Ultrafast X-rays: What are they good for?

Phil Bucksbaum

Siegman School 2016

Stanford | PULSE INSTITUTE

SLAC NATIONAL ACCELERATOR LABORATORY

Atomic, Molecular, and Optical Science (AMO)

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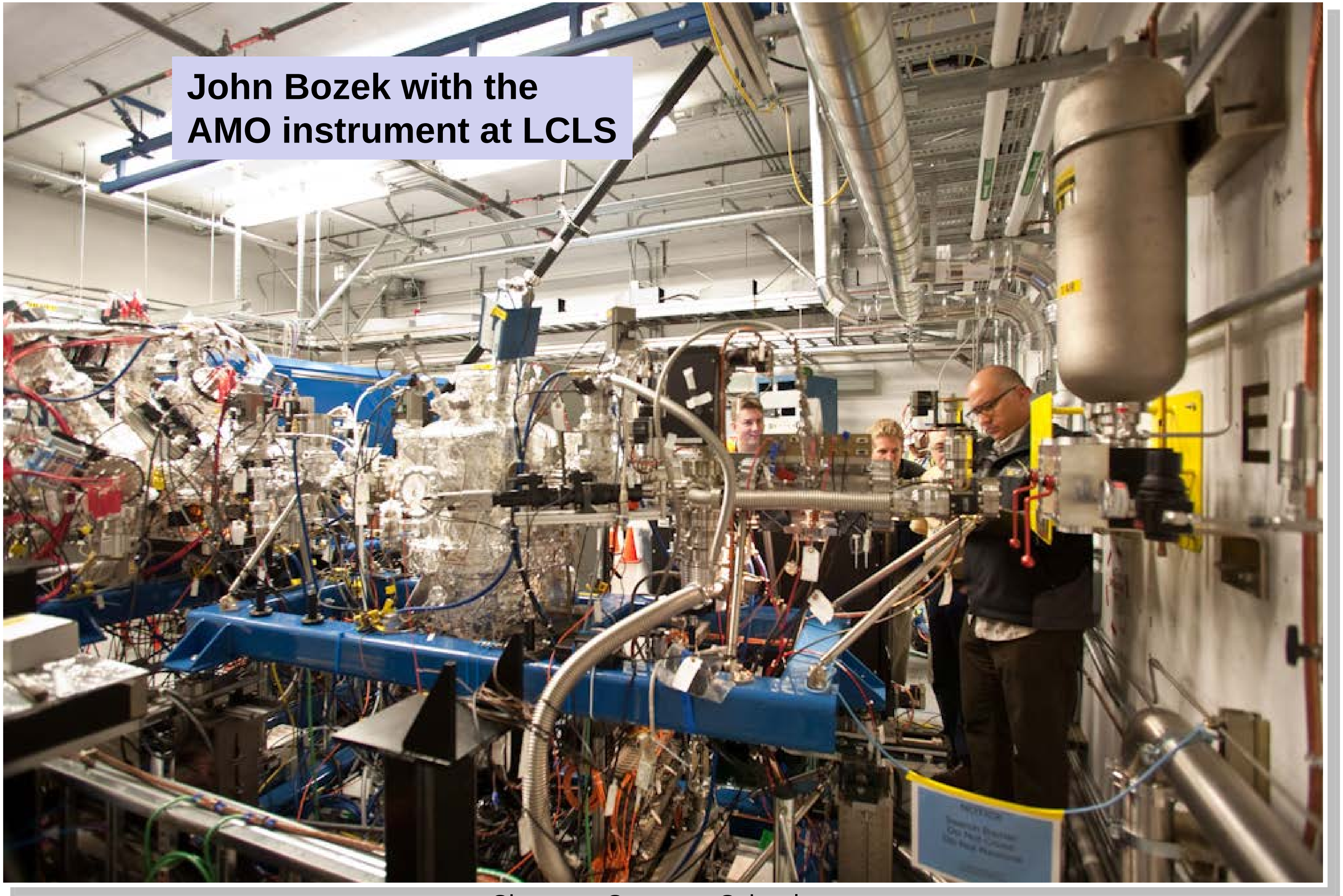
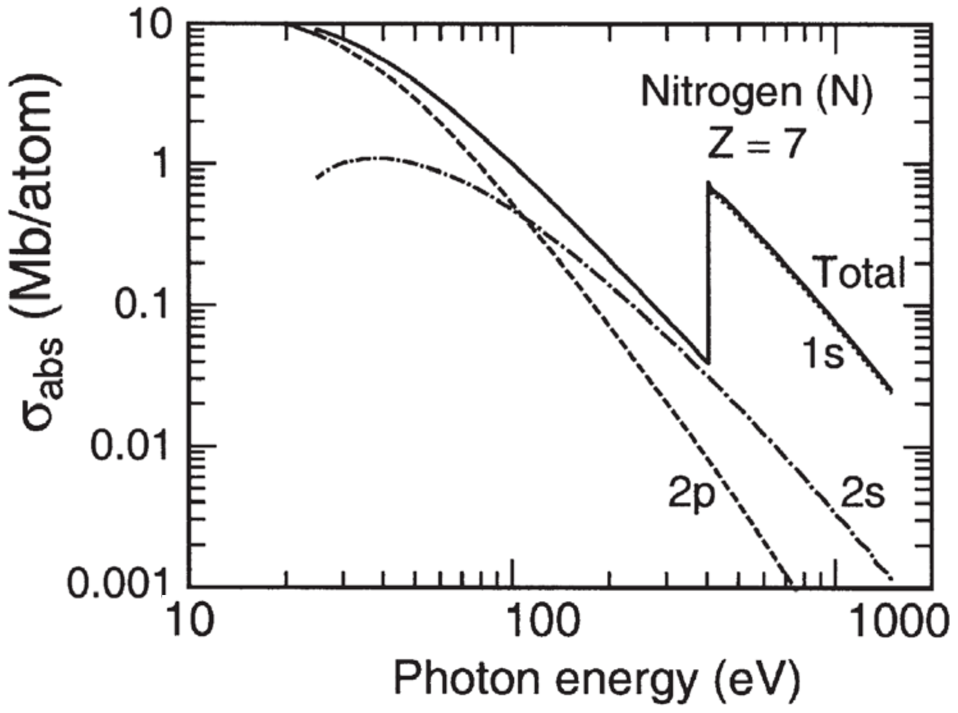
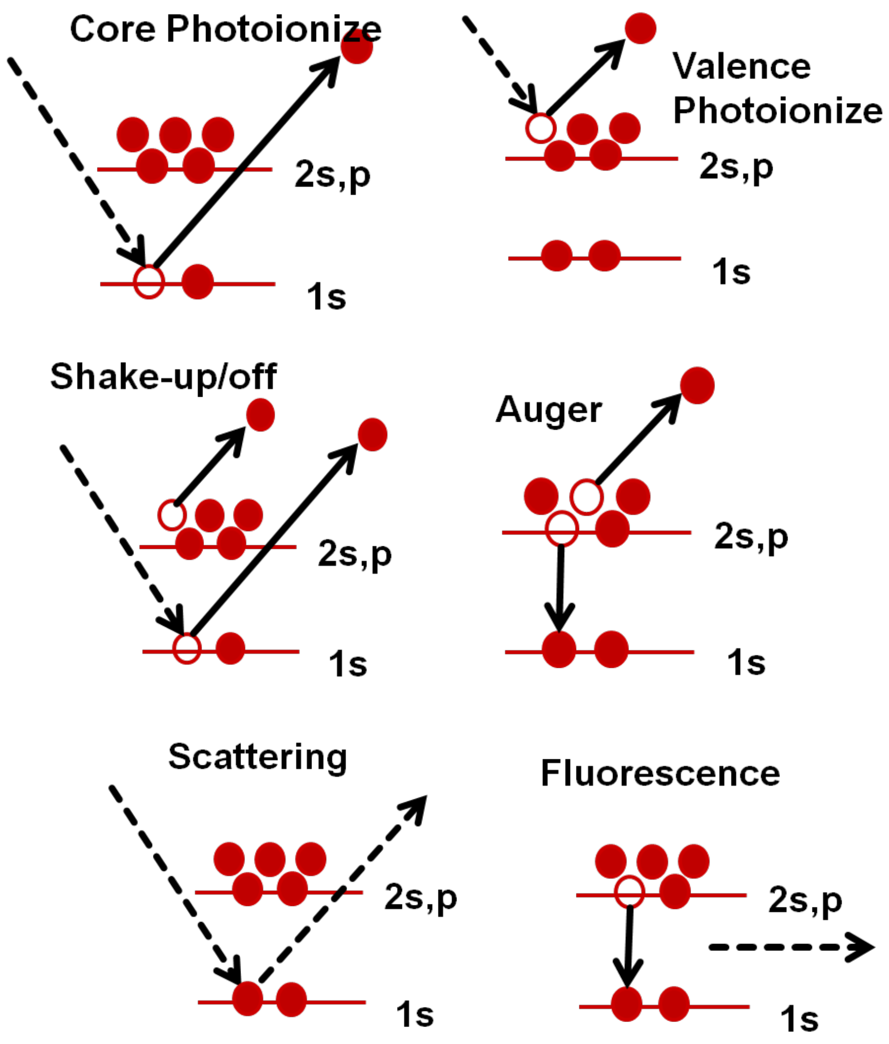
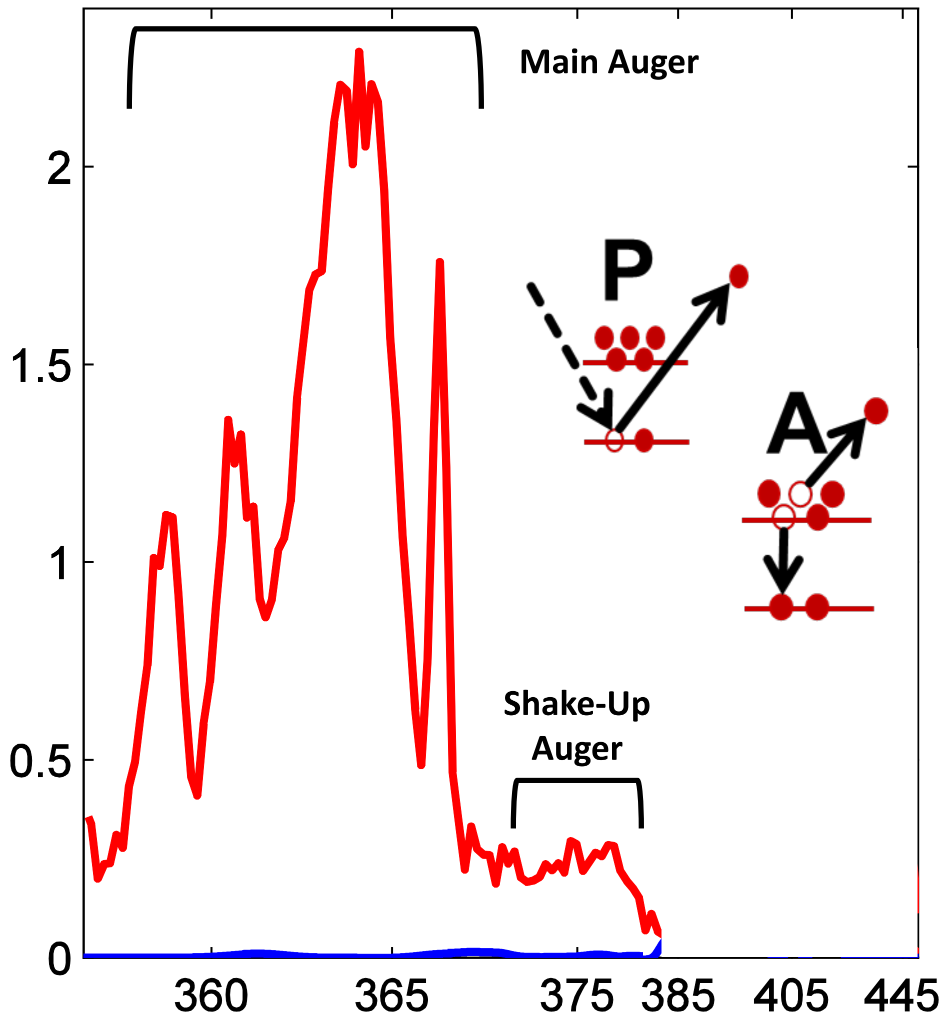


X-ray interactions with atoms



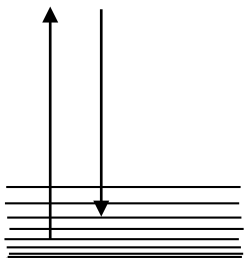


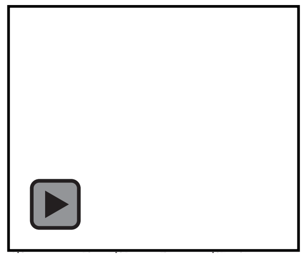
Auger spectrum from N_2

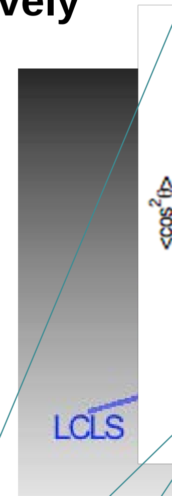


Ultrafast measurements: Catching Molecules in transient states.

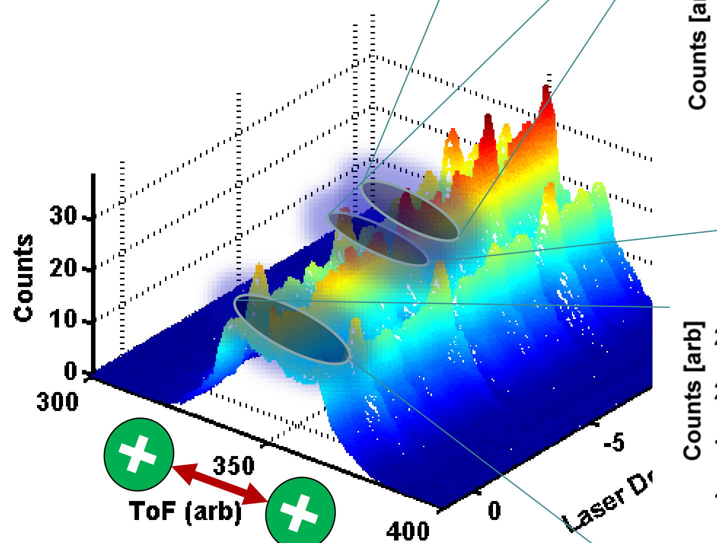
- **800 nm Ti:Sapphire laser is used to impulsively align molecular nitrogen along the laser polarization direction**

