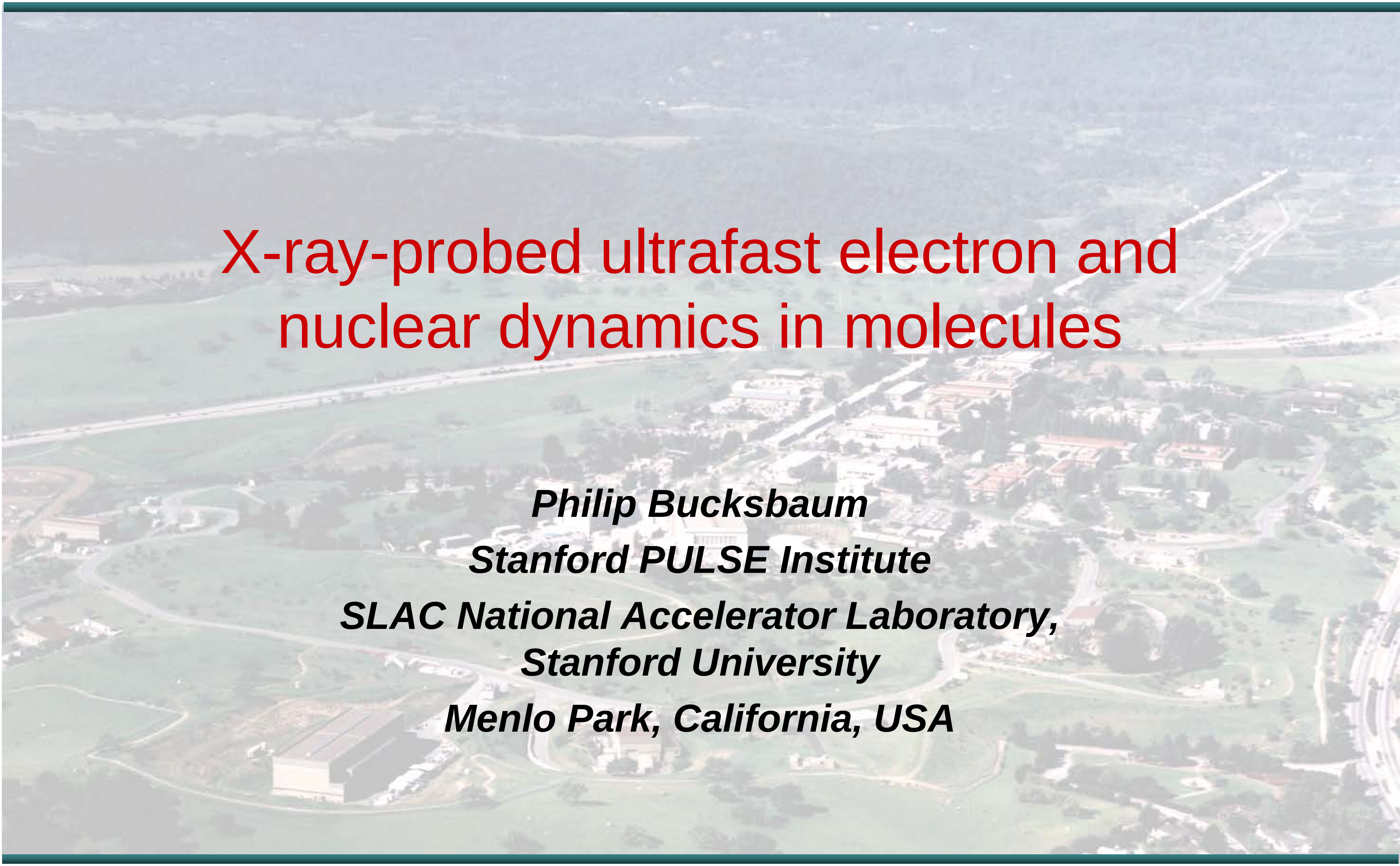
PULSE STANFORD



X-ray-probed ultrafast electron and nuclear dynamics in molecules

Philip Bucksbaum

Stanford PULSE Institute

SLAC National Accelerator Laboratory,
Stanford University

Menlo Park, California, USA

Ultrafast AMO Physics at the Stanford PULSE Institute

Phil Bucksbaum

Markus Guehr

David Reis

Todd Martinez

Adi Natan

James Cryan

Kelly Gaffney

Bucksbaum group on quantum control, attosecond processes, and strong fields

Song Wang

Julien Devin

Vladimir Petrovic

Jaehee Kim

Shungo Miyabe

Chelsea Liekhus-Schmaltz

Matthew Ware

Lucas Zipp

Andrei Kamalov

Greg McCracken

Funding: NSF, DOE

Lots of contributors

- **Bucksbaum group**
  - **Adi Natan**
  - **Song Wang**
  - **Julien Devin**
  - **Matthew Ware**
  - **Adrei Kamalov**
  - **James Cryan**
  - **Ryan Coffee**
  - **Vlad Petrovic**
  - **Chelsea Liekhus-Schmaltz**
  - **Greg McCracken**

- **PULSE and LCLS collaborators**
  - **Markus Guehr**
  - **Todd Martinez**
  - **Kellly Gaffney**
  - **David Reis**
  - **Shambhu Ghimire**
  - **Shungo Miyabe**
  - **Cristoph Bostedt (75% LCLS)**
  - **Mariano Trigo**
  - **Mike Glownia**
  - **Hermann Durr**
  - **Timor Osipov**

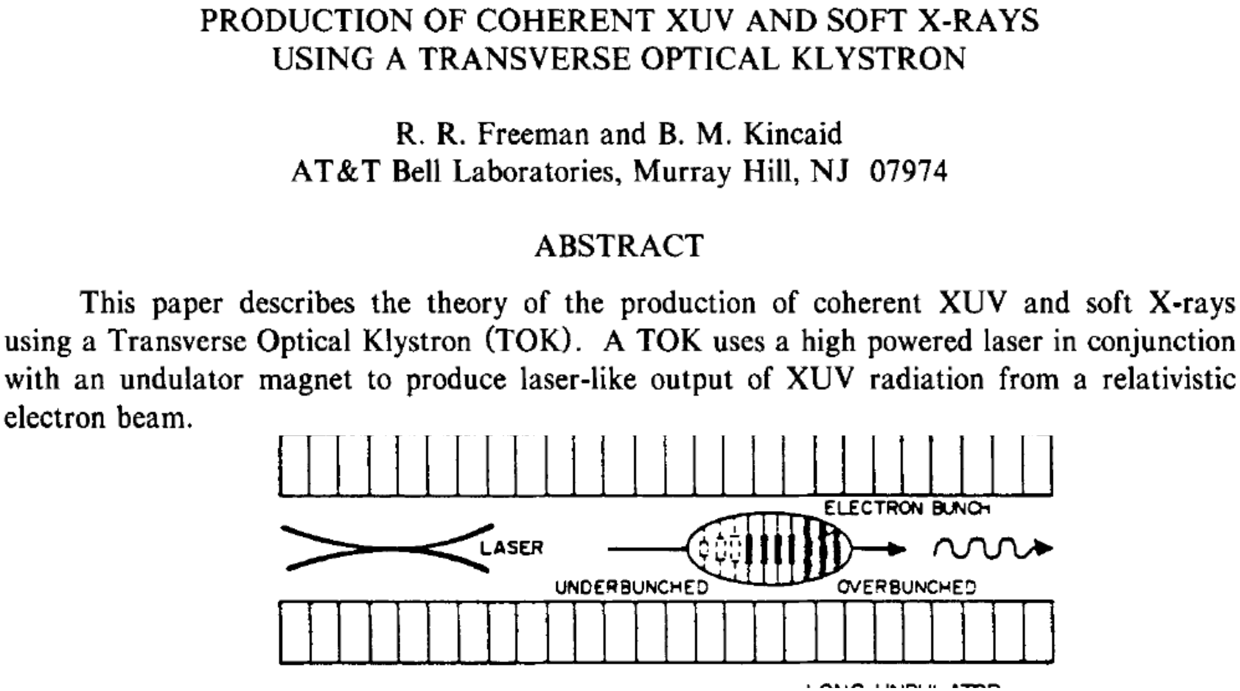
- **Alumni in the past three years**
  - **Limor Spector (went to McKinsey)**
  - **Brian McFarland (went to LANL)**
  - **James Cryan (went to LBNL)**
  - **Mike Glownia (went to LCLS)**
  - **Fenglin Wang (went to CFEL)**
  - **Joe Farrell (graduated)**
  - **Doug Broge (graduated)**
  - **Ben Barbrel (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**
  - **Katsumi Midorikawa, RIKEN**
  - **Roseanne Sension, UM**
  - **Limor Spector, McKinsey**
  - **Fenglin Wang, and others, CFEL**

Some earlier projects and influences

- **Jeff Bokor: The Bell Labs "XUV Laser" project**
- **Mike Duguay, Bill Silfvast, Roger Falcone, Dennis Matthews, …**
- **Rick Freeman, Brian Kincaid, Claudio Pellegrini: Transverse Optical Klystron at Brookhaven**
- **Pierre Agostini, Anne l'Huillier: High Harmonics Generation**
- **Kent Wilson: Ultrafast plasma x-rays at UCSD**
- **Chuck Shank: Ultrafast Thomson source, slicing source**

1983:

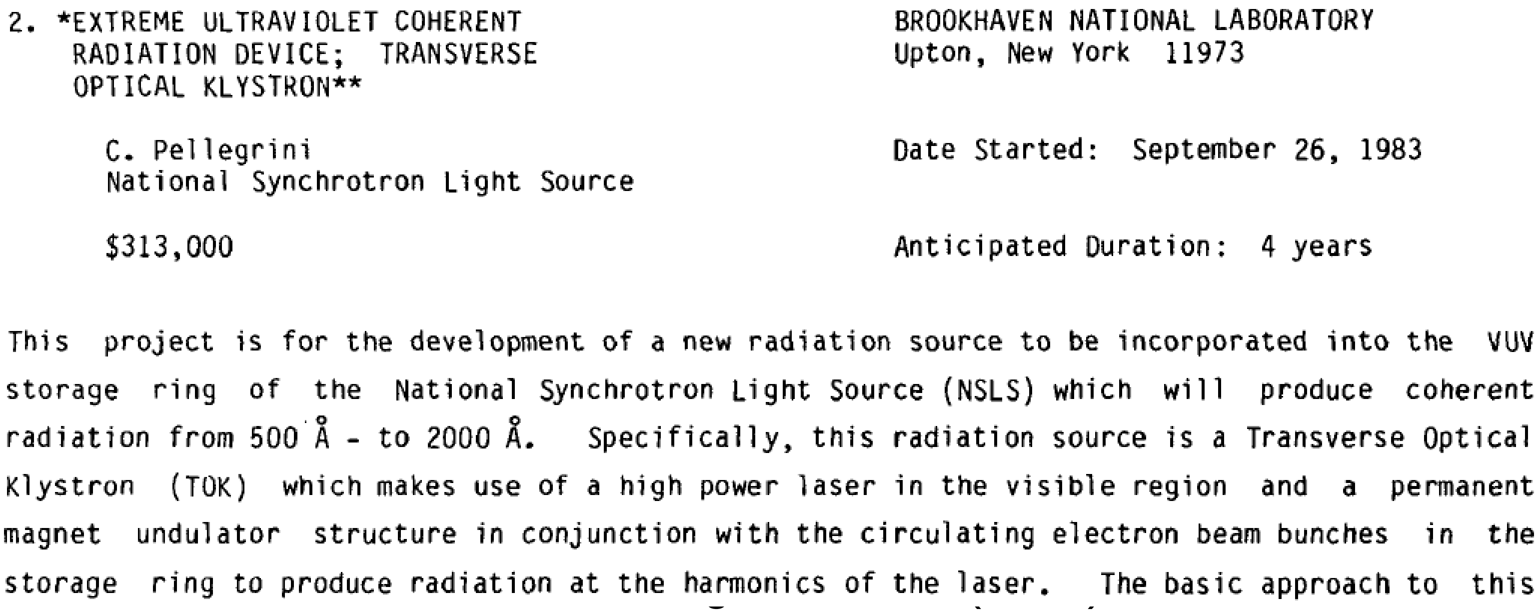


PRODUCTION OF COHERENT XUV AND SOFT X-RAYS USING A TRANSVERSE OPTICAL KLYSTRON

R. R. Freeman and B. M. Kincaid
AT&T Bell Laboratories, Murray Hill, NJ 07974

ABSTRACT

This paper describes the theory of the production of coherent XUV and soft X-rays using a Transverse Optical Klystron (TOK). A TOK uses a high powered laser in conjunction with an undulator magnet to produce laser-like output of XUV radiation from a relativistic electron beam.



