Fundamental Interactions in Chemical, Atomic and Molecular Physics

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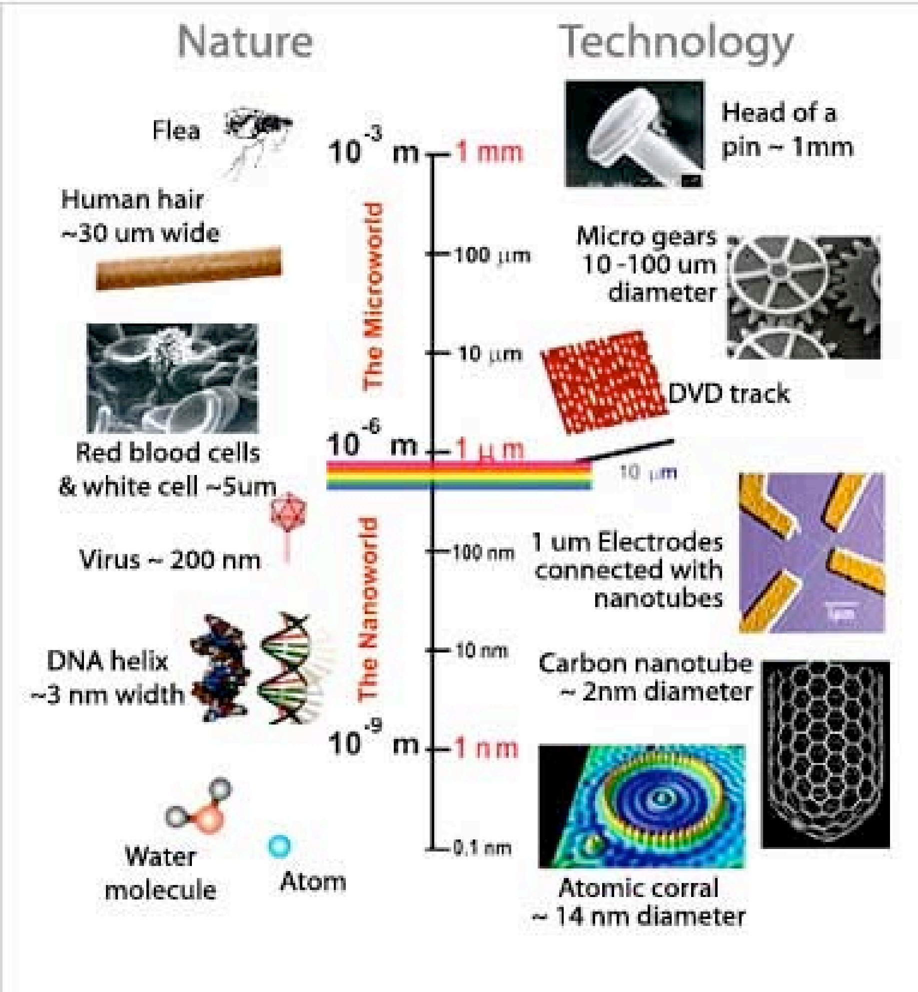
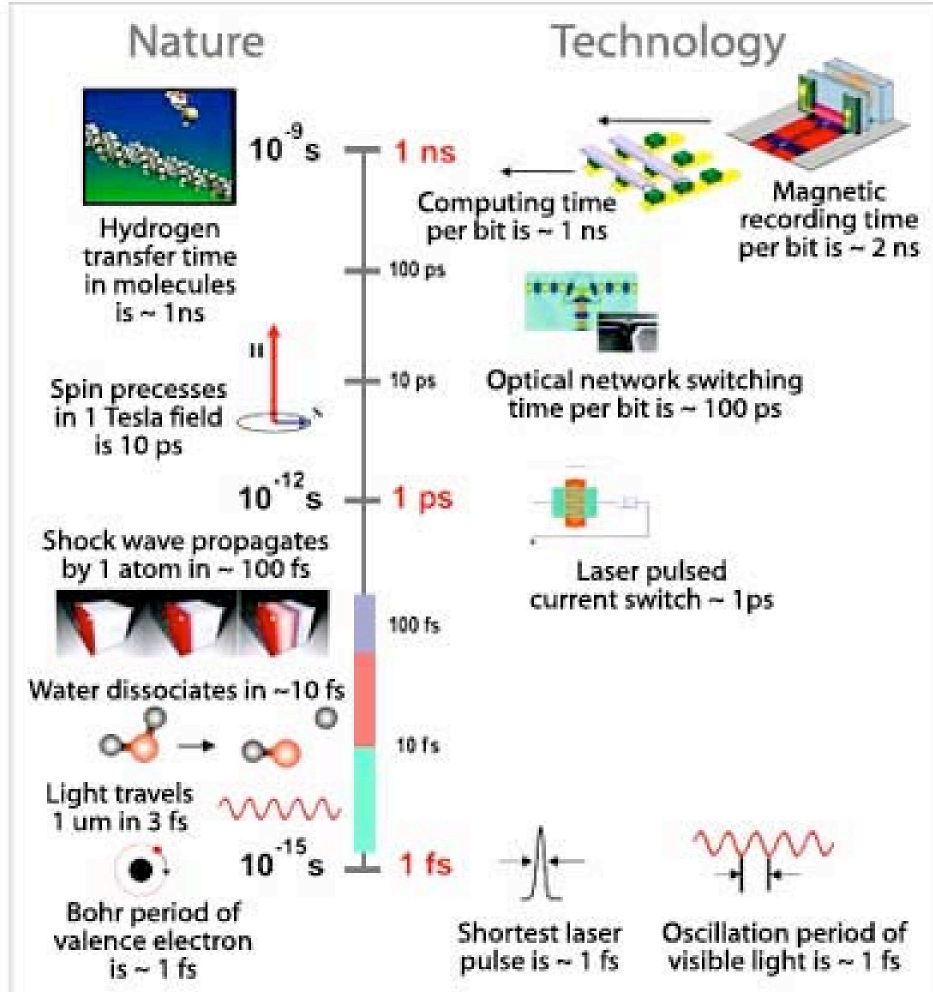
Focus on Short Pulse X-ray Project