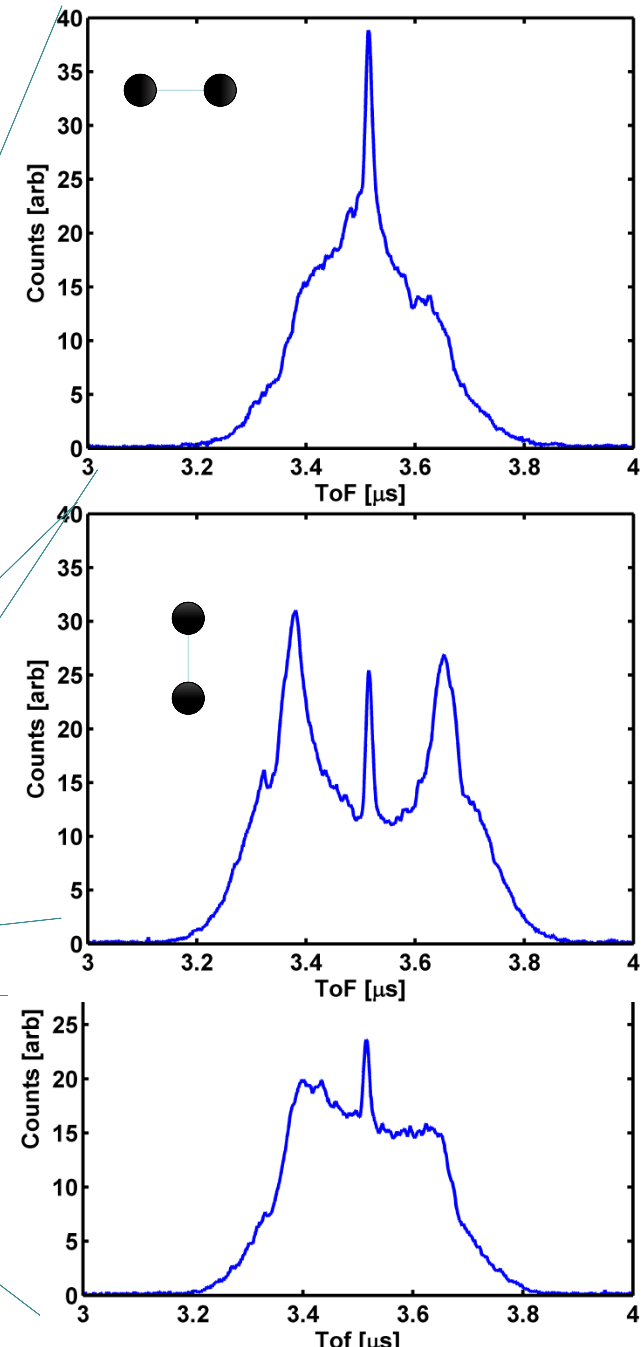






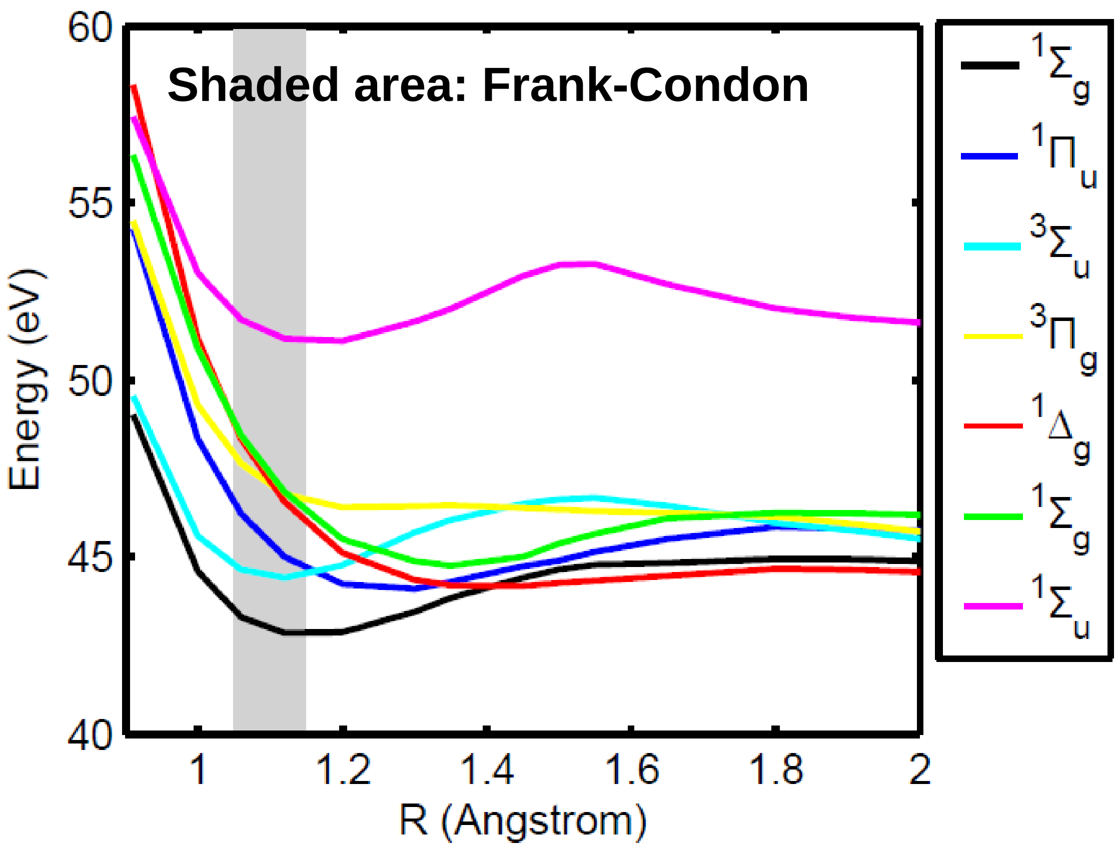
- **Dissociation following ionization by 1100 eV x-rays**

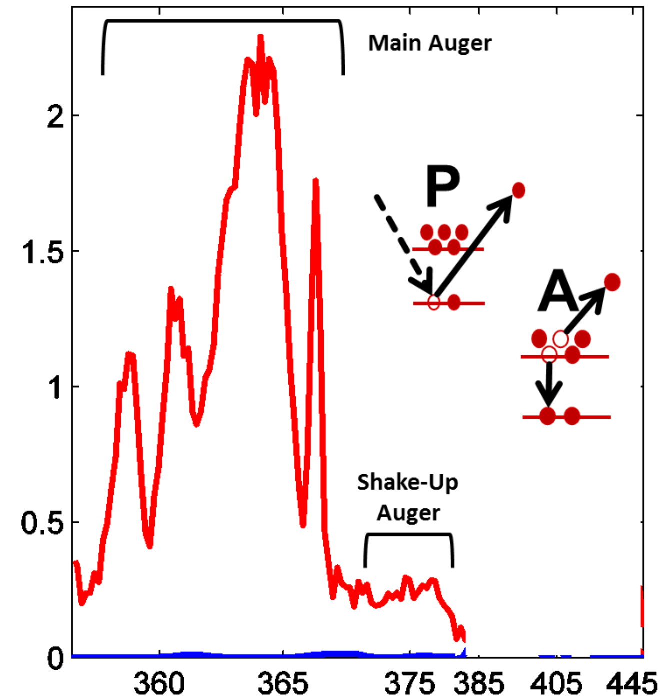




Glownia, J. M., J. Cryan, et al. (Opt. Express 18, 17620 (2010).

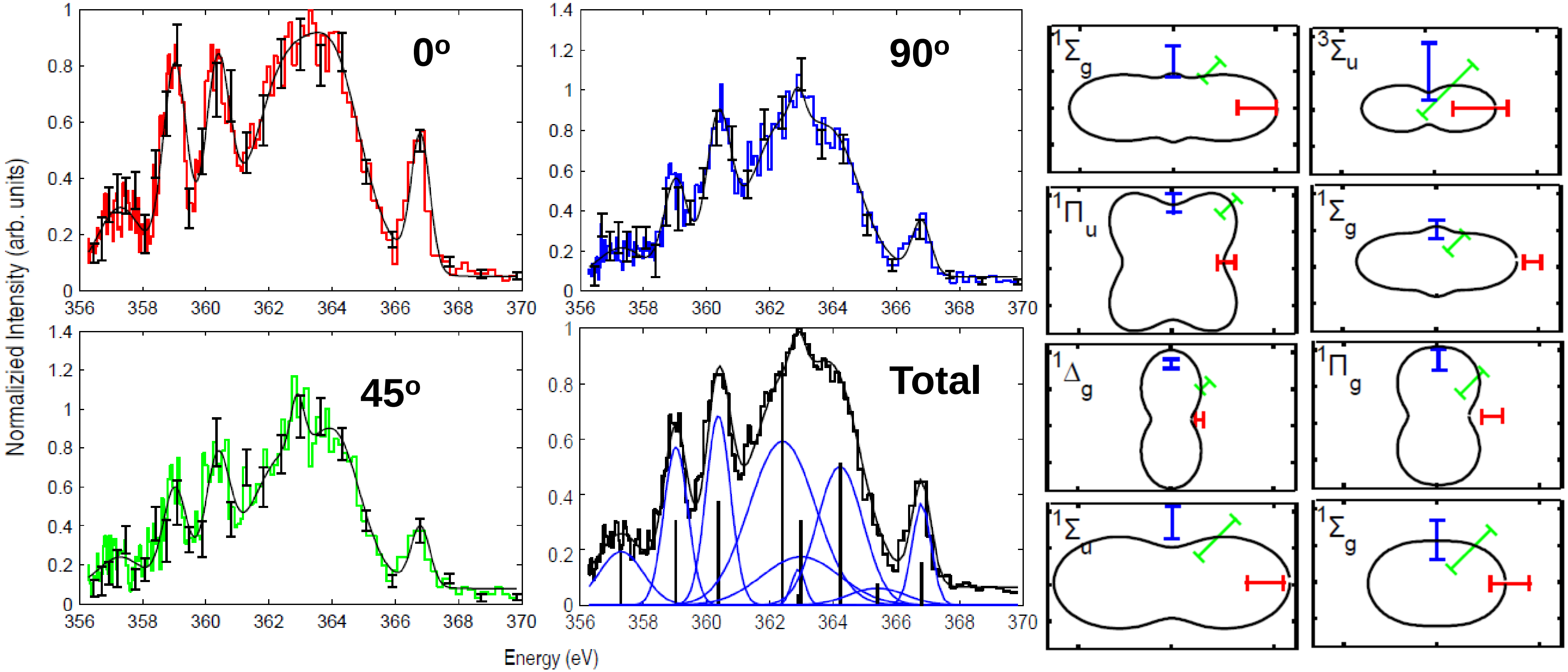
Transient state studies: N_2^{++} Potential Energy Surfaces





R. W. Wetmore and R. K. Boyd, J. Phys. Chem. 90, 5540 (1986).

Auger electron energies observed in the molecular frame from $N_2 \rightarrow N_2^+ \rightarrow N_2^{2+}$ at 1.1keV



(Cryan et al, J. Phys. B 45 055601 (2012))

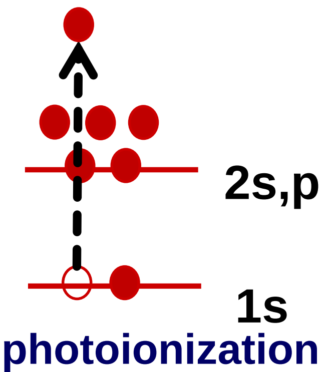
Strong fields: 1-photon, 1-electron ionization

consider a 1-photon K-shell transition:

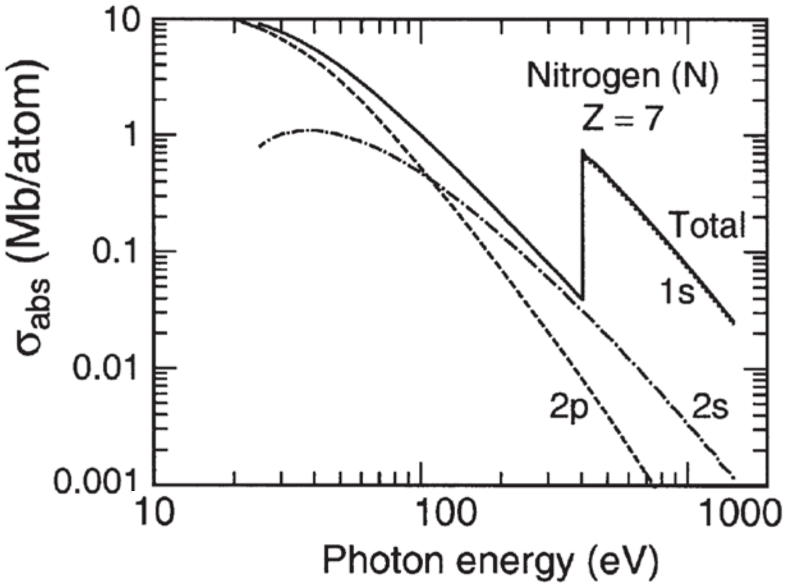
$\sigma_K \approx 10^{-18}$ **cm**^{2}

$\Gamma_K = \sigma_K F_{lcls} \approx 10^{15}$ **s**$^{-1}$ **(*saturated*)**

$t_K = 1/\Gamma_K = 1$ **fs**



- **rapid enough to ionize more than one electron.**
- **fast enough to compete with atomic relaxation.**



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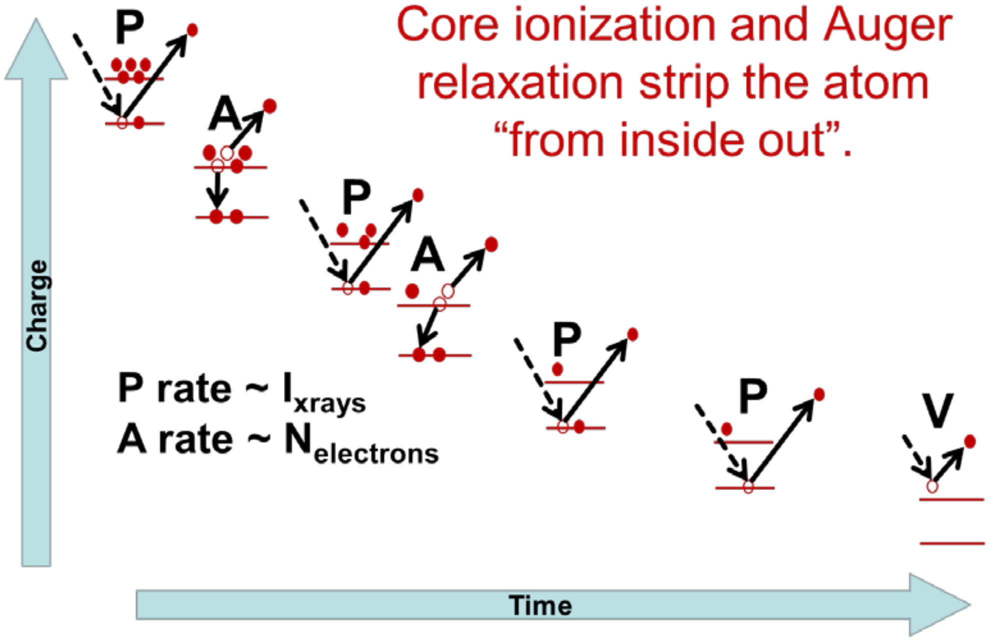
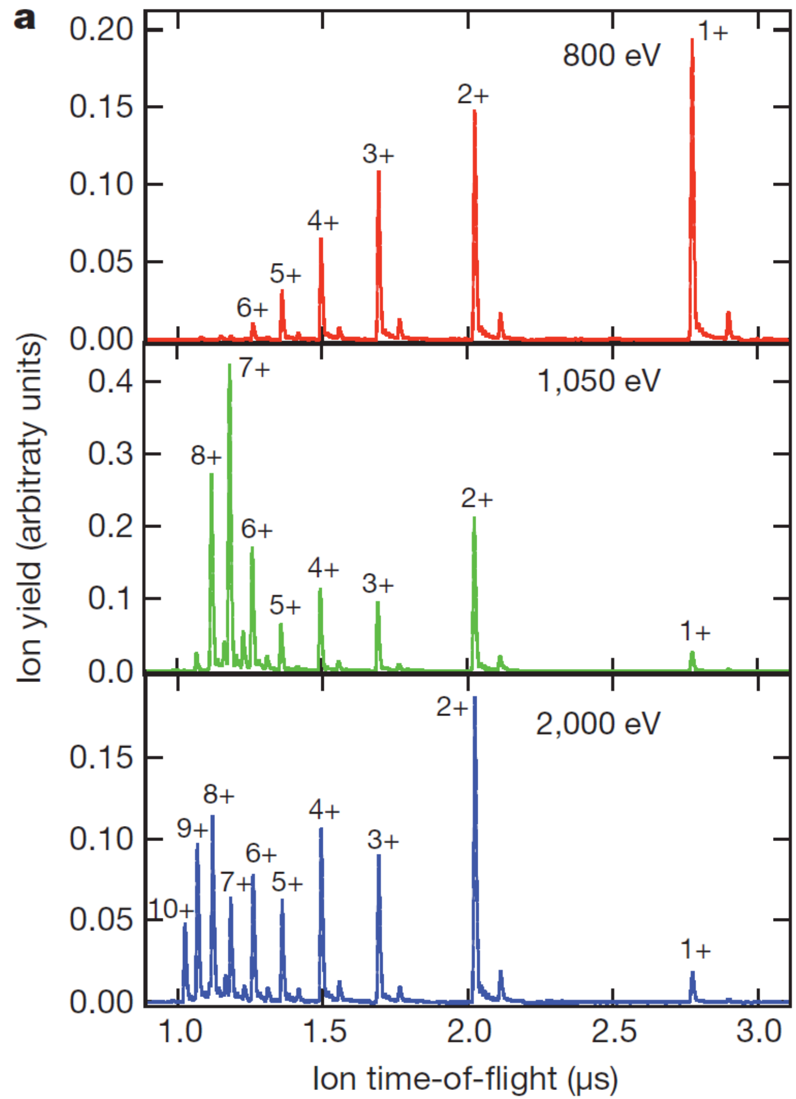
Ne^{10+} at the focus:

Core ionization and Auger relaxation strip the atom “from inside out”.