2. *EXTREME ULTRAVIOLET COHERENT
RADIATION DEVICE; TRANSVERSE
OPTICAL KLYSTRON**

BROOKHAVEN NATIONAL LABORATORY
Upton, New York 11973

C. Pellegrini
National Synchrotron Light Source

Date Started: September 26, 1983

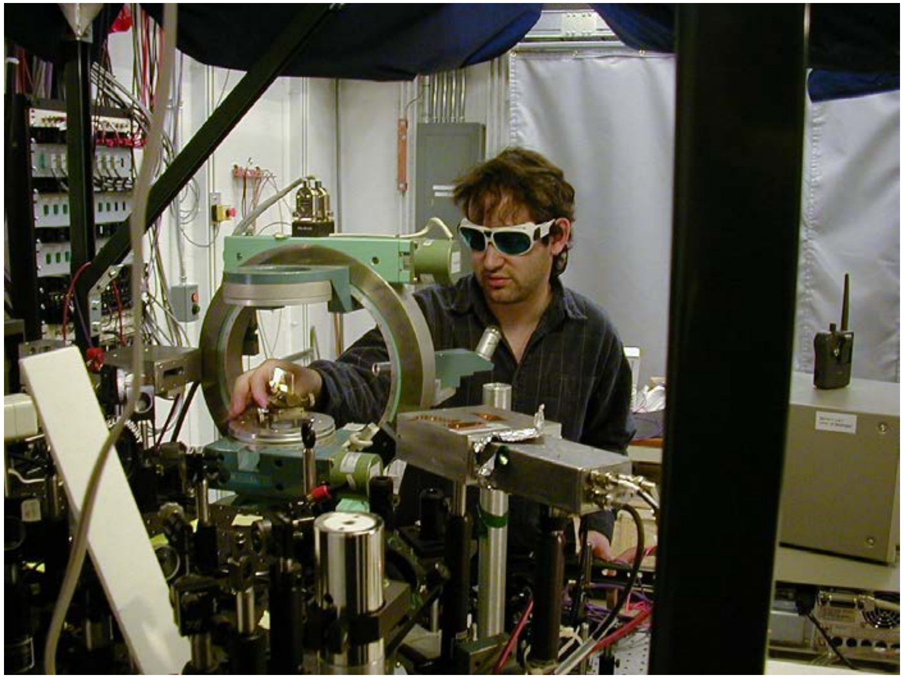
$313,000

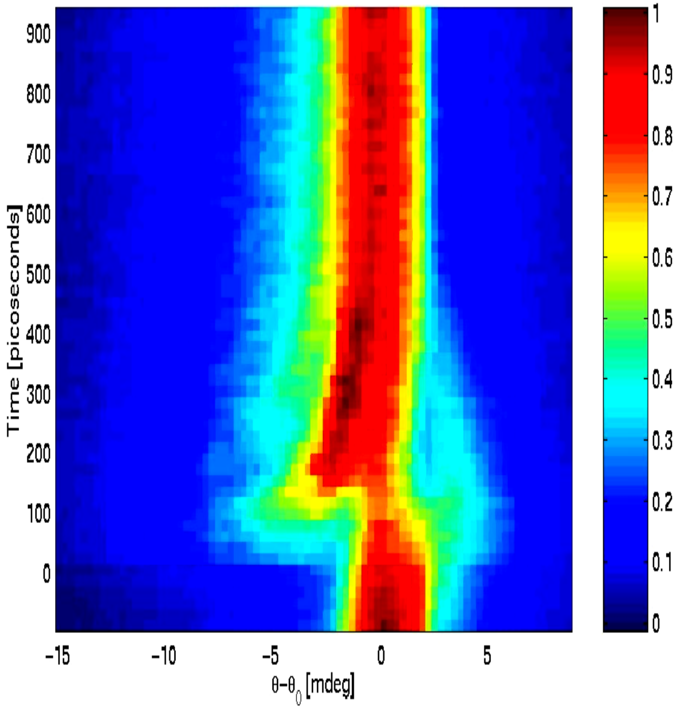
Anticipated Duration: 4 years

This project is for the development of a new radiation source to be incorporated into the VUV storage ring of the National Synchrotron Light Source (NSLS) which will produce coherent radiation from 500 Å - to 2000 Å. Specifically, this radiation source is a Transverse Optical Klystron (TOK) which makes use of a high power laser in the visible region and a permanent magnet undulator structure in conjunction with the circulating electron beam bunches in the storage ring to produce radiation at the harmonics of the laser. The basic approach to this

APS Sector 7, 2000 Impulsive excitation of coherent acoustic phonons in InSb.

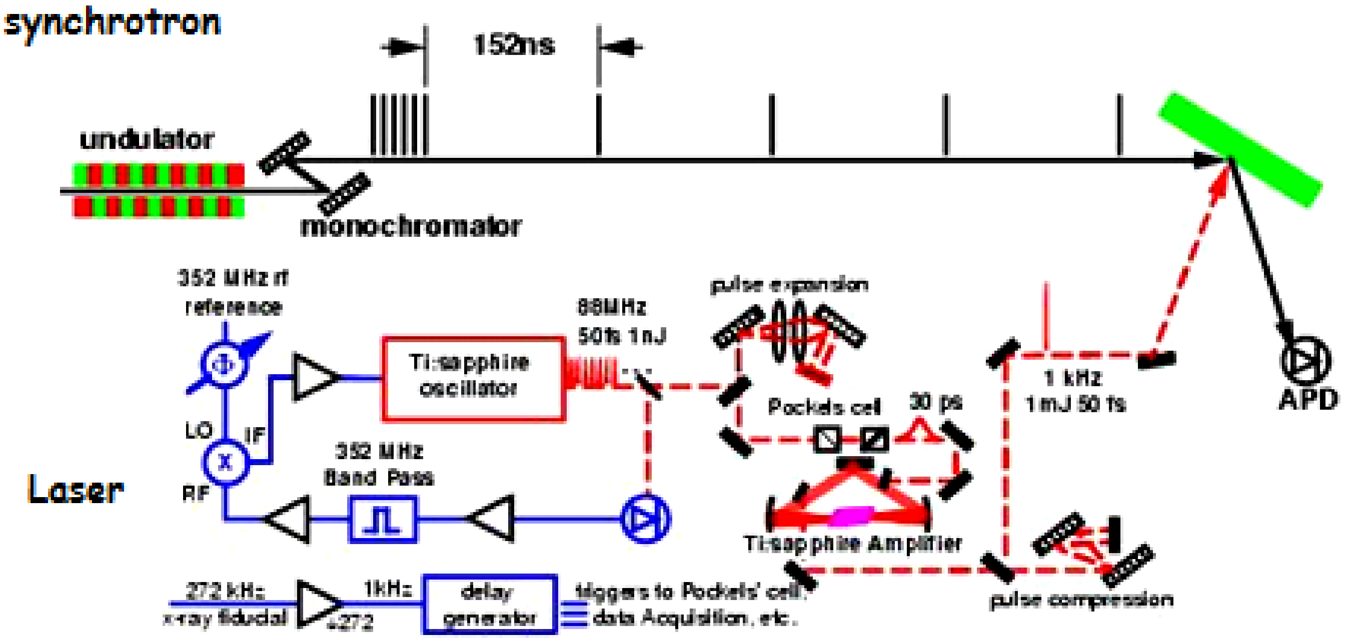
An ultrafast laser kicks the crystal, and the x-rays probe the response.





MHATT-CAT: Roy Clarke, Steve Dierker, Ron Pindak, Walter Lowe
D. Reis et al., Physical Review Letters 86, 3072 (2001).

- Pump-probe uses "slow" detectors to study ultrafast dynamics.
- Temporal resolution limited by probe pulse: ~100 ps at synch.
- Pump-probe delay must be held fixed << the pulse duration. (especially important at synchrotron sources).



Launching and probing impulsive dynamics with strong ultrafast pulses

$$H\psi(\vec{x},t) = i\dot{\psi}(\vec{x},t)$$

$$(H_0 + H_{\mathrm{int}}(t))\psi(\vec{x},t) = i\dot{\psi}(\vec{x},t)$$

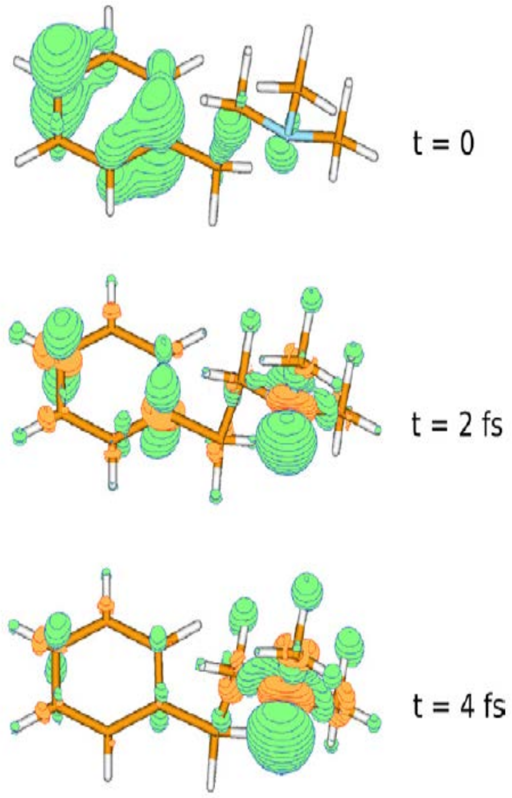
H_{int} can be both the shutter speed and the starter pistol

Impulse limit: The “shutter speed” must be fast compared to the natural motion. In quantum mechanics, this means Δτ < ħ/ΔE

The applied field must be strong enough to alter the natural dynamics.