Ultra-Small



Ultra-Fast



Convey three concepts

- *Storage ring sources are complementary to XFELs for ultrafast x-ray science*

- *Multiple timescales are of importance*

- *APS can be the leader for time-resolved x-ray science for times > 1 ps.*

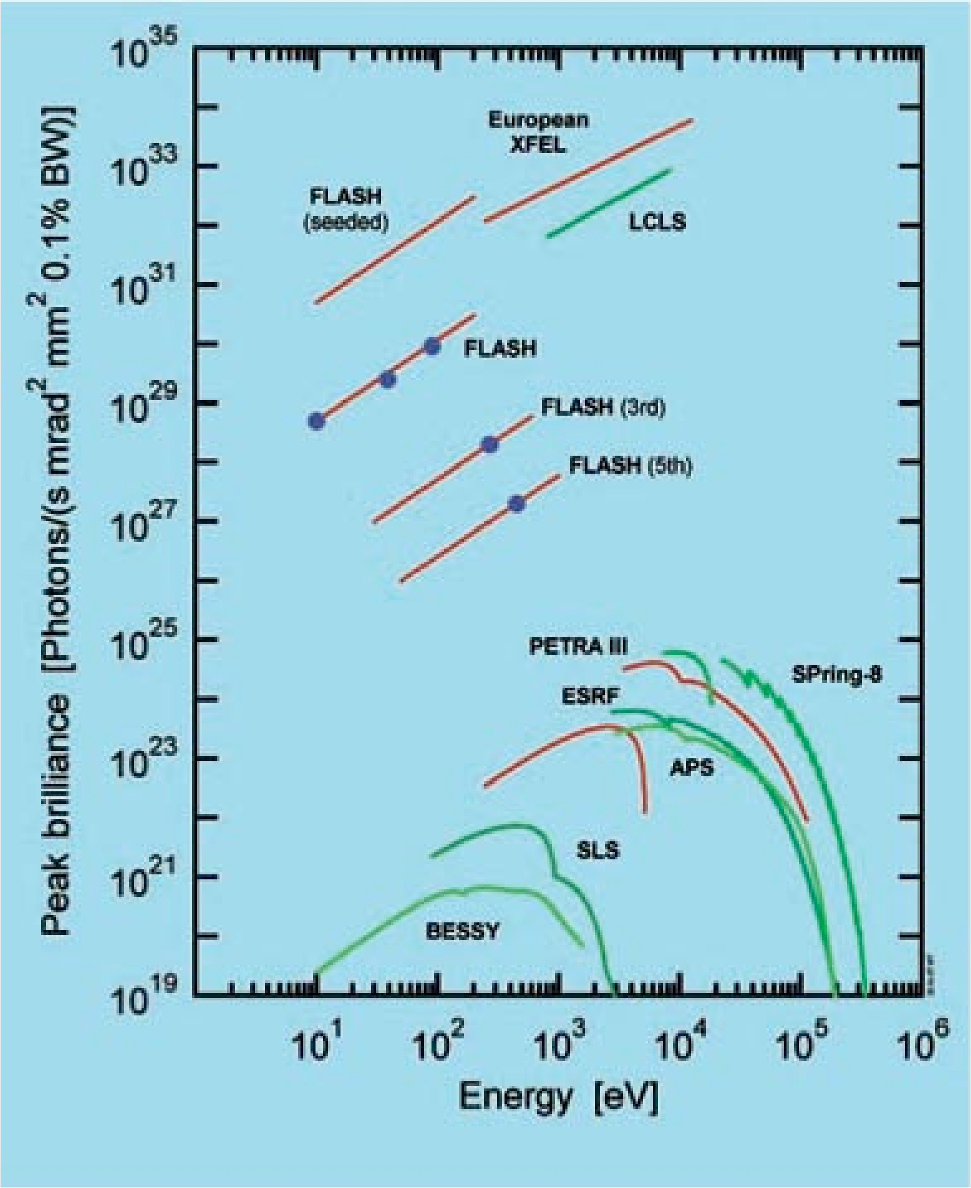
Fundamental question: *what is the response of atoms, molecules and materials to electromagnetic (and other) excitations?*

From equilibrium structure to dynamics

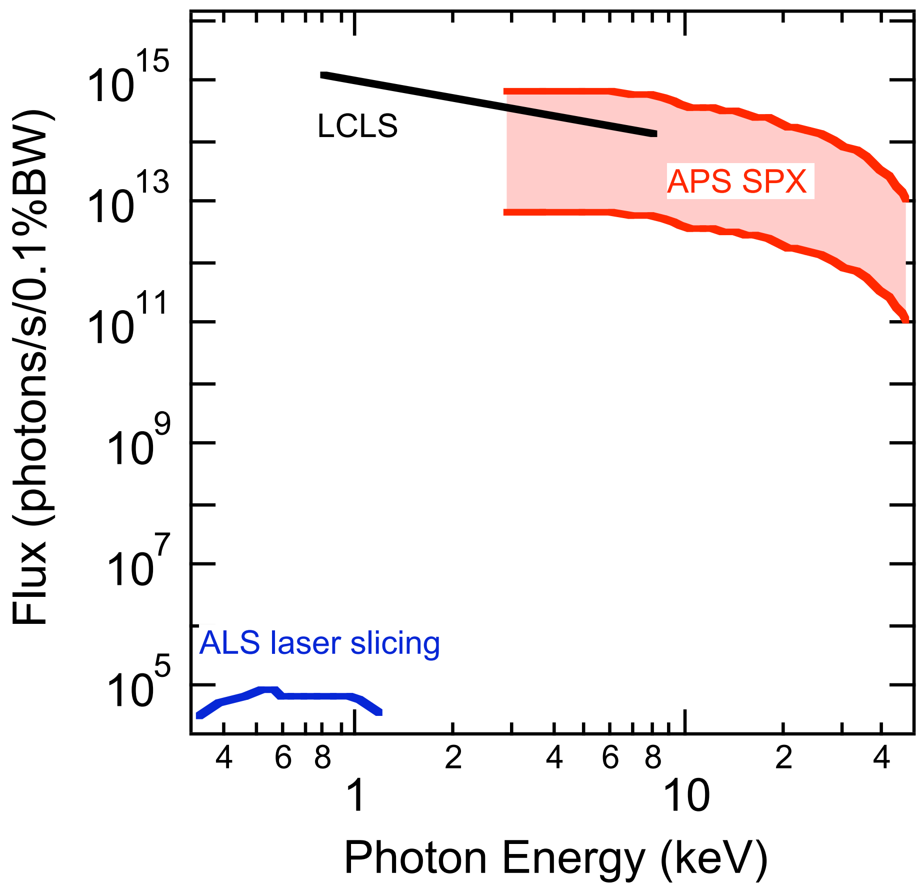
From observation to control

Ultrafast x-ray probes enable joint resolution of picoseconds and picometers

Peak brilliance - the oft-cited figure of merit



APS flux is comparable to that of LCLS!