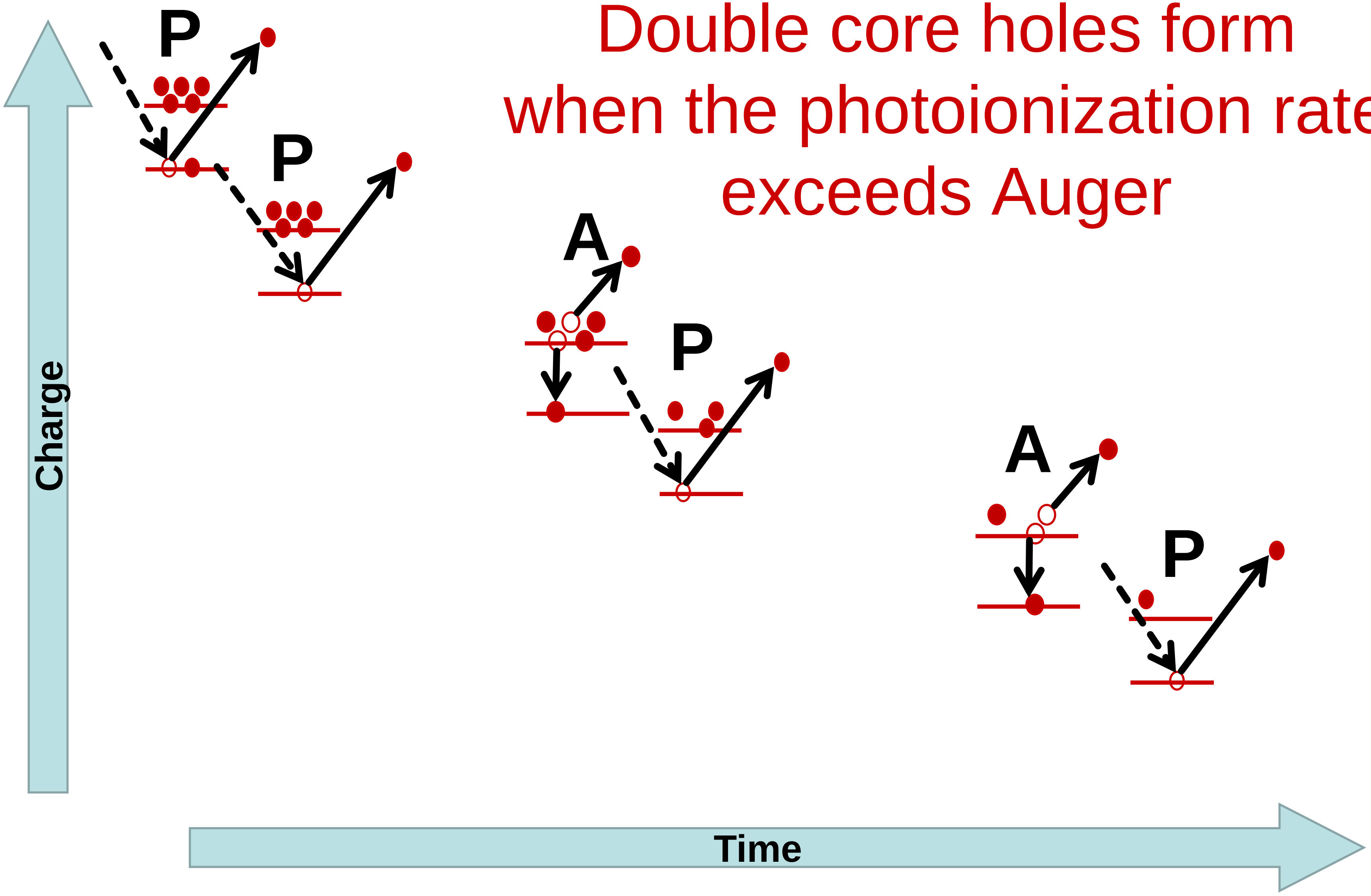
P rate ~ I_{xrays}
A rate ~ $N_{electrons}$



Young, et al., Nature 466, 56 (2010)

Strong and Ultrafast: Hollow atoms

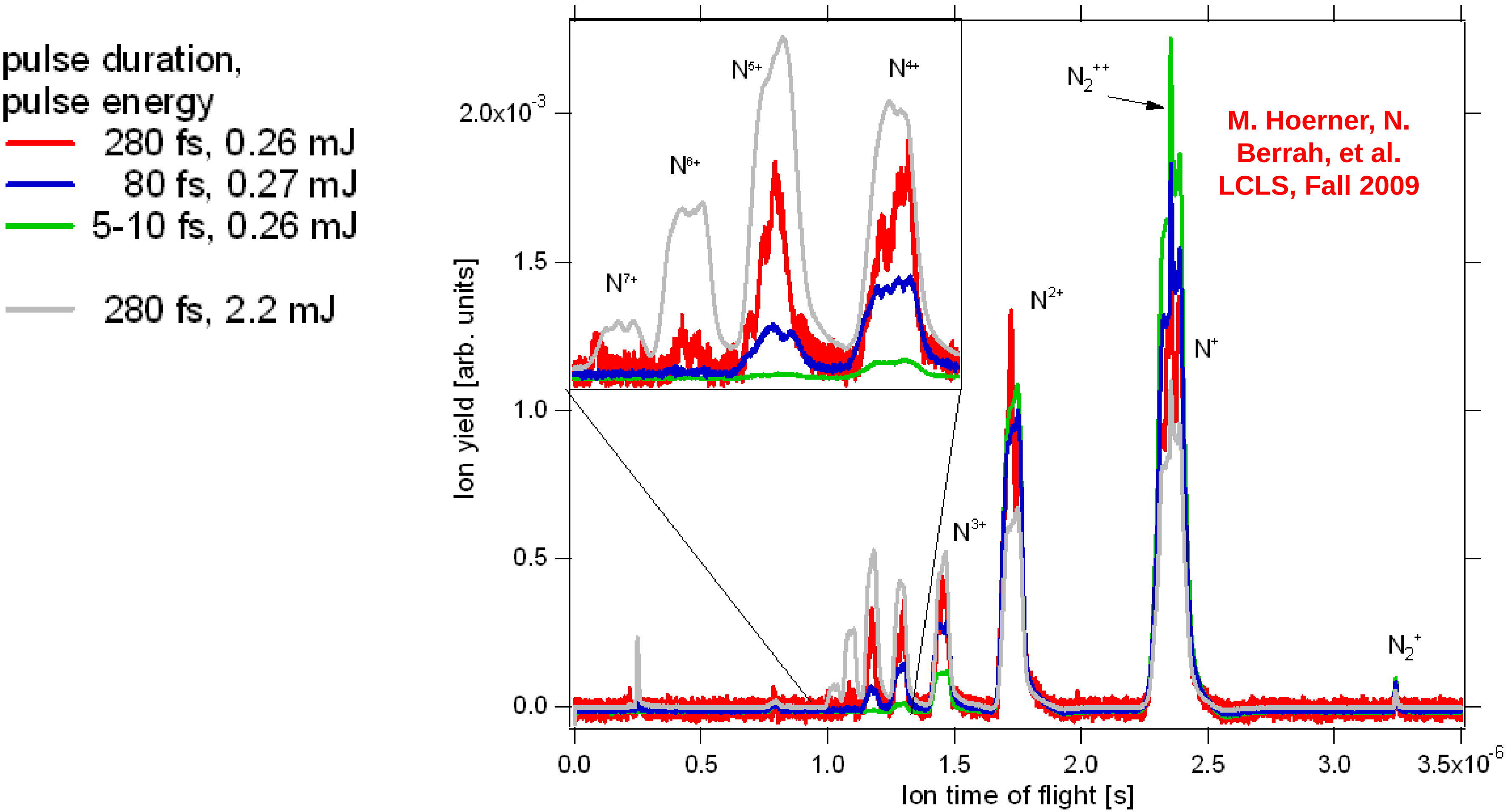
Double core holes form when the photoionization rate exceeds Auger



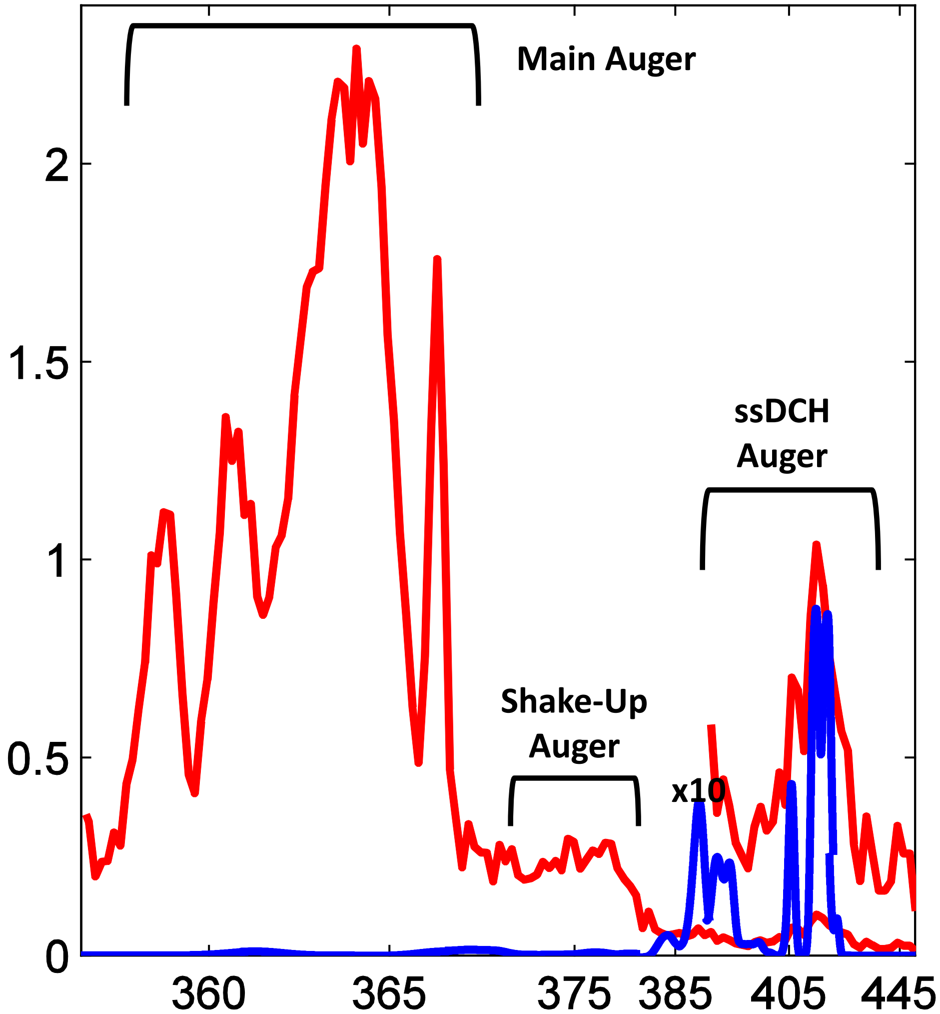
Hollow atom formation at LCLS

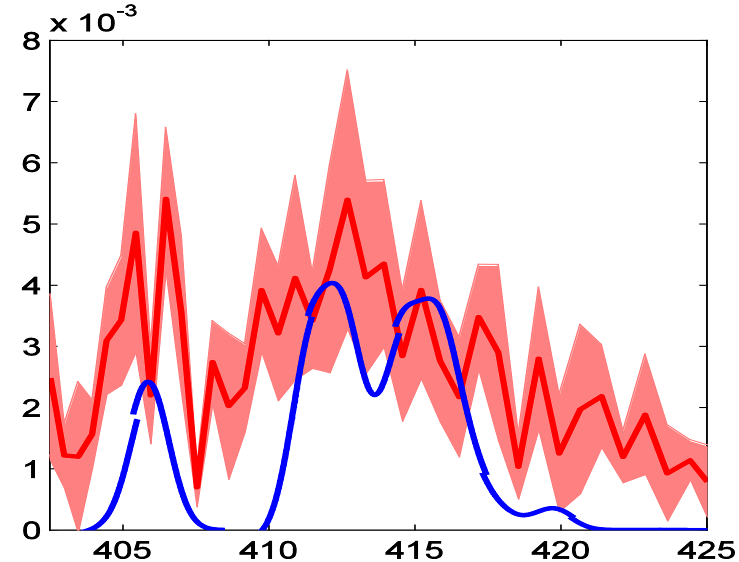
Hoener, M., L. Fang, et al. <u>Phys. Rev. Lett. 104(25): 253002</u> (2010).

Frustrated ionization in N2



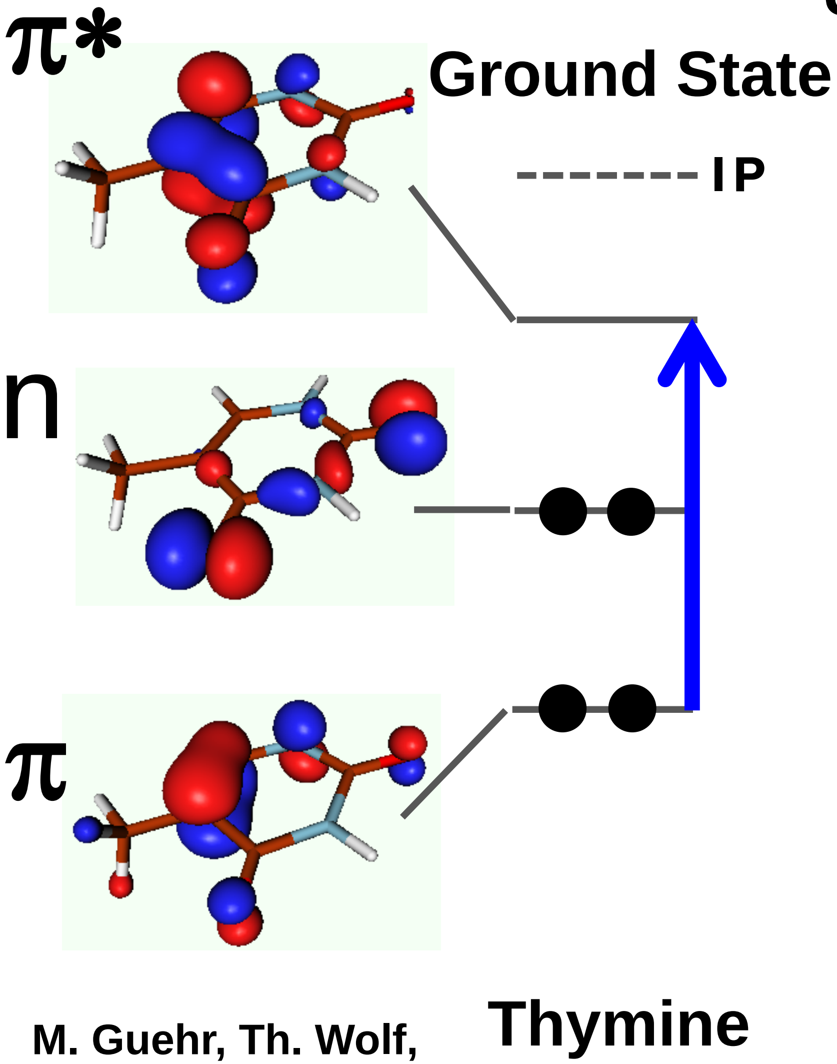
High Energy Auger Spectrum of N_2 from LCLS shows clearer evidence for double core hole formation

