Attosecond Science with XFELs

Campaign at LCLS:
Real-time Observation of Ultrafast Electron Motion using Attosecond XFEL Pulses

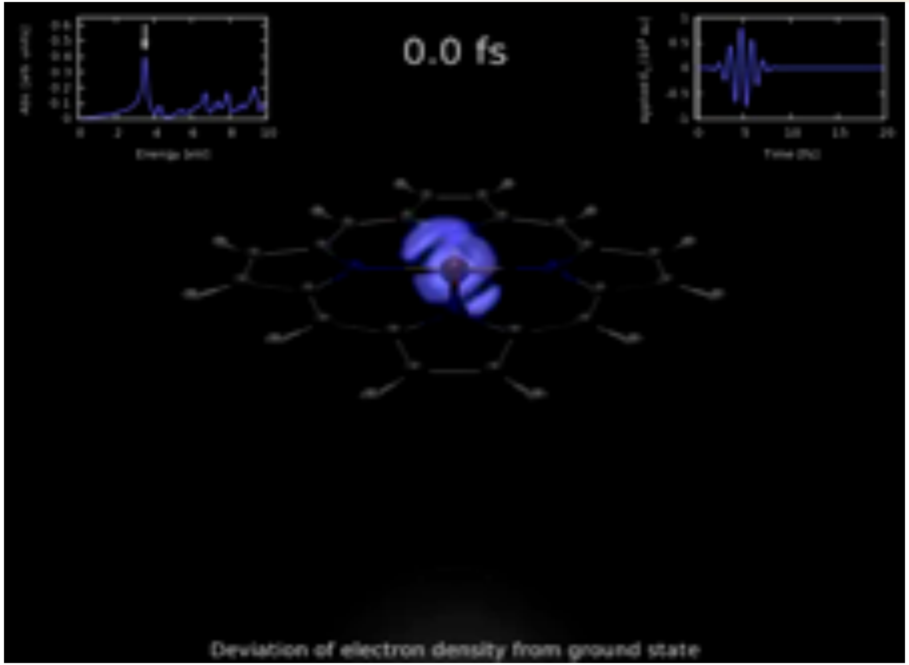
James P. Cryan

Non-Linear Multidimensional Methodologies for Studying Chemical Sciences
December 9-10, 2020

U.S. DEPARTMENT OF ENERGY
Office of Science

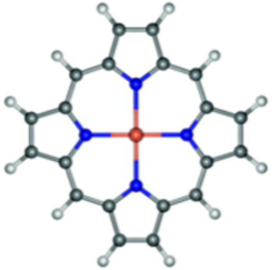
SLAC NATIONAL ACCELERATOR LABORATORY

Coherent Electronic Motion



Environmental Molecular Sciences Laboratory (EMSL) @ PNNL:
https://www.youtube.com/watch?v=ZYsktRlhMOg
J. Chem. Theory Comput. **7**, 1344–1355 (2011)

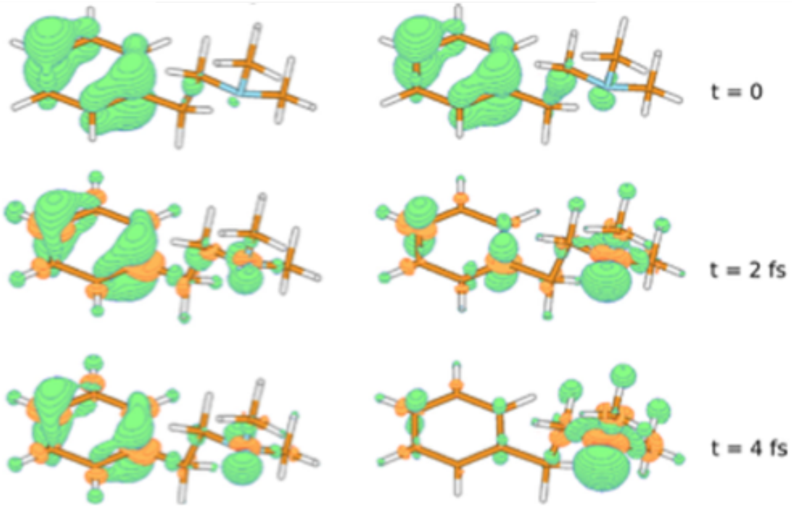
- Electron motion is the means by which light energy is harnessed in photochemistry.
- Goal: track the evolution of electrons on their natural time scales.
- Determine how attosecond scale electronic dynamics (and coherence) effects longer timescale, femtosecond motion.
  - Understand the first step in chemistry



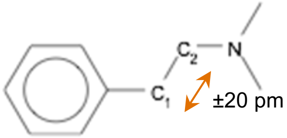
Zinc porphyrin

Electronic Wavepackets

- The moving electric charge is described as a coherent superposition of electronic states that evolve on the sub-femtosecond timescale.
- Coupling of electronic and nuclear motion is important for the dynamics, and leads to possible charge transfer.
- Requires sub-femtosecond temporal resolution **and** atomic resolution.

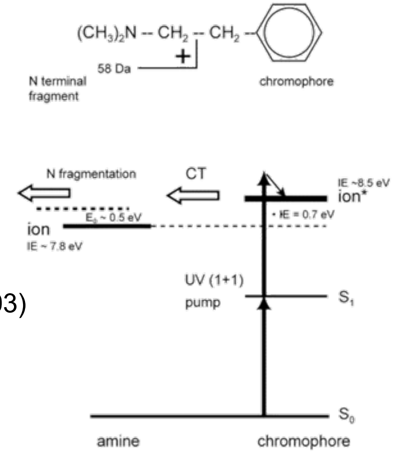


Lunnemann CPL **450** 232-235 (2008)