The hierarchy of timescales in molecules

- **Free electrons:** No resonances below 1MeV; response limited only by c
- **Inner electrons in atoms** can be bound by kilovolts and confined to fractions of an Angstrom, implying **attosecond motion.**
- The time scale for **binding electron** motion in small molecules is determined by their Angstrom sizes and Rydberg binding energies to be **femtoseconds or shorter.**
- The **molecules can also bend and stretch,** on time scales of **tens or hundreds of femtoseconds.**
- Finally, the whole vibrating molecule is usually **rotating** in space, and these rotations can be **many picoseconds.**



Lunnemann et al., Chem Phys Lett 450 232 (2008)

Stimulated Raman in the impulse limit: A swift kick

- **Kramers Heisenberg**

$$\frac{d\sigma}{d\Omega} = (N+1)\frac{\omega^3\omega'}{c^4}\left|\vec{\varepsilon}\cdot\alpha_{km}\cdot\vec{\varepsilon}'\right|^2,$$

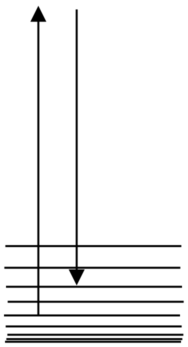
$$(\alpha_{km})_{ij} = \frac{1}{\hbar}\sum_n\left\{-\frac{\mu^i_{nm}\mu^j_{kn}}{\omega-\omega_{nk}-i\Gamma}\right\},$$

- **Impulse limit:**

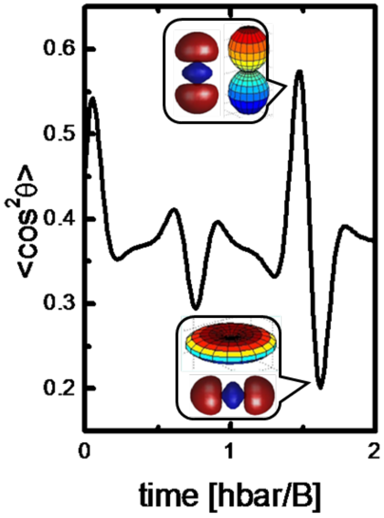
$$N = (I_0/\omega^3\alpha), \qquad F_0 = \int dt I_0.$$

- **Total rate**
  - $P = \int dE(d\sigma/d\Omega)F_0.$
  - $\boldsymbol{I_0^2}$

Impulsive Stimulated Rotational Raman Scattering: Quantum alignment of molecules

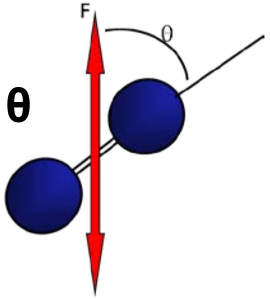


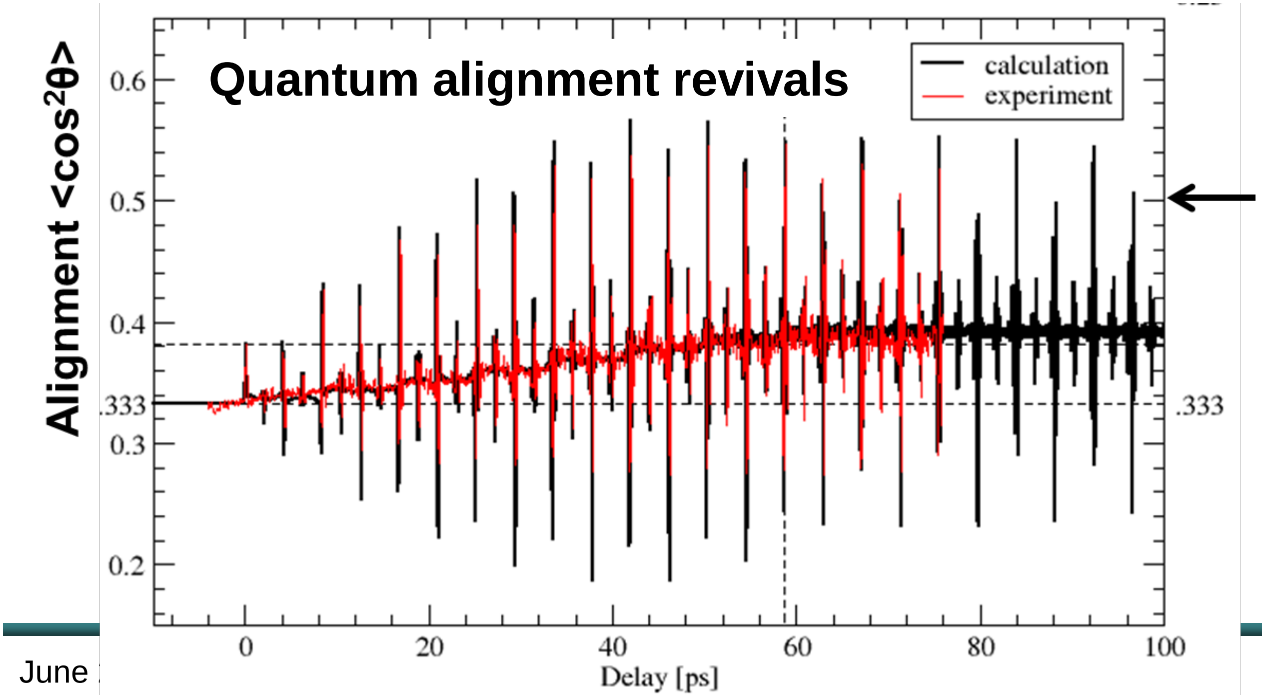
$\tau_{pump} < \tau_{rotation}$



Molecular Alignment potential

$$H = -1/4\ \Delta\alpha\ E^2 \cos^2 \theta$$





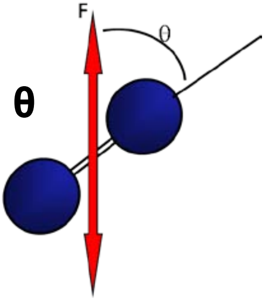
Shaped pulse solution (Eight 100 fs kicks over 64 ps) to optimize alignment

Cryan, et al. PRA, *80, 063412 (2009).*

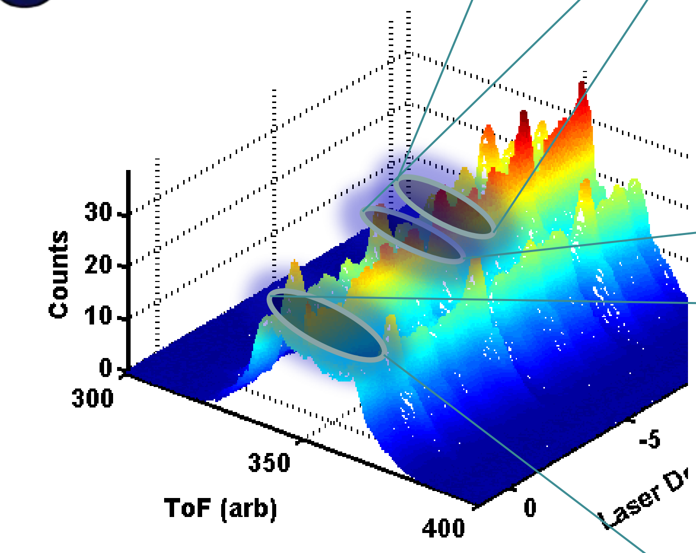
LCLS measurements on aligned molecules

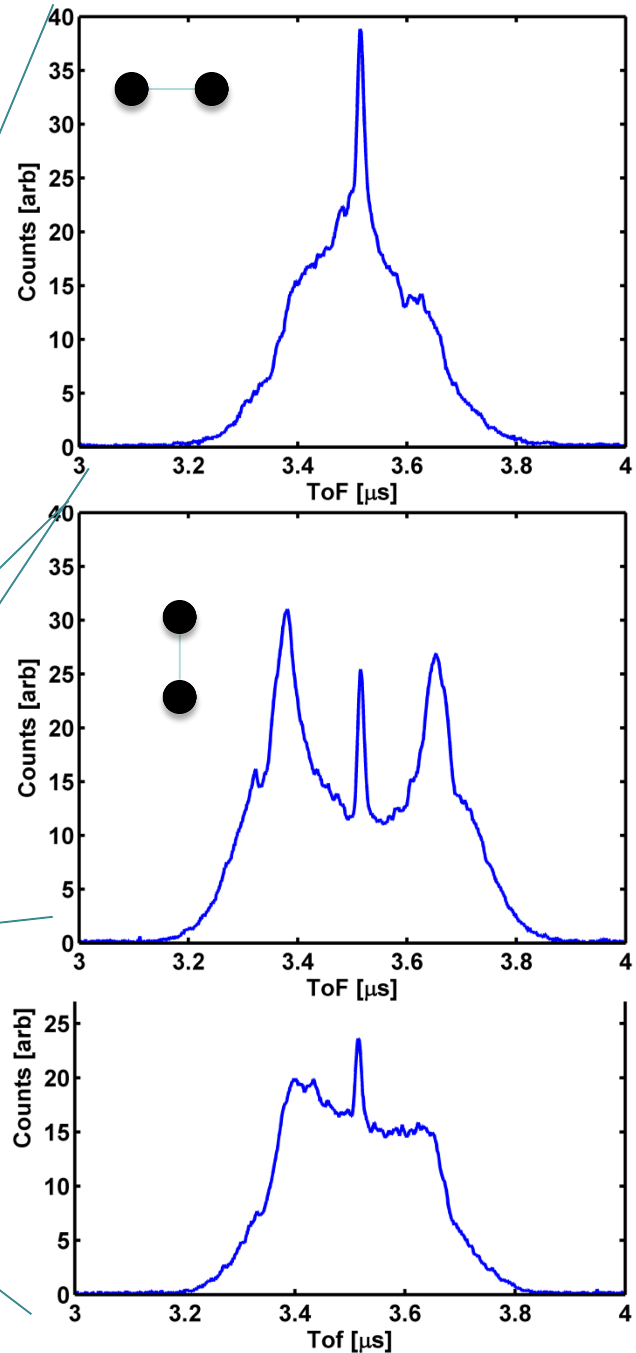
- **800 nm Ti:Sapphire laser is used to impulsively align molecular nitrogen along the laser polarization direction**
- **Dissociation following ionization by 1100 eV x-rays**

$H = -1/4\ \Delta\alpha\ F^2 \cos^2\theta$

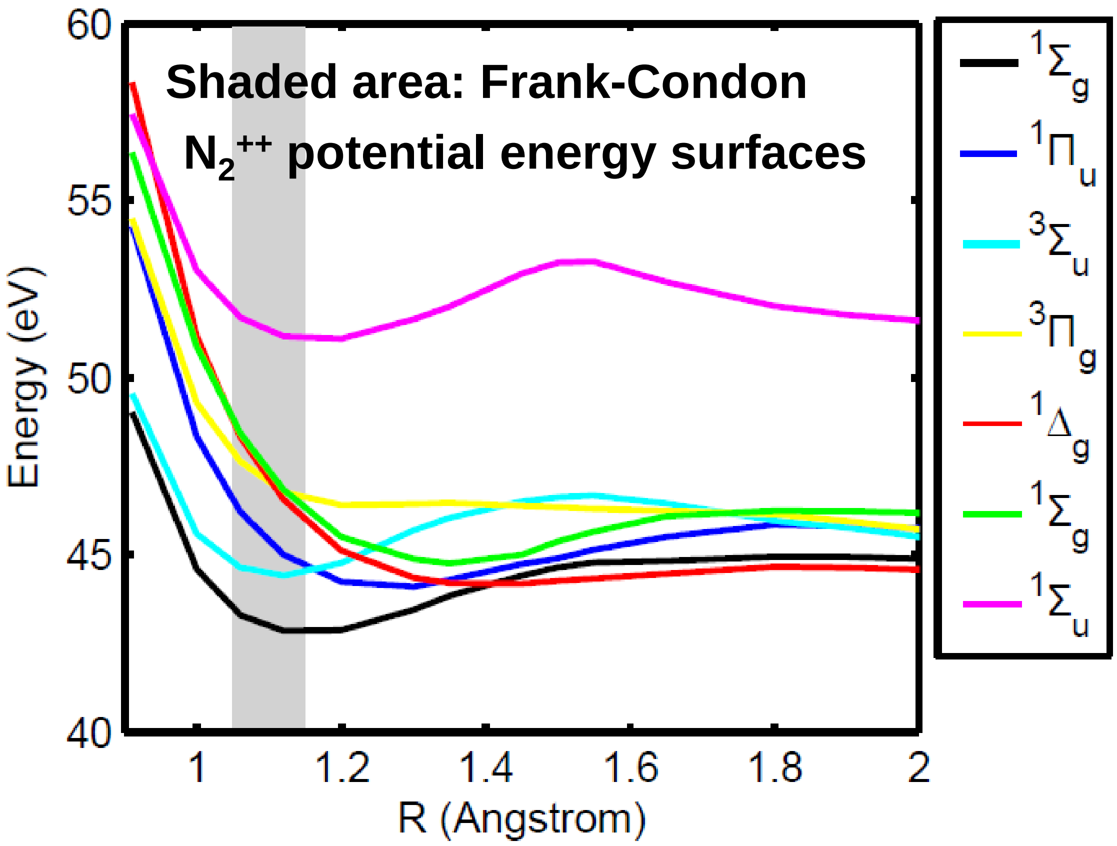


Glownia, J. M., J. Cryan, et al. (Opt. Express 18(17): 17620-17630 (2010).