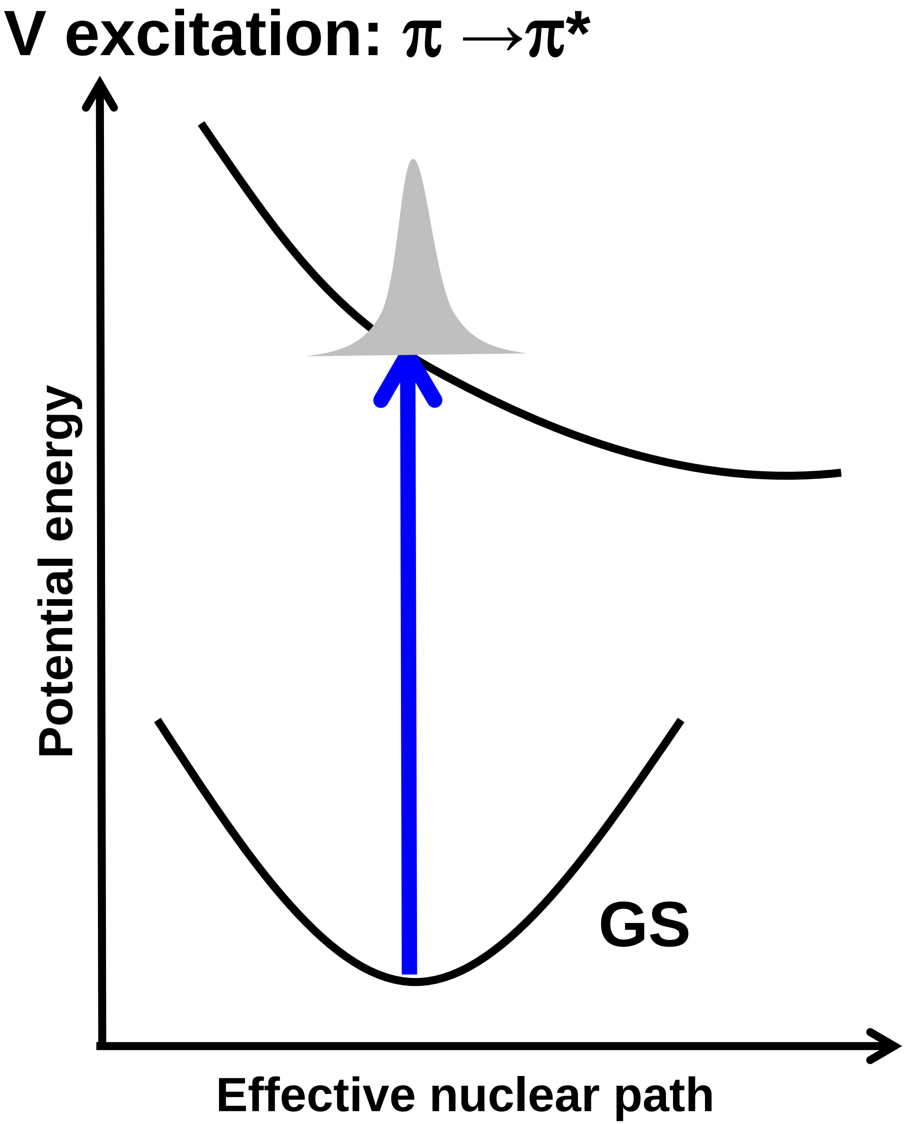




Cryan PRL 105, 083004 (2010)

Ultrafast electron dynamics: Nucleobase photoprotection





M. Guehr, Th. Wolf, PULSE/Potsdam

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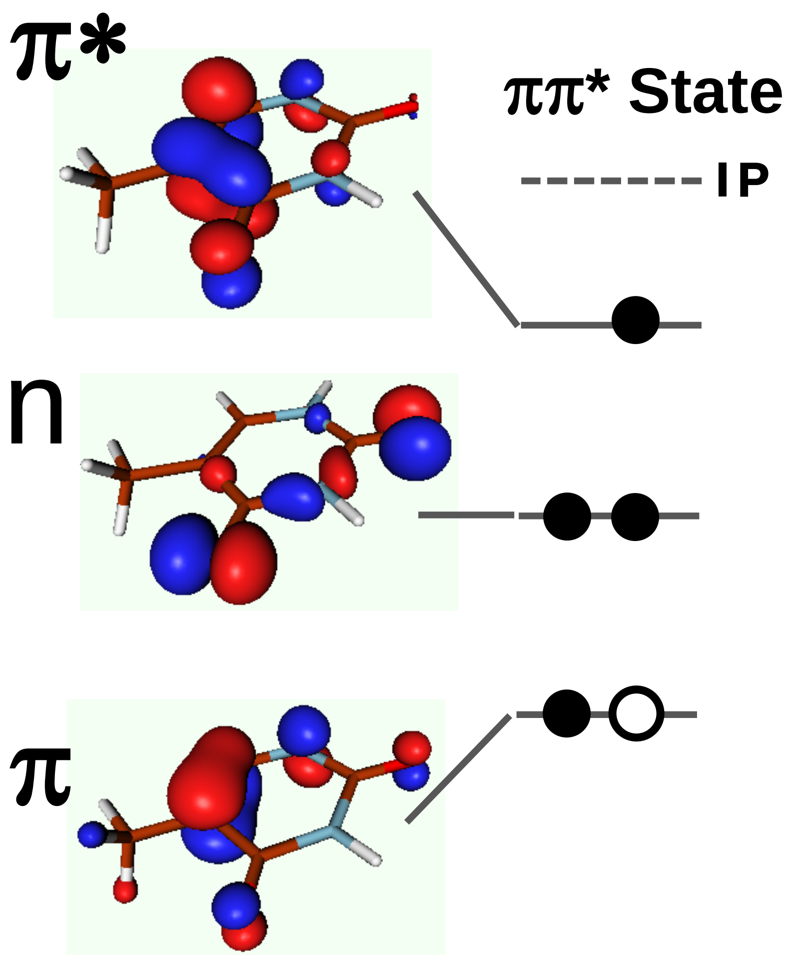
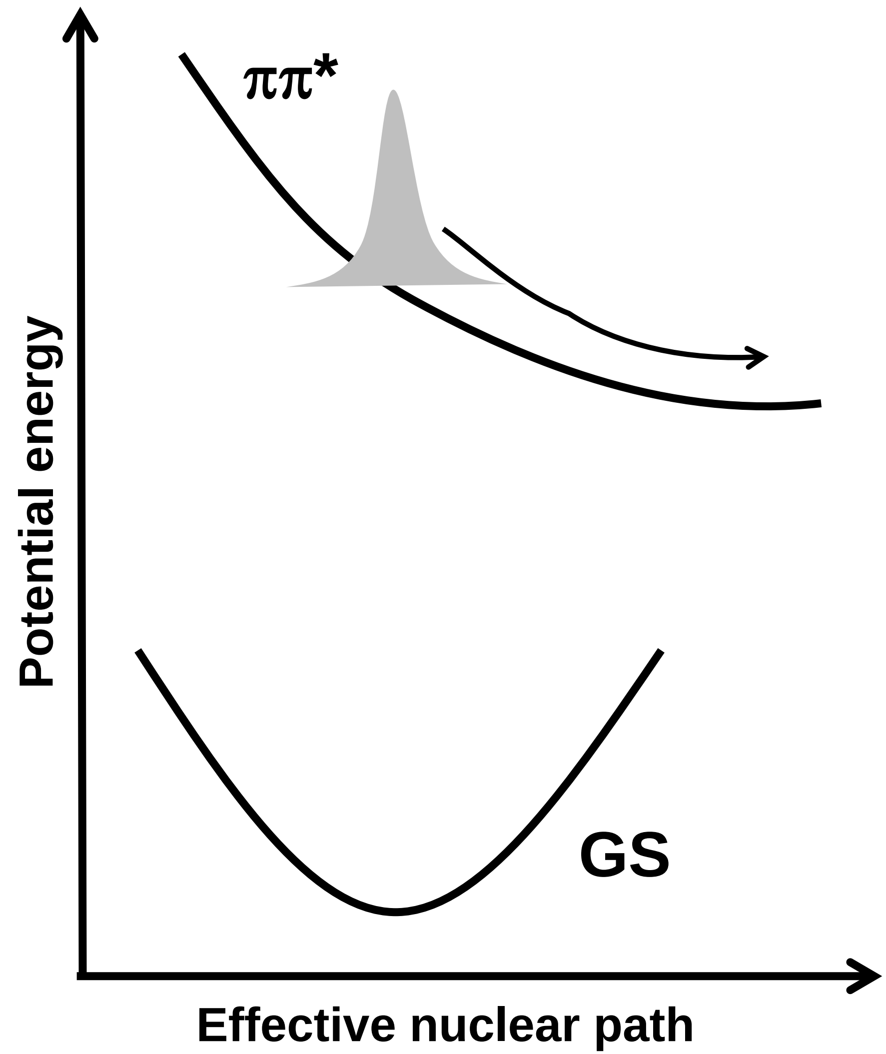
Ultrafast electron dynamics: Nucleobase photoprotection