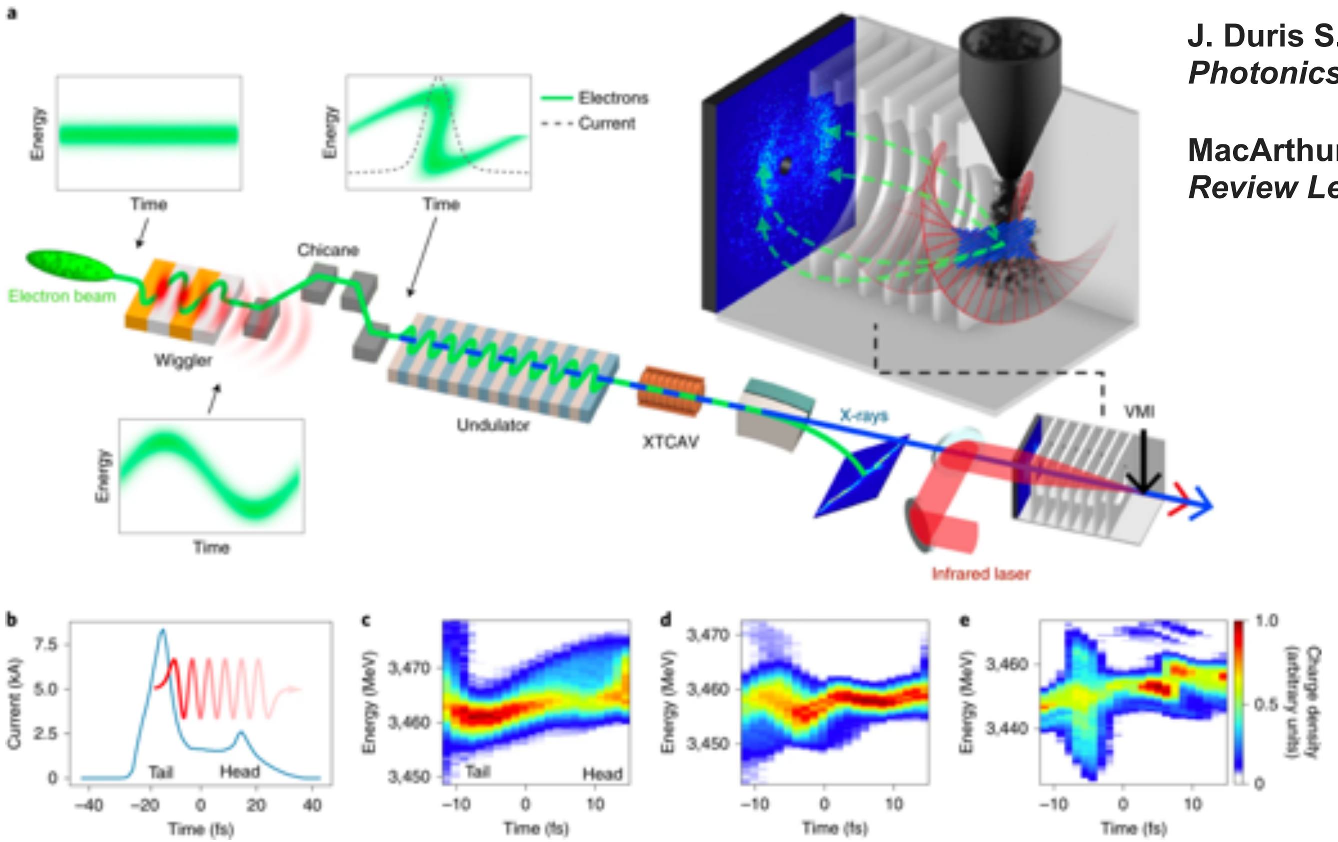


2-phenylethyl-N,N-dimethylamine

R. Weinkauf, L. Lehr, A. Metsala
J. Phys. Chem. A **107** 2787-2799 (2003)



XLEAP: X-ray Laser-Enhanced Attosecond Pulse Generation

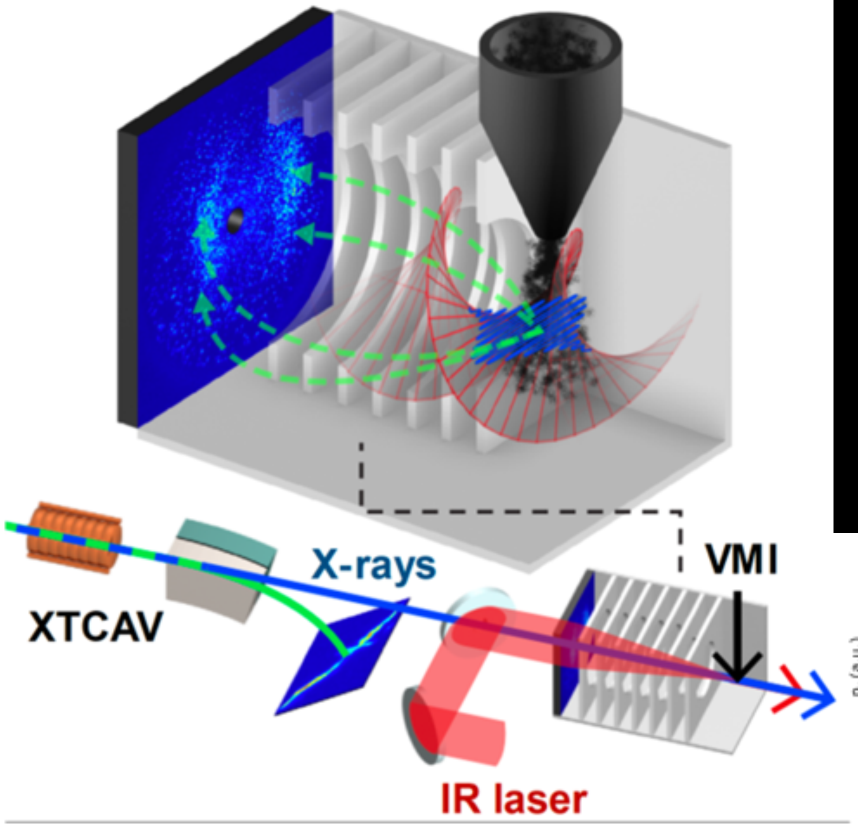


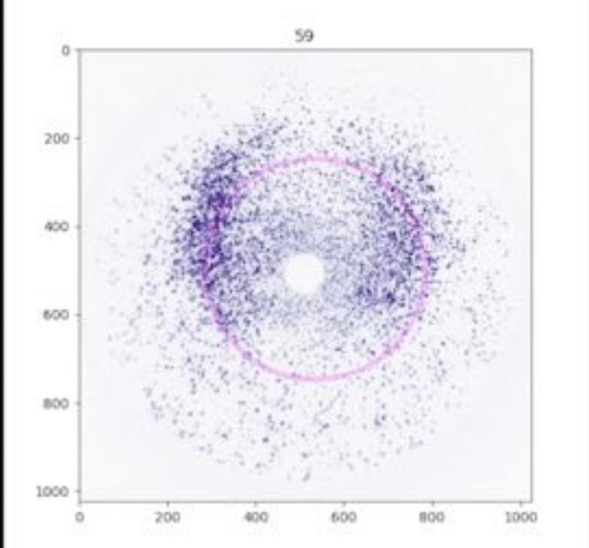
J. Duris S. Li, et al. *Nature Photonics* 14.1 (2020): 30-36.

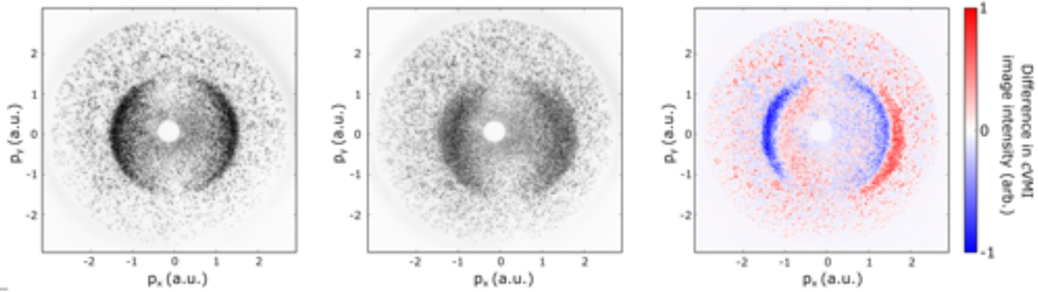
MacArthur, James P., et al. *Physical Review Letters* 123.21 (2019): 214801.

Original concept using laser: Zholents PRSTAB 8, 040701 (2005).

