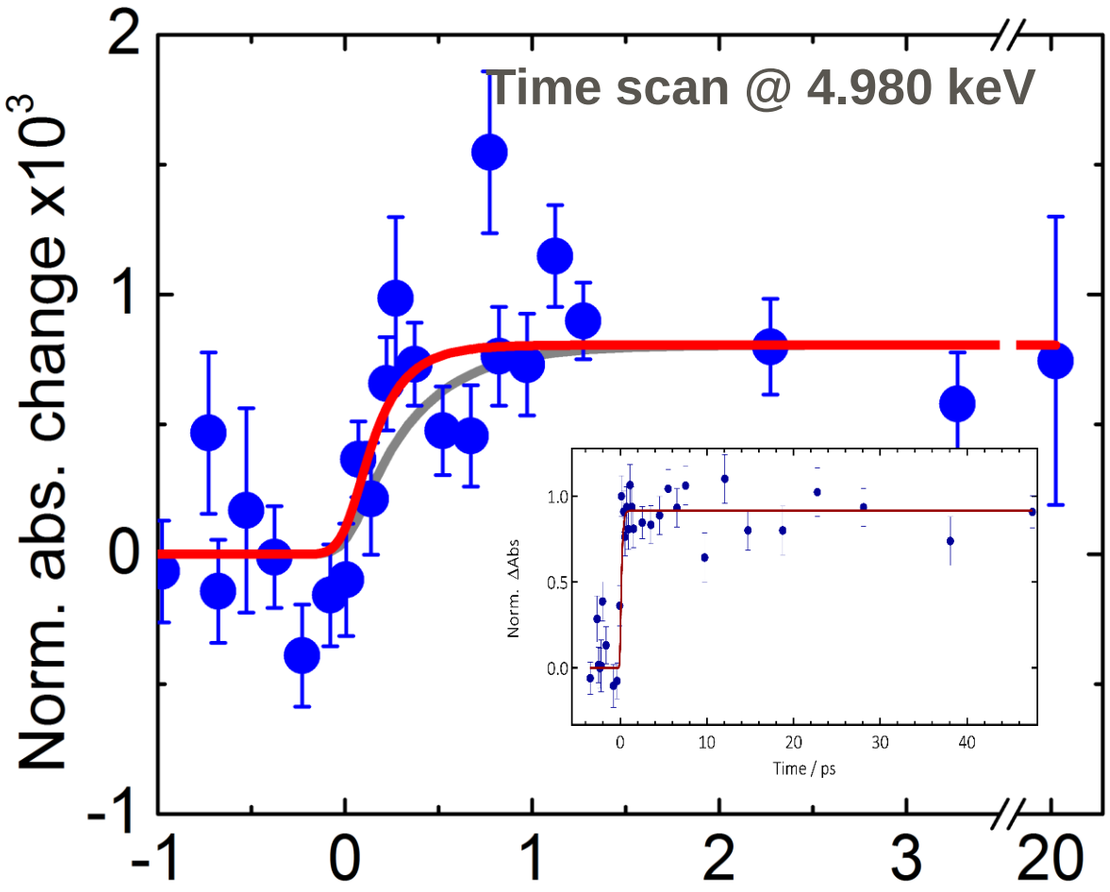


-1 eV-shifted amorphous minus anatase spectrum

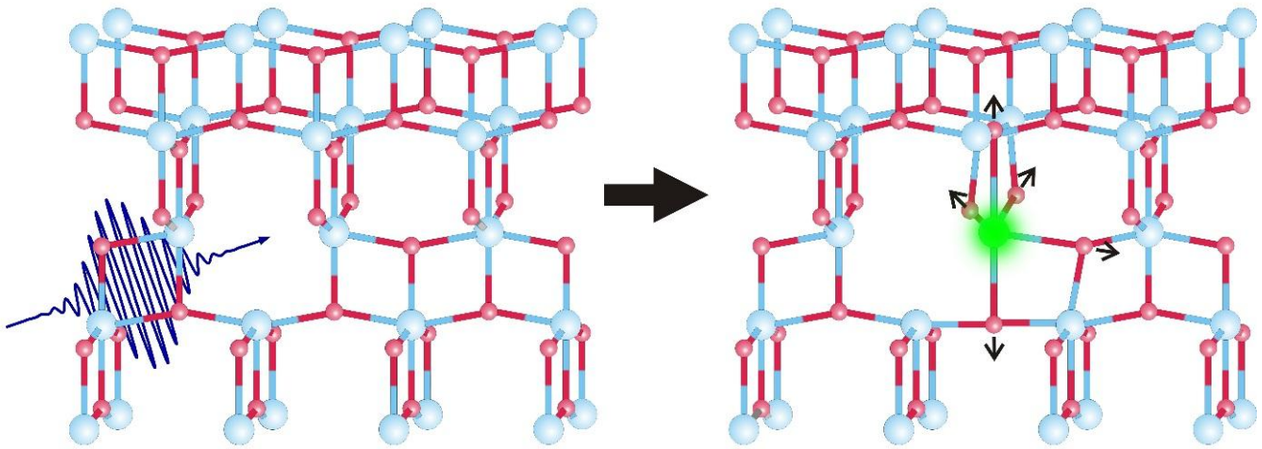
Electron trapping occurs at pentacoordinated defects
Bulk case: trapping deep inside surface shell
