

Using Attosecond XFELs to Probe Ultrafast Electron Dynamics

James P. Cryan

Stanford PULSE Institute

Linac Coherent Light Source

SLAC National Accelerator Laboratory

New Scientific Capabilities at European XFEL

March 25-27, 2019

Stanford

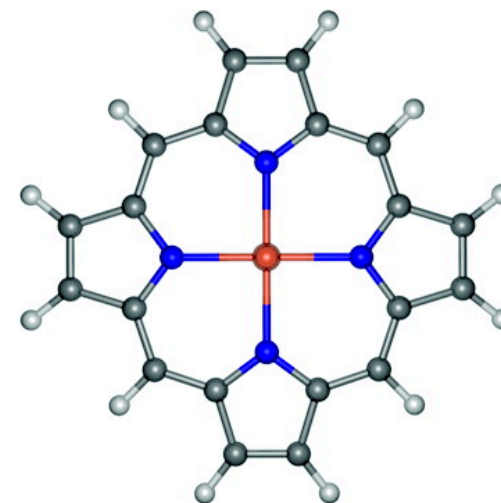
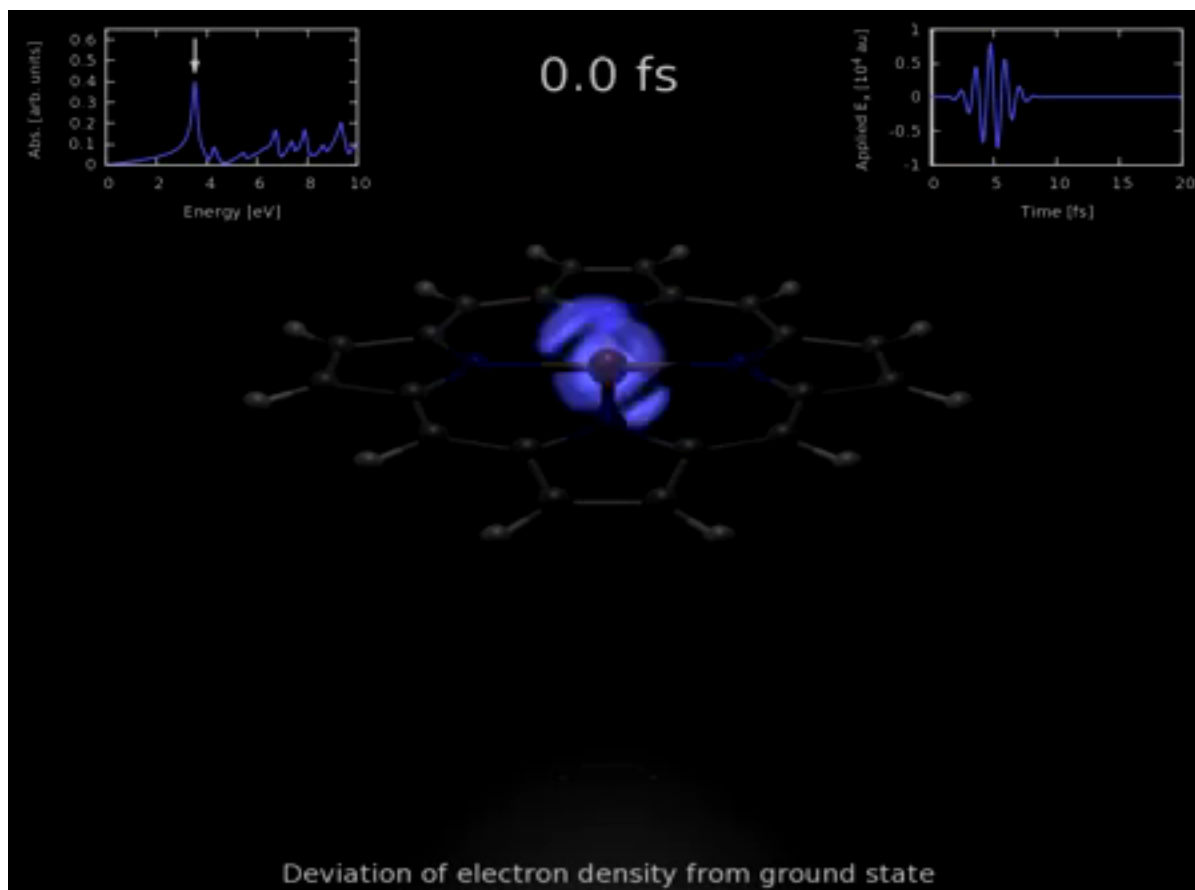
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LCLS

Coherent Electronic Phenomena

- Electron motion is responsible for all chemistry
- Our goal is to track the evolution of electrons on their natural time scales
- We want to determine what role attosecond scale electronic coherence has on longer timescale, femtosecond motion (Chemistry).



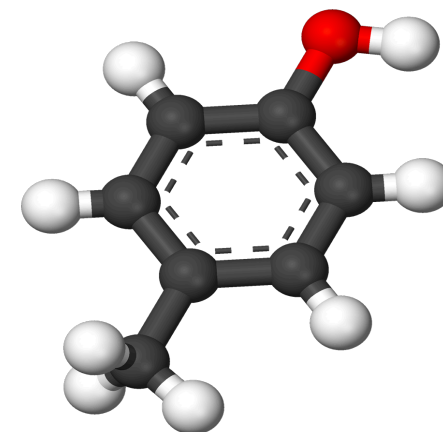
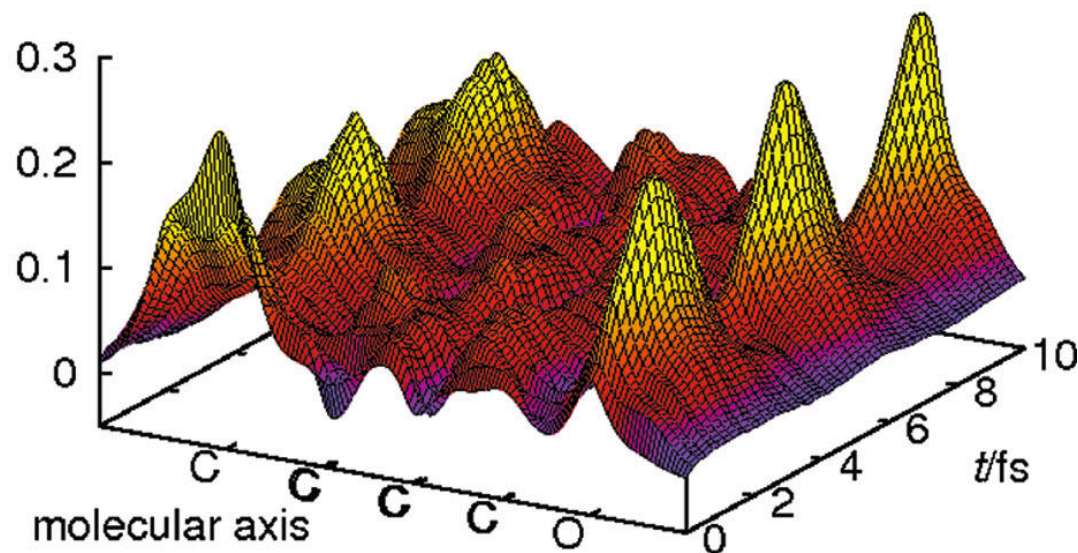
Zinc porphyrin