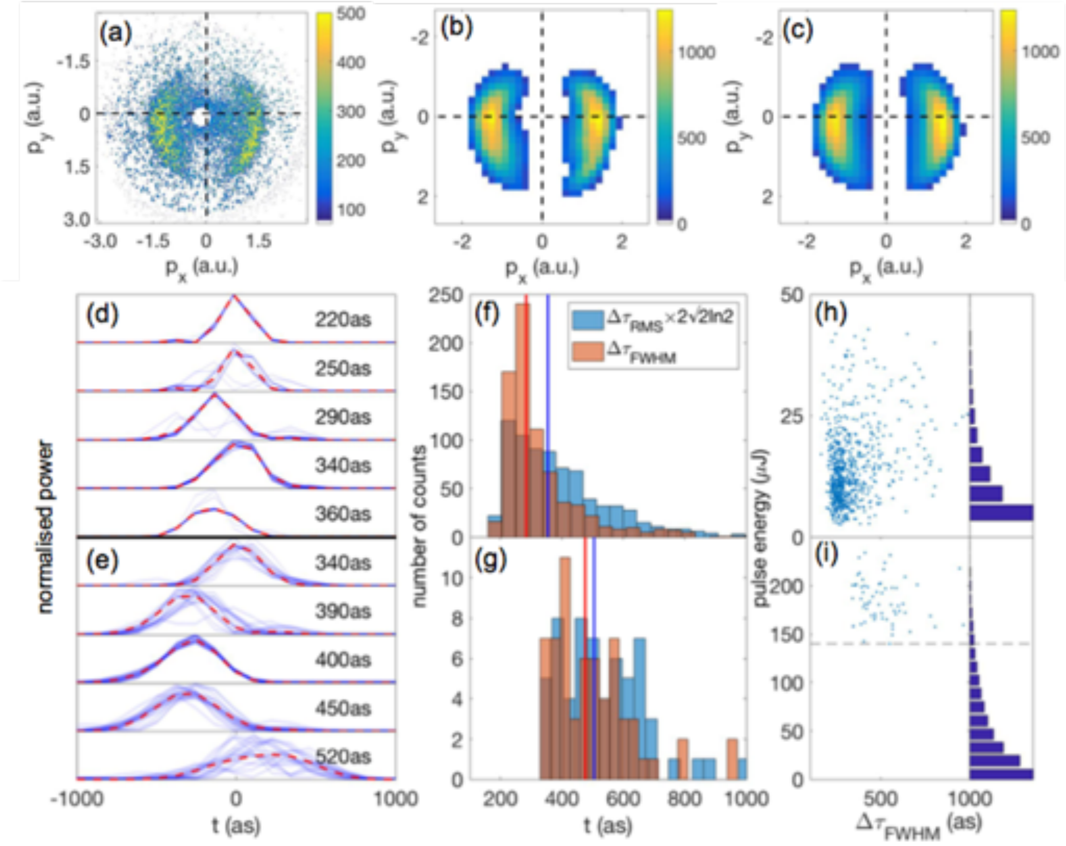
Angular Streaking



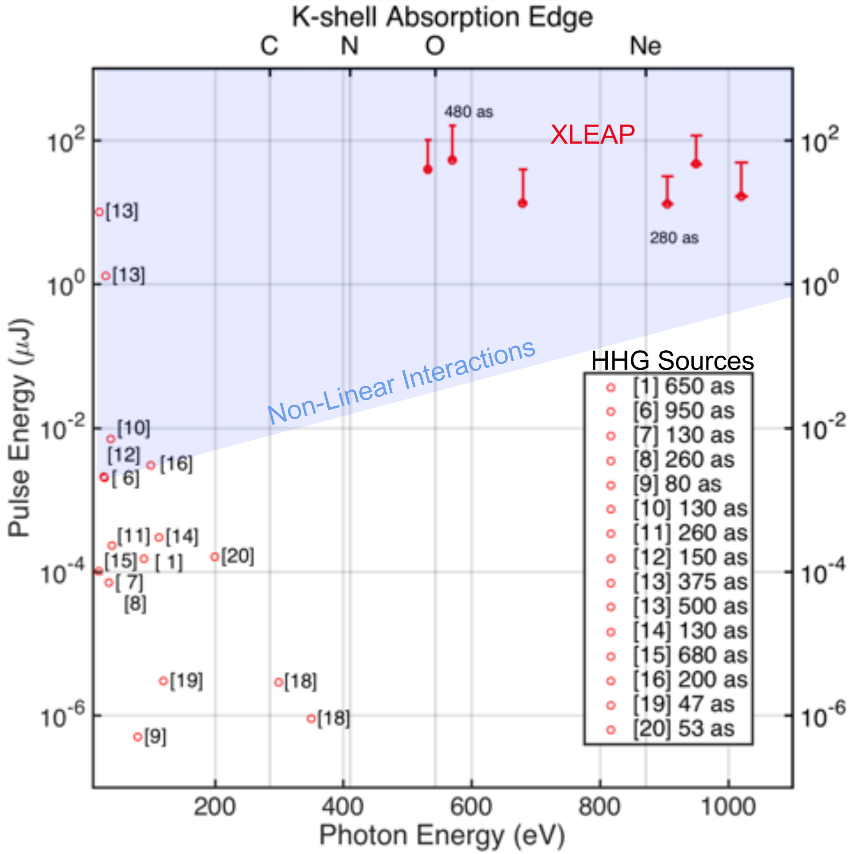




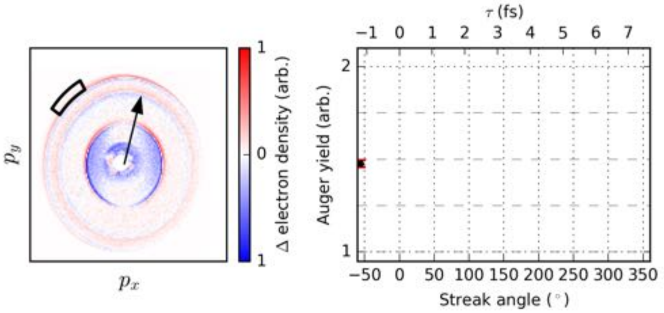
XLEAP Results

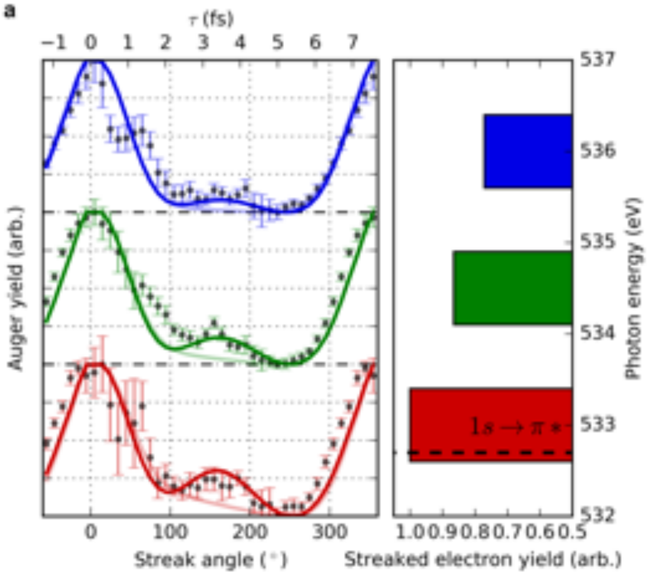


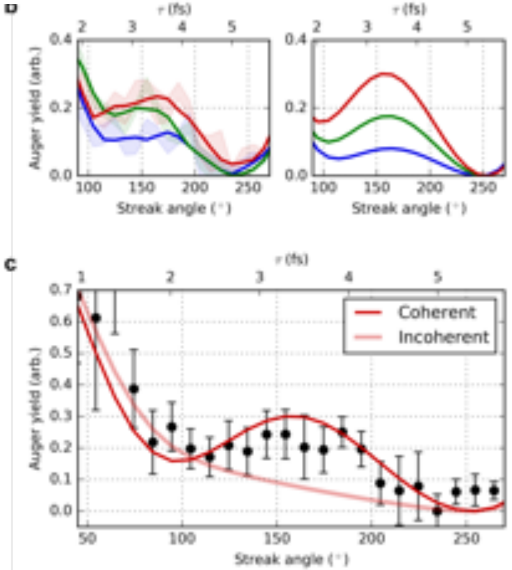
Scientific Impact

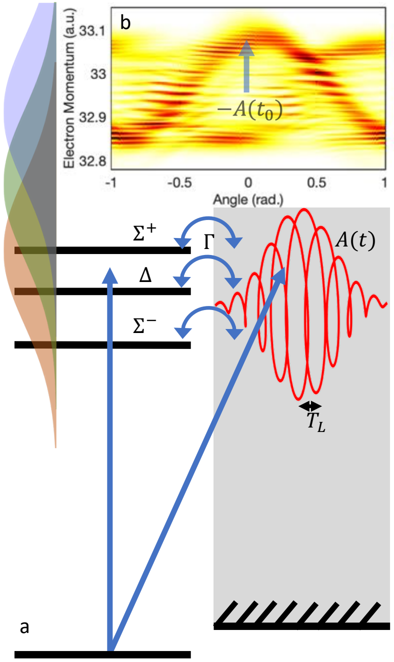