Injection: trapping on the outer surface
Similar results obtained for Rutile TiO2

Rittmann-Frank et al, Ang. Chem. Int. Ed. (2014)
Buddarz et al, Chimia (2017)

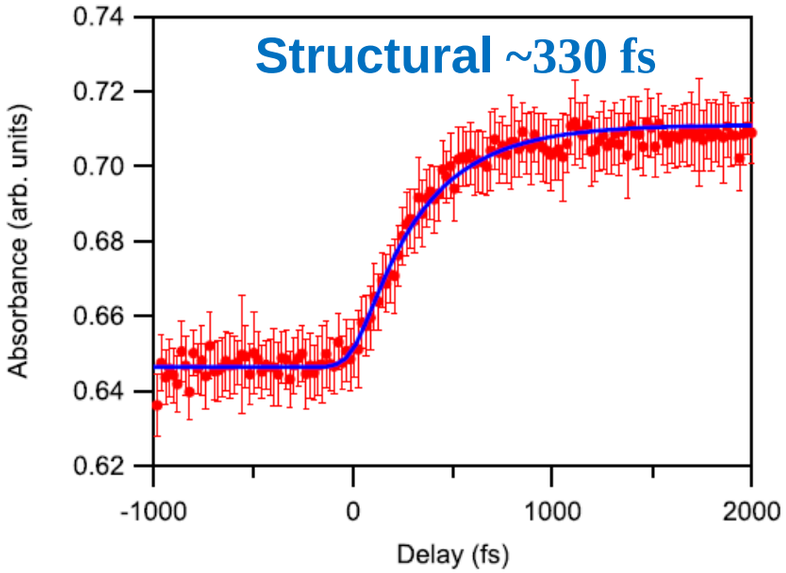
Femtosecond X-ray absorption studies of electron trapping