APS flux curves

Undulator A

λ_u = 3.3 cm

length = 2.4 m

Storage ring advantages

Tunability

Stability

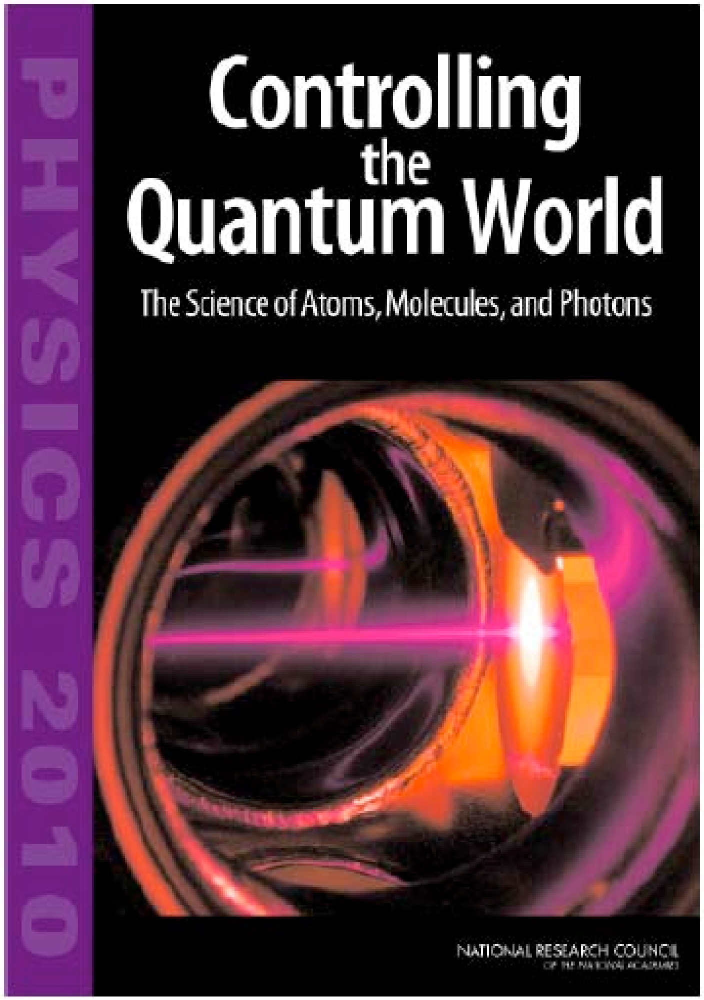
Higher x-ray energy

FEL advantages

Shorter pulses

Higher peak intensity

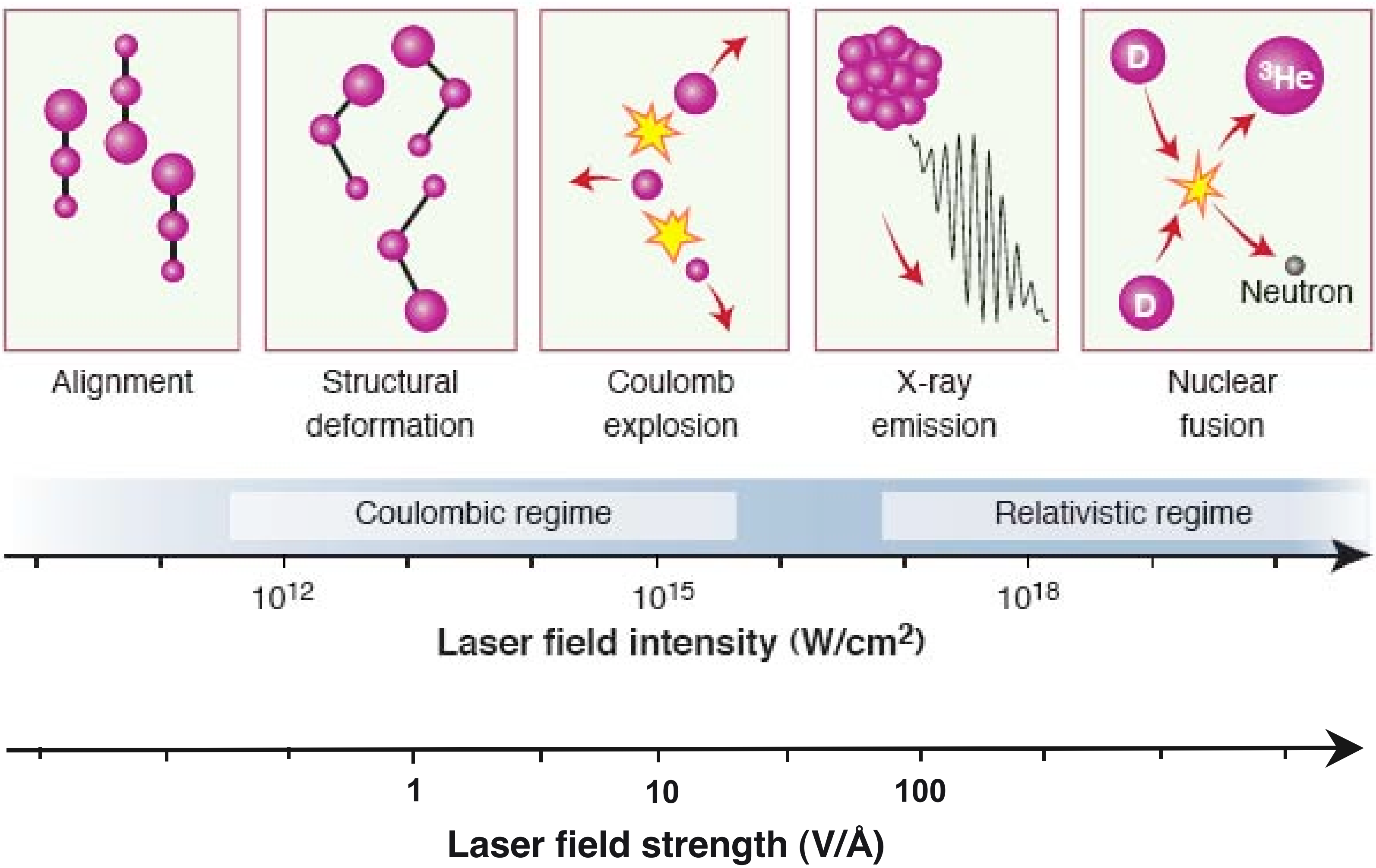
Atomic & Molecular Physics - Dream & Challenge:
Can we control the inner workings of atoms, molecules and matter with photon technology?



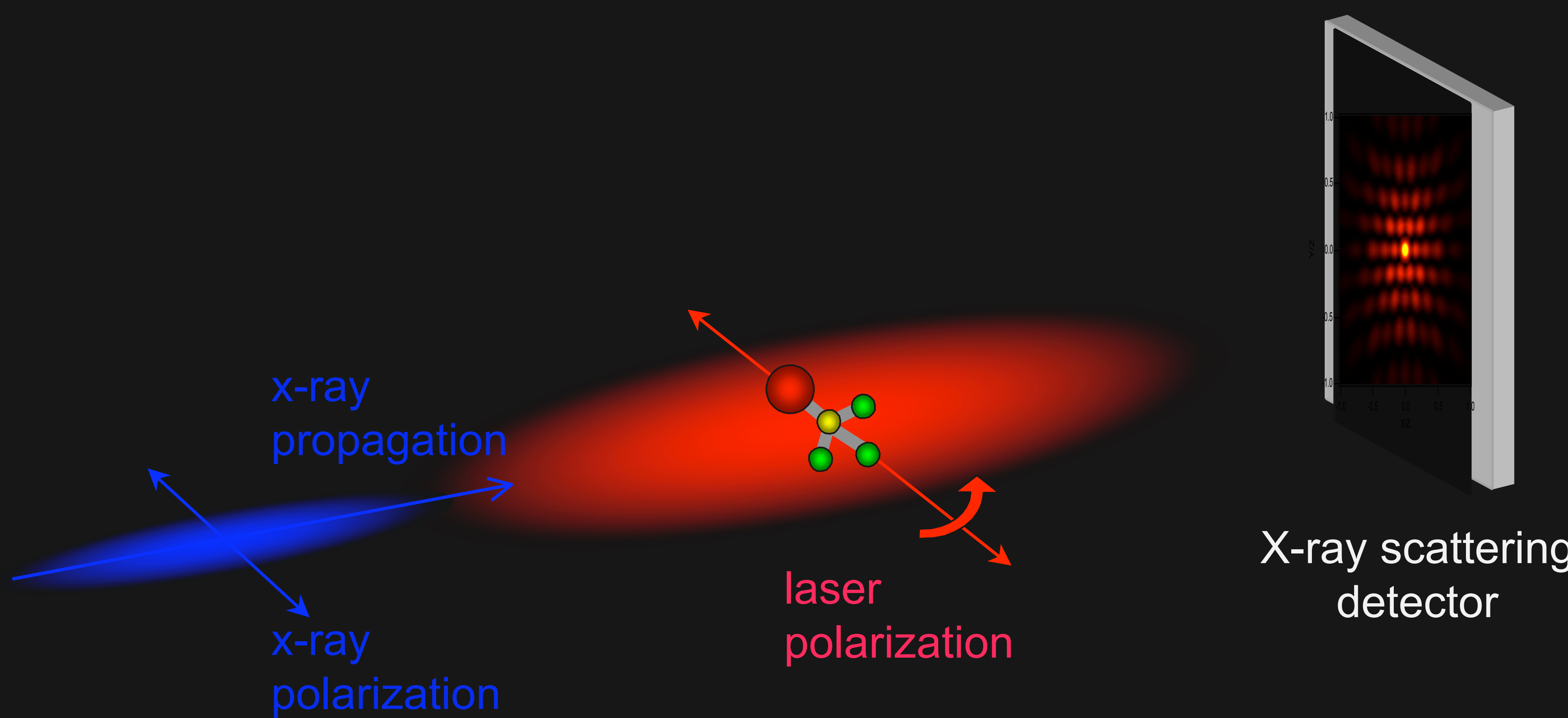
BES Grand Challenge

Science of the past has been to observe and understand matter in its natural and perturbed states. Grand challenge of the 21st century is to control matter, electron flow at the atomic scale with new tools.