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

Coherent Electronic Phenomena

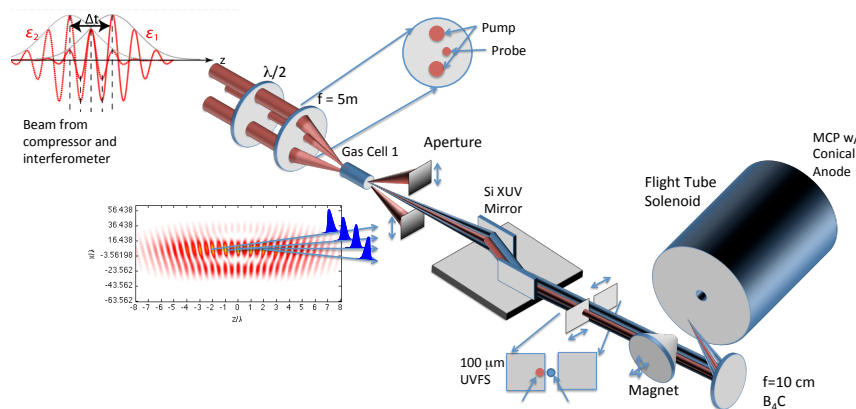
- **Ultrafast X-rays are the ideal tool to create and probe coherent electronic phenomena**
 - **Sub-femtosecond duration**
 - **Atomic site-specificity.**

hole density $Q(z, t)$



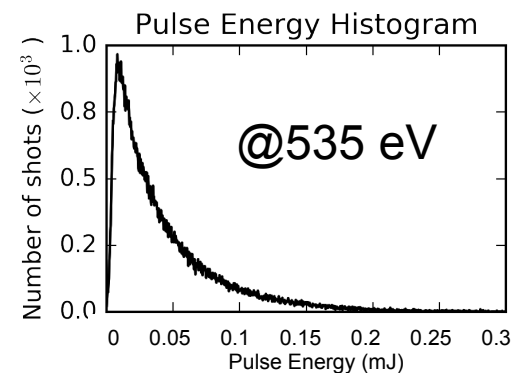
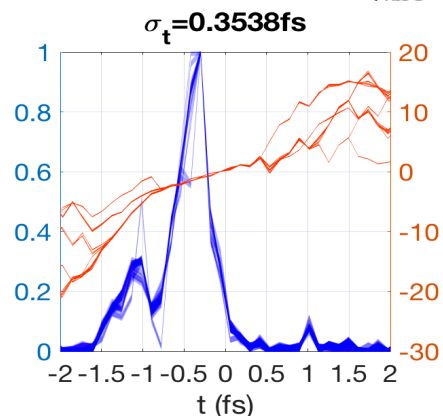
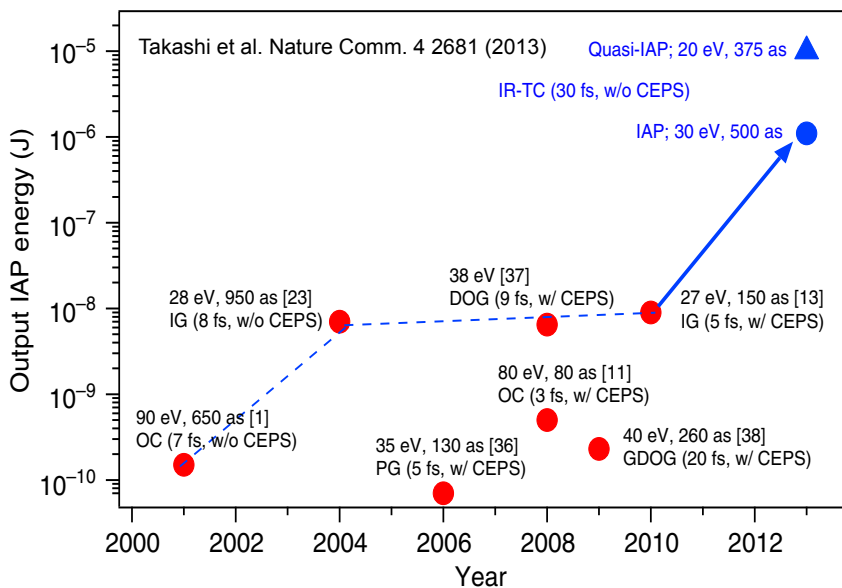
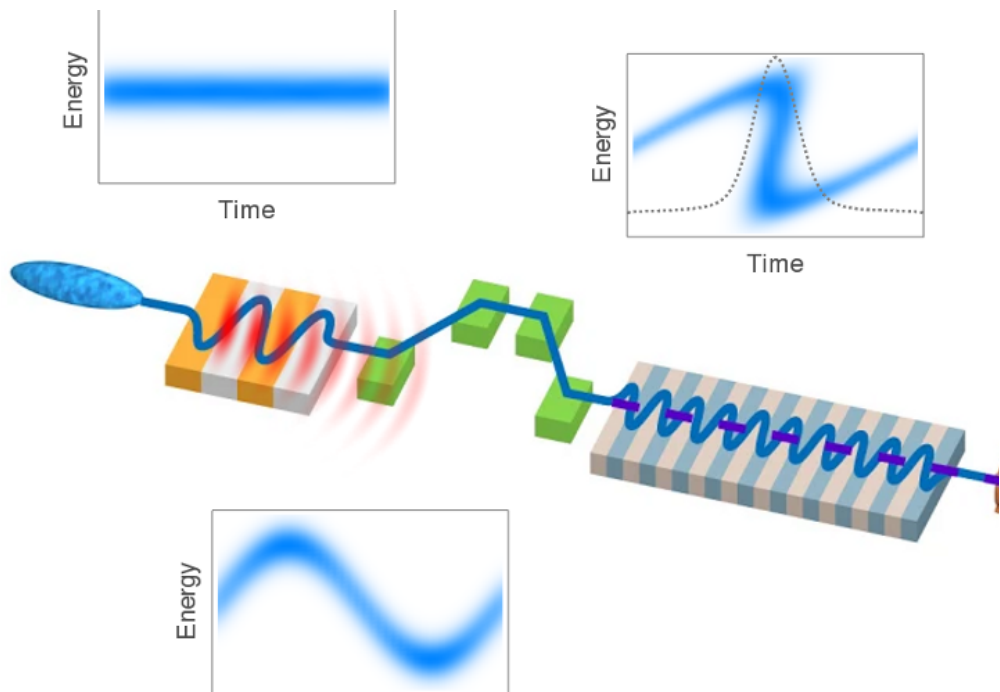
Tools for Probing Charge Dynamics