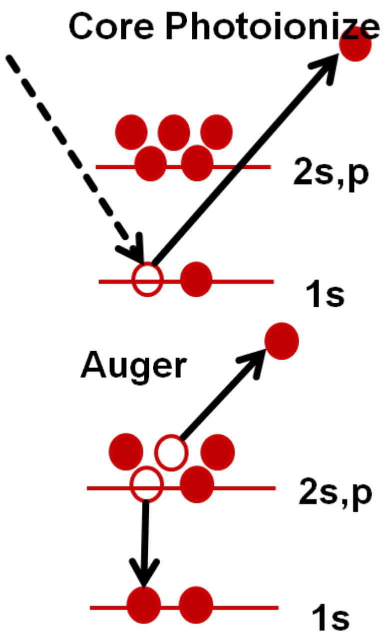


Transient state studies: N_2^{++} Potential Energy Surfaces



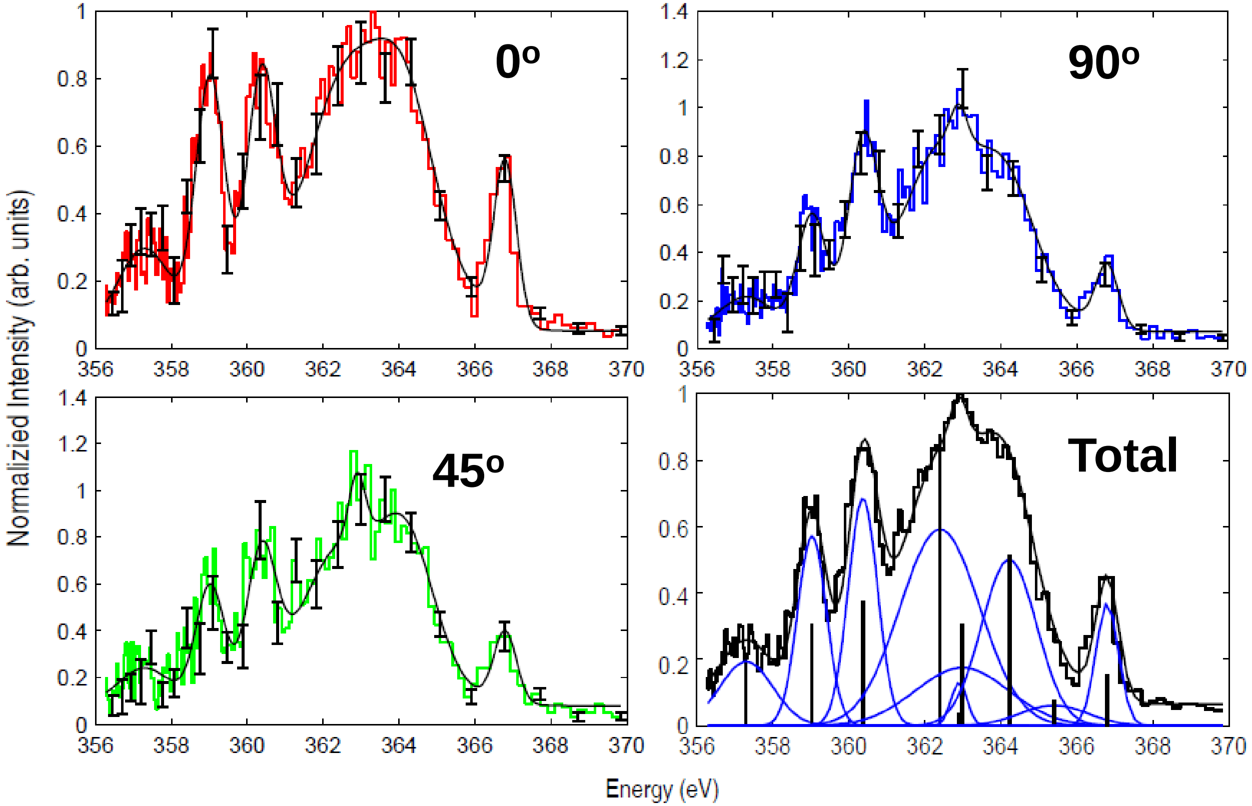
R. W. Wetmore and R. K. Boyd, J. Phys. Chem. 90, 5540 (1986).

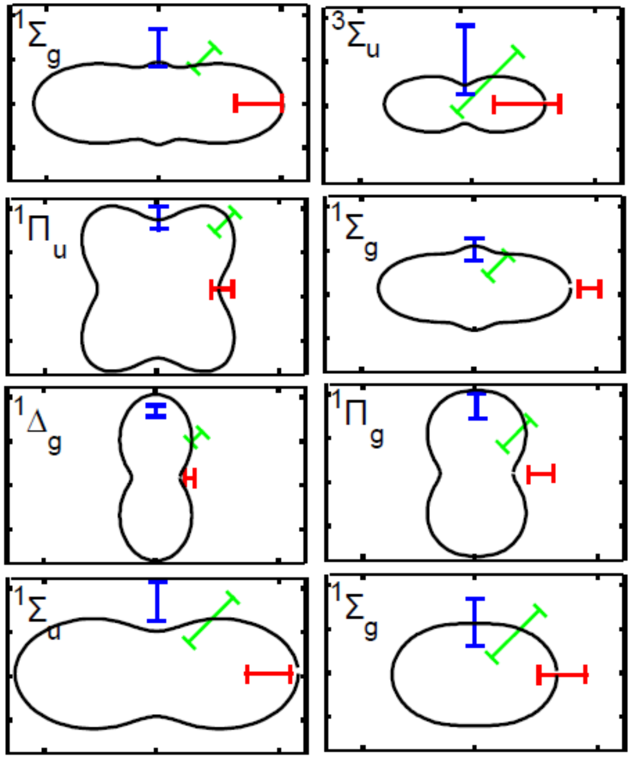
$\Gamma_K = \sigma_K F_{lcls} \approx 10^{15}\ s^{-1}$



Impulsive dynamics
If Auger time
$t < h/\Delta E$

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



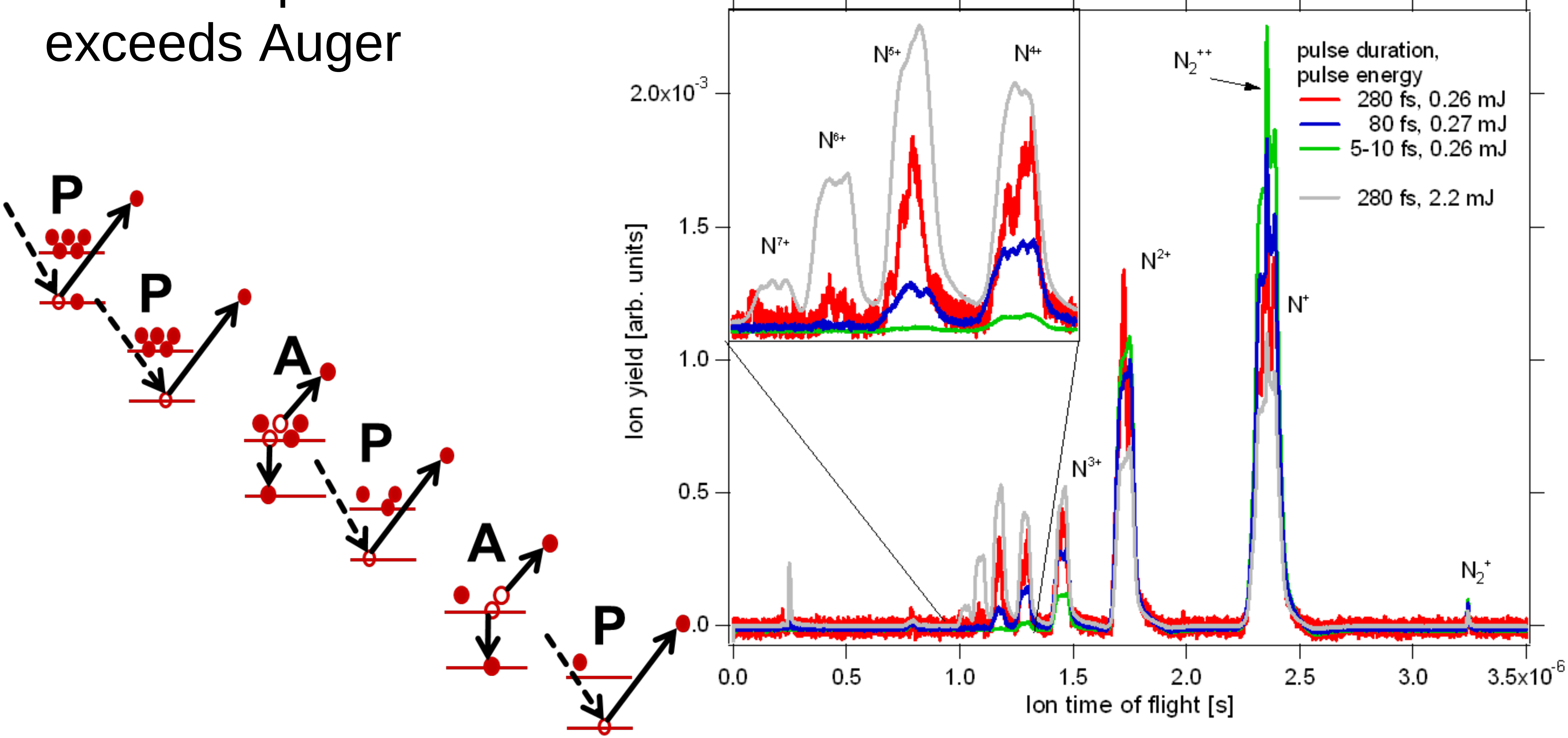


(Cryan et al, J. Phys. B 45 055601 (2012))