Control atomic and molecular dynamics with EM fields

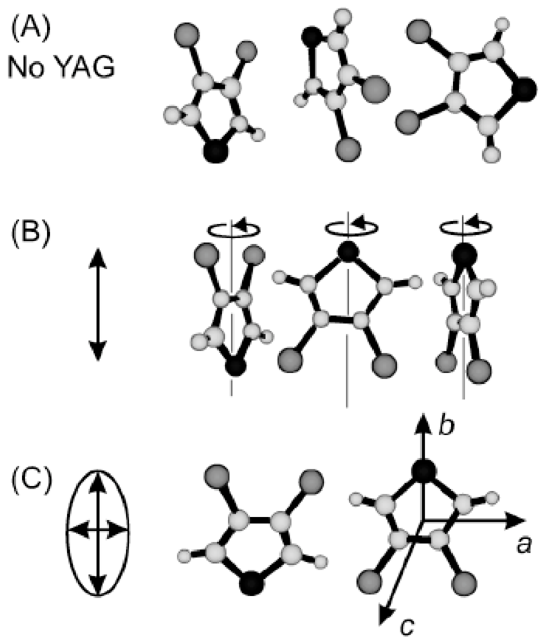


X-ray microprobe of laser aligned molecules

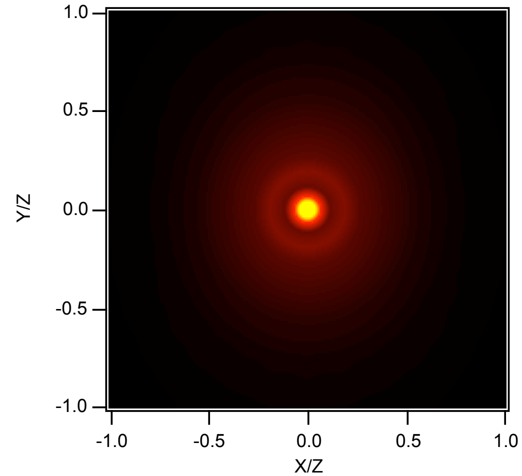


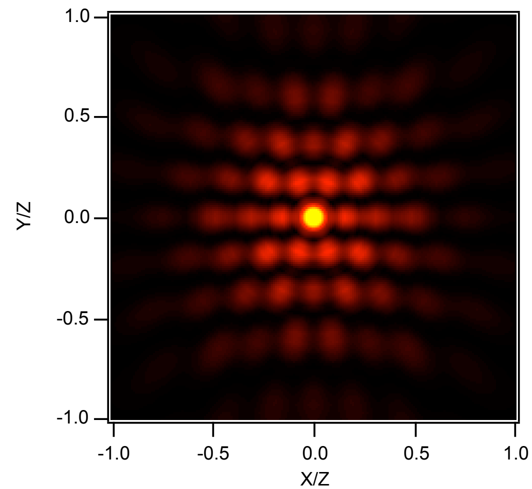
Molecular goniometer: alignment of all three Euler angles

3-D alignment w/elliptically polz'd fields
3,4 dibromothiophene



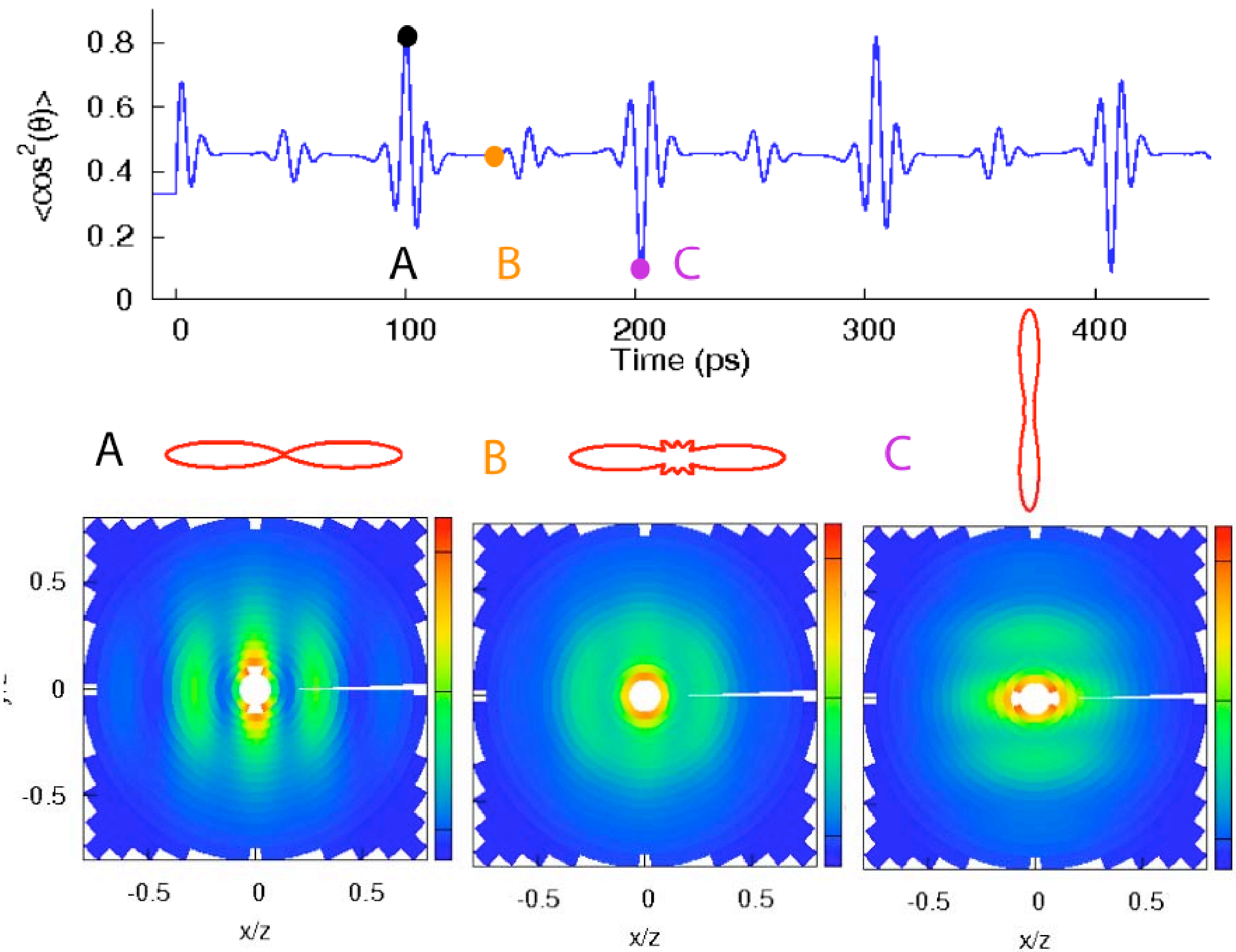
J.J. Larsen et al., PRL 85, 2470 (2000)