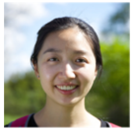
Time Resolving Auger Emission





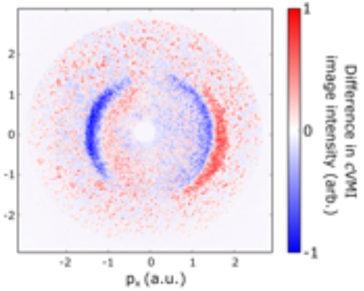




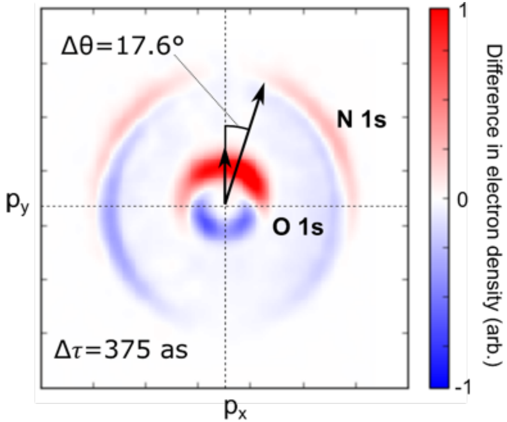


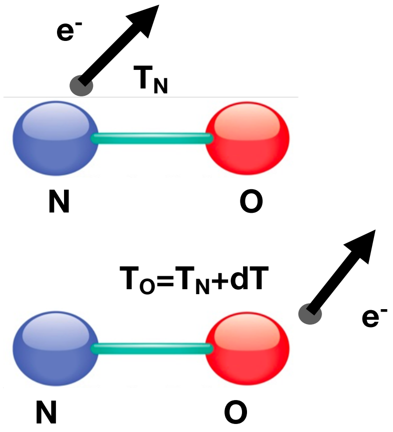

Siqi Li Taran Driver

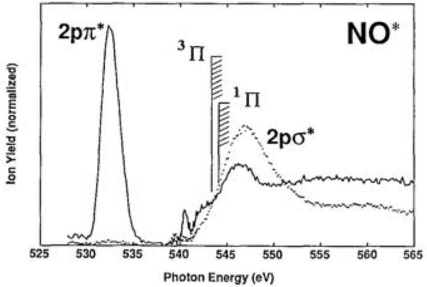
Attosecond Photoemission Delays in Nitric Oxide