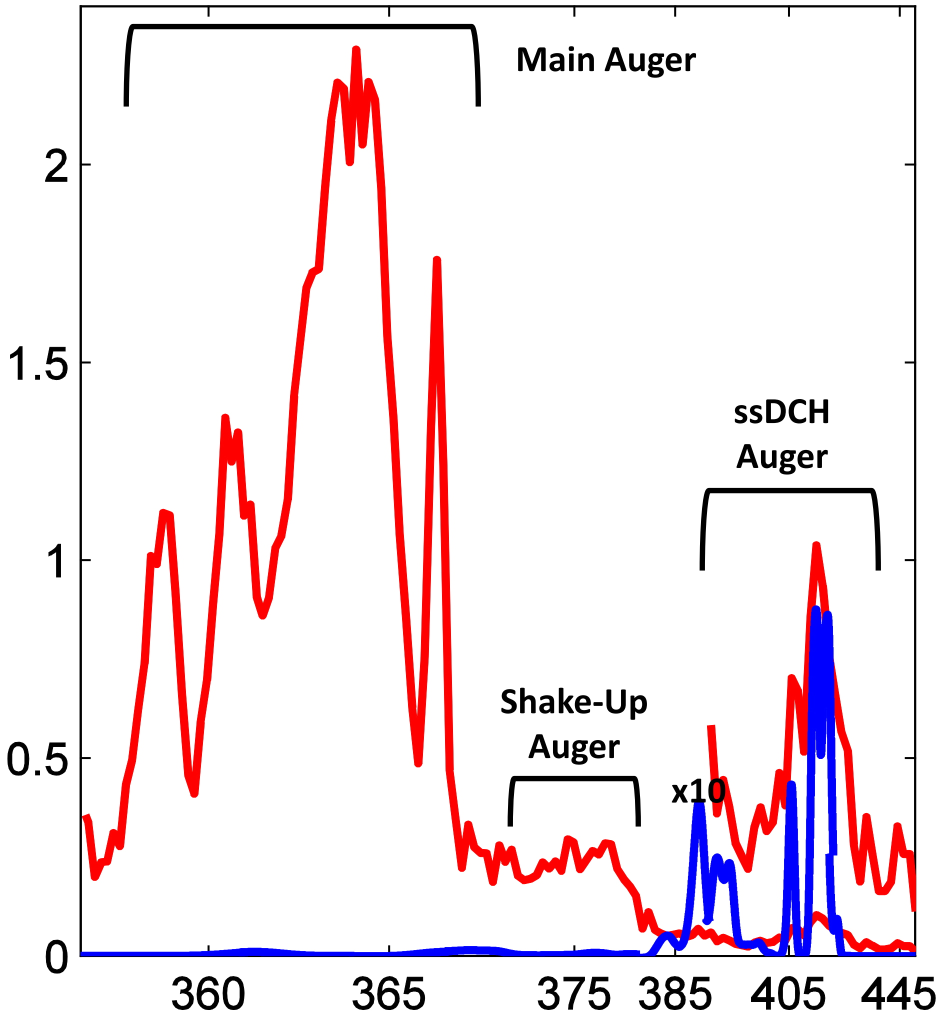
X-ray production of hollow atoms

Double core holes form when the photoionization rate exceeds Auger

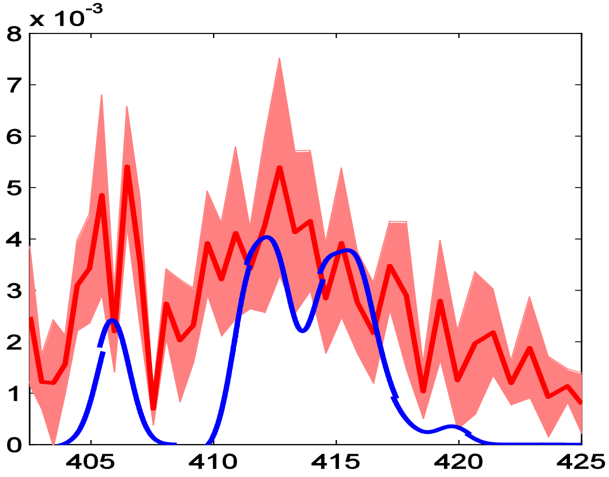
Hoener, M., L. Fang, et al. Phys. Rev. Lett. 104(25): 253002 (2010).



Auger spectrum from hollow N_2 (Double core vacancies).



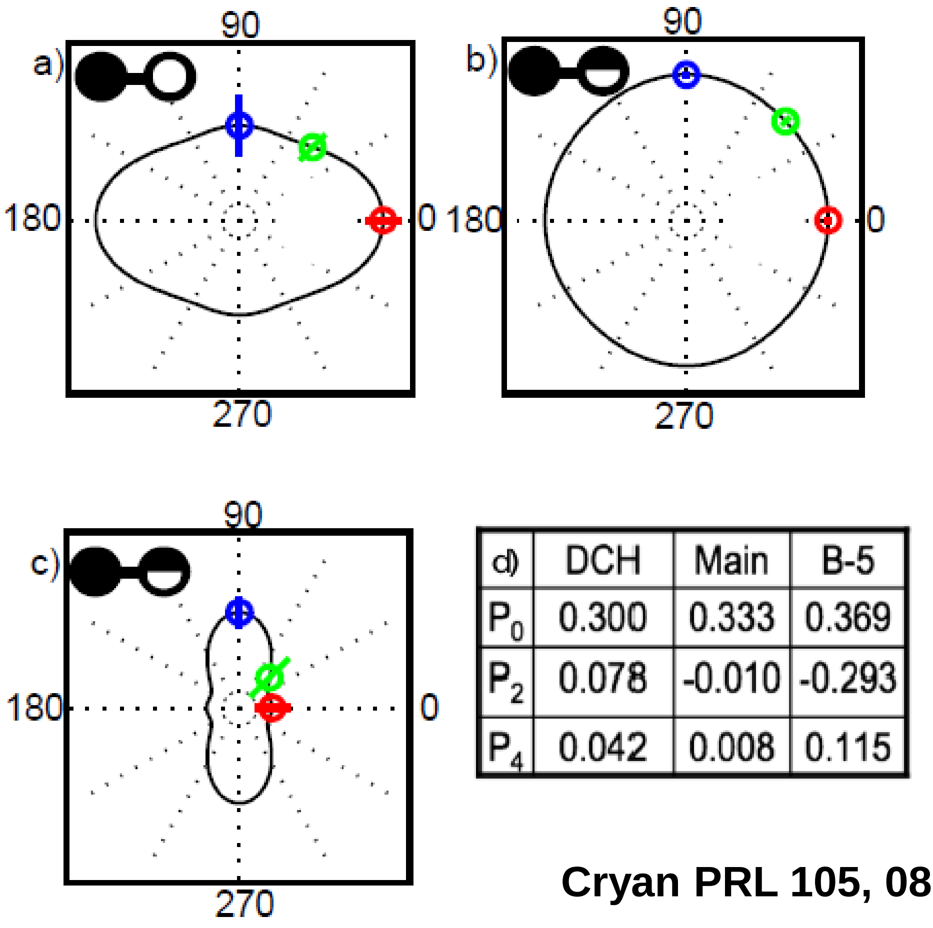
Single-site double core Auger spectrum



Cryan PRL 105, 083004 (2010)

Cryan, J. P., Glownia, J. M., Andreasson, J., Belkacem, A., Berrah, N., Blaga, C. I., Bostedt, C., Bozek, J., Buth, C., Dimauro, L. F., Fang, L., Gessner, O., Guehr, M., Hajdu, J., Hertlein, M. P., Hoener, M., Kornilov, O., Marangos, J. P., March, A. M., Mcfarland, B. K., Merdji, H., Petrovi\Ifmmode \Acutec\Else \'C\Fi, V. S., Raman, C., Ray, D., Reis, D., Tarantelli, F., Trigo, M., White, J. L., White, W., Young, L., Bucksbaum, P. H. & Coffee, R. N.

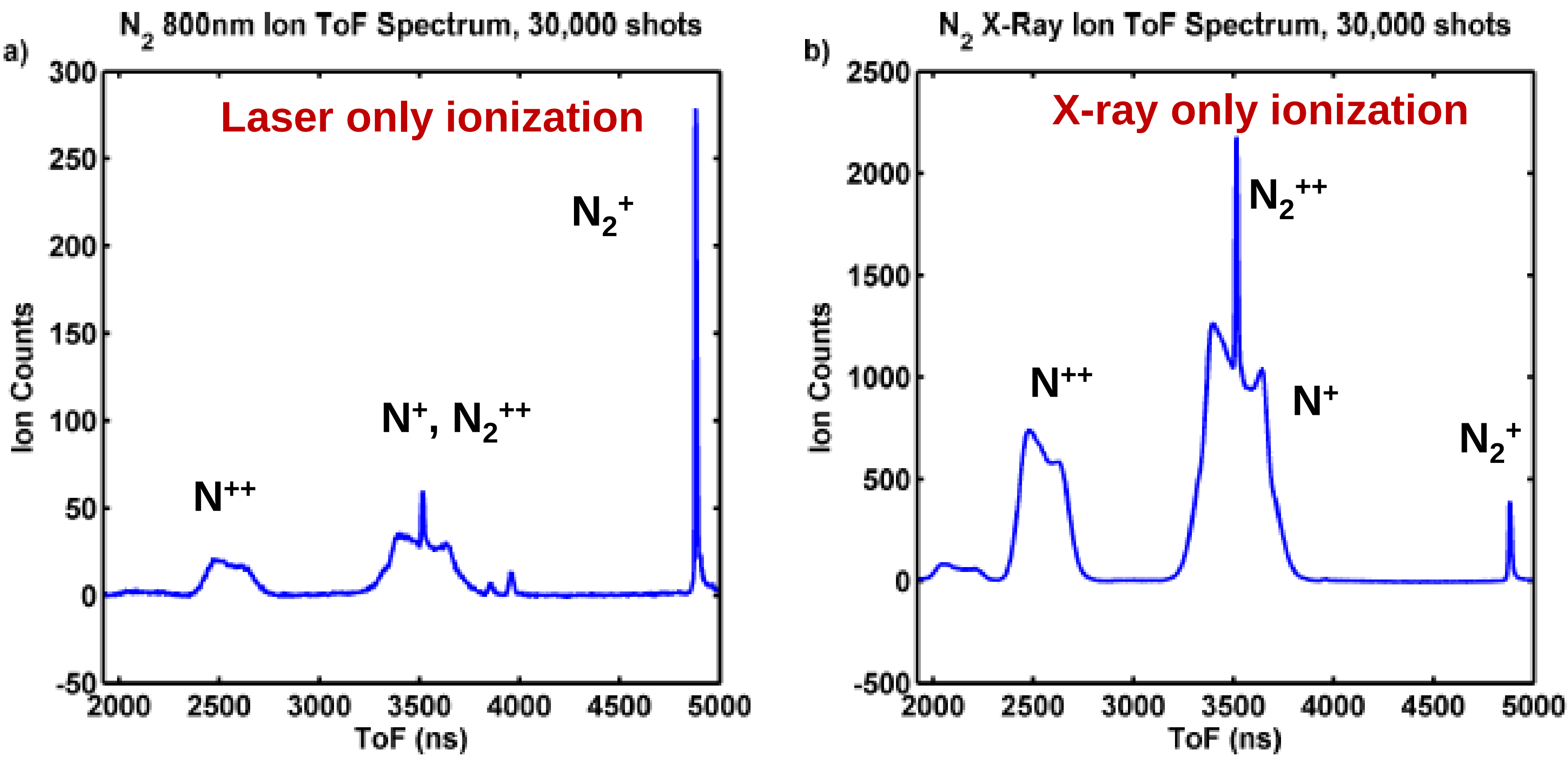
ssDCH Auger anglular distributions



d)	DCH	Main	B-5
P_0	0.300	0.333	0.369
P_2	0.078	-0.010	-0.293
P_4	0.042	0.008	0.115

Cryan PRL 105, 083004 (2010)