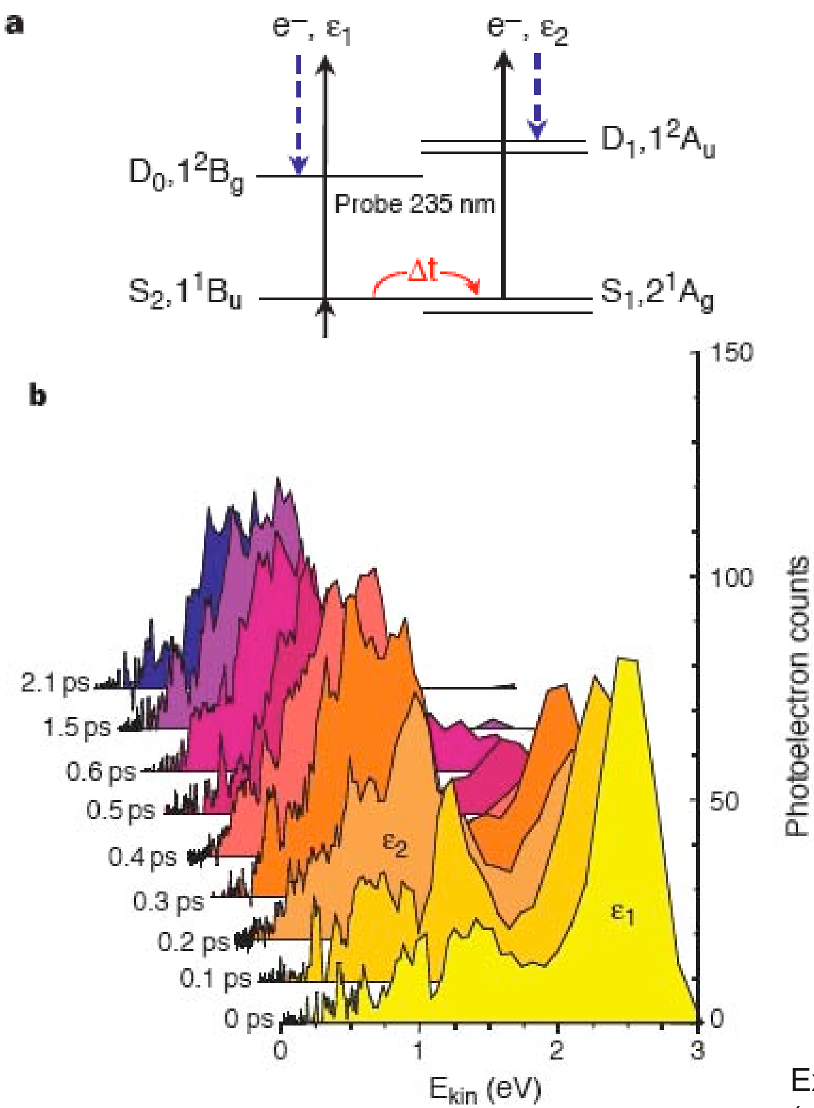
Calculations by Robin Santra

Studies of aligned molecules in field-free environment: Br_2



Figures from Phay Ho

Pump-Probe Studies of Radiationless Transitions

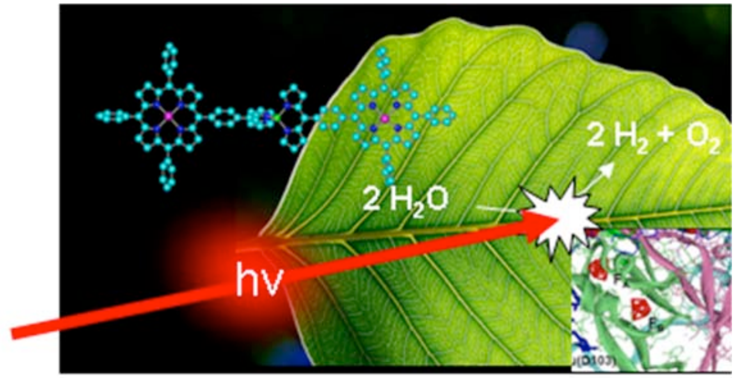


- *Time-resolved photoelectron spectroscopy at optical wavelengths shows evolution of electronic character through a radiationless transition*
- *Time-resolved near-edge x-ray absorption could also characterize the evolution of the unoccupied orbitals during this process*
- *X-ray probes could also directly monitor changes in localization of the electron density*
- *Time-resolved pump-probe diffraction could reveal electronic-structure driven changes in geometry*

Example shows the time-resolved photoelectron spectra of a linear polyene (all-trans 2,4,6,8 Decatetraene), revealing the radiationless transition from the S_2 to the S_1 state. From V. Blanchet et al., Nature **401**, 52 (1999).

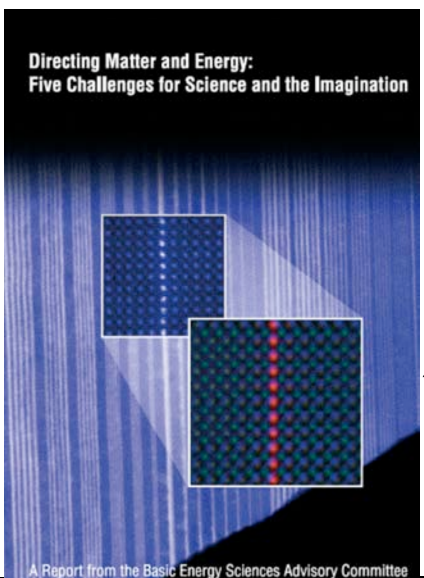
Use-inspired Grand Challenge:

Solar energy: rational design of materials that couple ultrafast light-excited states to chemistry



- *High-Priority National Research Need*
- *Basic Research Problem*
- *Aligned with DOE Grand Challenges in Science and Energy Research Mission*

Grand Challenges for Basic Energy Sciences

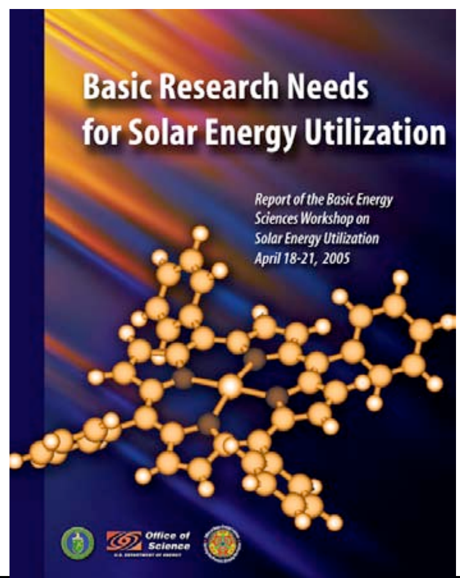


How Do We Design Revolutionary New Forms of Matter with Tailored Properties?

How Do Remarkable Properties of Matter Emerge from Correlations of Atomic or Electronic Constituents?

How Do We Characterize and Control Matter Far Equilibrium?

BES Mission in Solar Energy Research



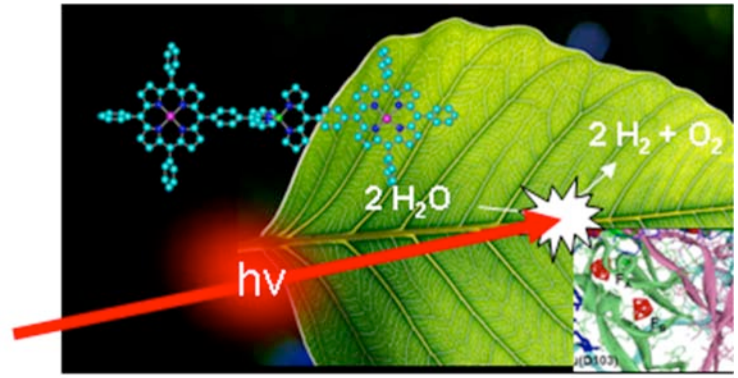
Photon Management:

Control Of Carrier Excitation, Charge Transport, And Energy Migration

Solar-powered Catalysts For Energy-rich Fuels Formation

Solar Energy Challenge:

Discovery of materials that couple ultrafast light-excited states to chemistry

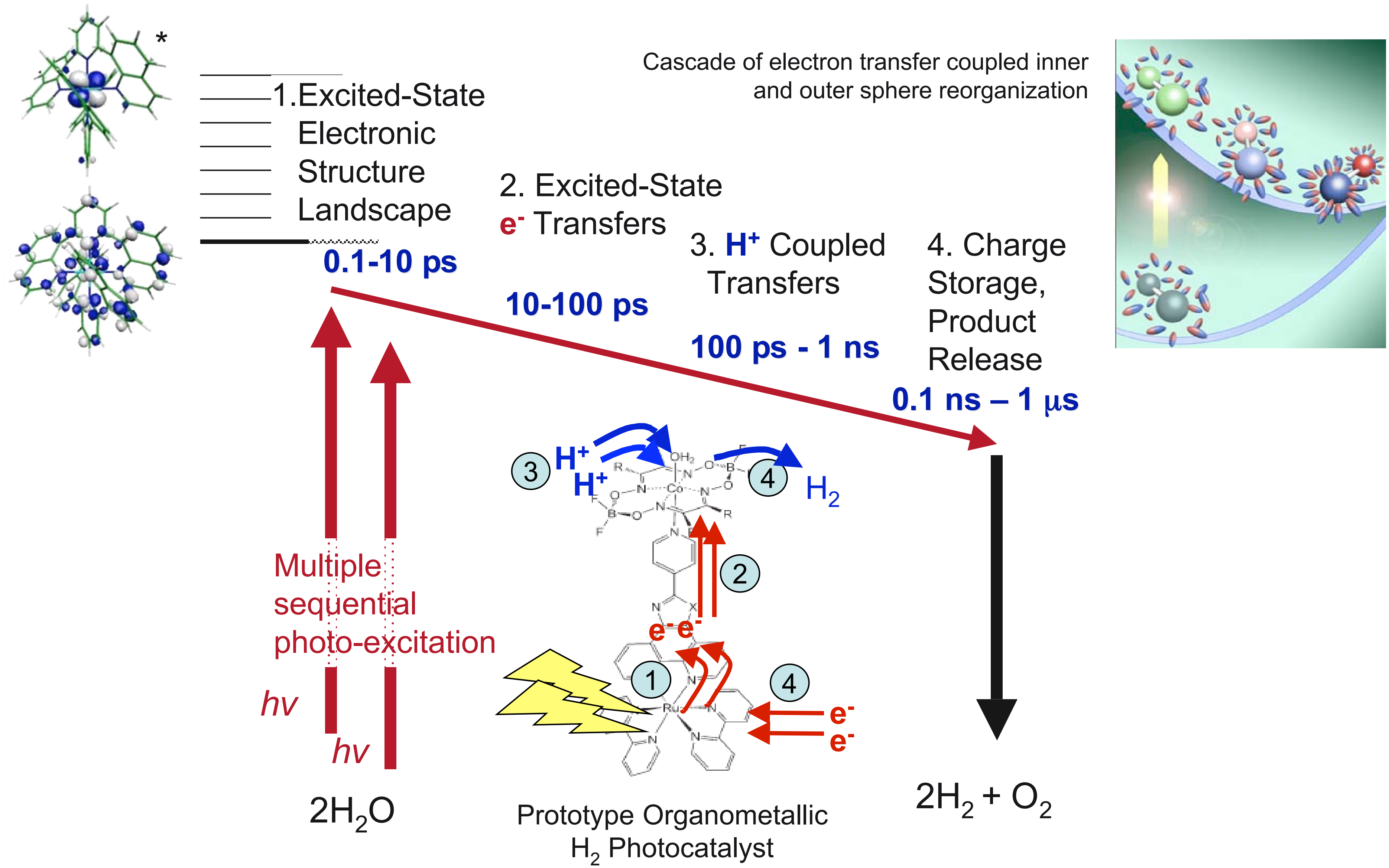


Science Drivers:

- *Understanding solar energy conversion through structure determination of excited states*

- *SPX would enable first-of-a-kind opportunities to resolve chemical structure in the excited-state across the timescales most critical to chemical energy conversion processes*

Solar Chemical Energy Conversion Involves a Cascade of Multiple Excited-State Electronic and Atomic Structure Changes



*www.chemphys.lu.se/research/projects/solarcalc/RuBQP_MOs.jpg

Laser-Initiated Time-Resolved (LITR) X-ray Techniques Offer Means to Measure Excited-State Inner and Outer Sphere Dynamics

LITR-X-ray Spectroscopy

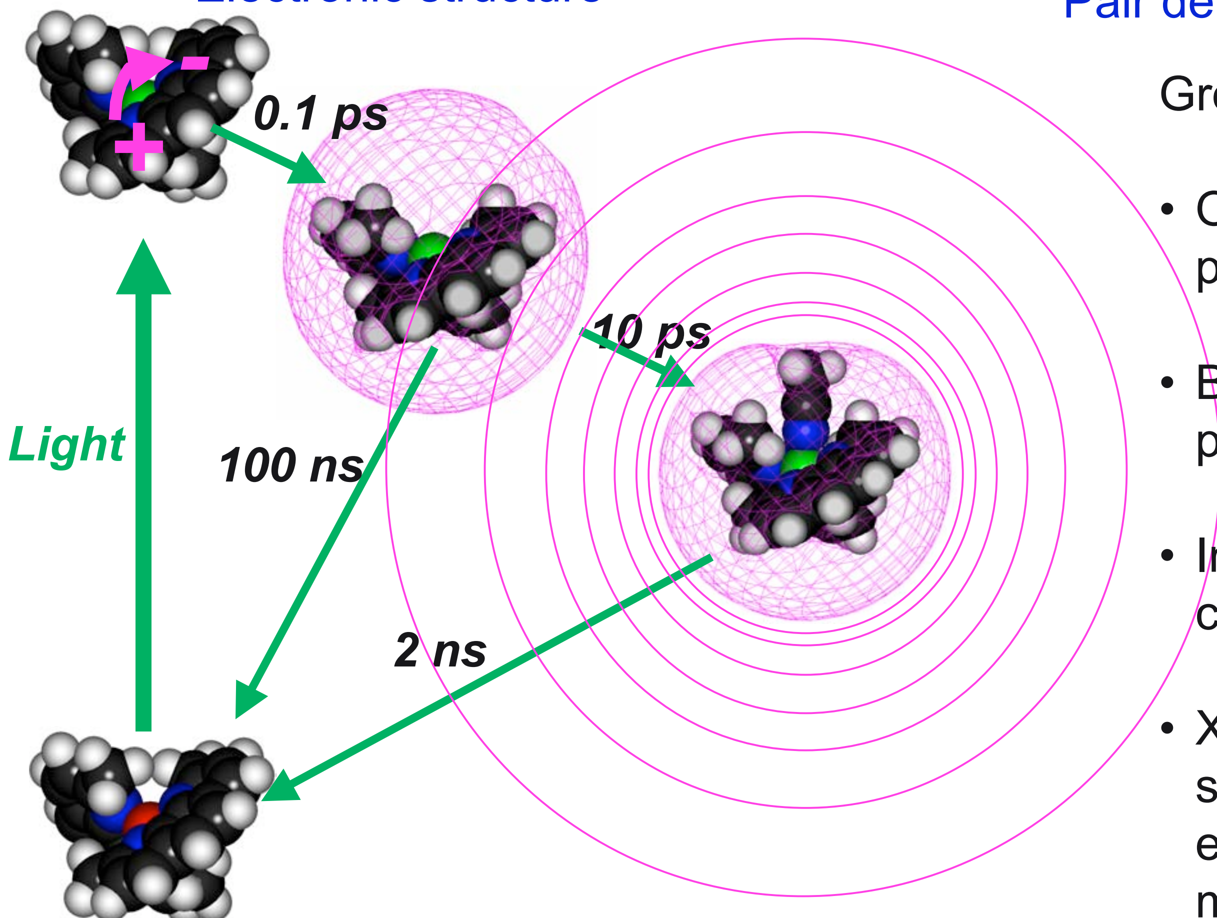
Probes inner sphere:

- Metal oxidation state
- Coordination geometry
- Electronic structure

LITR-X-ray Scattering

Probes outer sphere:

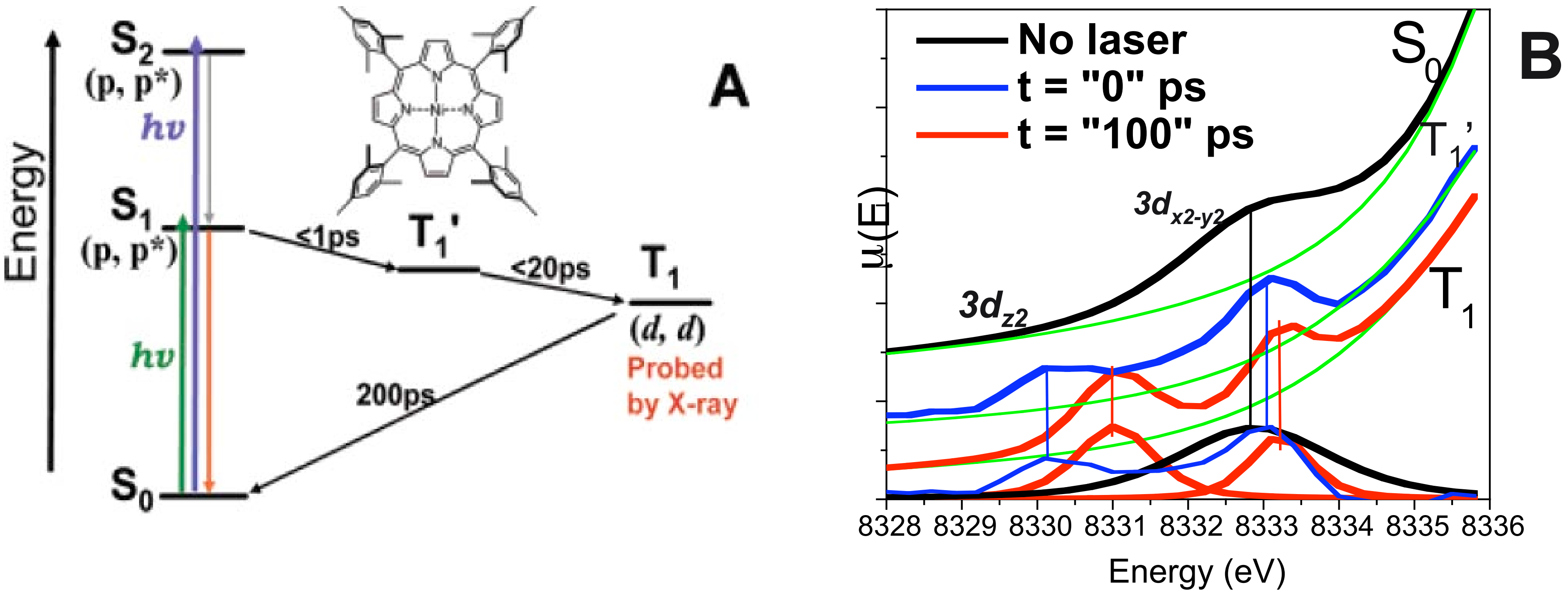
- Molecular shape
- Interactions with solvent
- Pair density distribution functions