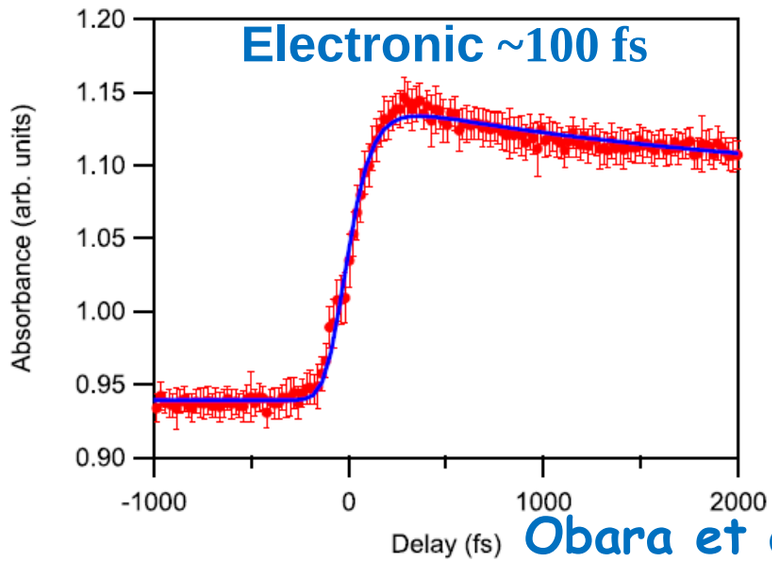


Electron trapping time <200 fs



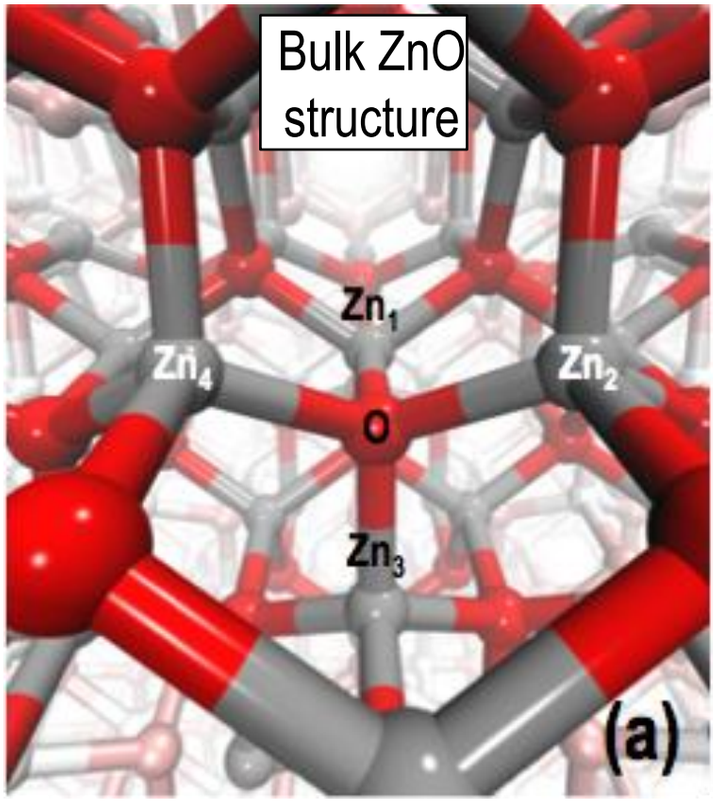
Santomauro *et al*, Scient. Rep. (2015)