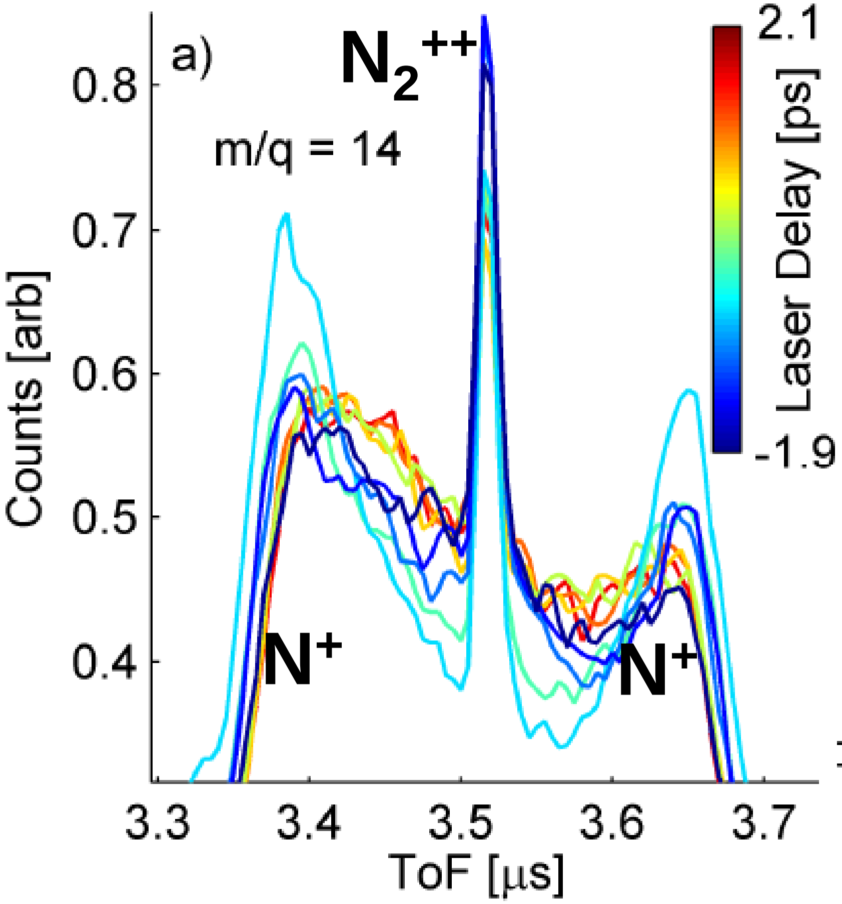
Laser vs X-ray laser multiple ionization

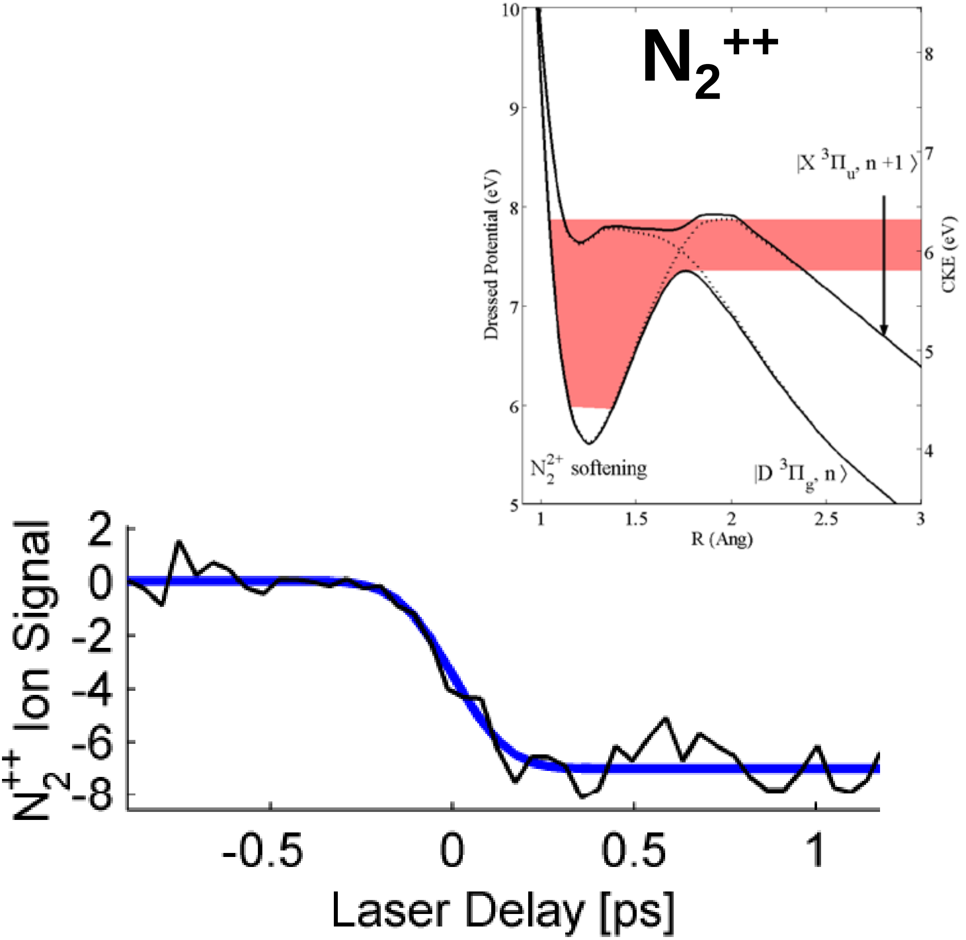


X-ray fragmentation of molecular nitrogen shows dissociation into charged fragments out to N^{7+}

J.M. Glownia

The N_2^{++} can be probed by 800 nm dissociation.

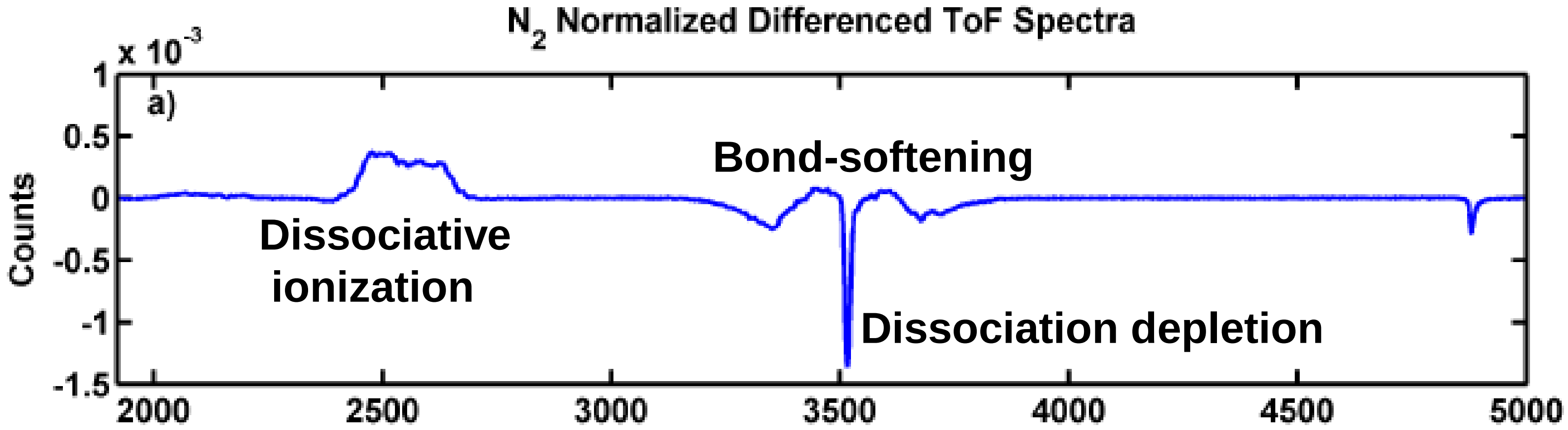




Glownia, J. M., et al. (2010). Opt. Express 18(17): 17620-17630.

Strong field dissociation

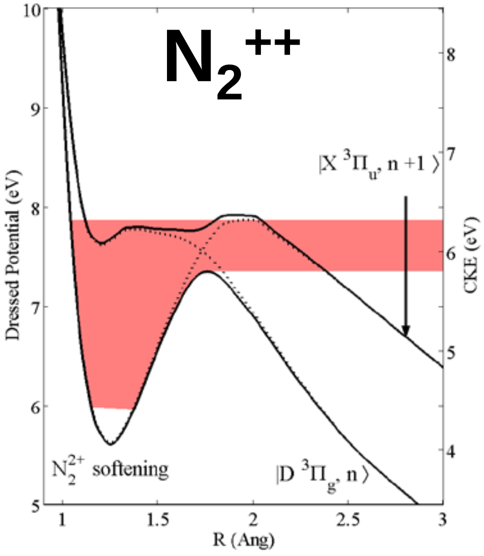
(X-rays followed by IR laser) – (X-rays alone)



Bond-softening

Dissociative ionization

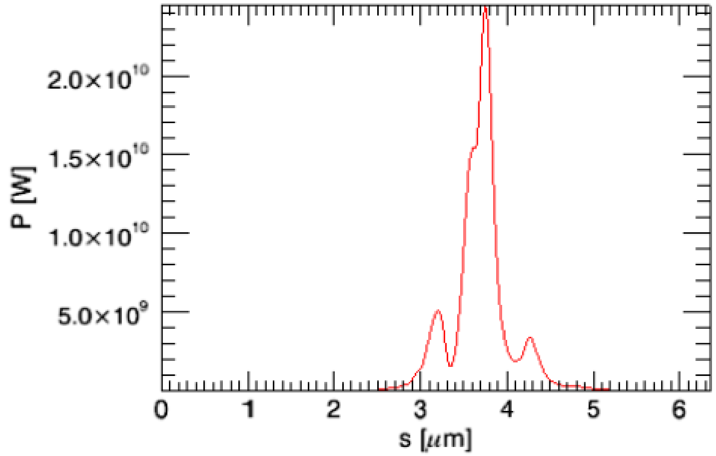
Dissociation depletion

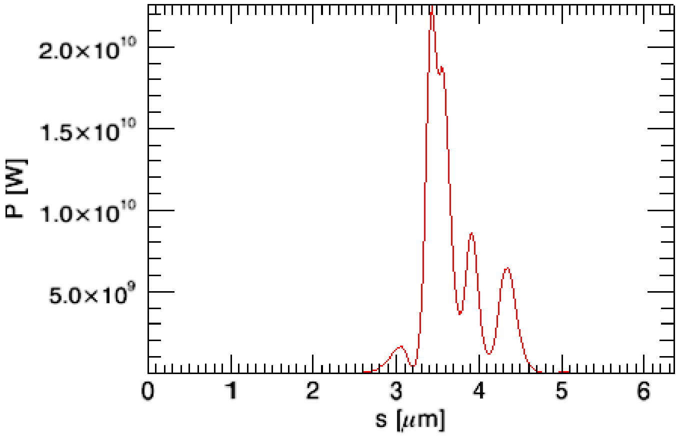


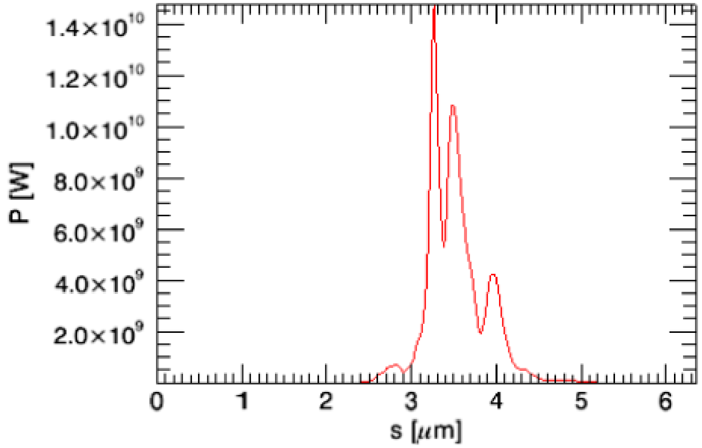
N_2^{++}

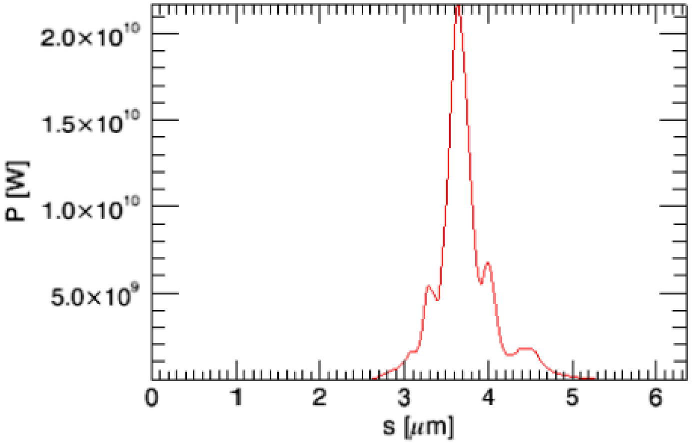
What impulsive Raman can we observe with single SASE spikes at LCLS?