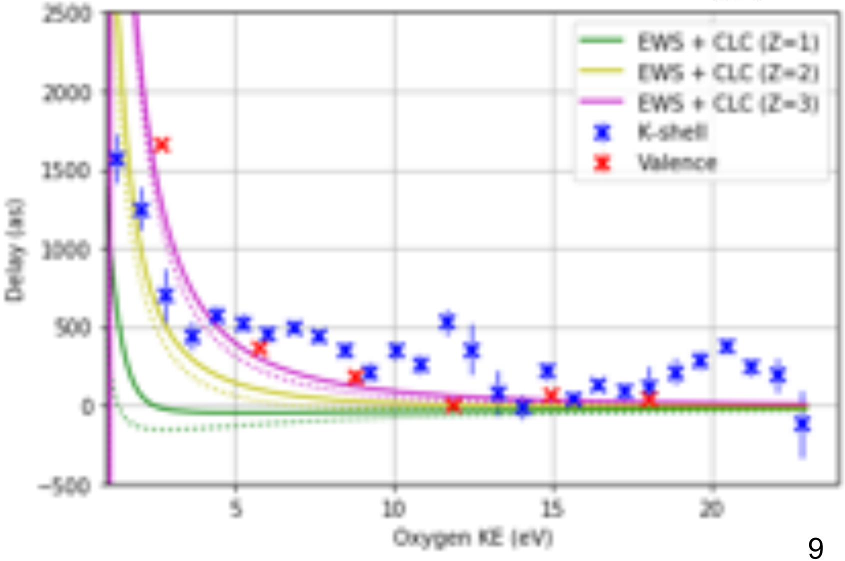


$$\Delta\tau = \frac{\Delta\theta}{2\pi}\times T$$



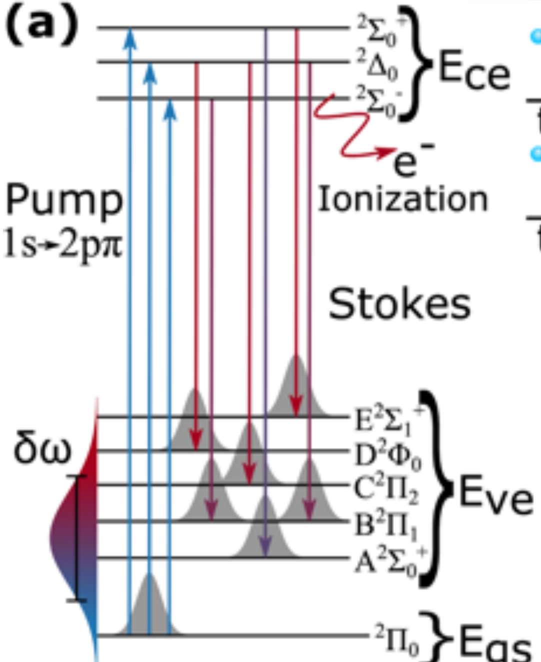


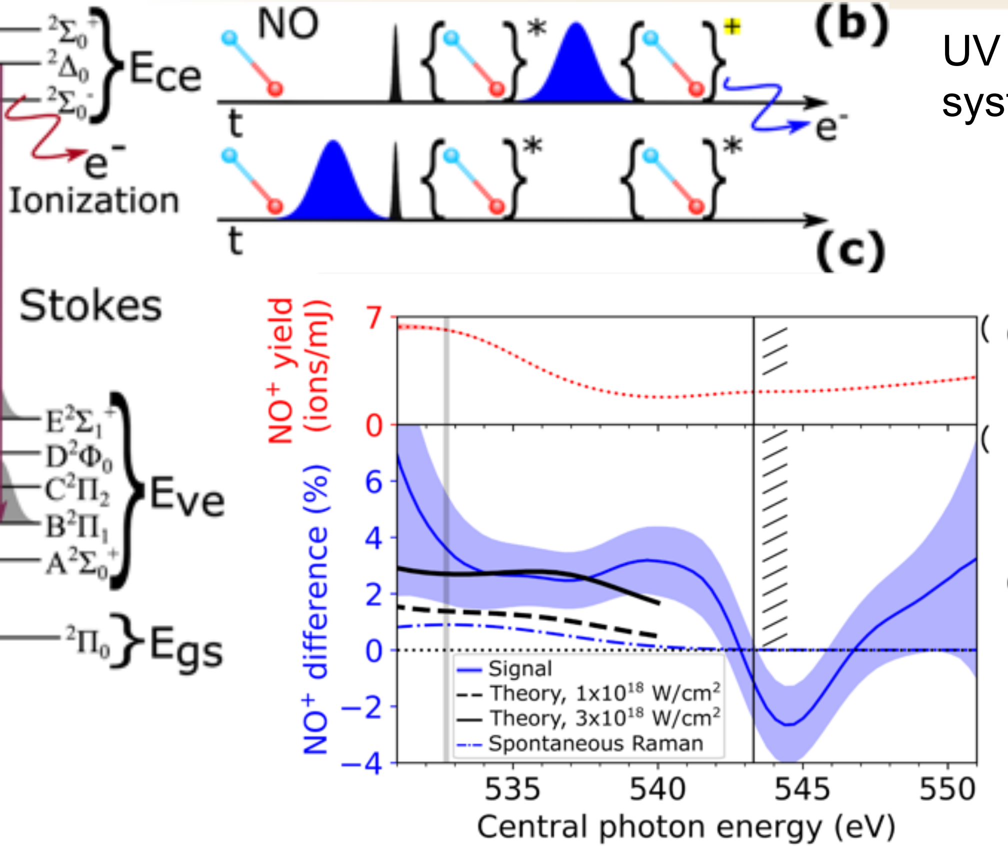




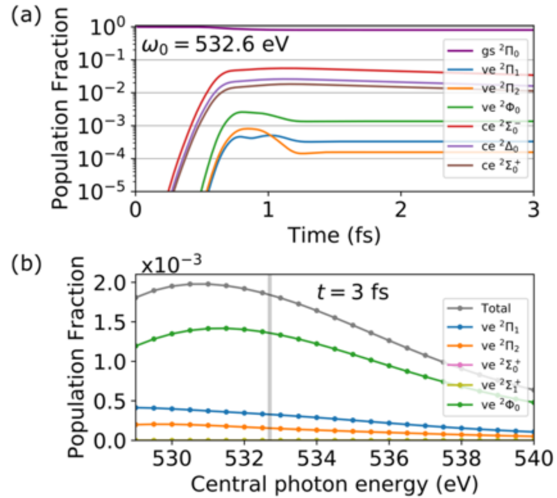
First Science: Impulsive Raman Redistribution

SLAC



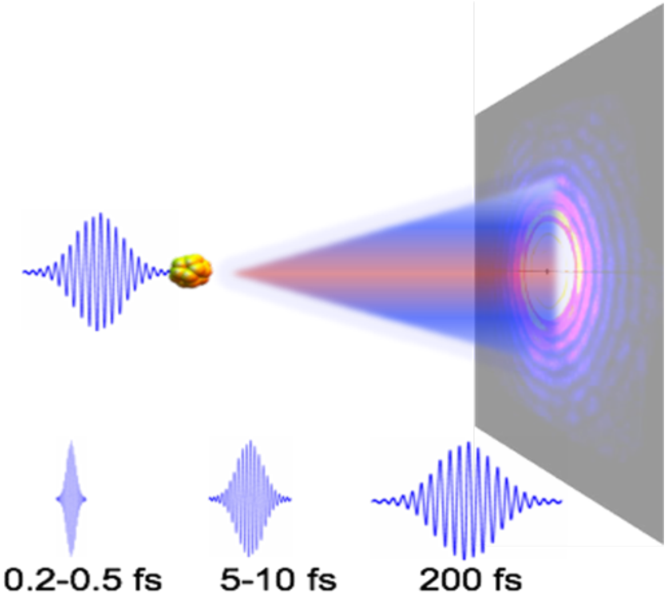


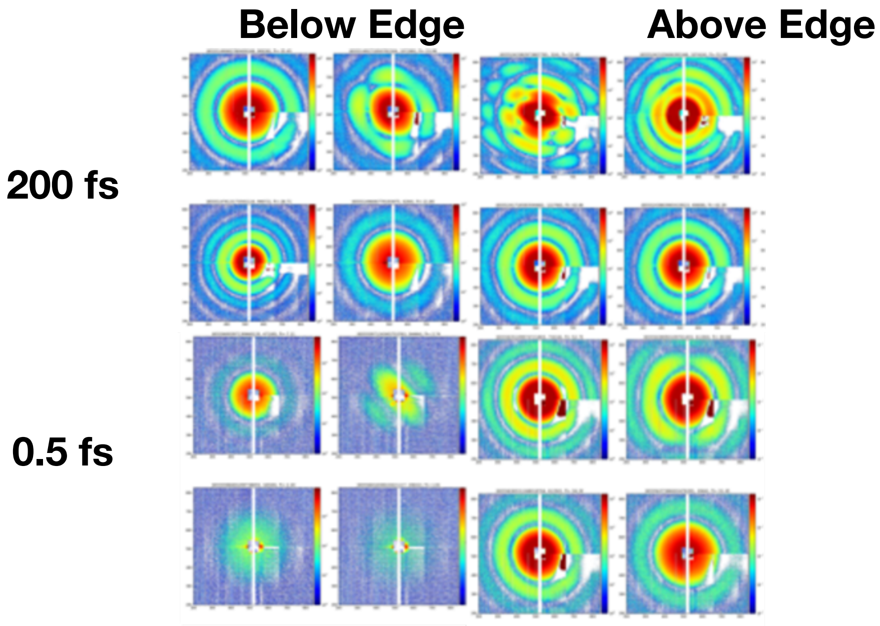
UV Probe ONLY ionizes system in valence excited state



J. Cryan, J. O’Neal

Attosecond Single-Shot Imaging





Imaging Xe clusters with variable pulse duration
Vary photon energy across Xe M-edge (~700 eV)