Groundbreaking Applications in

- Organometallic photocatalysts
- Bio-mimetic host-guest photocatalysts
- Interfacial photovoltaic charge transfer
- X-ray data-based electronic structure and coordinate excited-state dynamic modeling

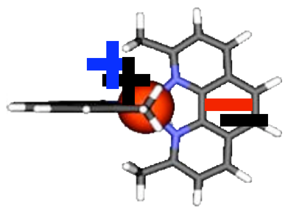
Example: Measurement of Excited-State Electronic Structure Relaxation in the Triplet State of a Ni-Porphyrin Using LITR-XANES



Chen et al, JACS, 2007

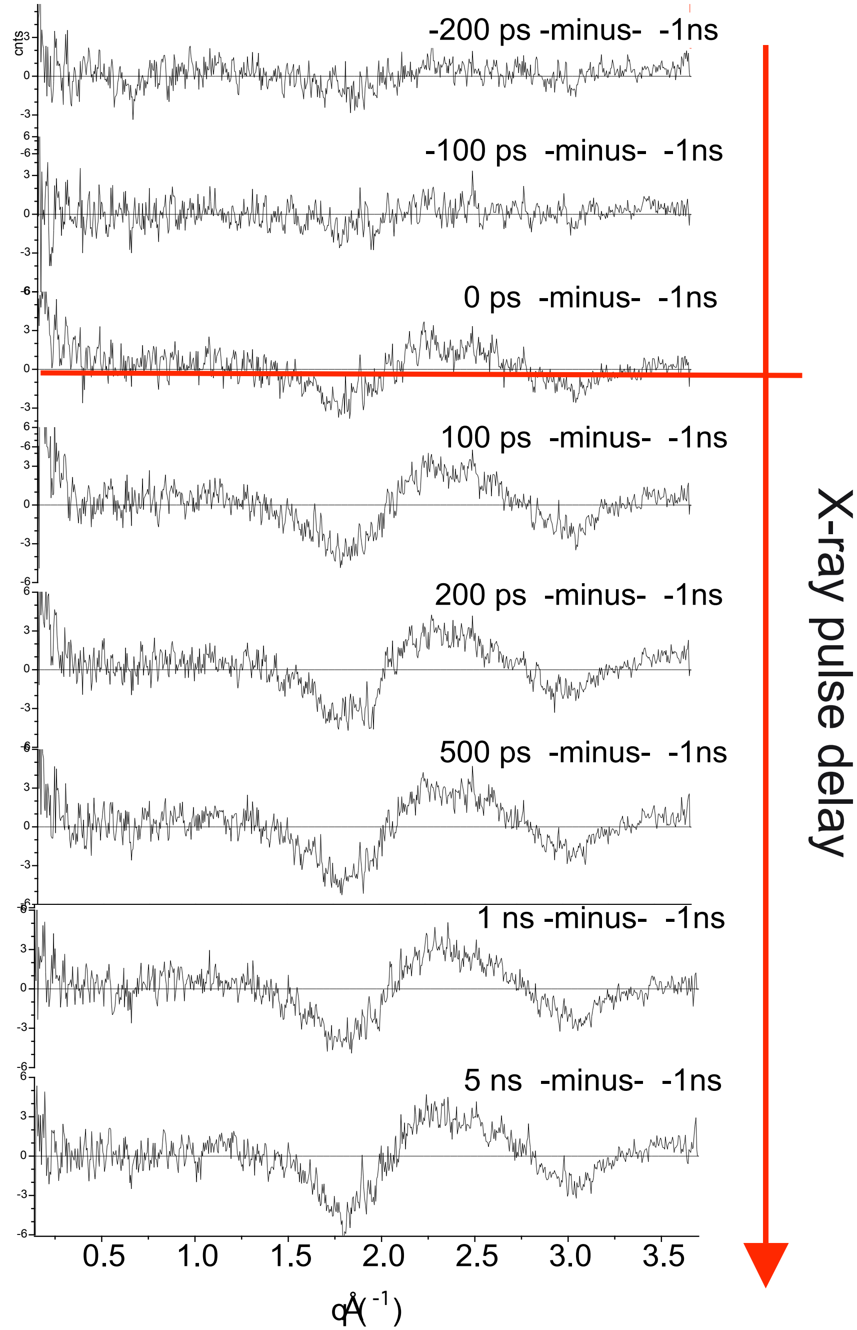
Example: Outer Sphere Relaxation in the MLCT Excited-State using LITR-SAXS