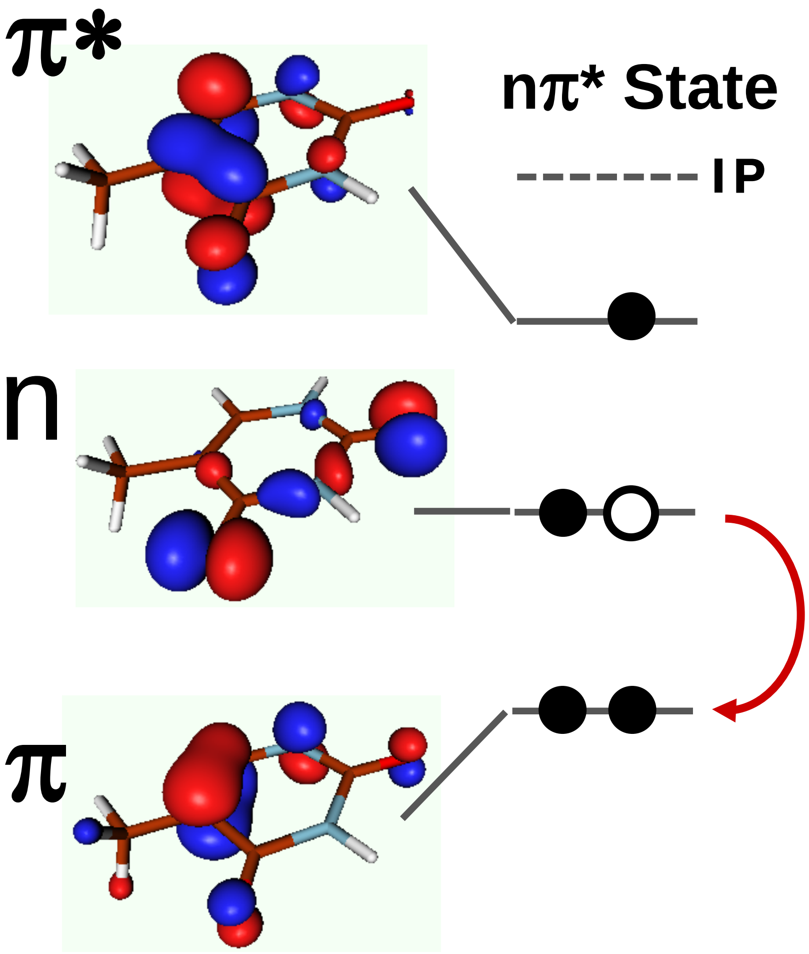


Thymine

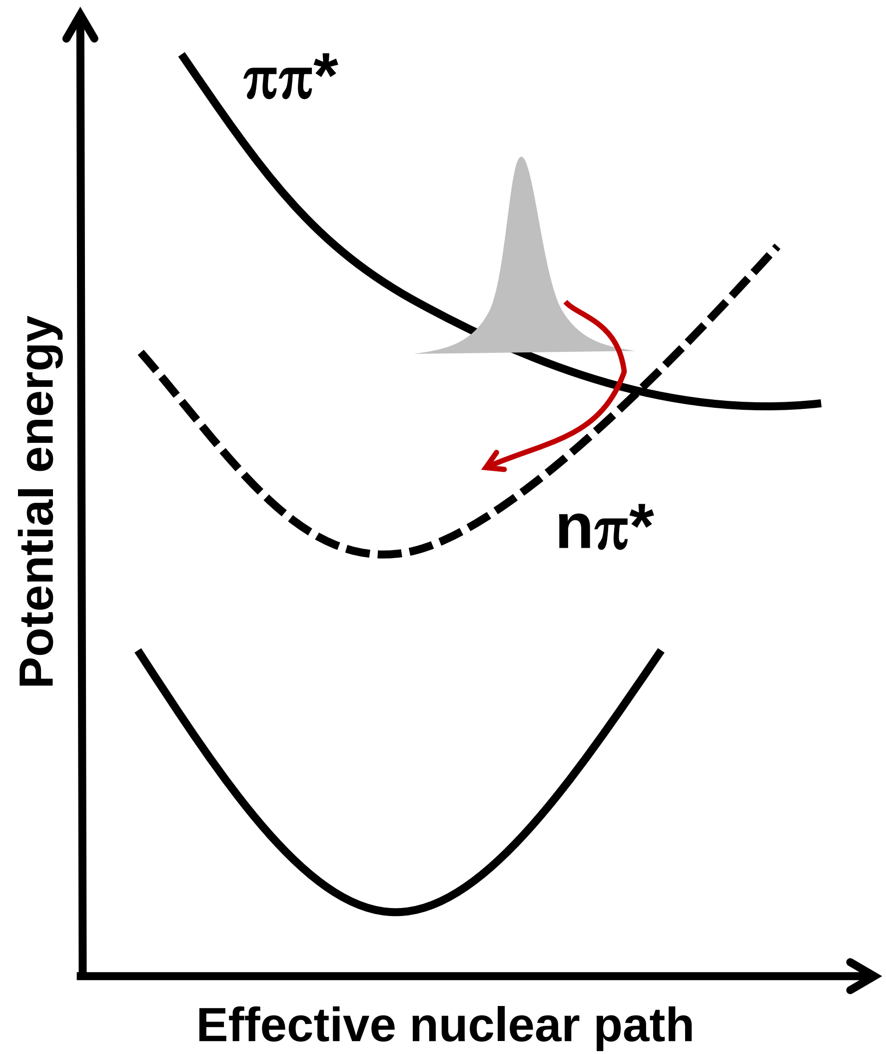
UV excitation: π →π*



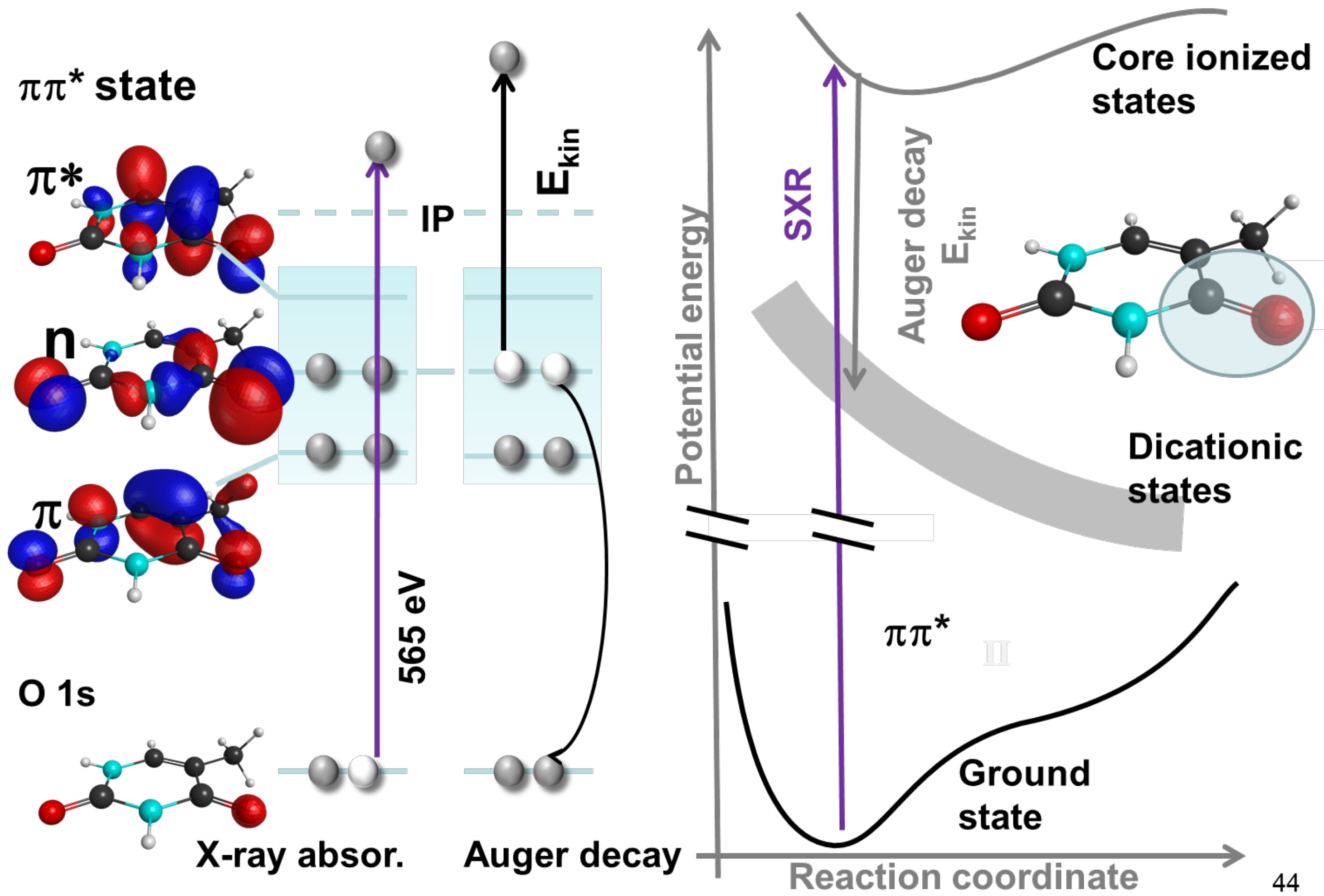
Non-Born-Oppenheimer dynamics



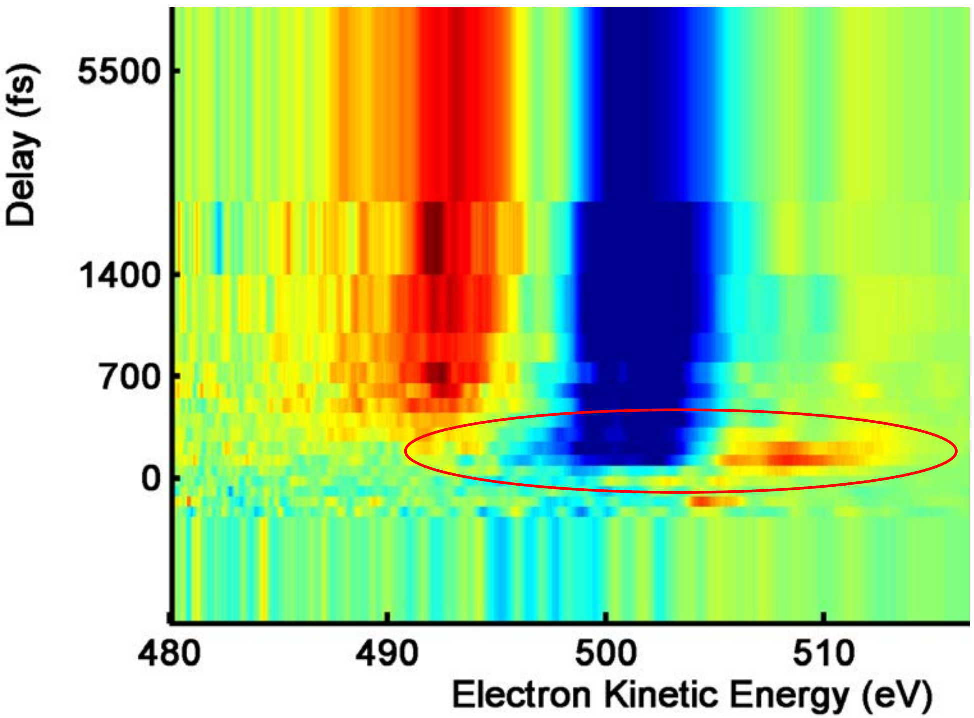
Thymine



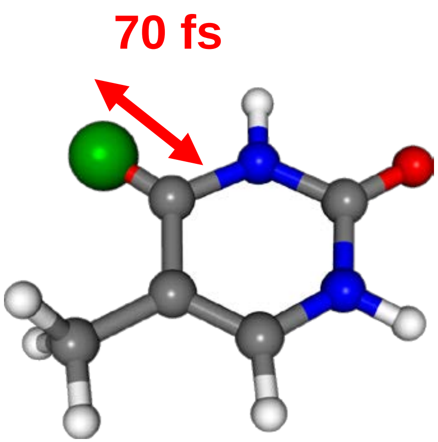
Auger energy is sensitive to valence charge near the oxygen atom.



Localized structural evolution: Time-resolved Auger Electron Spectroscopy

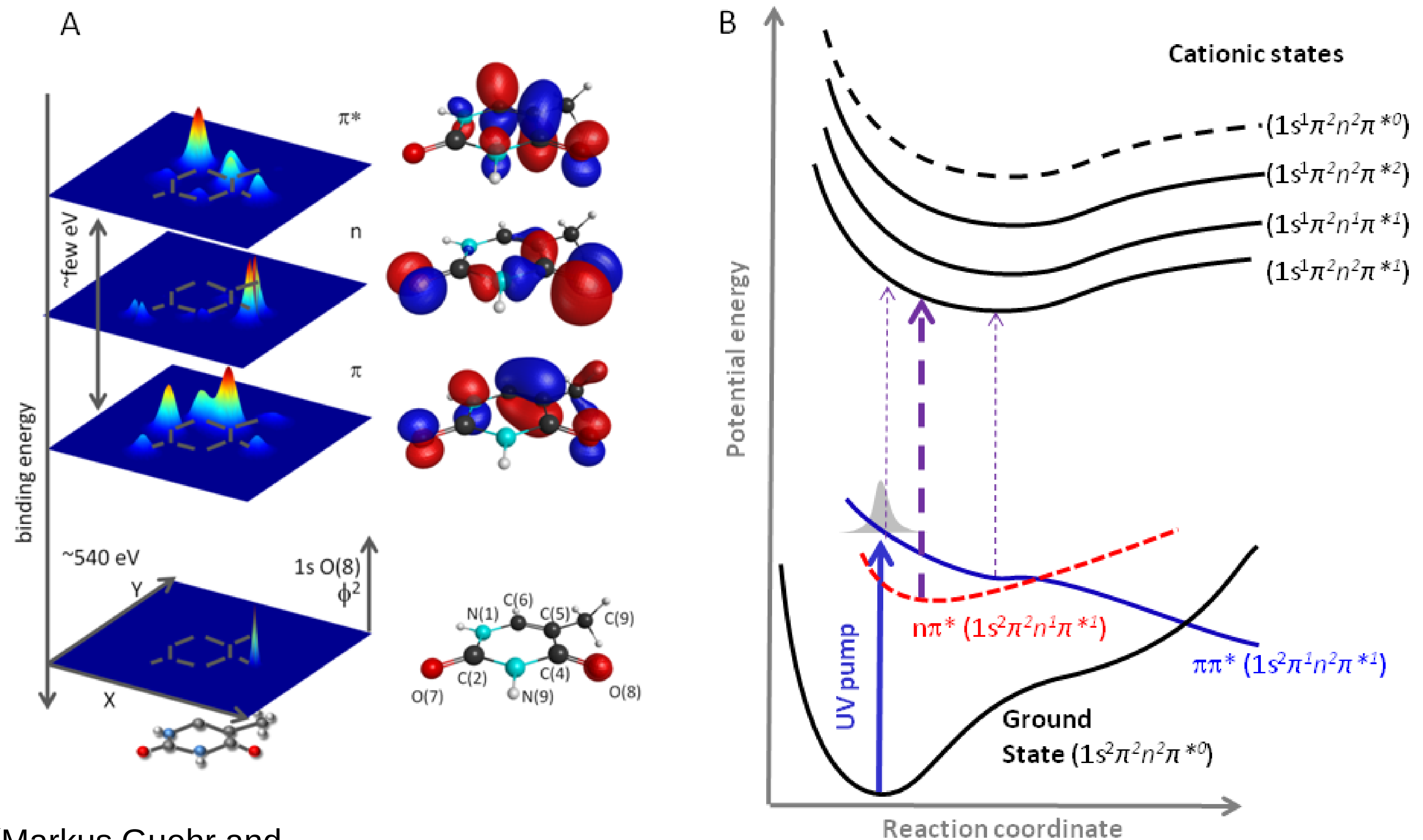


Geometry change: 0.15 Å
Spectral change: several eV



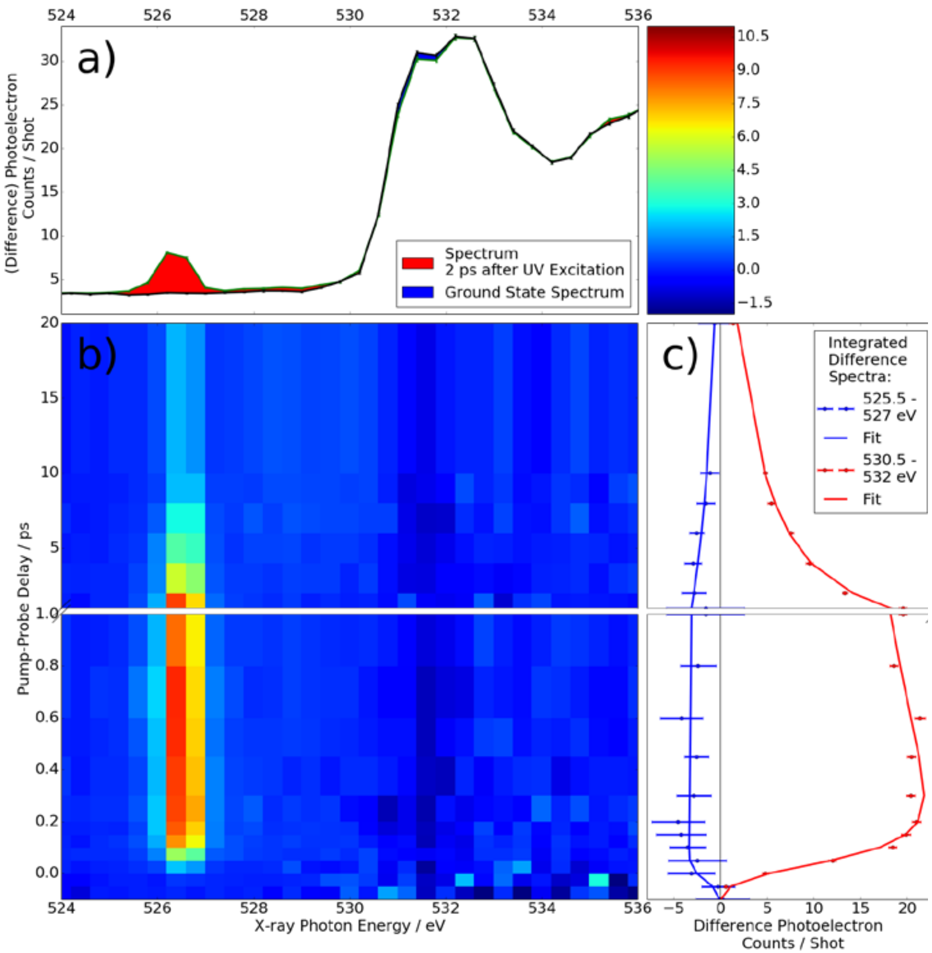
McFarland et al. *Nature Commun.* 2014, *5*, 4235

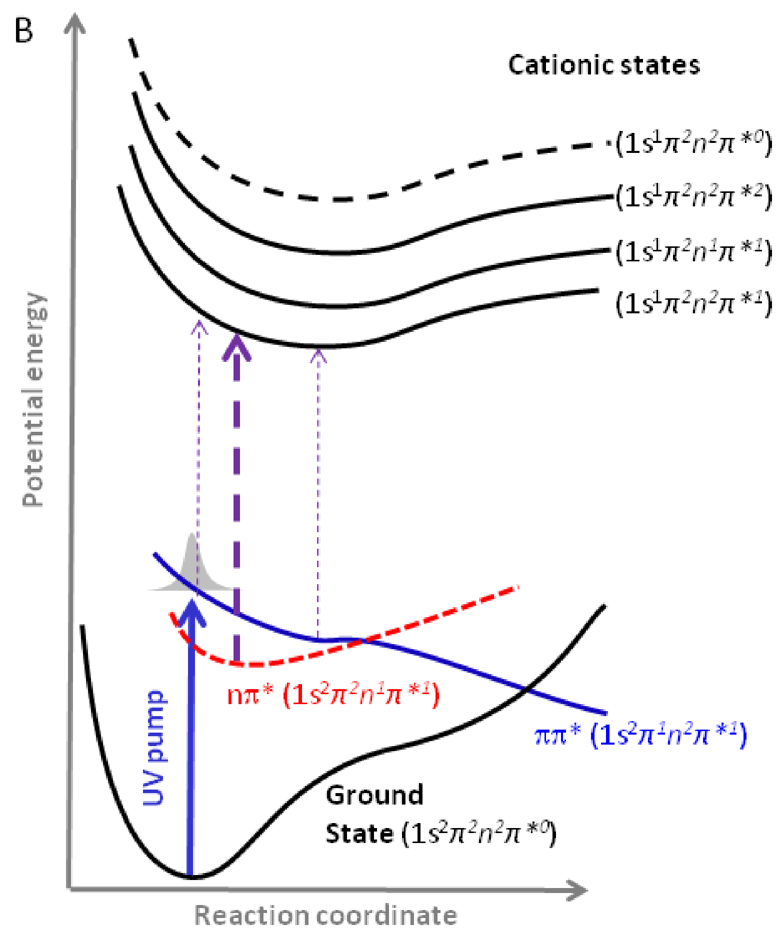
Probing ultrafast $\pi\pi^*$-$n\pi^*$ transitions via oxygen K-edge resonant absorption:



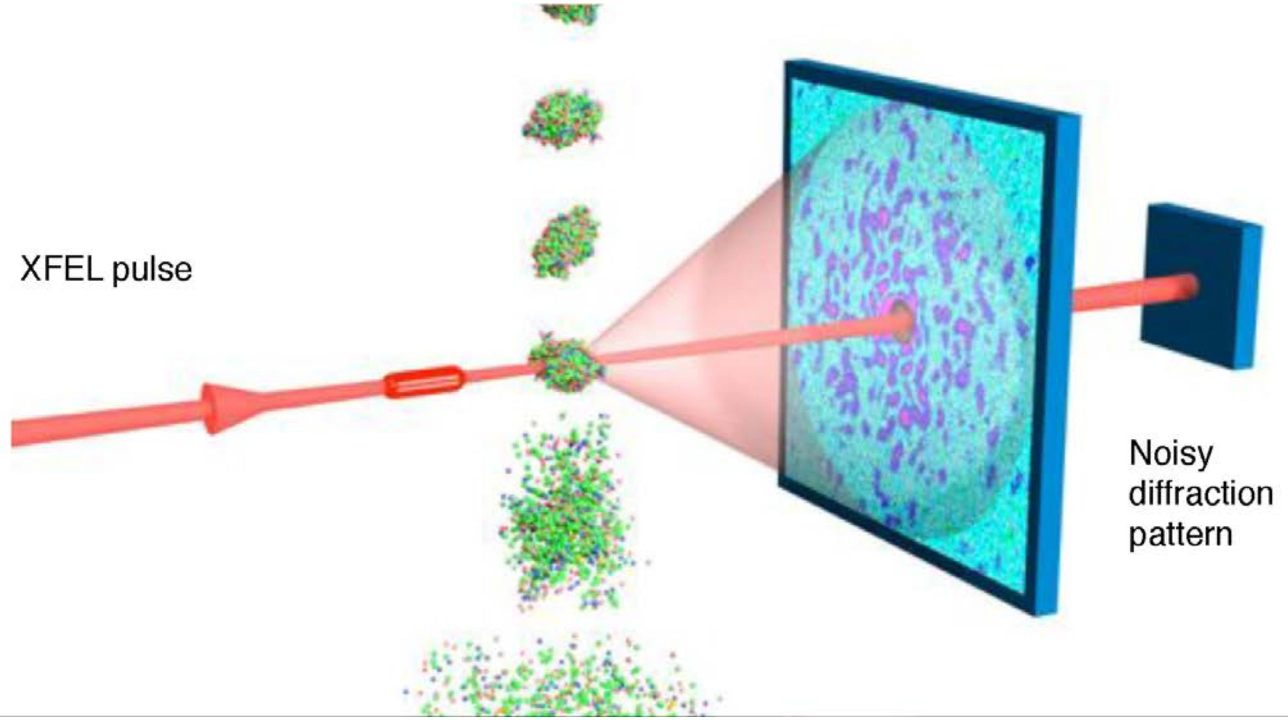
(Markus Guehr and Thomas Wolf, et al.)