T. Gorkhover

Science Campaigns @ LCLS

Expansion of PRP access channel

- Target high-impact science ares exploiting LCLS capabilities
- Support comprehensive research efforts requiring multiple LCLS beamtimes (e.g. including synthesis, experiment, theory etc.)
- Open, competitive access based on peer-review
- Scientific scope and impact well above standard PRP proposal, and:
  - Clear justification for campaign, and need for LCLS capabilities (partnership)
- Review: PRP-plus
  PRP augmented by high-level external area experts, SAC input/oversight on portfolio
- Opportune time – increased competition and capacity (local, worldwide)

Opportunity for LCLS to target a few high-reward "grand challenge" science areas

Attosecond Campaign @ LCLS

Real time Observation of Ultrafast Electron Motion Using Attosecond XFEL Pulses

Impact:

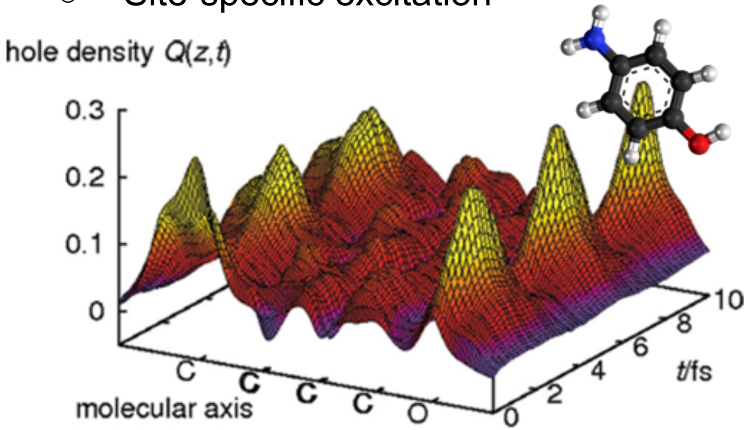
- Meaningful comparison between experiment and theory.
  - X-ray observables of charge migration are within reach of the current state-of-the-art for computational modelling.
  - Validate speculative models. (Little experimental data to compare to)
- Understand the role of electronic coherence in the earliest stages of chemical dynamics.
  - Electronic motion mediates chemical change
- Development of methods to probe ultrafast electrons dynamics are useful to a broad range of fields.

Objectives:

- Demonstrate the creation and control of nonstationary electronic states in small molecular systems.
- Follow charge migration across the molecular backbone, and study the coupling of charge motion to nuclear dynamics.
- Develop nonlinear X-ray techniques for probing ultrafast dynamics.

Impulsive Interactions Create Non-Stationary States

- X-ray interactions induce ultrafast charge motion
- "Fast" Removal of an Electron
  - Creates coherent electronic superposition
  - Ionization of highly correlate inner valence electrons
- Stimulated X-ray Raman Scattering (SXRS): A "swift kick" for initiating charge motion
  - Nonlinear X-ray technique
  - Site-specific excitation



The Impulse Limit:

$$\tau \ll \frac{2\pi\hbar}{\Delta E}$$

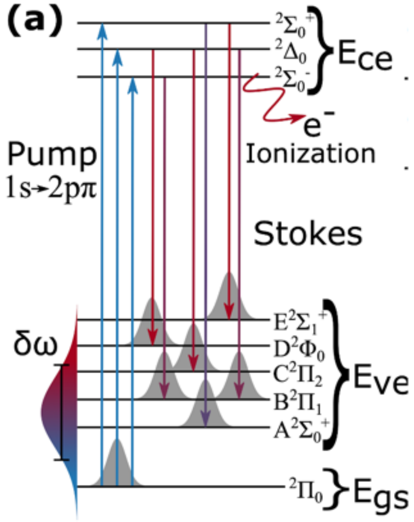
Interaction timescale

Natural timescale for system

$$\psi(t=0^+) = e^{-iP}\psi(t=0^-)$$

$$P = \int_0^{\tau} H'(t')\,dt'$$

State of the system



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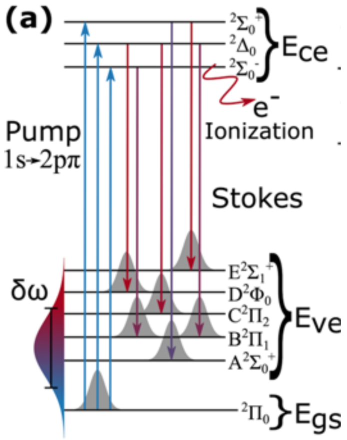

The Impulse Limit:

$$\tau << \frac{2\pi\hbar}{\Delta E}$$

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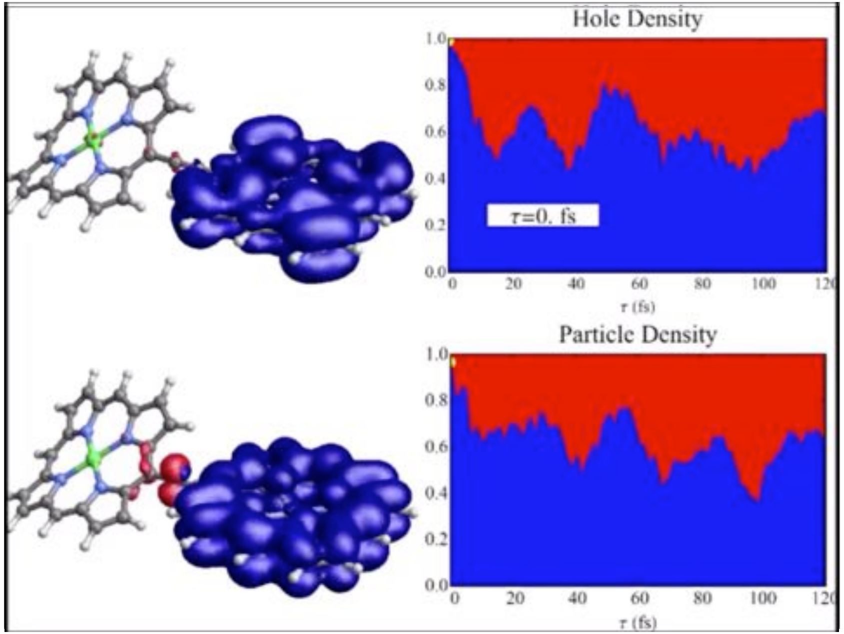
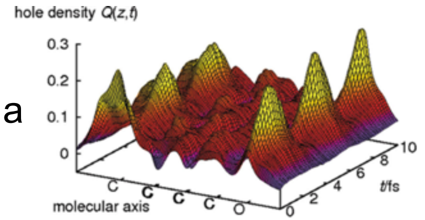


Milestones of the Campaign

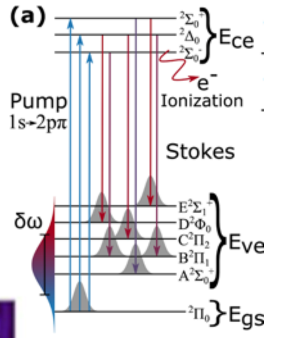
SLAC

Real time Observation of Ultrafast Electron Motion Using Attosecond XFEL Pulses

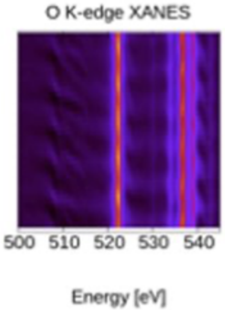
Cryan, Walter, and Marinelli



1. <u>Impulsive Ionization</u>: Sudden ionization of inner valence electrons will create a coherent superposition of cationic states. The evolution of the non-stationary electronic state will be probed with a second X-ray pulse.