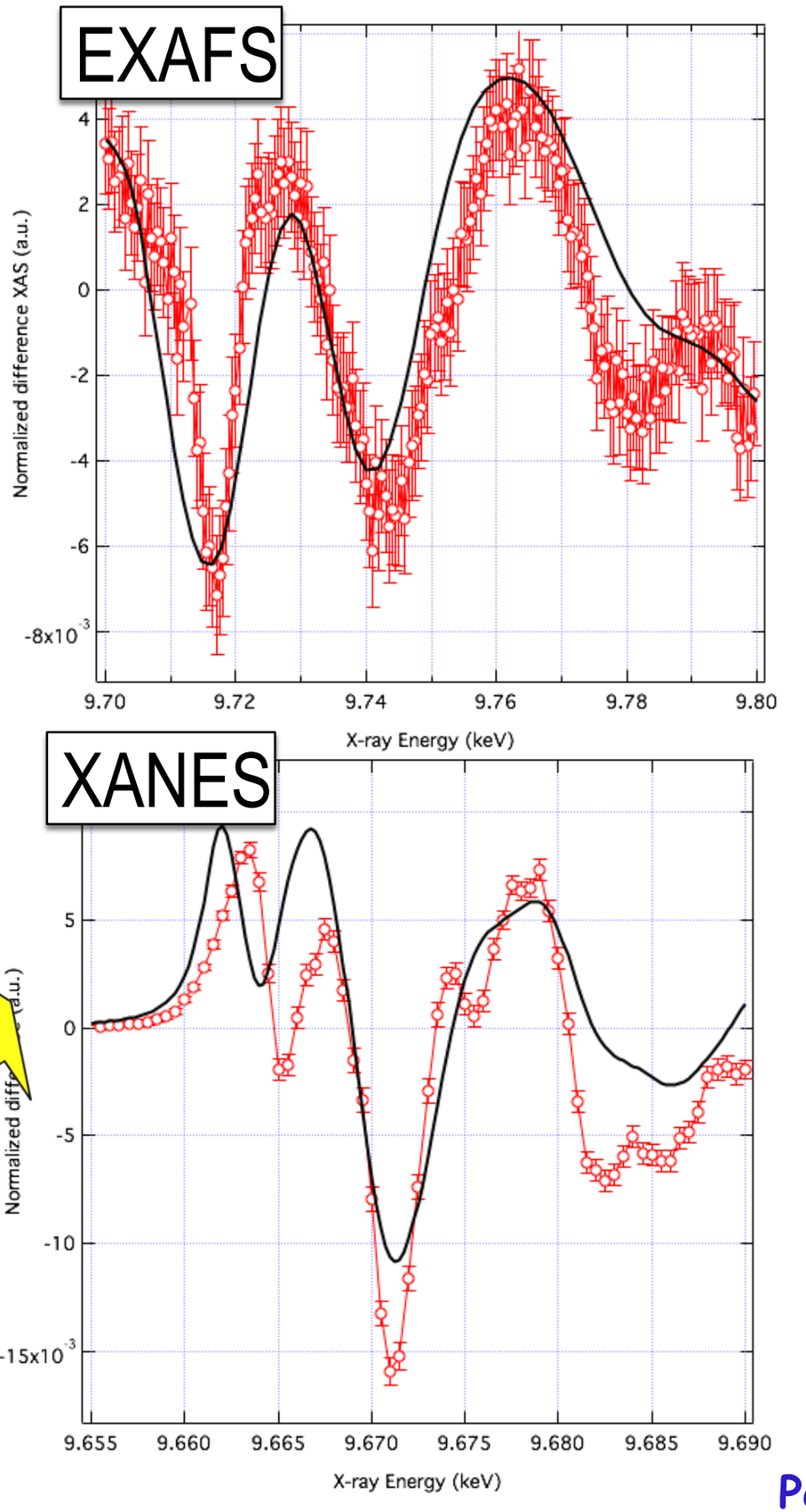


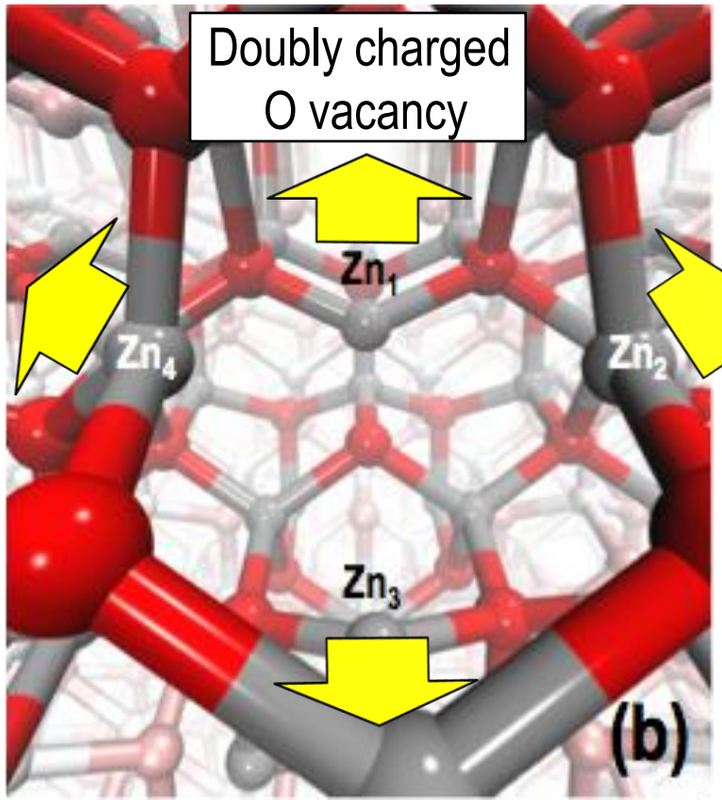


Obara et al, Struct. Dyn. (2017)