HHG Based Sources



XLEAP;
530 eV, 400 as

FEL Based Sources

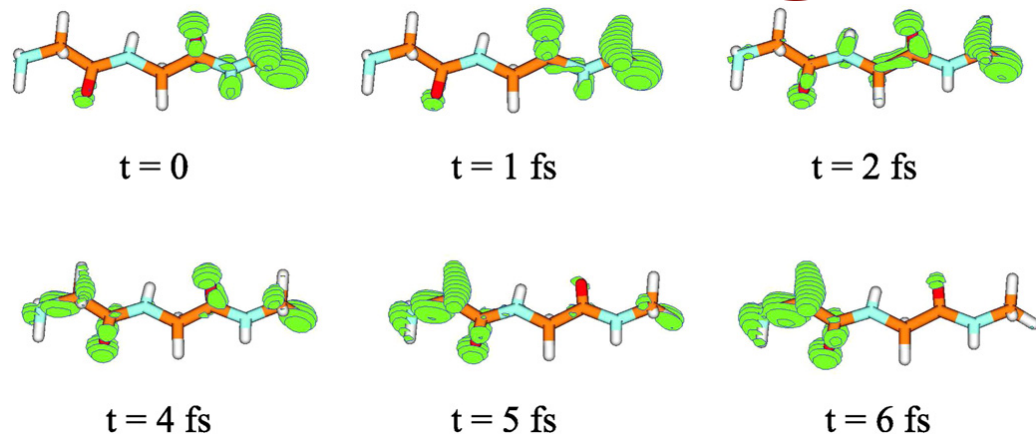


Opportunities for Attosecond Measurements of Electron Dynamics

- **The attosecond scale is the timescale for electronic motion on the atomic length scale.**
- **Coherent charge motion (Charge Migration)**
 - **Superpositions of electronic states will evolve on the sub-femtosecond timescale**
 - **Could offer the possibility to control the charge localization in molecules.**
- **Time-resolving electron correlation.**
 - **The exchange–correlation term in the many-body Hamiltonian can have large effects on electronic configuration of a molecule, and thus the chemical bonding.**
 - **Non-sequential ionization**
 - **Auto-ionization, Auger Decay**

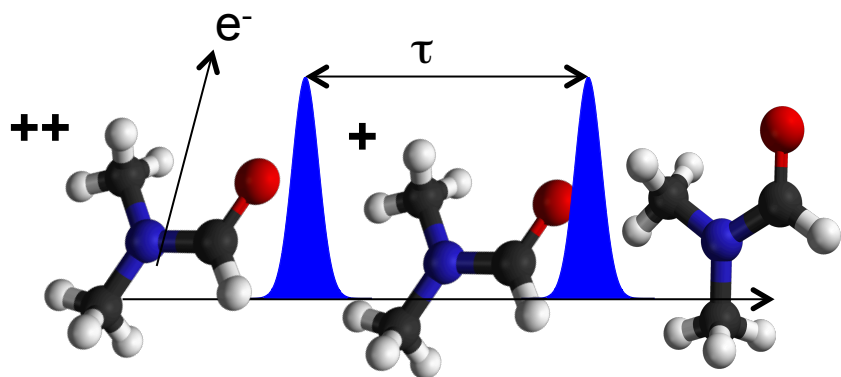
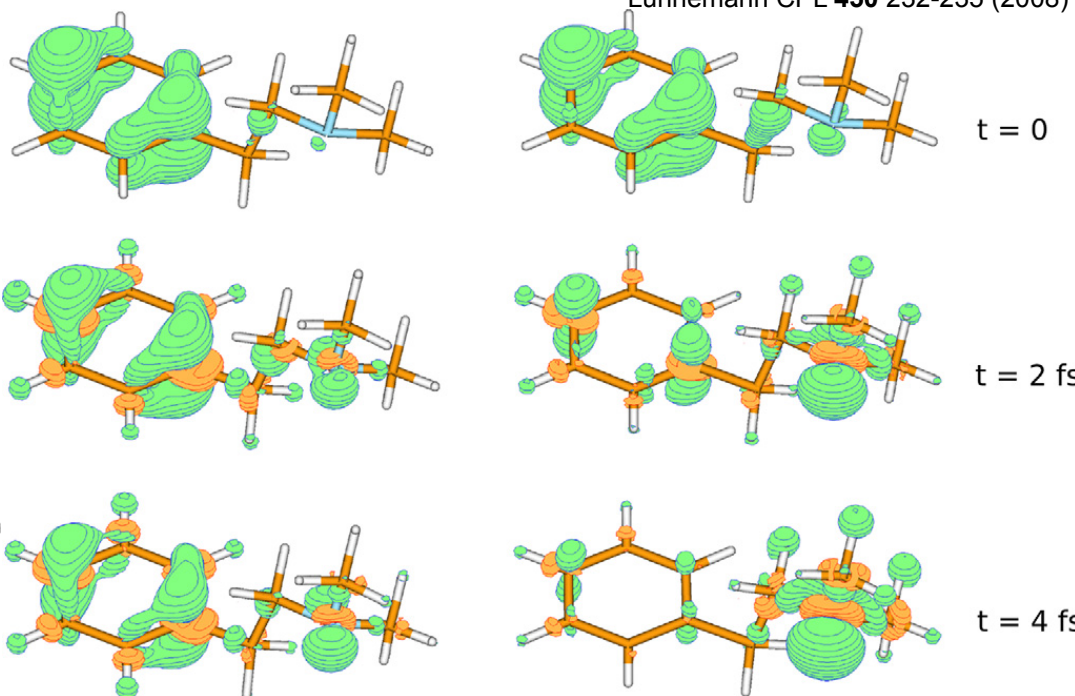
Ultrafast Charge Migration

- Superpositions of electronic states will evolve on the sub-femtosecond timescale.
- Nuclear motion will alter the coherence
- We want to determine what role attosecond scale electronic coherence has on longer timescale, femtosecond motion (Chemistry).
- Attosecond-pump/attosecond-probe

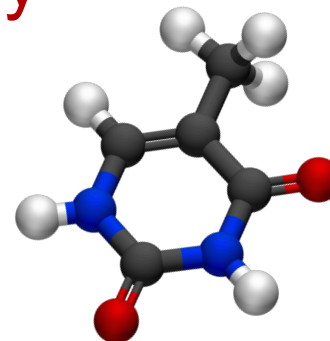


Kuleff *Chem. Phys.* **414** 100 2013

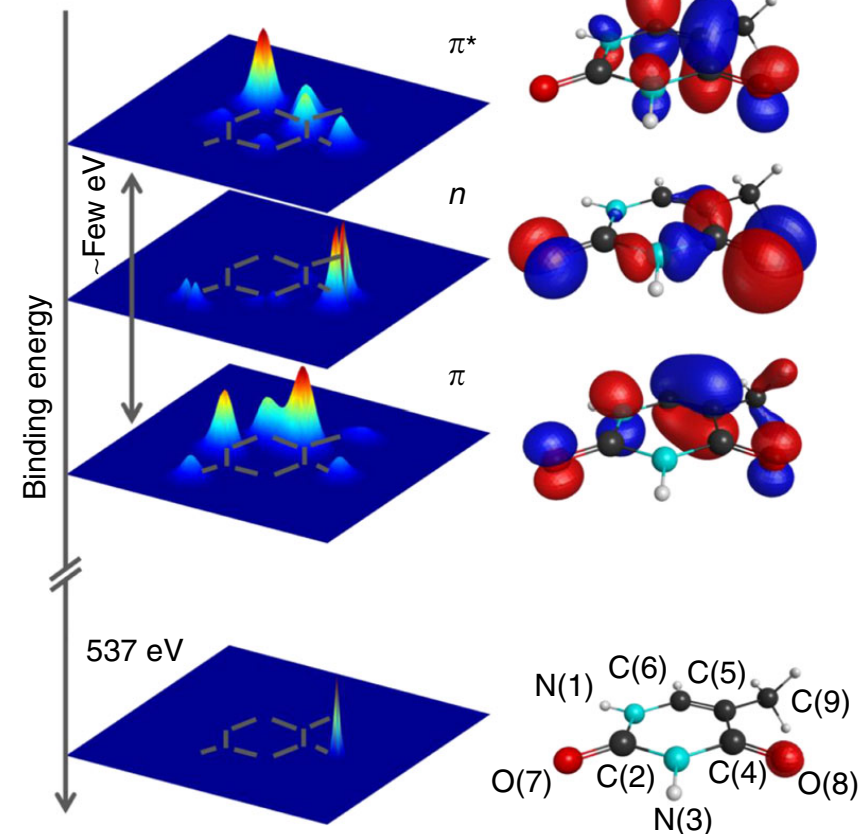
Lunnemann *CPL* **450** 232-235 (2008)