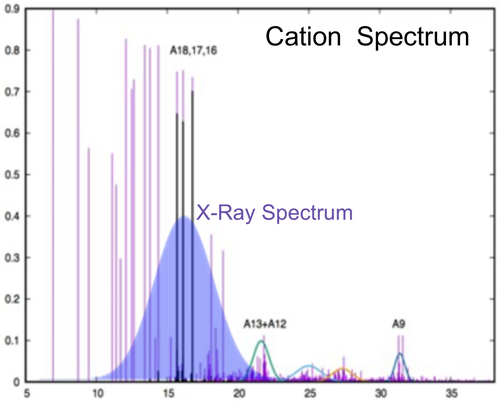


2. <u>Characterize and control impulsive stimulated X-ray Raman scattering (SXRS)</u>: Creation and control of non-stationary electron wavepackets in molecules. Impulsive SXRS provides a controlled method for creating localized electronic excitations in the neutral molecule.

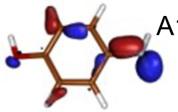


3. <u>Probing impulsive SXRS with X-ray Absorption:</u> This is the final goal of the campaign.

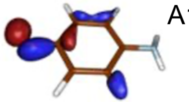
Impulsive Ionization



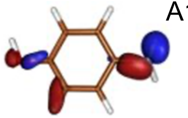
Excitation Energy (eV)



A18

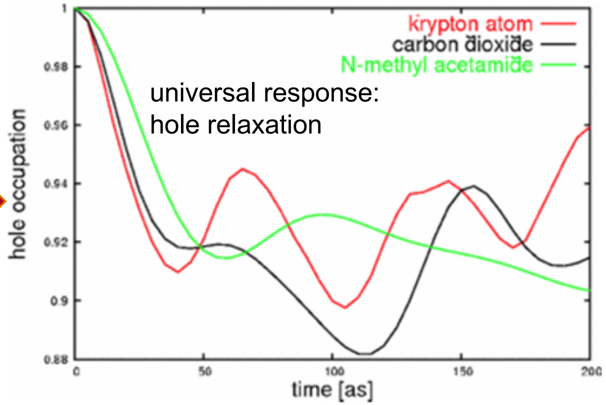


A17

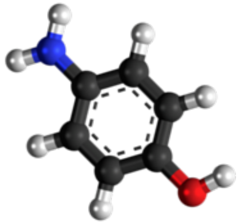


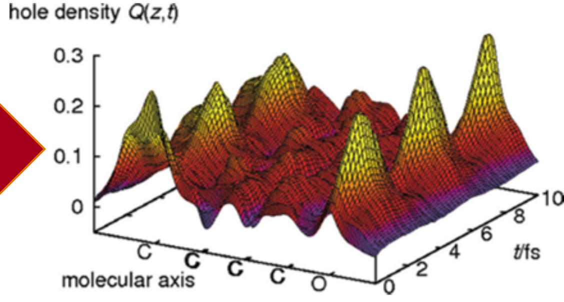
A16

Calculation courtesy of Vitali Averbukh and Premysl Kolorenc



Breidbach PRL **94** 033901 (2005)

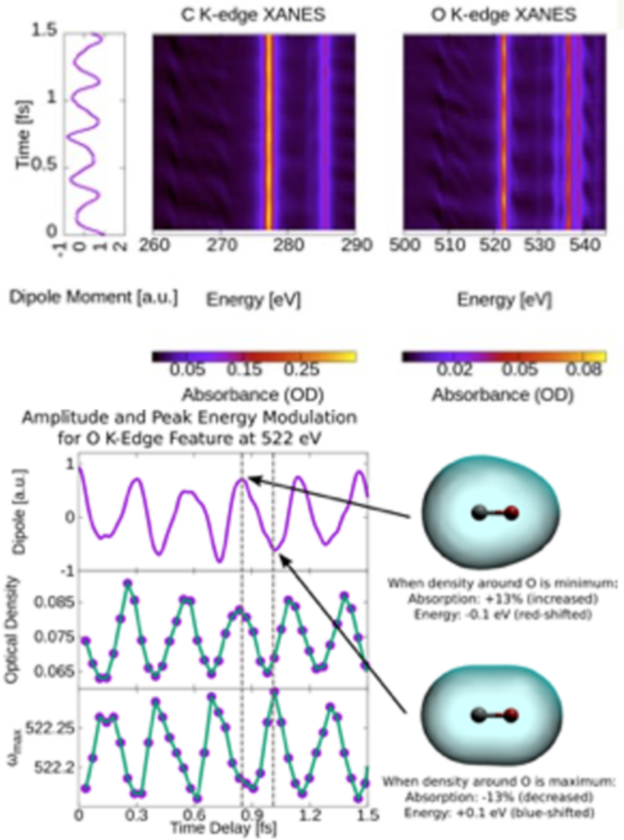




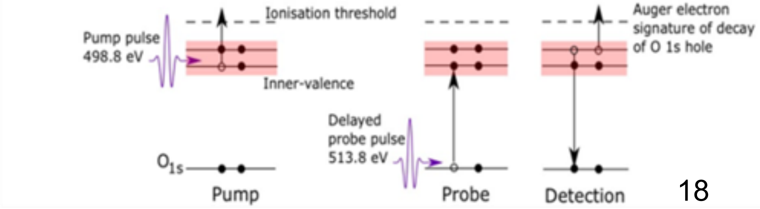
Kuleff et al. JPC A 114 8676 (2010)

Probing Charge Motion with X-rays

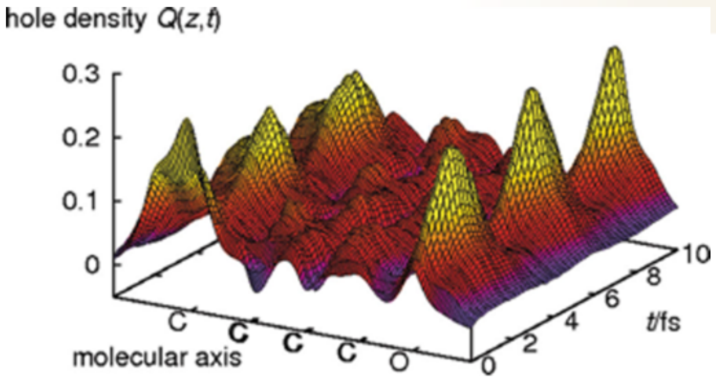
- X-rays Observables:
    - Sensitive to the local molecular environment at a specific site
- Gas phase photoemission based methods:
    - Photoelectrons, Auger electrons
    - XAS: Absorption can be monitored by measuring Auger electron yield
    - XPS: Lower energy photoelectrons produced by second X-ray pulse
        - Sensitivity of XPS to charge migration is an open question.
- Members of the campaign are calculating the sensitivity of X-ray observables to coherent electron motion



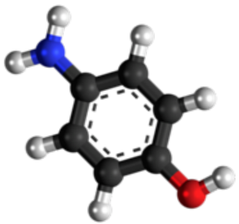
Preliminary Simulation from Ken Lopata (LSU)