NEXAFS spectrum indicates a rapid decay to the nπ* state



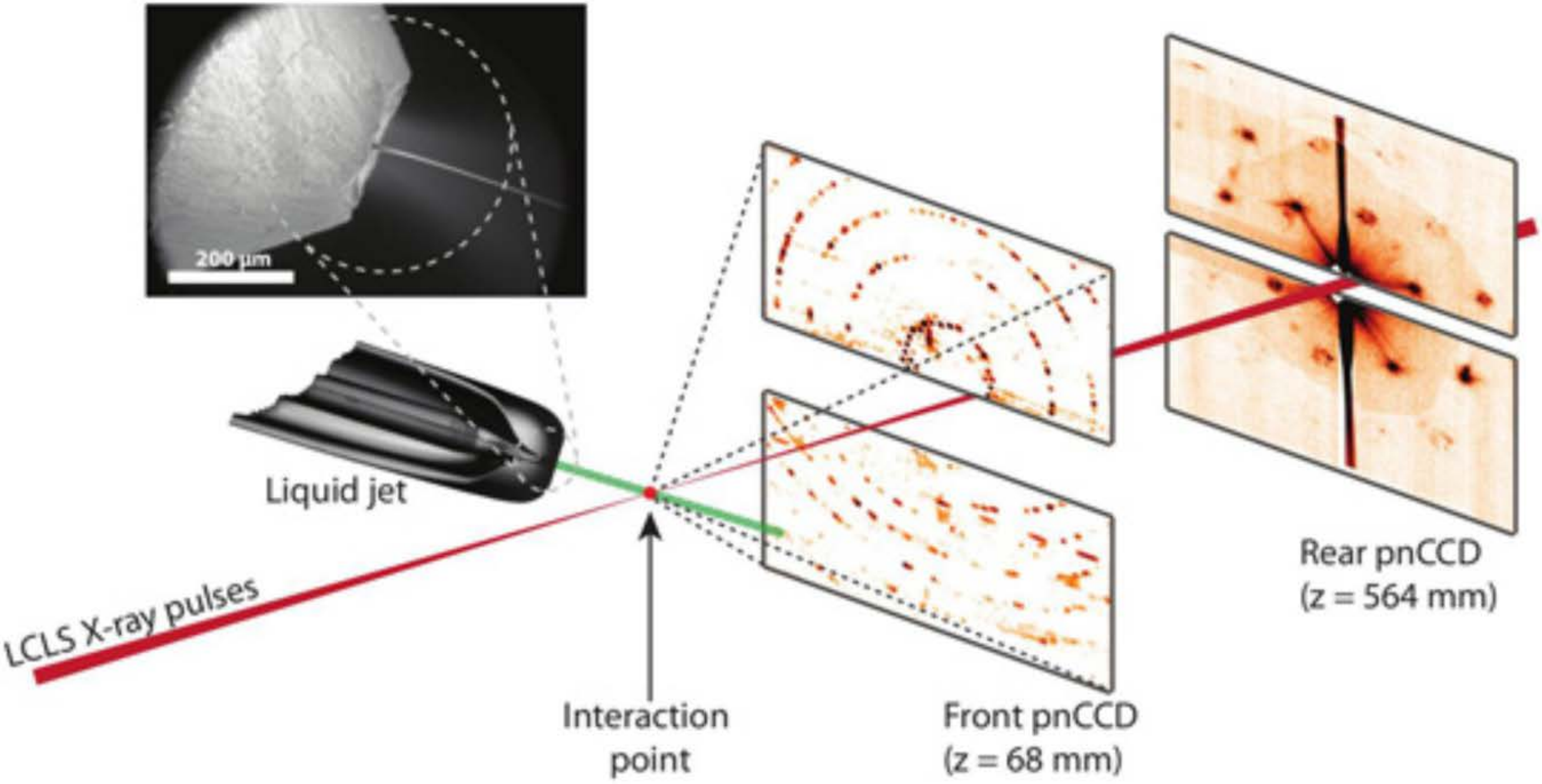


Hard x-rays at X-FELs: Single particle imaging paradigm



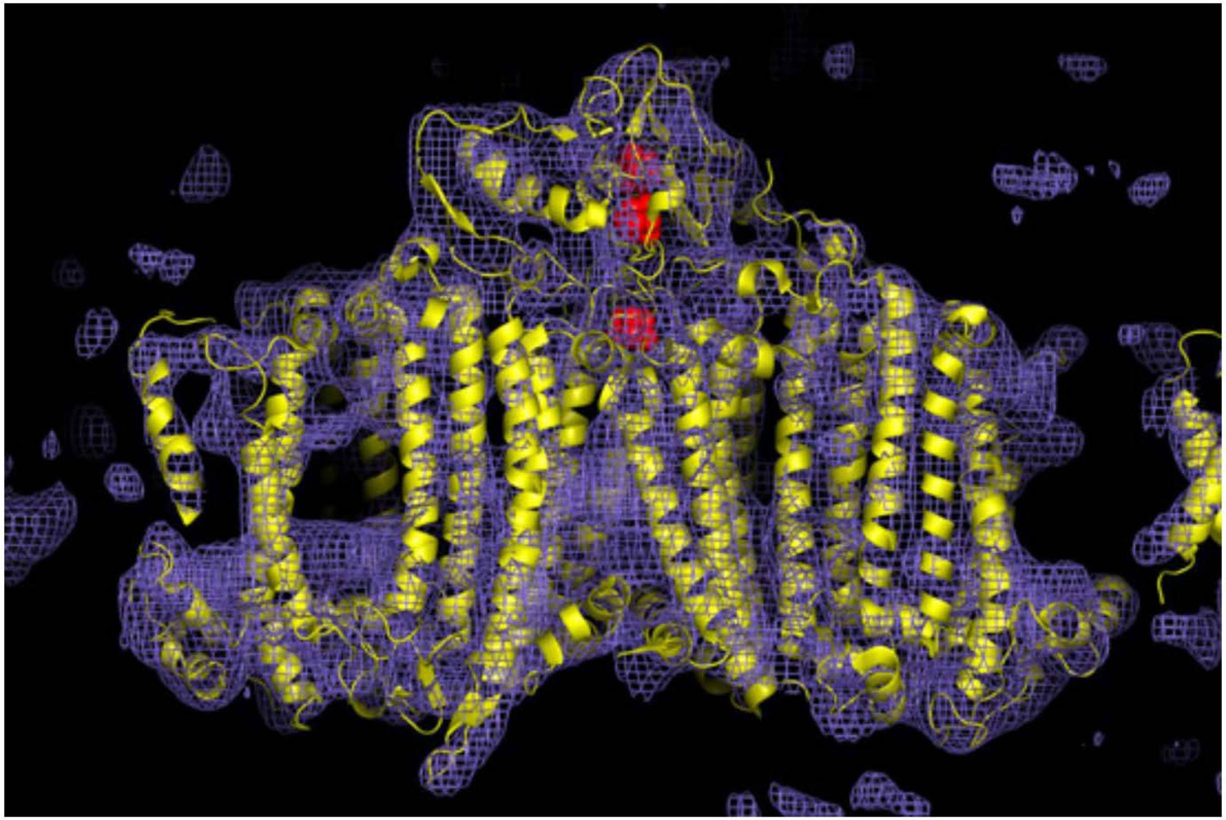
- **Ultrashort pulses outrun damage: diffract before destroy**
- **High intensities: A diffraction image on every spot.**
- **High repetition: Millions of images.**

Serial femtosecond nanocrystallography



Chapman et al., Nature 470, 73 (2011)

PS-II structure from LCLS



Chapman, et al. Nature 470, 73 (2011)

Photoinduced atomic motion can be viewed directly with hard X-ray scattering.

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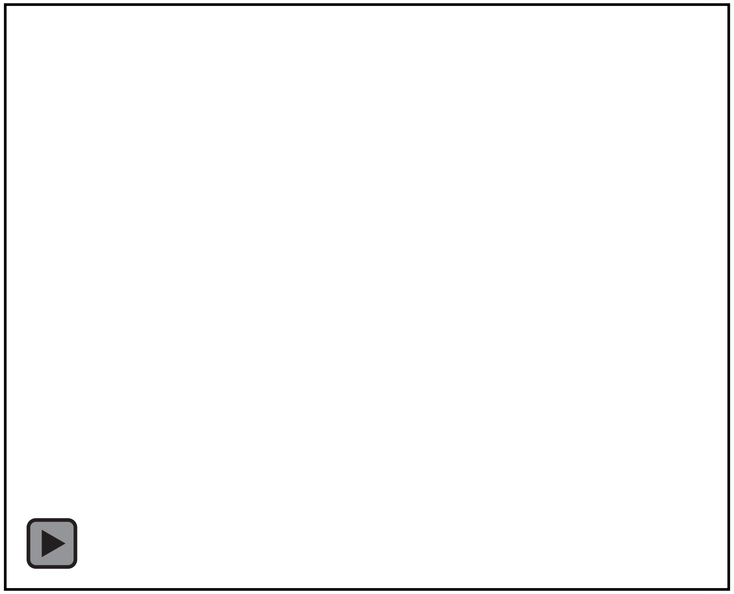
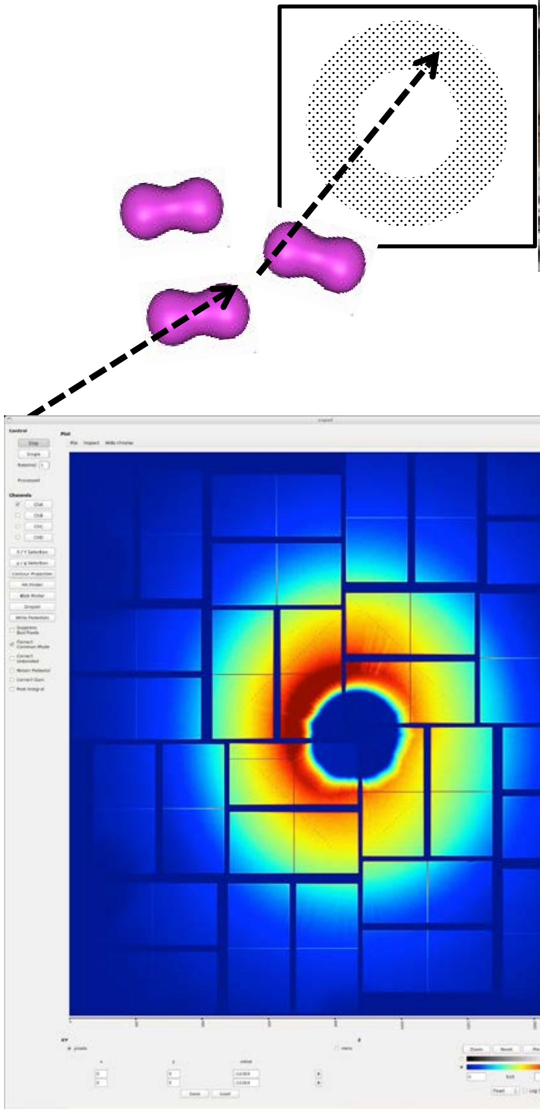
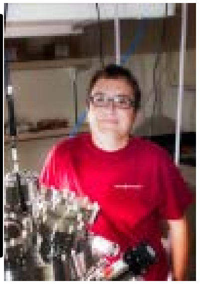
$$f(\vec{Q},t) = \int d^3x\rho(\vec{x},t)e^{i\vec{Q}\cdot\vec{x}}$$