X-Ray Absorption Spectroscopy



- X-ray absorption probes overlap of valence orbitals with core electrons
- Very useful for ultrafast photochemistry



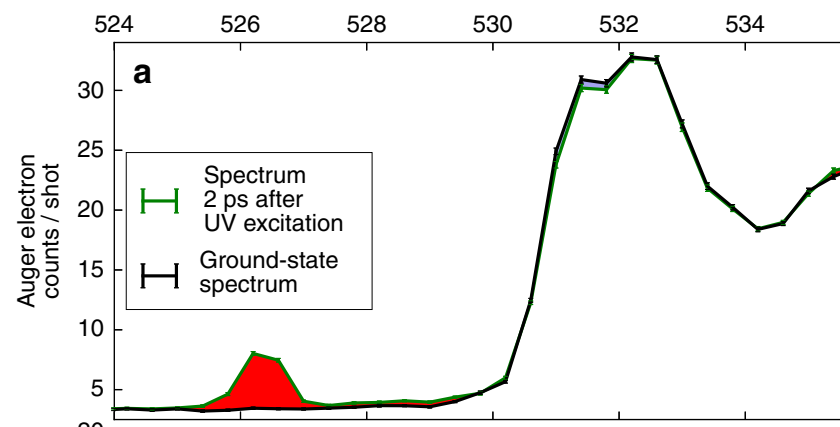
ARTICLE

DOI: 10.1038/s41467-017-00069-7

OPEN

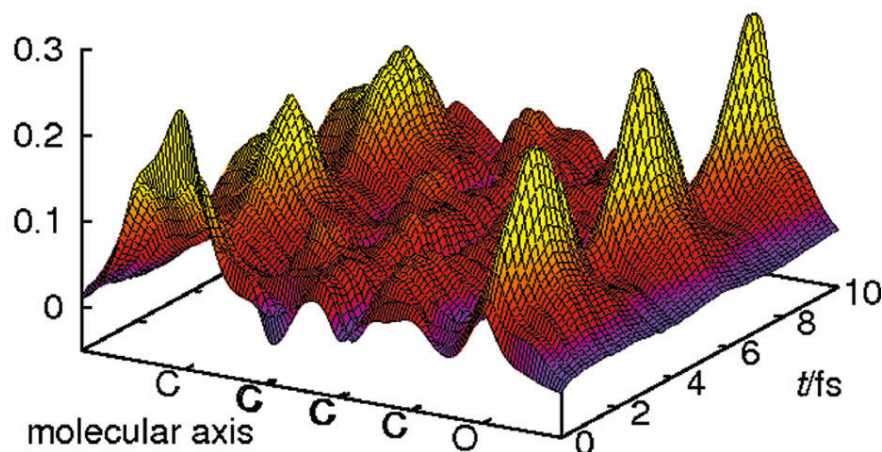
Probing ultrafast $\pi\pi^*/n\pi^*$ internal conversion in organic chromophores via K-edge resonant absorption

T.J.A. Wolf¹, R.H. Myhre^{1,2}, J.P. Cryan¹, S. Coriani^{3,4}, R.J. Squibb⁵, A. Battistoni¹, N. Berrah⁶, C. Bostedt^{7,8,9}, P. Bucksbaum^{1,10}, G. Coslovich⁷, R. Feifel⁵, K.J. Gaffney^{1,11}, J. Grilj¹², T.J. Martinez^{1,13}, S. Miyabe^{1,13,14}, S.P. Moeller⁷, M. Mucke¹⁵, A. Natan¹, R. Obaid⁶, T. Osipov⁷, O. Plekan¹⁶, S. Wang¹, H. Koch^{1,2} & M. Gühr^{1,17}