Average photon number: 2.4x10^{11} , with 20% fluctuation.
Estimated time-bandwidth product ~ 3 times Fourier-transform limit.



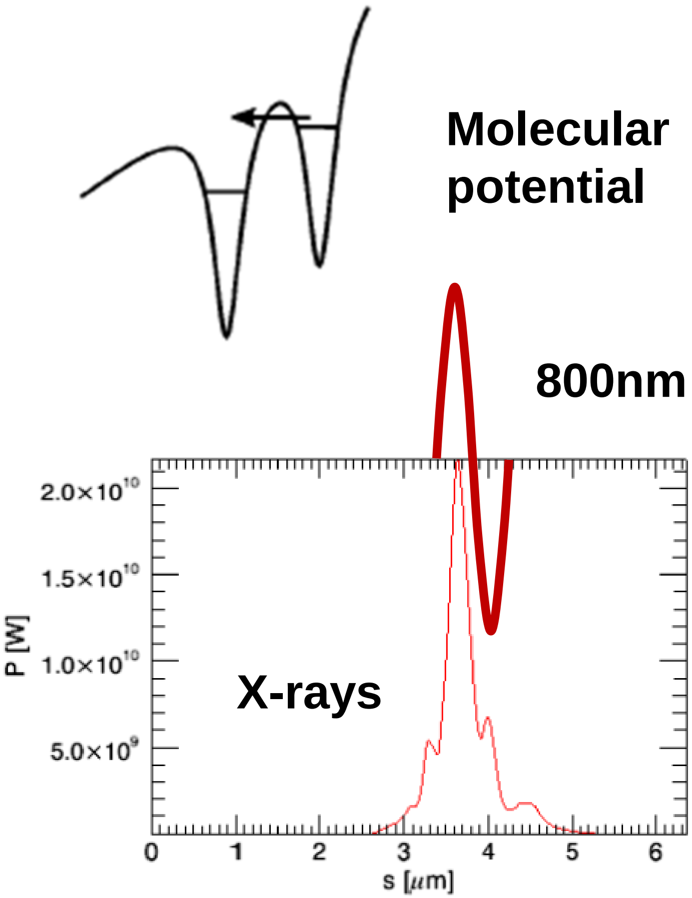


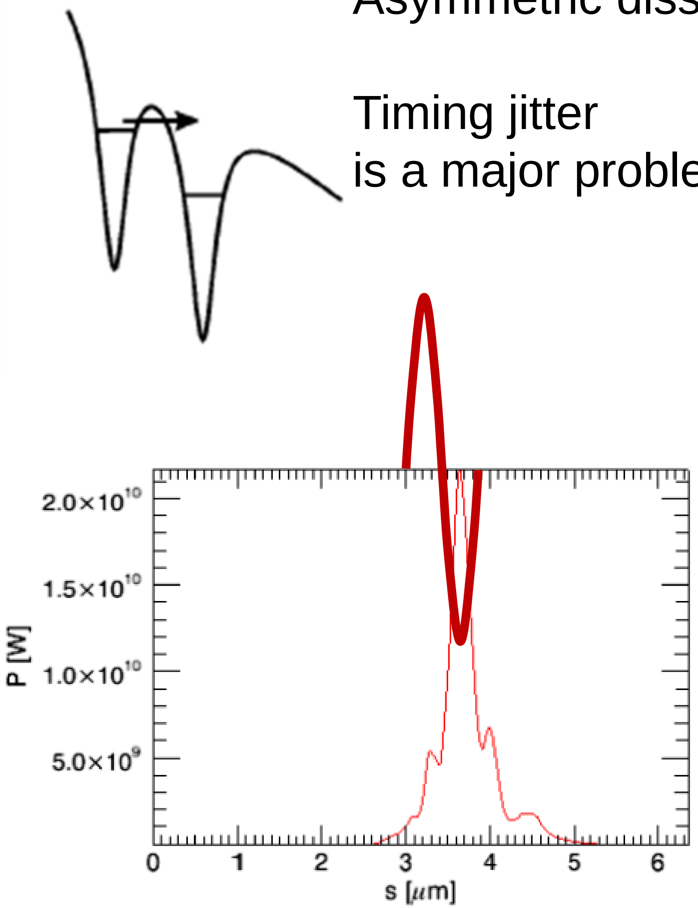




Simulation: Jo Frisch and Yuantao Ding, 15Angstrom

Sub-cycle x-rays can interrogate molecules distorted by a strong visible laser

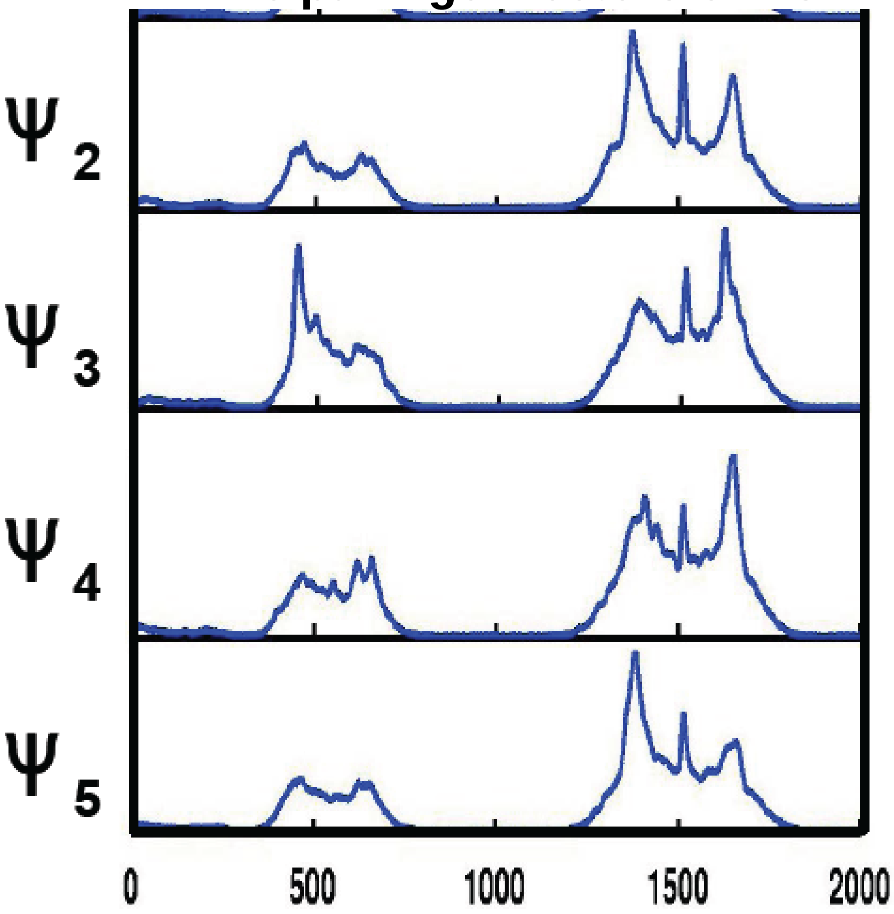




Look for strong g-u coupling
Asymmetric dissociation

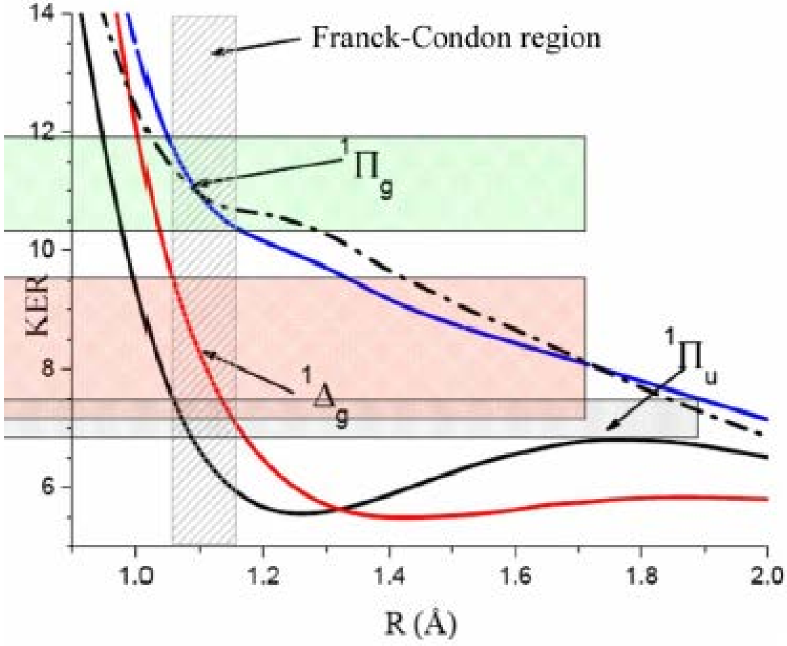
Timing jitter
is a major problem

Only slight evidence for charge-asymmetric dissociation in SVD-sorted data



Pincipal Eigenvectors of PCA

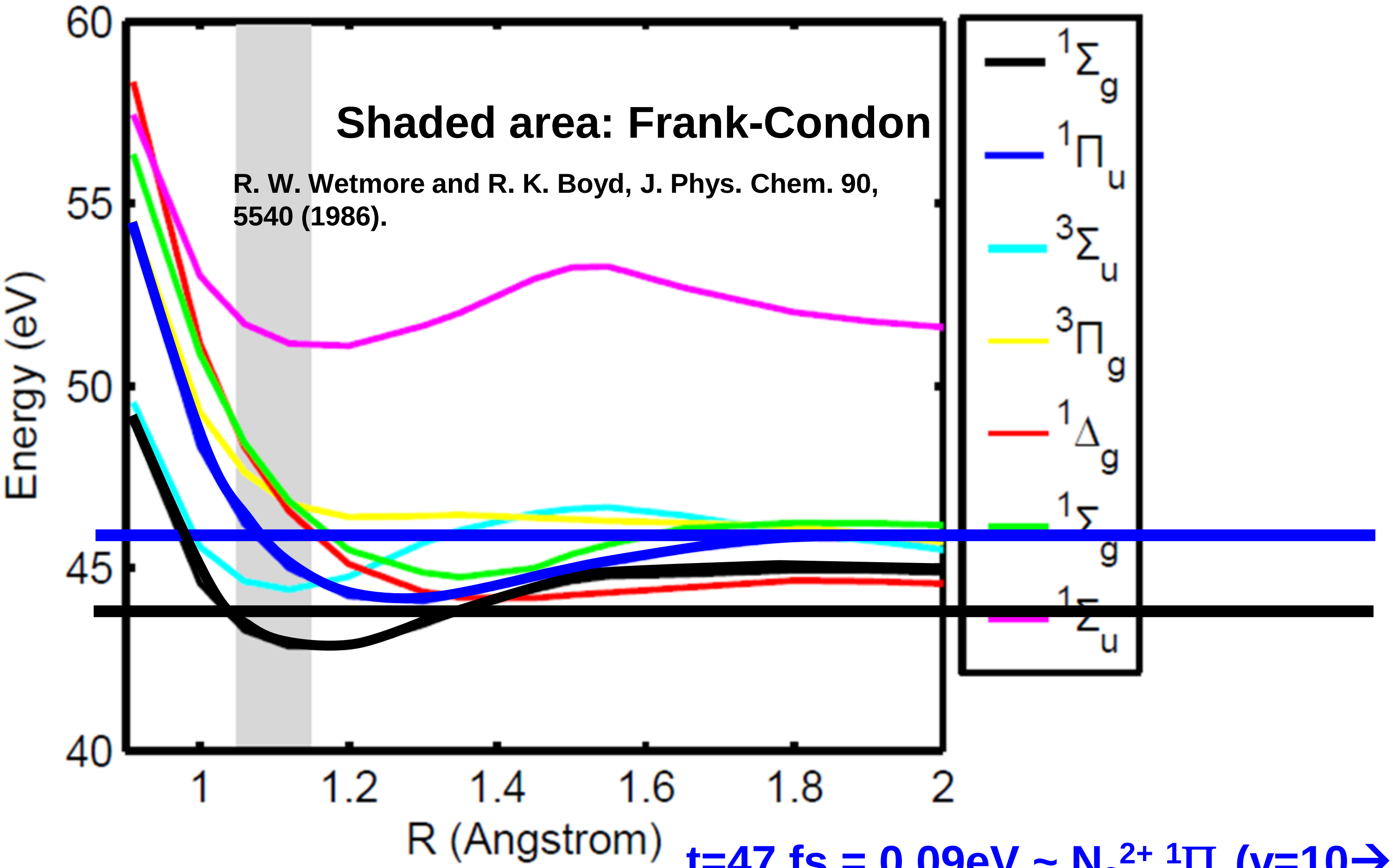
Ourmazd and Fung, unpublished



The Nitrogen dication

Dissociation channels of some transient dication states might undergo asymmetric dissociation under the influence of strong fields. Analysis has not been conclusive.