Example: Diatomic Iodine



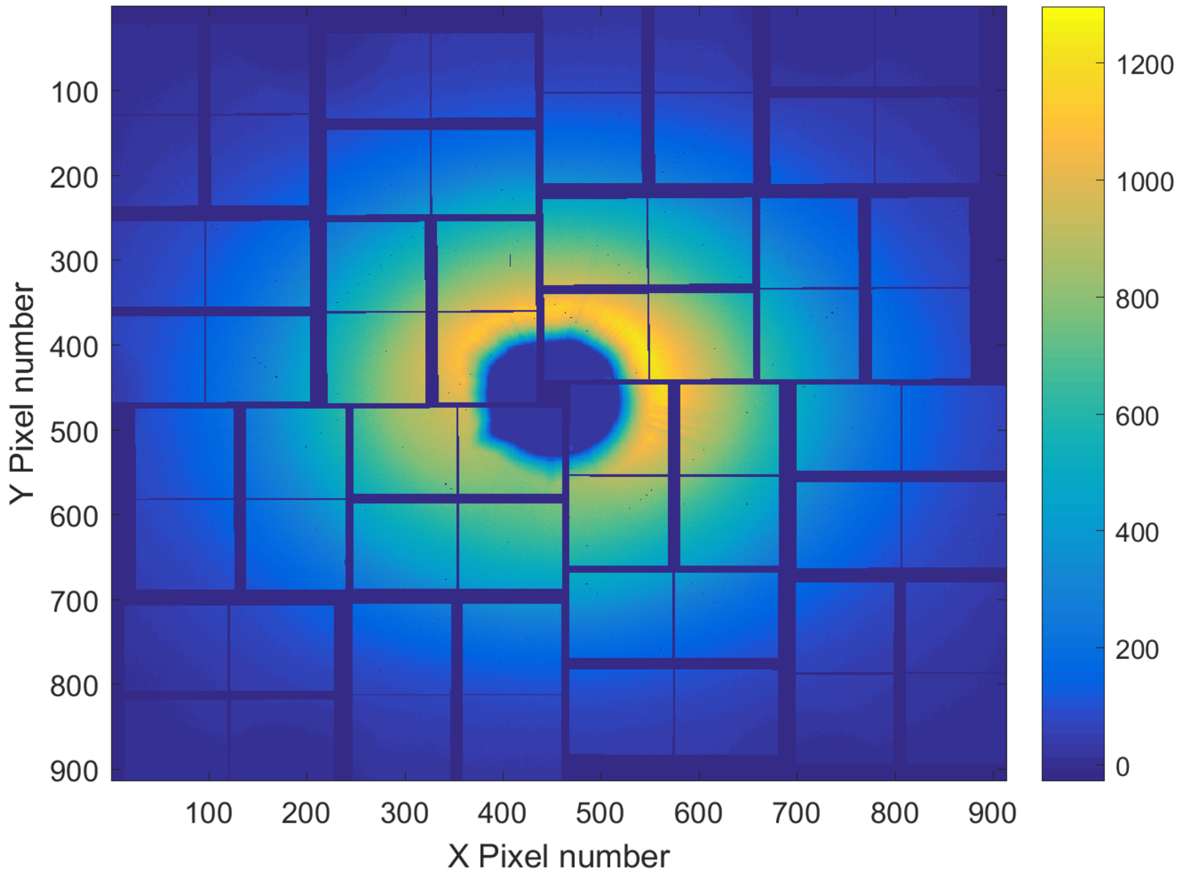




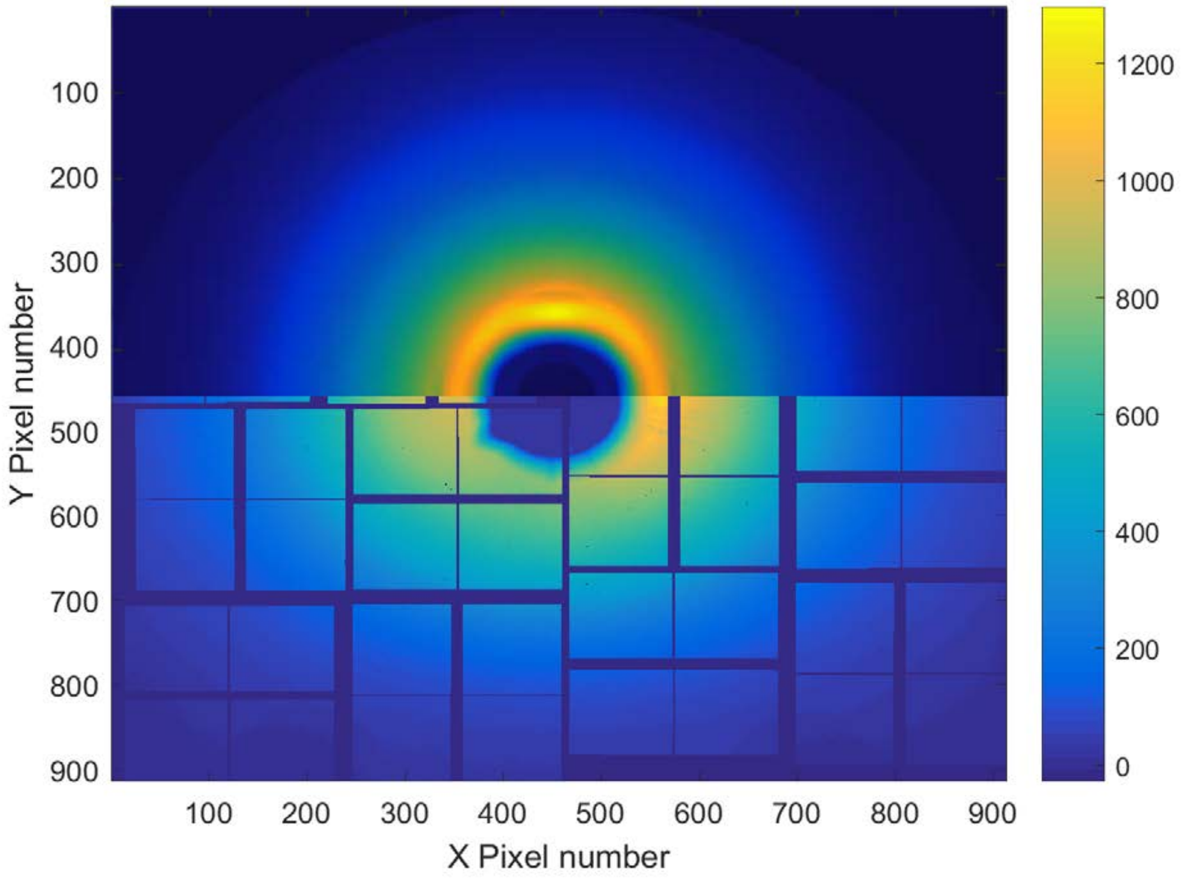
Mike Glownia

9keV, 50fs, 1mJ

CS-PAD (2.5Mpx) detector



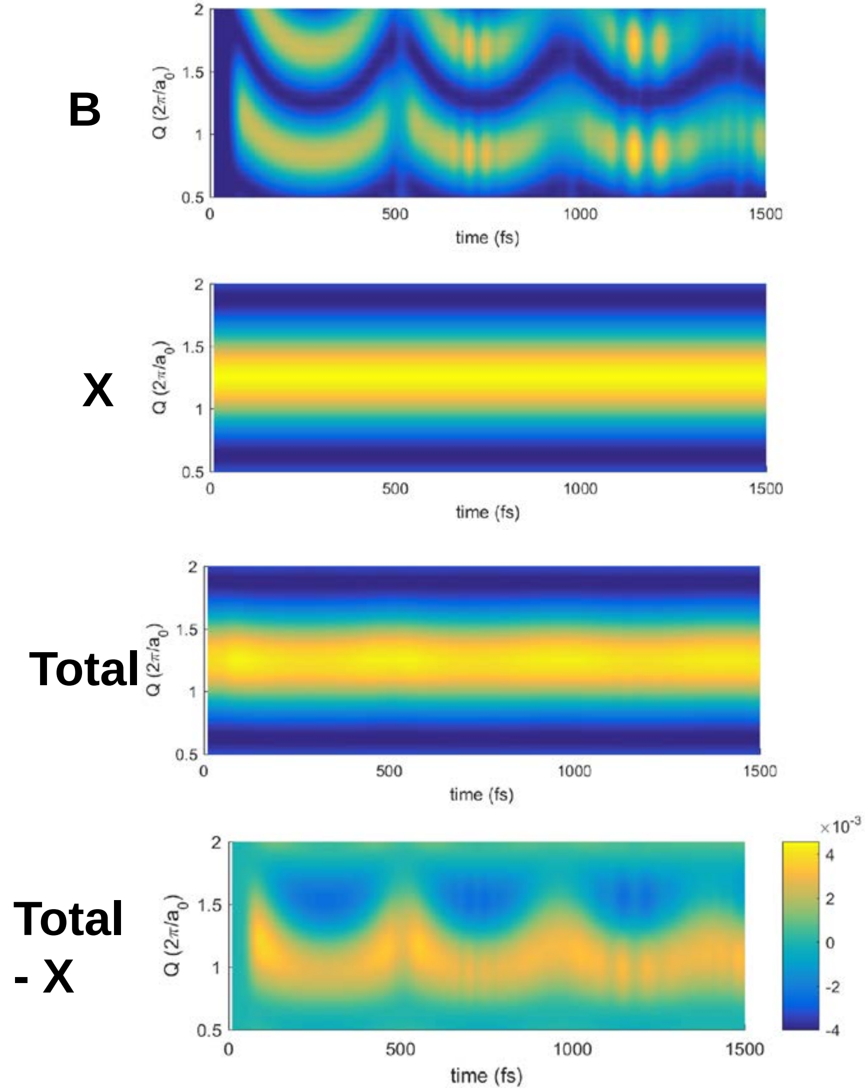
Project each $S(Q_r,t)$ onto first 10 Legendre polynomials $P_L(\cos\theta)$



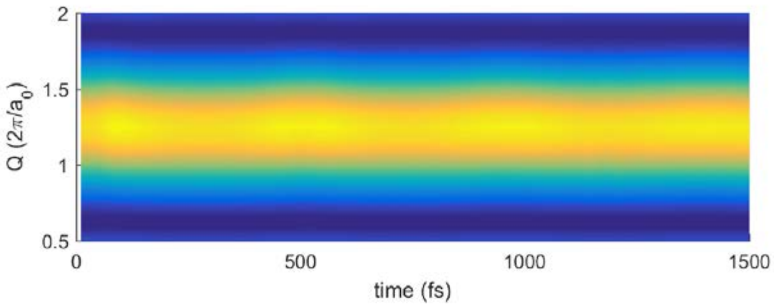
Signal comes from the entire charge distribution

$$f(\vec{Q},t) = \int d^3x \rho(\vec{x},t) e^{i\vec{Q}\cdot\vec{x}}$$

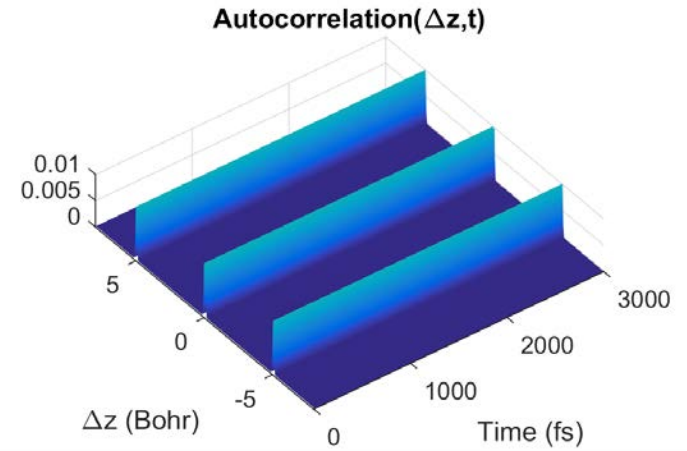
$$\rho_X(\vec{x}) = \sum_{v=0}^{\infty} \rho_v(\vec{x}) e^{-E_v/k_BT}$$



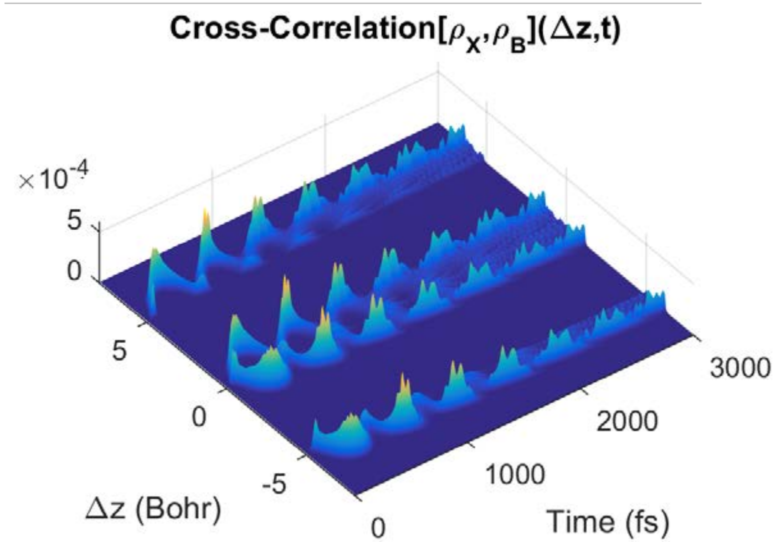
Extracting the molecular movie from the scattering data.



$FFT^{-1} \rightarrow$



$$\mathcal{AC}[\rho(\vec{x},t)] \equiv \rho(\vec{x},t) \otimes \rho(\vec{x},t)$$
$$= \mathcal{F}^{-1}(f(\vec{Q},t)f^*(\vec{Q},t))$$



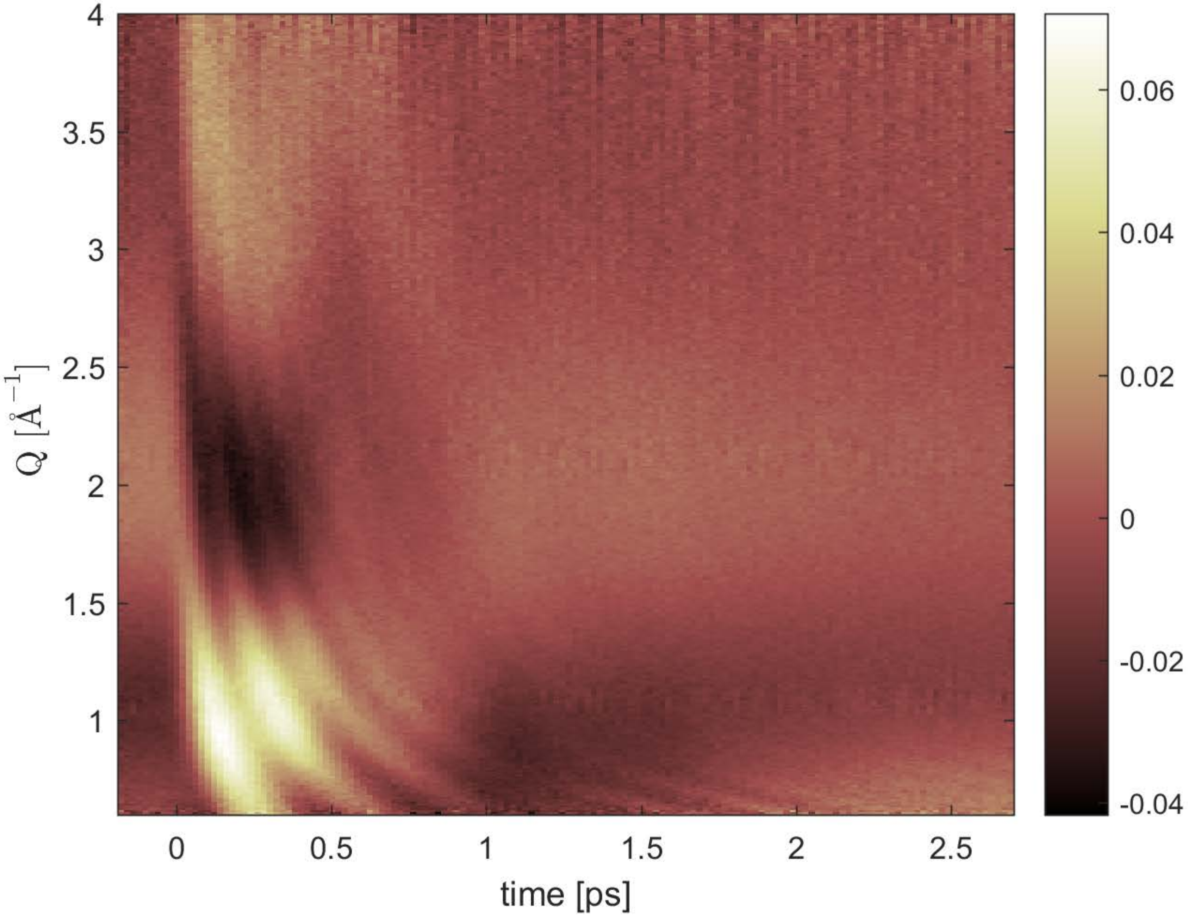
$$\mathcal{AC}[\rho(\vec{x},t)] = \mathcal{AC}[\rho_X(\vec{x})] + \mathcal{AC}[\rho_B(\vec{x},t)]$$
$$+2\mathcal{CC}[\rho_X(\vec{x}), \rho_B(\vec{x},t)]$$

$$2\ \mathcal{CC}[\rho_X(\vec{x}), \rho_B(\vec{x},t)] \simeq \mathcal{AC}[\rho(\vec{x},t)] - \mathcal{AC}[\rho_X(\vec{x})]$$