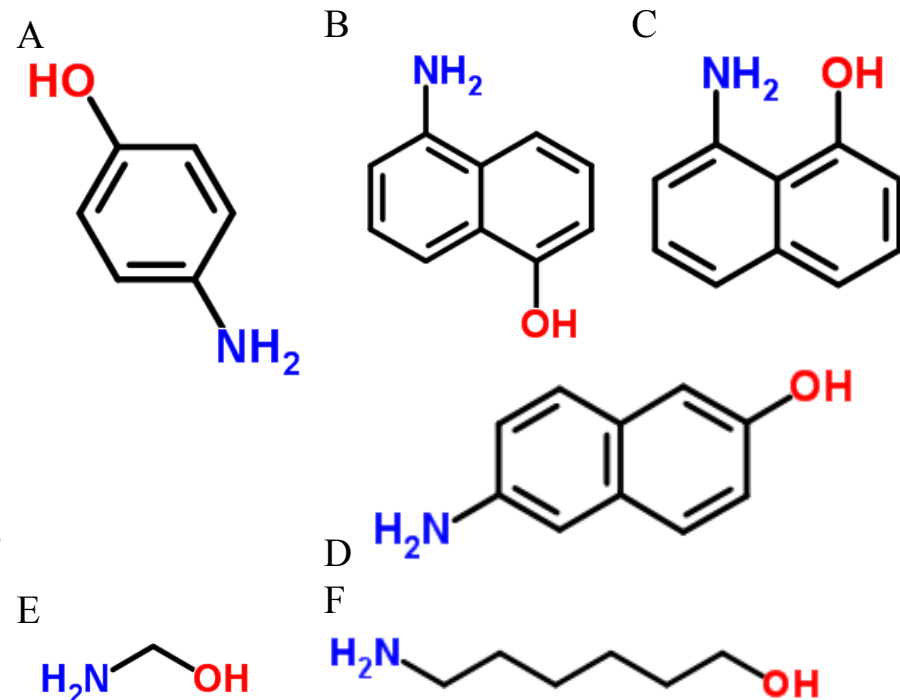


Molecular Effects on Electronic Coherence

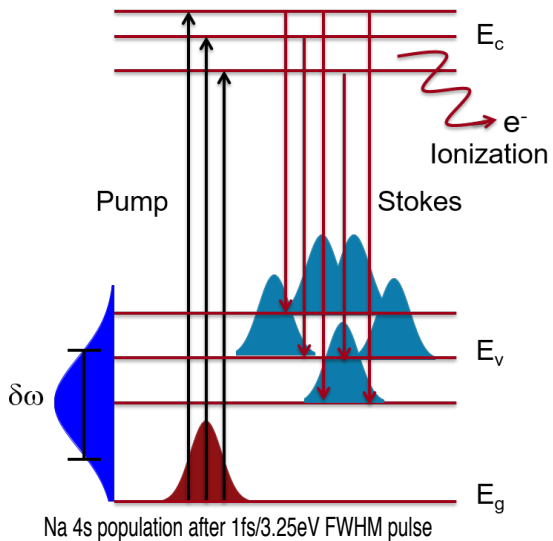
hole density $Q(z,t)$



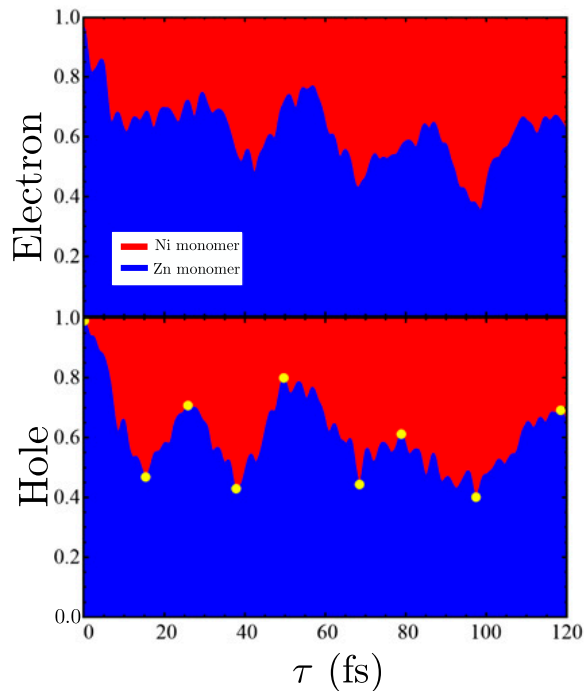
- Can coherent electronic excitations provide a route to by-pass IVR in controlling molecular reactions?
 - Chem. Phys. Lett. 285, 25-33 (1998)
 - Nat. Photonics 8 195-204 (2014)
- Measure coherence lifetime
- Effect of structure on charge migration.
 - Amino-phenol derivative chromophores.



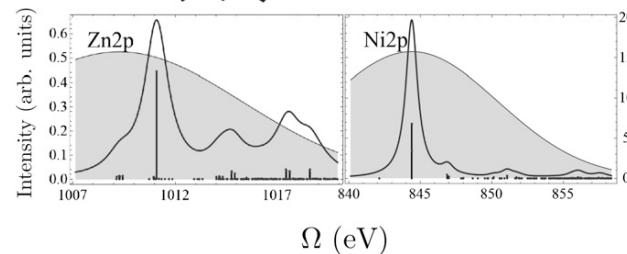
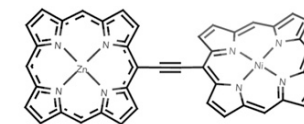
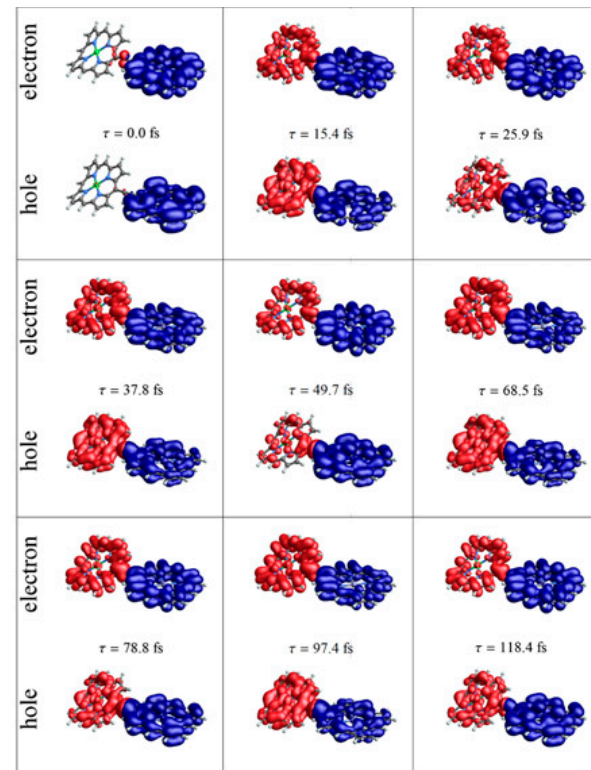
Impulsive Electronic Raman Scattering: A Swift Kick for Initiating Charge Motion



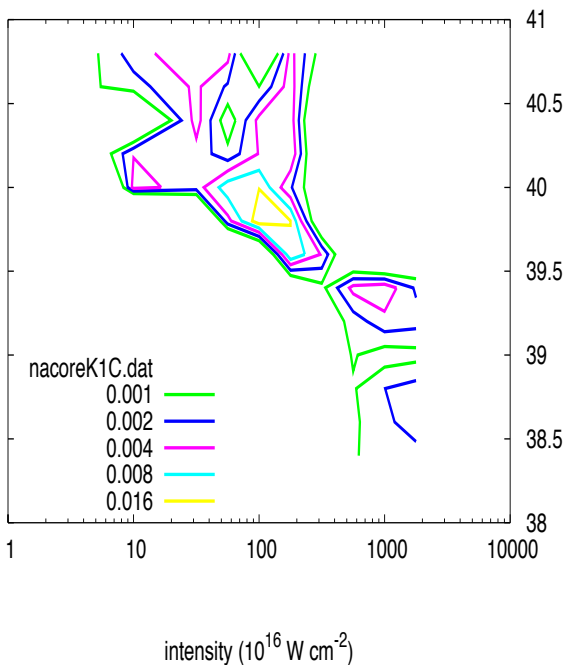
Zn2p Raman Wavepacket Densities



Biggs PNAS **110** 15597 (2013)