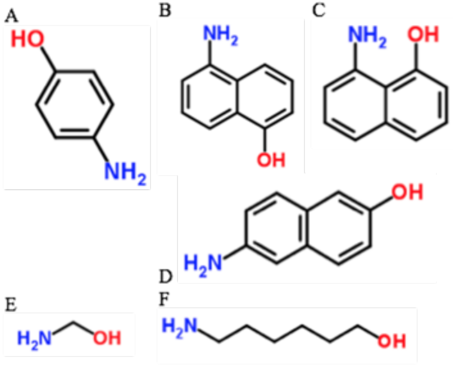


Model System



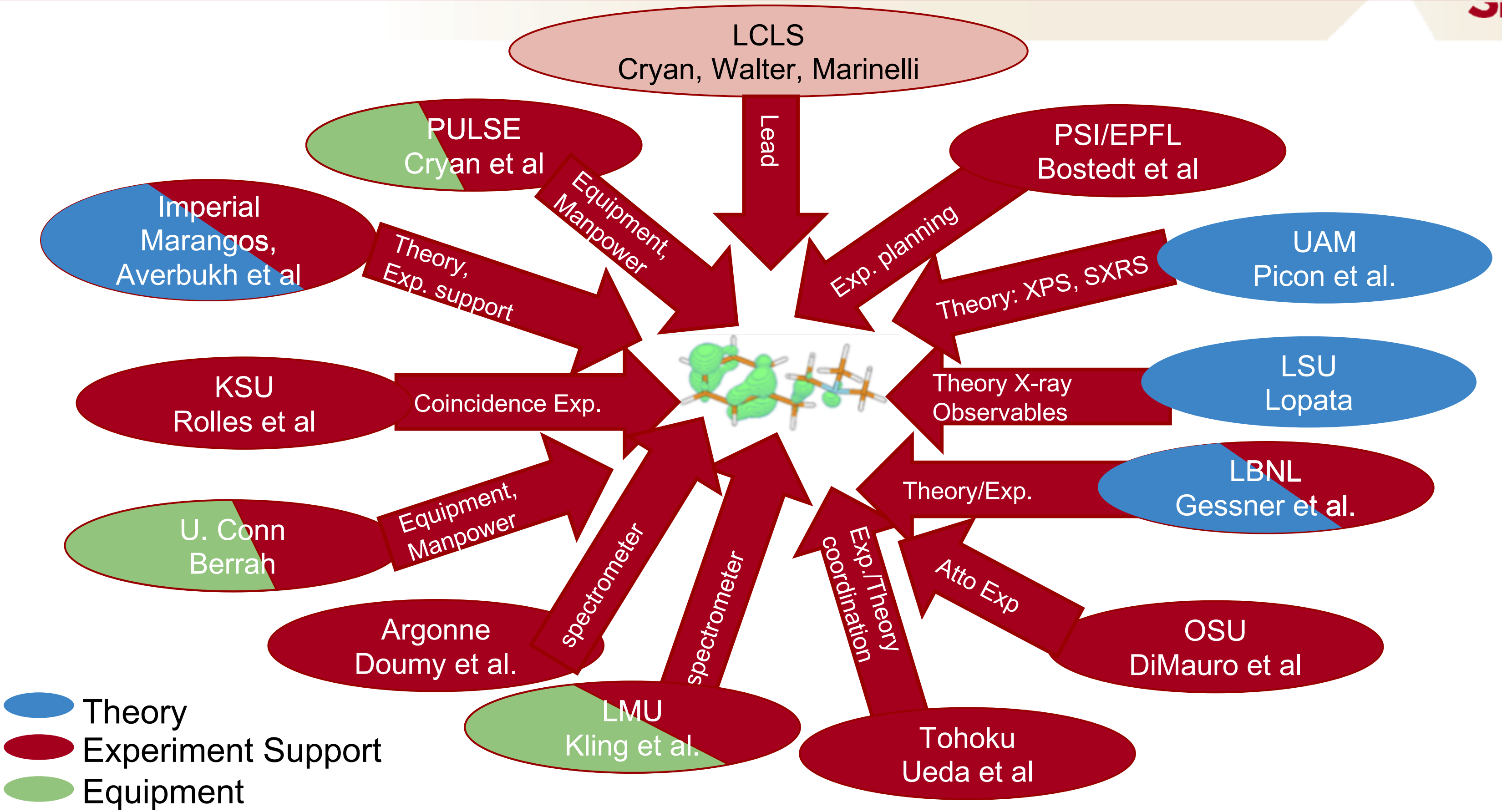
Kuleff et al. JPC A 114 8676 (2010)





- Aminophenol
- nitrogen and oxygen sites to produce and probe charge motion
- change substitution to look at effect of molecular structure
- change “backbone” to investigate rigidity on “molecular wire”
- effect of separation on charge migration

The Team

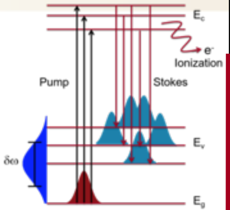


LCLS
Cryan, Walter, Marinelli
Lead
PULSE
Cryan et al
Equipment,
Manpower
PSI/EPFL
Bostedt et al
Exp. planning
Imperial
Marangos,
Averbukh et al
Theory,
Exp. support
UAM
Picon et al.
Theory: XPS, SXRS
KSU
Rolles et al
Coincidence Exp.
LSU
Lopata
Theory X-ray
Observables
LBNL
Gessner et al.
Theory/Exp.
U. Conn
Berrah
Equipment,
Manpower
Argonne
Doumy et al.
spectrometer
LMU
Kling et al.
spectrometer
Tohoku
Ueda et al
Exp./Theory
coordination
OSU
DiMauro et al
Atto Exp
Theory
Experiment Support
Equipment

Milestones in the Campaign

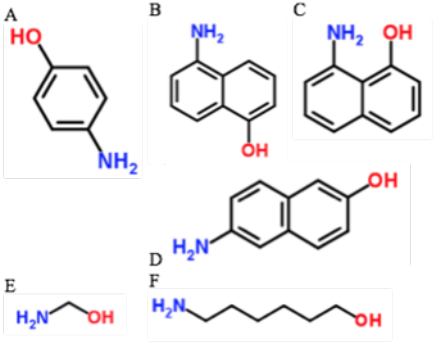
Peter, James, and Ago engage User Community

Develop and submit proposal for ultrafast electron motion



Experiment on nonlinear techniques for charge motion

Experiment on X-ray observables of charge migration X-ray Photoelectron Spectroscopy



Development of Angle-resolved Spectroscopy Instrument

Recommission Attosecond Operations

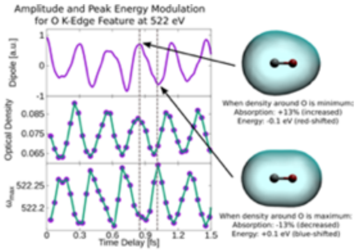
Development of Coincidence Endstations

Rebuild TMO | Run 18 - Cu | Run 19 - Cu | Run 20 - Cu/SC | Run 21 - SC

Campaign team to help in commissioning

Today

Experiment on X-ray observables of charge migration X-ray Absorption Spectroscopy



SXRS pump/probe experiment

Investigate the properties of the molecular system

Mike Dunne proposes a campaign exploiting the new attosecond capabilities

Experiment on X-ray observables of charge migration Coincidence Methods