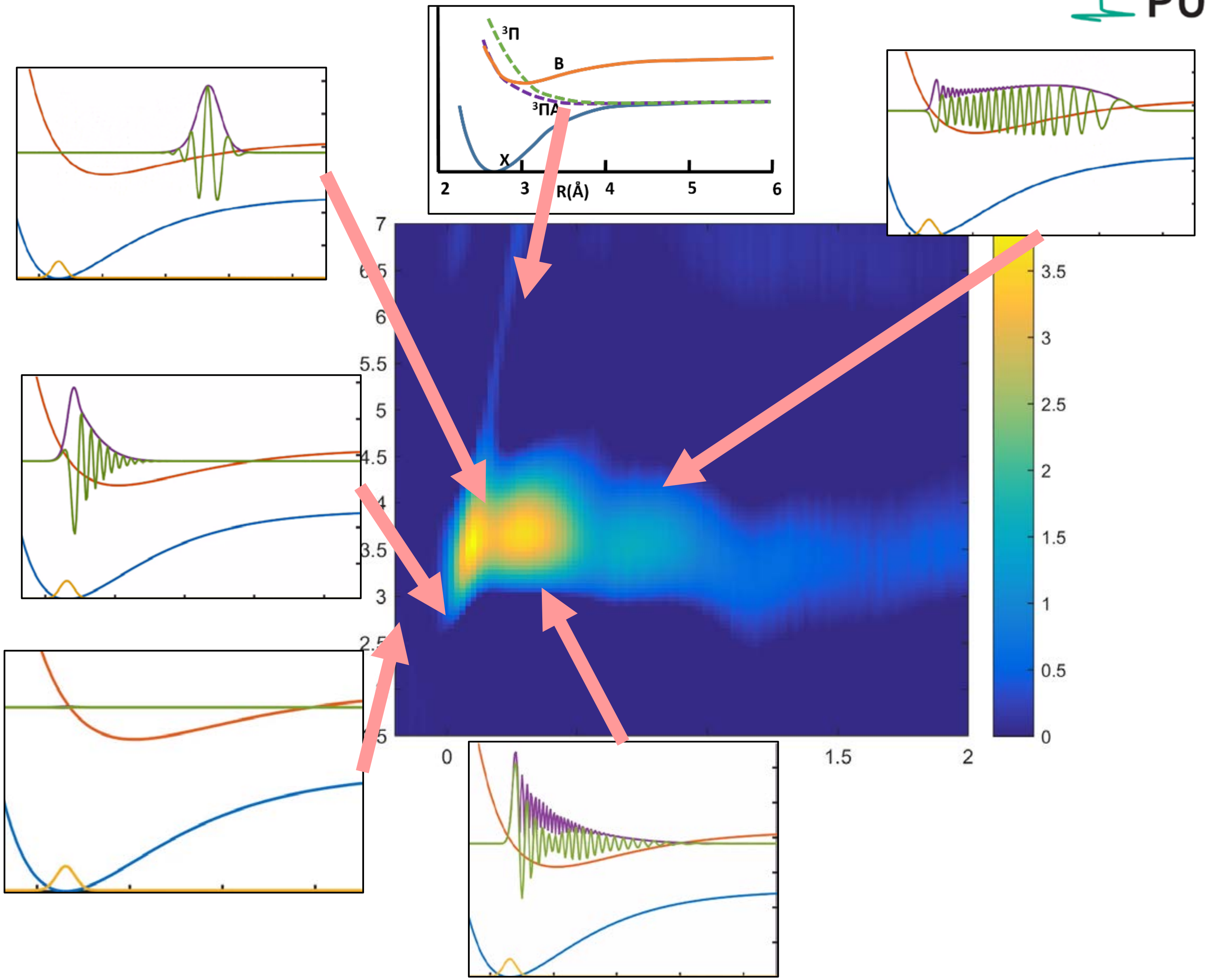
The cross correlation is a hologram where the ground charge distribution creates the reference scattered wave.

M. J. J. Vrakking and T. Elsaesser, Nat Photon 6, 645–647 (2012).

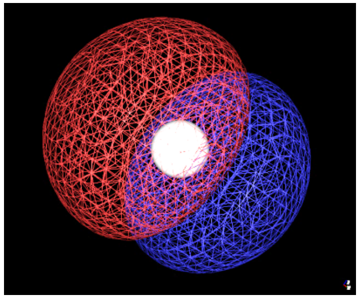
$P_2(\cos\theta)$ component of $S(Q,t)$



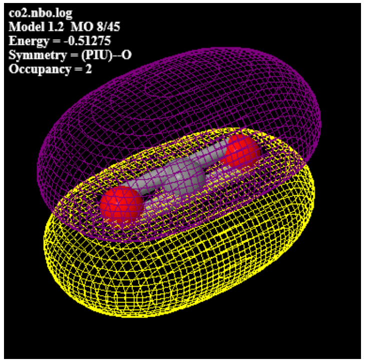
The movie



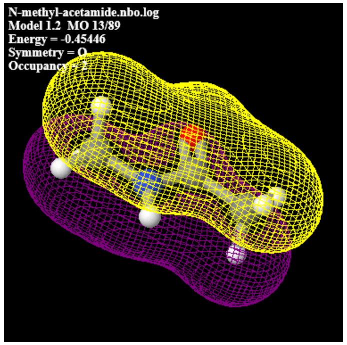
The future: X-ray-induced attosecond electron motion



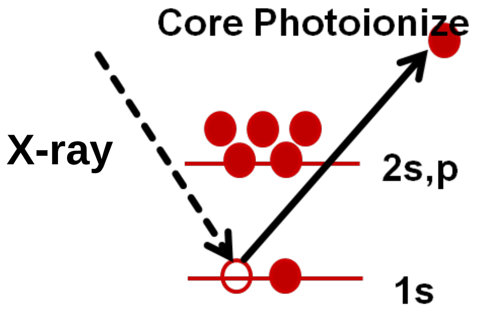
Kr 2p

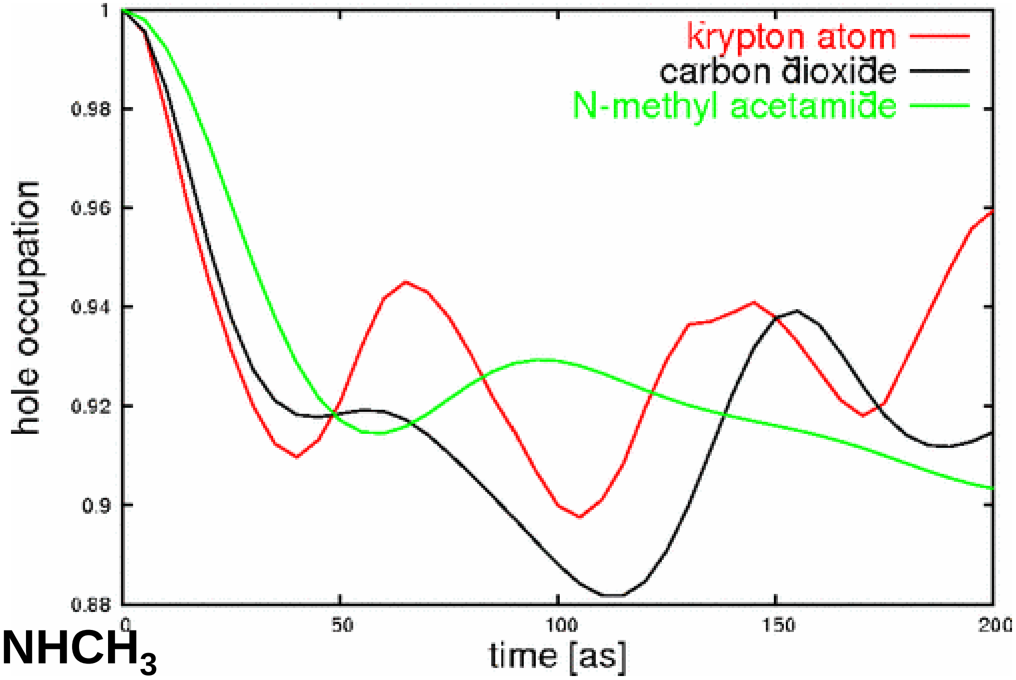


CO_2
$1\pi_u$



$CH_3CONHCH_3$
3π





J. Breidbach and L. S. Cederbaum
Phys. Rev. Lett. 94, 033901 (2005)

Attosecond X-ray Free Electron Lasers

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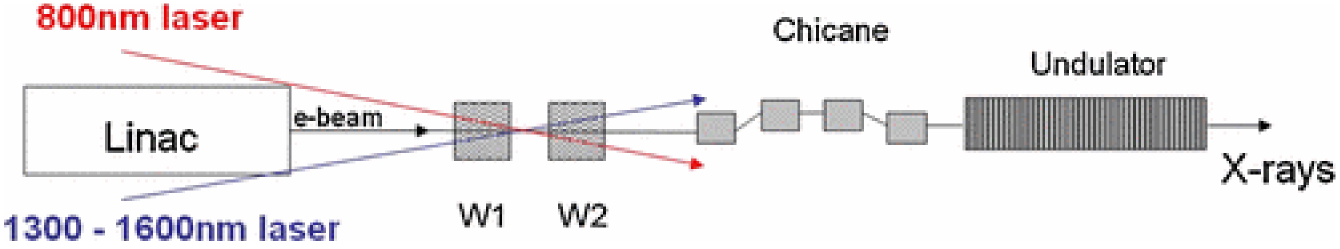
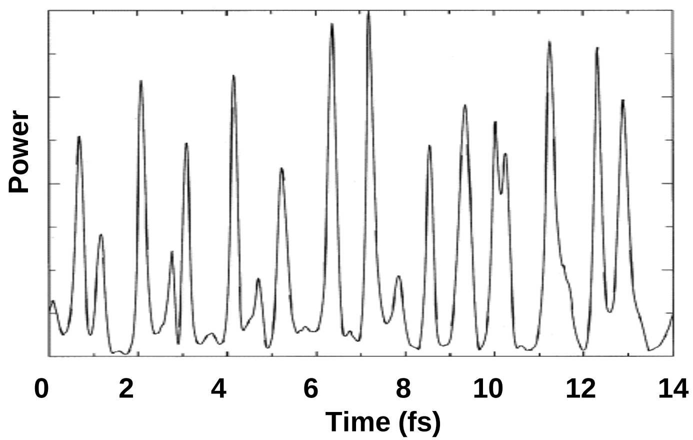
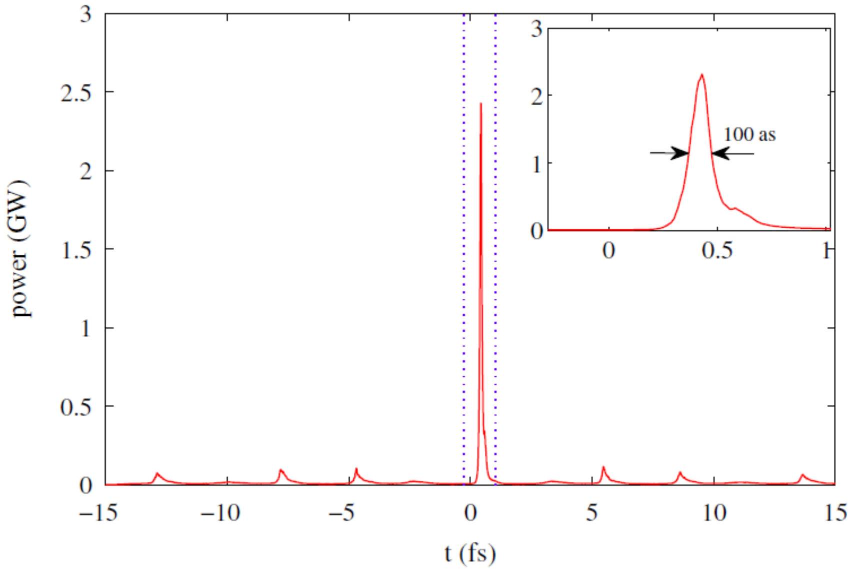
Laser pre-modulated electrons tame SASE



Typical SASE:



Single spike SASE:



Ding, Y., PRST 12, (2009).

Mapping electron dynamics with core excitation

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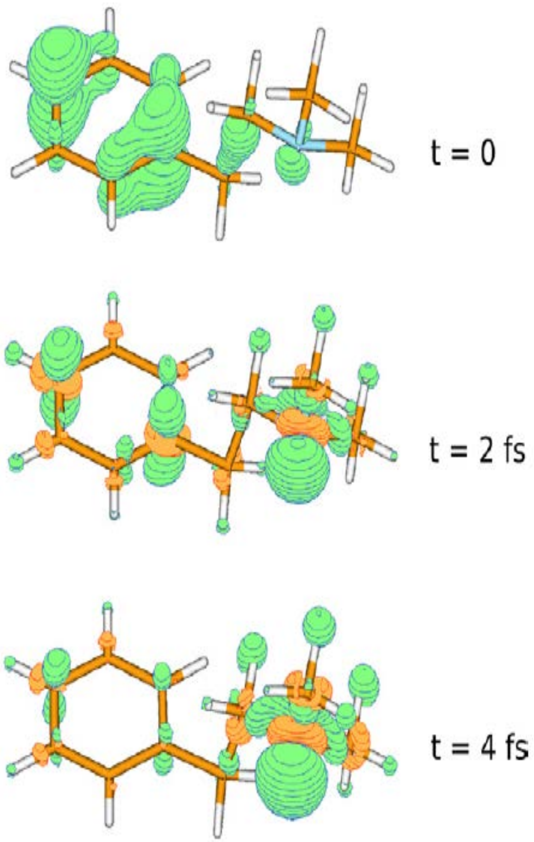
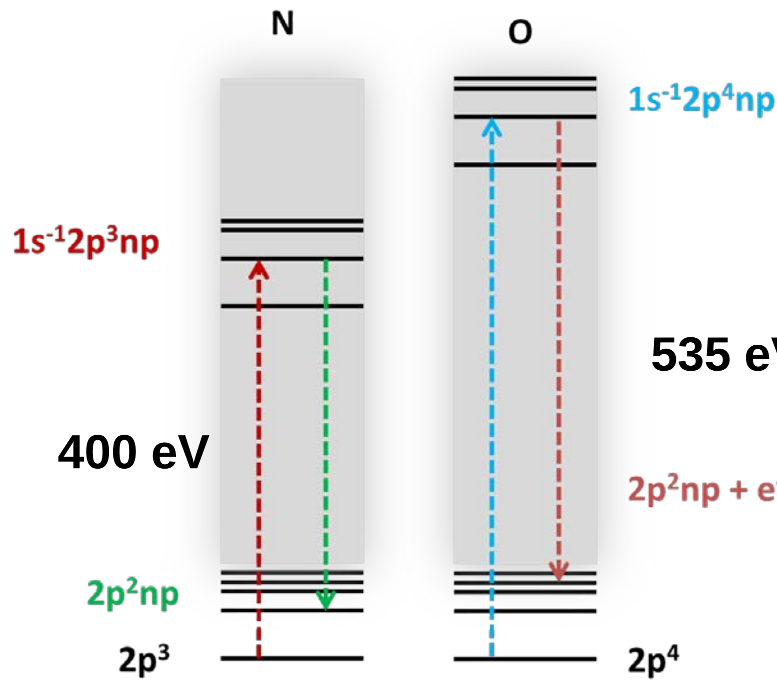
Core excitation creates localized electron disturbances. Correlation drives nonlocal electron transport in molecules

Example of how this could work: Send in three x-rays, k_1, k_2, and k_3 and read out the final Auger electron spectrum





Lunnemann et al., Chem Phys Lett 450 232 (2008); Mukamel et al., Ann Rev. P. Chem. 64, 101 (2013); Miyabe, S. & PHB, PRL 114, 143005 (2015)

Lots of contributors

- Bucksbaum group
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  - Matthew Ware
  - Adrei Kamalov
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  - Chelsea Liekhus-Schmaltz
  - Greg McCracken
  - Andreas Kaldun
- PULSE and LCLS collaborators
  - Todd Martinez
  - Kellly Gaffney
  - David Reis
  - Shambhu Ghimire
  - Shungo Miyabe
  - Cristoph Bostedt (75% LCLS)
  - Mariano Trigo
  - Mike Glownia
  - Hermann Durr
  - Timor Osipov
  - Thomas Wolf
  - Ryan Coffee
- Other alumni in the past three years
  - Limor Spector (went to McKinsey)
  - Brian McFarland (went to LANL)
  - Fenglin Wang (went to CFEL)
  - Joe Farrell (graduated)
  - Doug Broge (graduated)
  - Ben Barbrel (LBNL)
  - Jaehee Kim (NSF, graduates 12/14)
  - James White (NSF, startup)
- Outside collaborators (partial list)
  - Nora Berrah et al, U. Conn
  - Lou Dimauro et al, Ohio State
  - Artem Rudenko, K-State
  - Tamar Seideman, N'western
  - Linda Young et al, ANL
  - Ilya Averbukh, Weizmann
  - Jon Marangos et al, Imperial
  - Hamed Merdji, CEA
  - Roseanne Sension, UM
  - Fenglin Wang, and others, CFEL
  - Markus Guehr (U. Potsdam)

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