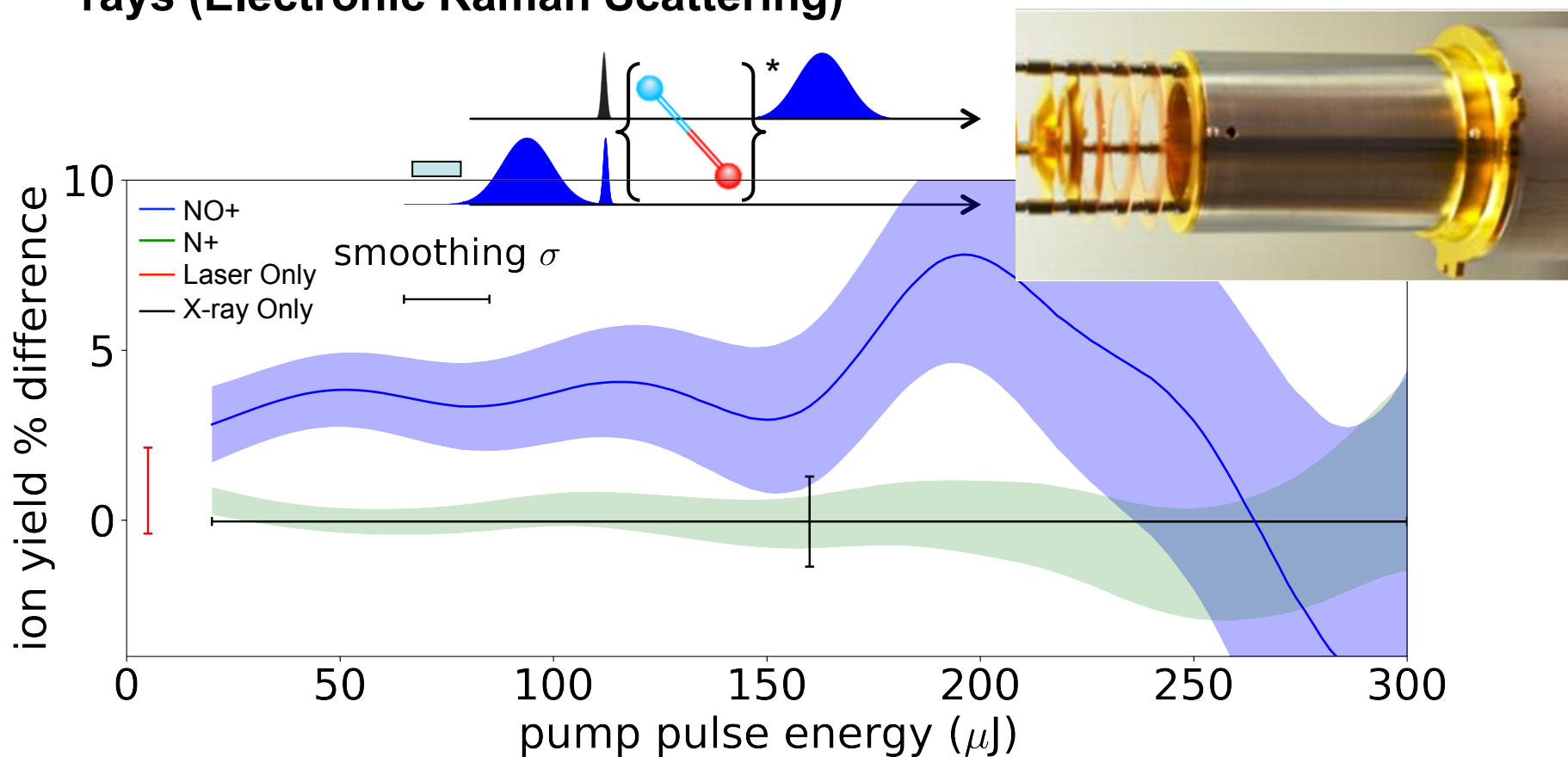


MCTDHF Calculation
(Haxton) arXiv:1609.04175



The Hunt for Impulsive Electronic Raman

- We see an increase of NO^+ ions when x-ray pulse precedes probe laser compared to the opposite.
- Ion Signal Consistent with excited state neutral production by X-rays (Electronic Raman Scattering)



Electron Correlations in Photoionization

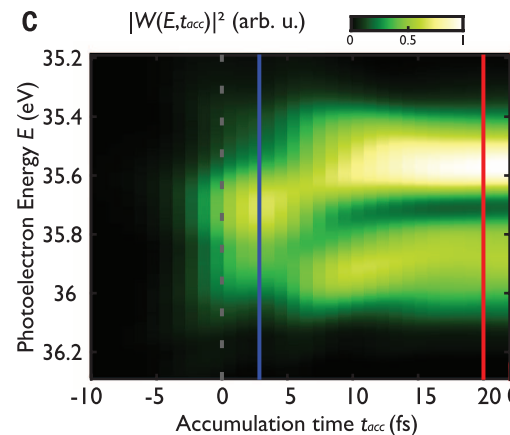
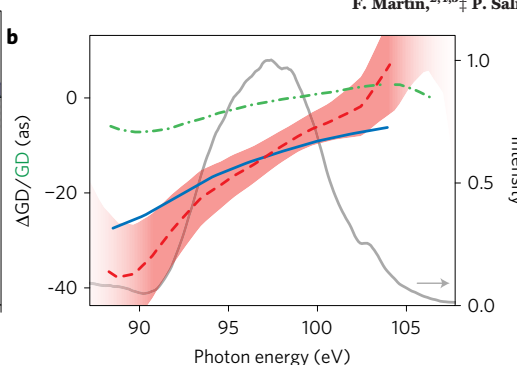
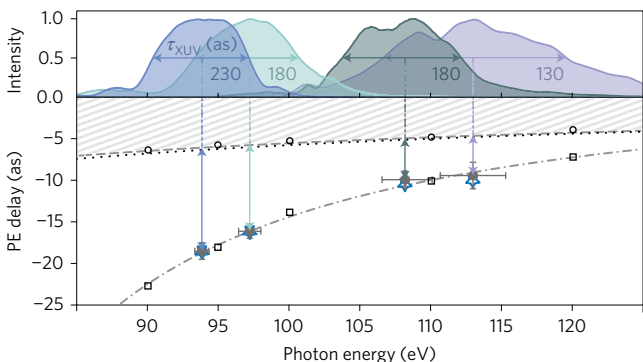
CHEMICAL PHYSICS

Attosecond dynamics through a Fano resonance: Monitoring the birth of a photoelectron

V. Gruson,^{1*} L. Barreau,^{1*} Á. Jiménez-Galan,² F. Risoud,³ J. Caillat,³ A. Maquet,³ B. Carré,¹ F. Lepetit,¹ J.-F. Hergott,¹ T. Ruchon,¹ L. Argenti,^{2,†} R. Taieb,³ F. Martín,^{2,4,5,†} P. Salières^{1,†}

Attosecond correlation dynamics

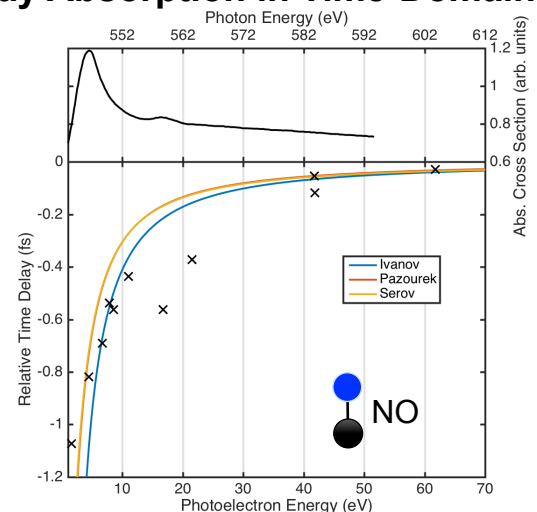
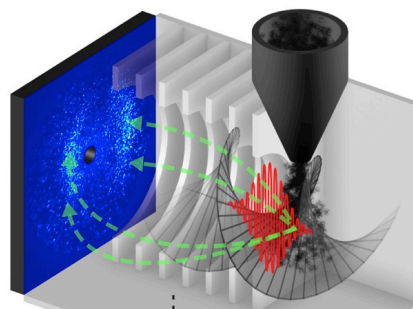
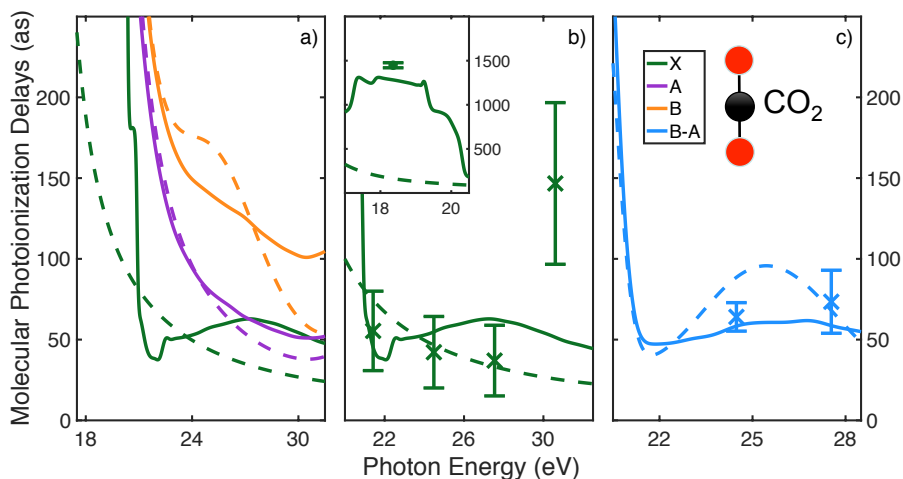
M. Ossiander,^{1,2*} F. Siegrist,^{1,2} V. Shirvanyan,^{1,2} R. Pazourek,³ A. Sommer,¹ T. Latka,^{1,2} A. Guggenmos,^{1,4} S. Nagele,³ J. Feist,³ J. Burgdörfer,³ R. Kienberger,^{1,2} and M. Schultze^{1,4*}