Hole trapping site at singly charged Oxygen vacancies in ZnO







Hole trapping sites are native singly-charge oxygen defects

$$V_O^{+} + h^{+} \rightarrow V_O^{++}$$

Expansion of the 4 neighbouring Zn atoms by ~20%

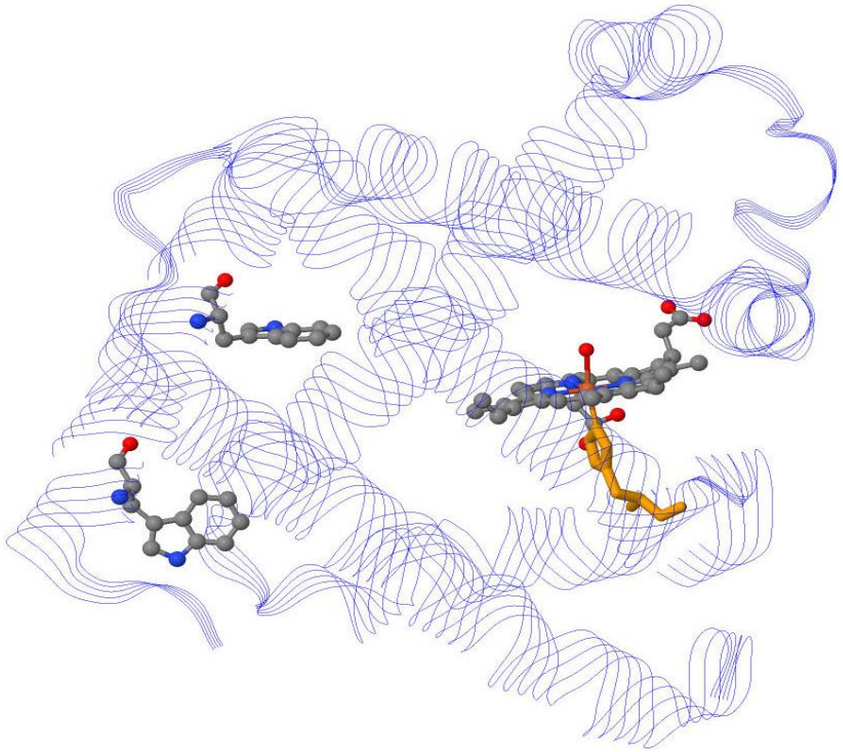
Strong signature in transient X-ray spectra

Hole trap is final state of green luminescence

Hole trapping occurs in approx. 1.2 ps

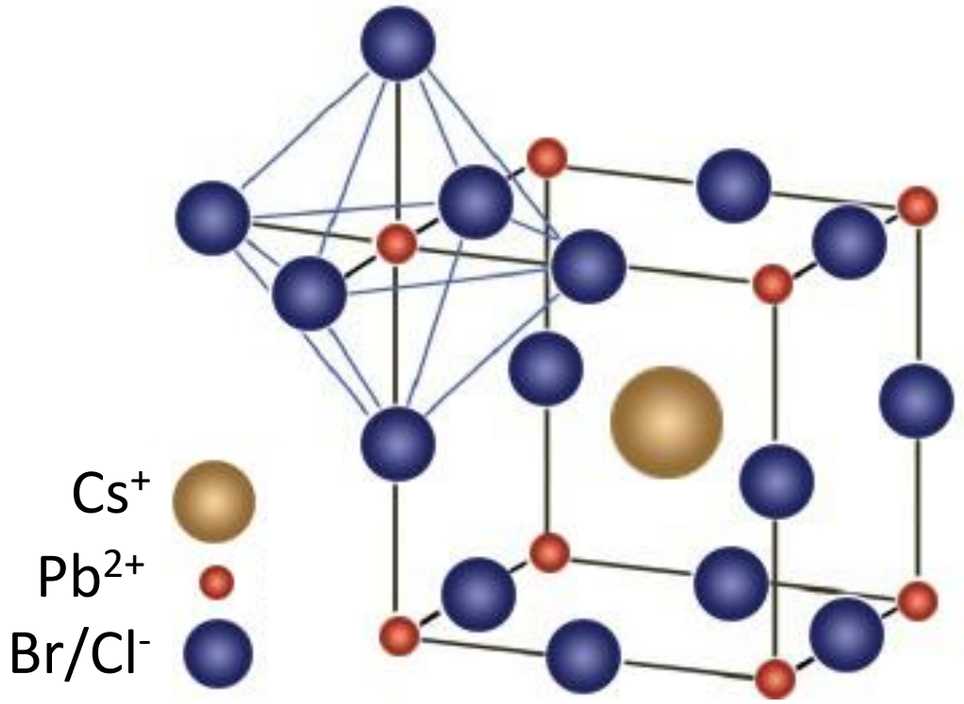
Penfold *et al*, Nature Comm. (2018)