Pump-probe, excited –minus- ground states difference scattering patterns

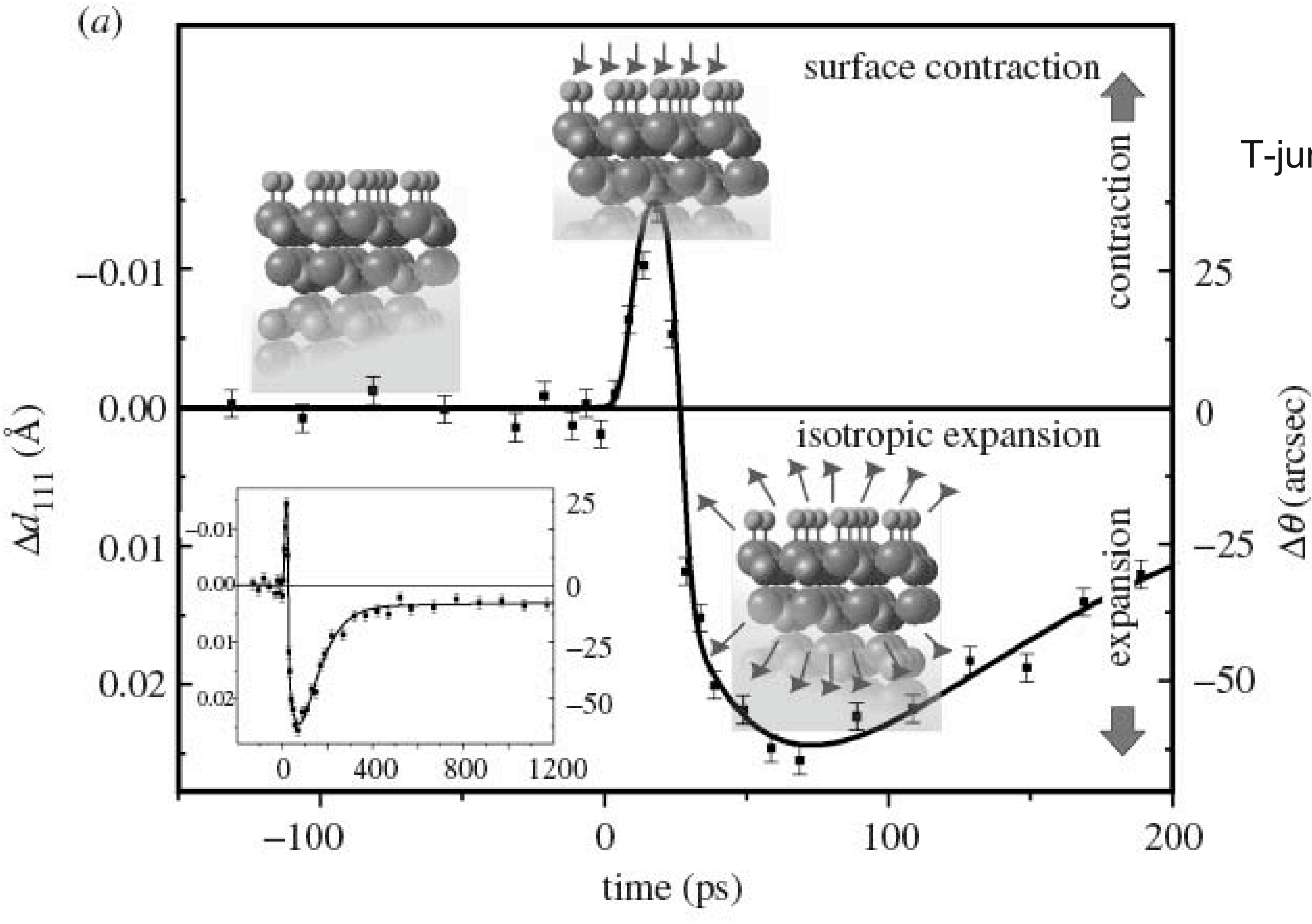


$[Cu^{I}(dmp)_2]^+$ $\xrightarrow[\sim 350\ ps]{h\nu,\ 20\ ps}$ **$[Cu^{II}(dmp^-)(dmp)L]^+$**

- High and small angle scattering features apparent at "0" ps
- Small angle decays consistent with MLCT lifetime
- Dynamics limited by100 ps resolution
- Signal-to-noise limited by current acquisition rate (1 kHz)



Surface dynamics on picosecond timescales

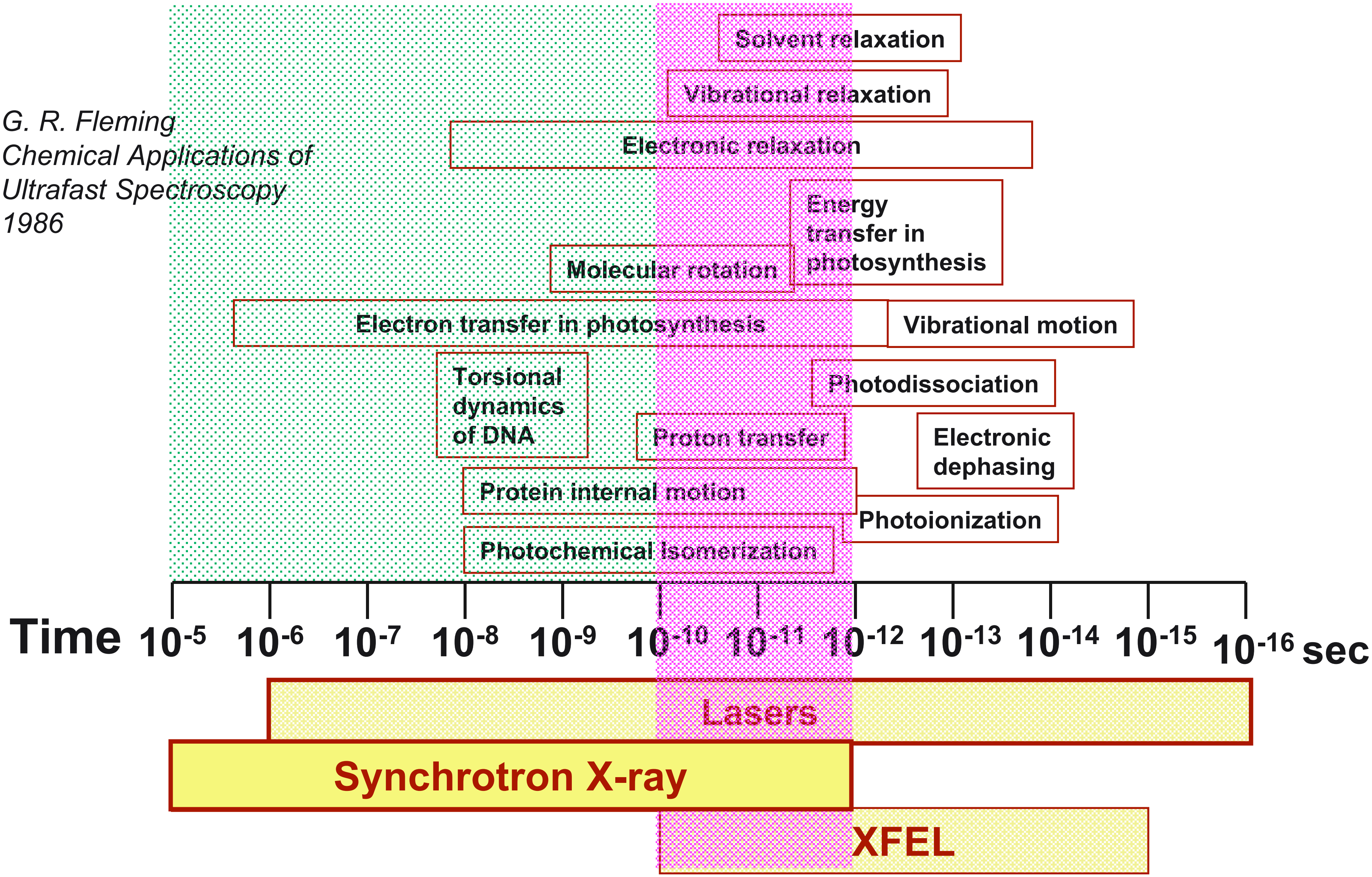


T-jump 1565°

Vigilotti et al., Angew. Chem 2004

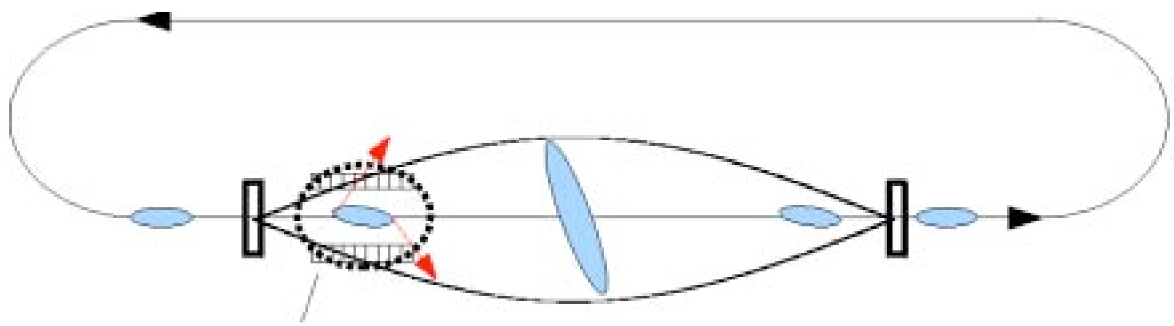
Multiple timescales in chemical processes

G. R. Fleming
Chemical Applications of Ultrafast Spectroscopy
1986



Summary

- SPX will dramatically expand APS capabilities and open research opportunities in AMO, chemistry, interfaces, devices, condensed matter



- Collaboration between APS machine, beamline, user scientists
- Maximize capability with beamlines ranging from soft to hard x-rays
- Maximize utility by providing 3 sets of pulse lengths (1, 10, 100 ps)
- Need optimal undulators, beamlines, optics (microfocus), detectors