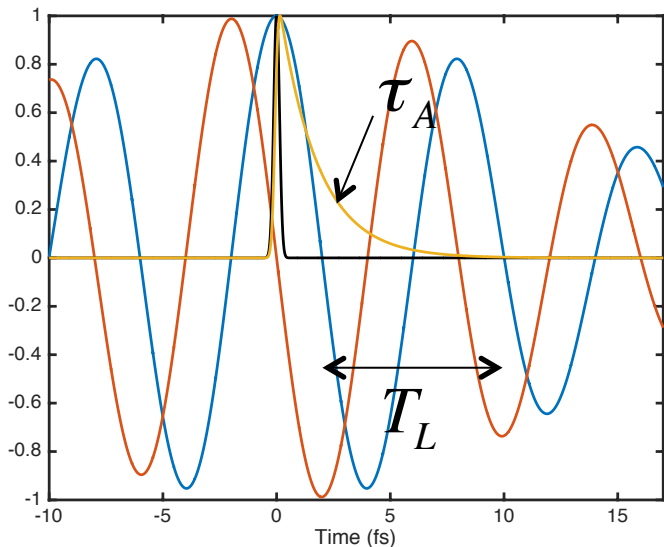
Inter-Channel Coupling in Molecular Systems in the Time Domain

A. Kamalov and J. P. Cryan in prep

Shape Resonance in X-ray Absorption in Time-Domain

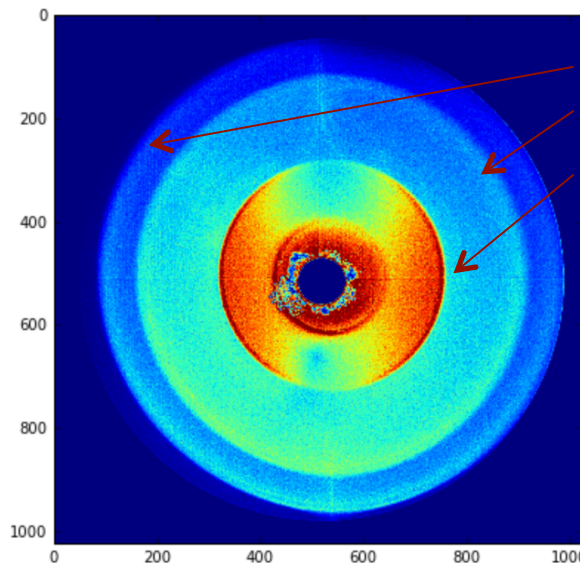


Time-Resolving Core-Hole Decay

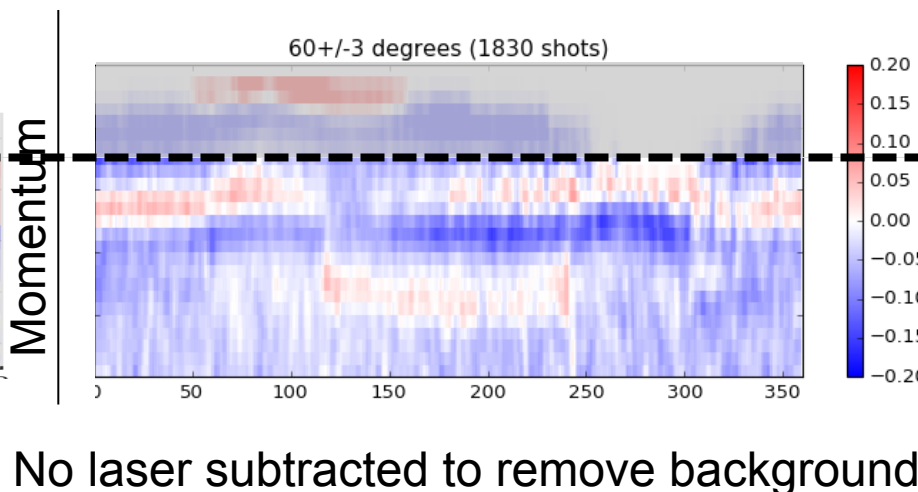
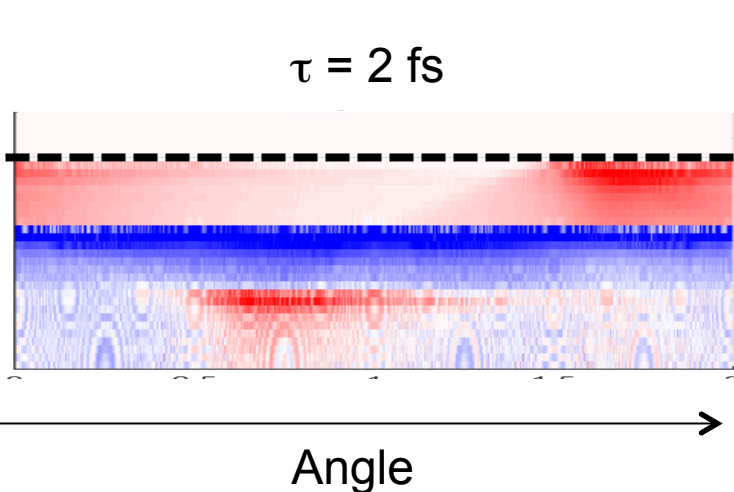


Simulated

$\tau = 2$ fs



Oxygen Resonant Auger
Nitrogen Normal Auger
Nitrogen Photoline



Oxygen
Resonant
Auger
Nitrogen
Normal
Auger

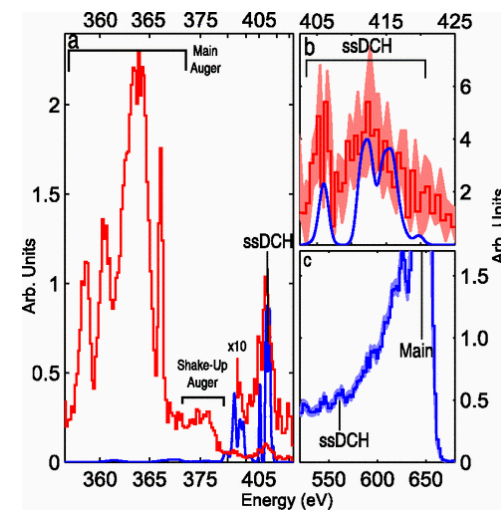
Nonsequential Ionization

- **Early LCLS experiments observed sequential ionization**

PRL 105, 083004 (2010) PHYSICAL REVIEW LETTERS week ending 20 AUGUST 2010

Auger Electron Angular Distribution of Double Core-Hole States in the Molecular Reference Frame