Ligand recombination in hemoproteins



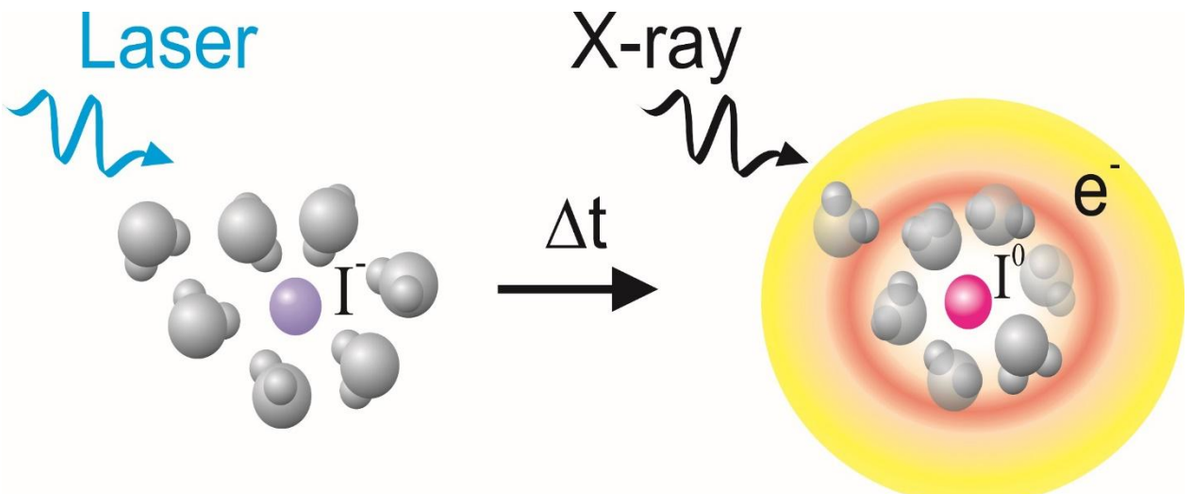
Silatani *et al*, PNAS (2015)

Charge carrier dynamics in perovskites



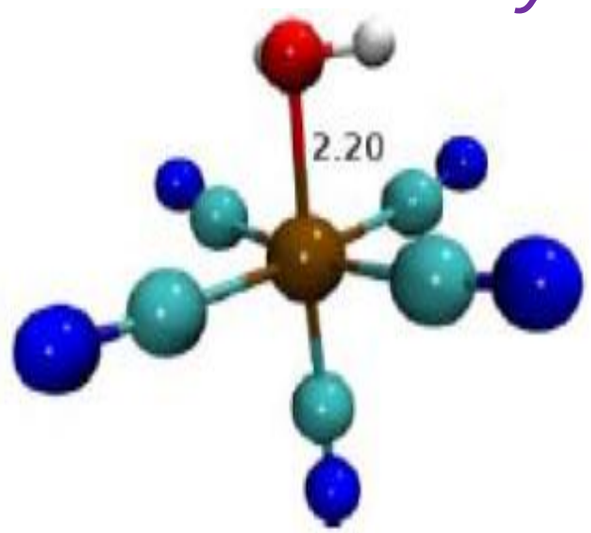
Santomauro *et al*, Struct. Dyn. (2017)

Electronic solvation dynamics



Pham *et al*, JACS (2007); JACS (2011)

Solution chemical dynamics



Reinhard *et al*, Struct. Dyn. (2014)