James P. Cryan,^{1,2,*} J. M. Glownia,^{1,3} J. Andreasson,⁴ A. Belkacem,⁵ N. Berrah,⁶ C. I. Blaga,⁷ C. Bostedt,⁸ J. Bozek,⁸ C. Buth,^{1,9} L. F. DiMauro,⁷ L. Fang,⁶ O. Gessner,⁵ M. Guehr,¹ J. Hajdu,⁴ M. P. Hertlein,¹⁰ M. Hoener,^{6,10} O. Kornilov,⁵ J. P. Marangos,¹¹ A. M. March,¹² B. K. McFarland,^{1,3} H. Merdji,^{1,13} V. S. Petrović,² C. Raman,¹⁴ D. Ray,^{12,15} D. Reis,^{1,3} F. Tarantelli,¹⁶ M. Trigo,¹ J. L. White,³ W. White,⁸ L. Young,¹² P. H. Bucksbaum,^{1,2,3} and R. N. Coffee^{1,8}



PHYSICAL REVIEW A 94, 043418 (2016)

Nonsequential two-photon absorption from the K shell in solid zirconium

Shambhu Ghimire,^{1,*} Matthias Fuchs,² Jerry Hastings,³ Sven C. Herrmann,⁴ Yuichi Inubushi,⁵ Jack Pines,⁴ Sharon Schwartz,⁶ Makina Yabashi,⁵ and David A. Reis^{1,7,†}

- **Nonsequential Double Ionization**

$$N_{SI}^{(S)} = \int dt N_{GS}(t) \sigma_1^{(1)} I(t) \propto \tau$$

$$N_{DI}^{(S)} = \int dt N_{SI}(t) \sigma_2^{(1)} I(t)$$

$$\propto \sigma_2^{(1)} N_{SI} \tau \propto \sigma_1^{(1)} \sigma_2^{(1)} \tau^2$$

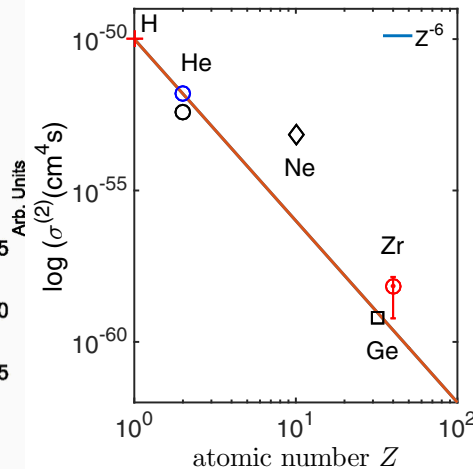
$$N_{DI}^{(NS)} = \int dt N_{GS}(t) \sigma^{(2)} I^2(t) \propto \sigma^{(2)} \tau$$

$$\sigma_1^{(1)} \sigma_2^{(1)} \gg \sigma^{(2)}$$

$$\frac{N_{DI}^{(S)}}{N_{DI}^{(NS)}} = \frac{\sigma_1^{(1)} \sigma_2^{(1)}}{\sigma^{(2)}} \tau$$

Short pulse suppress sequential process

- **Push far below core-hole lifetime**
- **Time-resolve electron emission**

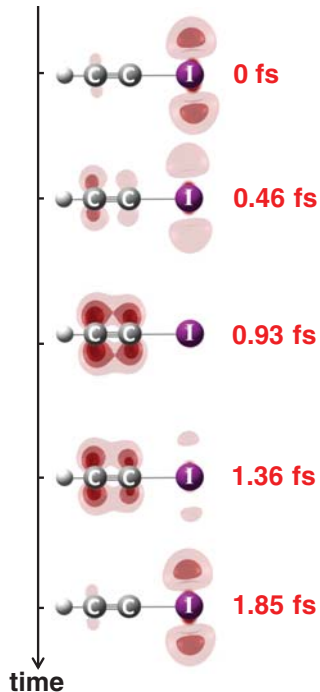


Molecules in Strong-Laser Fields

ATTOSECOND DYNAMICS

Measurement and laser control of attosecond charge migration in ionized iodoacetylene

P. M. Kraus,¹ B. Mignolet,^{2,3} D. Baykusheva,¹ A. Rupenyan,¹ L. Horny,¹ E. F. Penka,⁴ G. Grassi,¹ O. I. Tolstikhin,⁵ J. Schneider,¹ F. Jensen,⁶ L. B. Madsen,⁷ A. D. Bandrauk,⁴ F. Remacle,² H. J. Wörner^{1*}

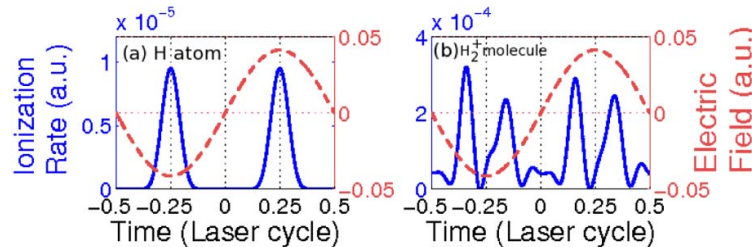


- Another route to studying ultrafast charge motion



Laser-driven nonadiabatic electron dynamics in molecules

M. R. MILLER, Y. XIA, A. BECKER,* AND A. JARÓN-BECKER



OPEN ACCESS

IOP Publishing

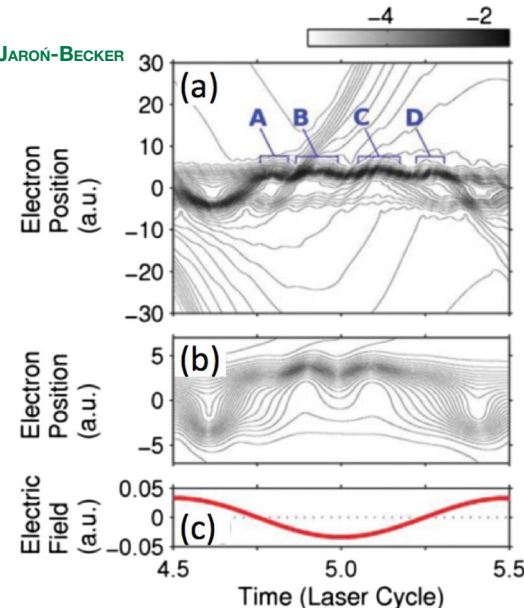
J. Phys. B: At. Mol. Opt. Phys. 50 (2017) 125601 (18pp)

Journal of Physics B: Atomic, Molecular and Optical Physics

<https://doi.org/10.1088/1361-6455/aa7098>

Enhanced ionisation of polyatomic molecules in intense laser pulses is due to energy upshift and field coupling of multiple orbitals

Sonia Erattupuzha¹, Cody L Covington², Arthur Russakoff², Erik Lötstedt³, Seyedreza Larimian¹, Václav Hanus¹, Sergiy Bubín⁴, Markus Koch⁵, Stefanie Gräfe⁶, Andrius Baltuška¹, Xinhua Xie (谢新华)¹, Kaoru Yamanouchi³, Kálmán Varga² and Markus Kitzler^{1,7}



- Probing on electron motion in strong-fields

Summary

- **Sub-femtosecond X-ray pulses provide a unique opportunity to study the motion of electrons on the atomic length scale.**
- **This is critical for understanding the role of electronic coherence in photochemical reactions**
- **Such technology would also allow for time-resolving electron-electron interactions (or correlations)**

- **Requirements:**
 - **10-200 μJ pulse energies**
 - **Sub-femtosecond pulse duration**
 - Within factor 3 of transform limit would be most useful.
 - **Soft X-ray ($< 1\text{keV}$)**
 - **Two-color pulses,**
 - 100's eV separations between colors.
 - Tunable delay (nice to scan through zero)
 - **1 μm^2 focus**
 - **Synchronized NIR laser field**