Search for vibrational coherencs on the N_2^{++} Potential Energy Surfaces



Shaded area: Frank-Condon

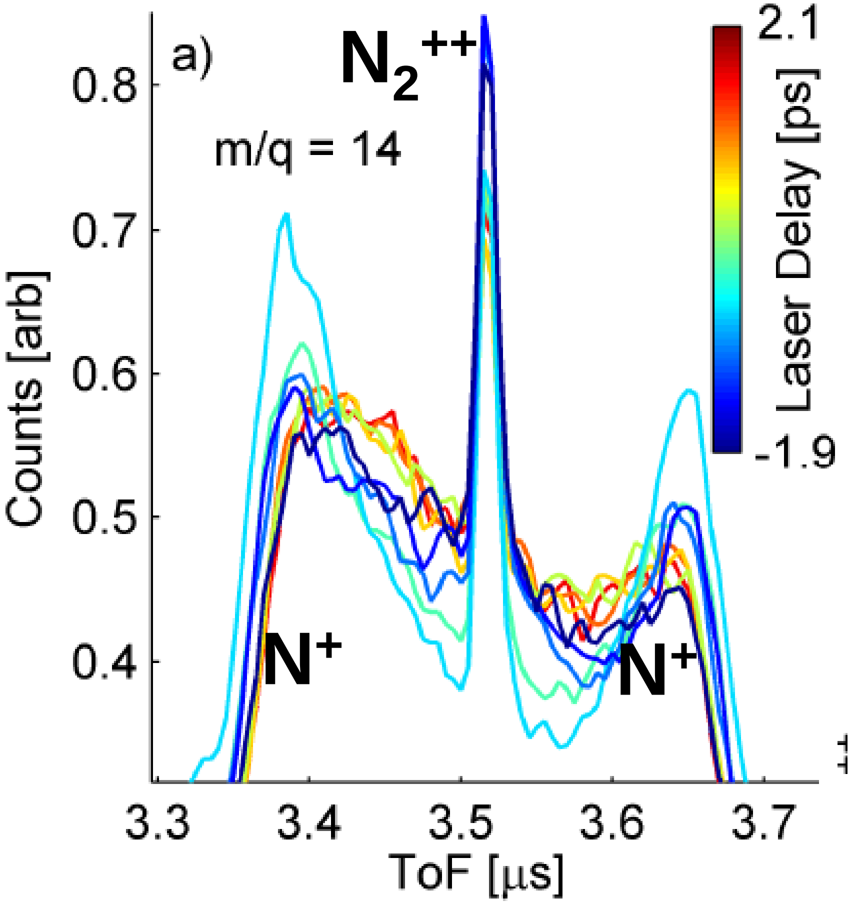
R. W. Wetmore and R. K. Boyd, J. Phys. Chem. 90, 5540 (1986).

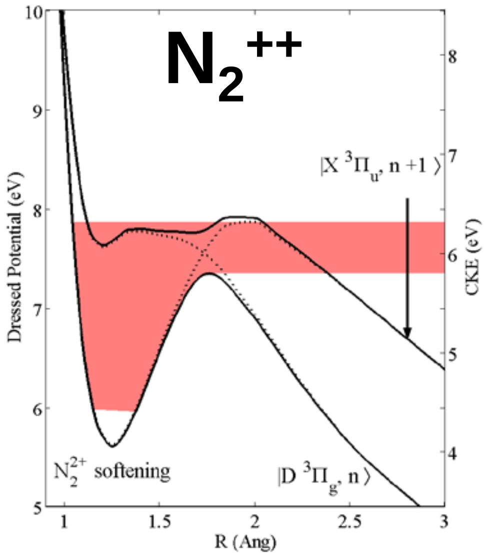
t=47 fs = 0.09eV ~ N_2^{2+} $^1\Pi_u$(v=10→11)

t=21 fs = 0.19eV ~ N_2^{2+} $X^1\Sigma_g$(v=3→4)

t=13 fs = 0.31eV ~ N_2^{+} $^2\Sigma_g$(v=0→1)

Inconclusive: searching for N_2^{++} vibrational wave packets probed by 800 nm dissociation.



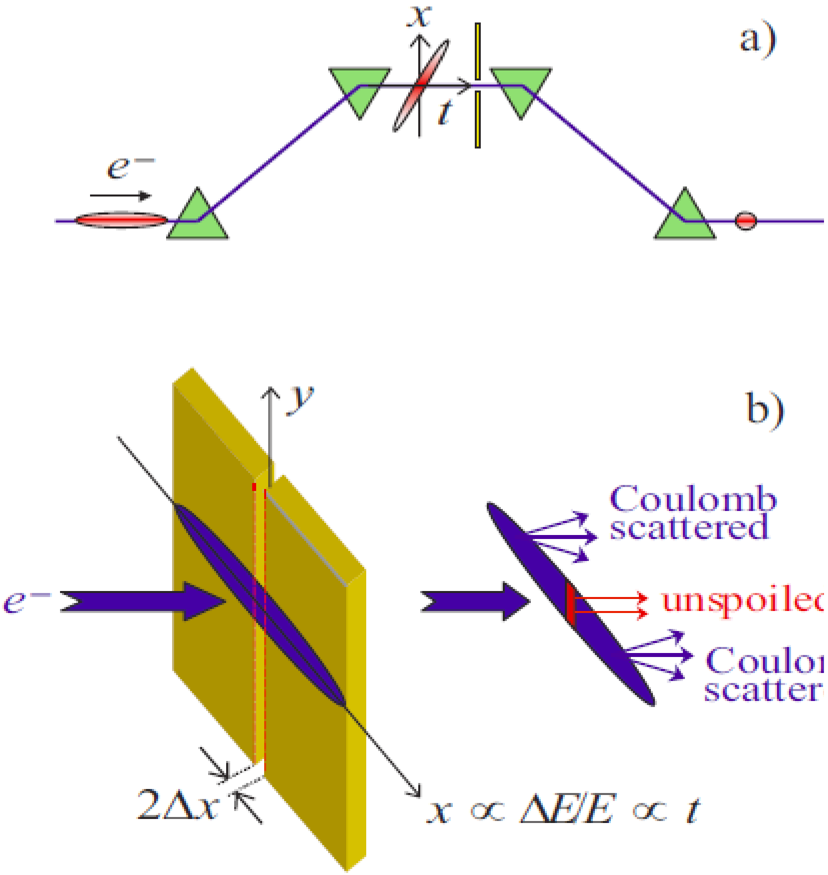


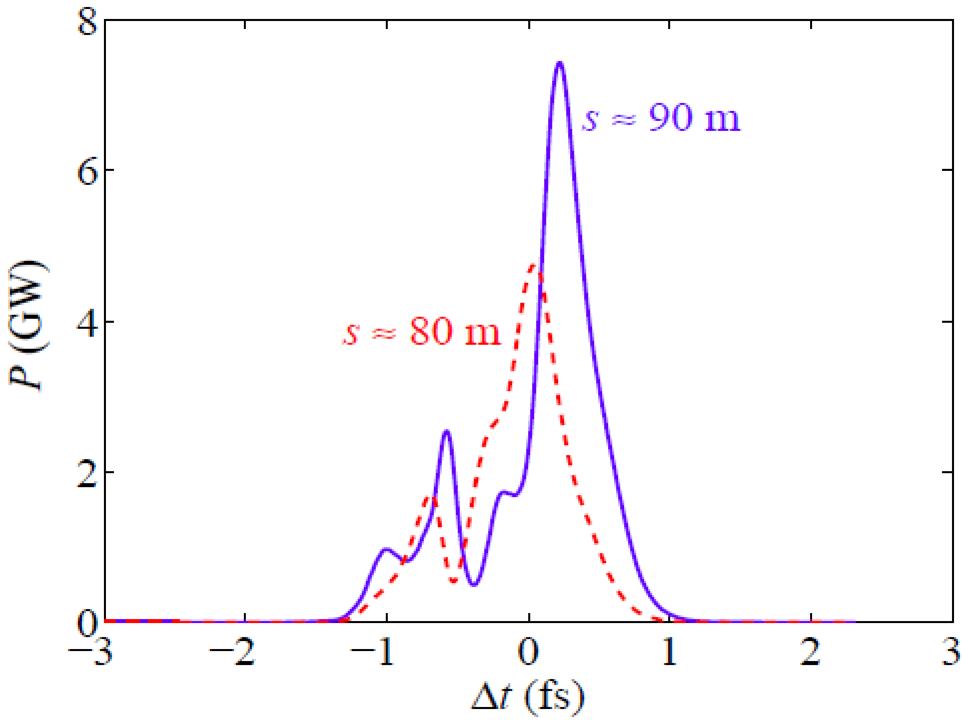
Pump-probe jitter obscures the femtosecond dynamics

Glownia, J. M., et al. (2010). Opt. Express 18(17): 17620-17630.

Shorter pulses at LCLS

Slotted spoiler to filter attosecond pulses from an x-ray FEL

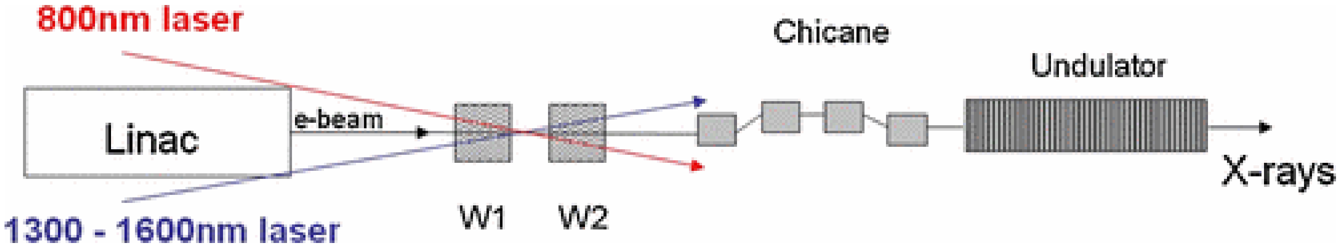




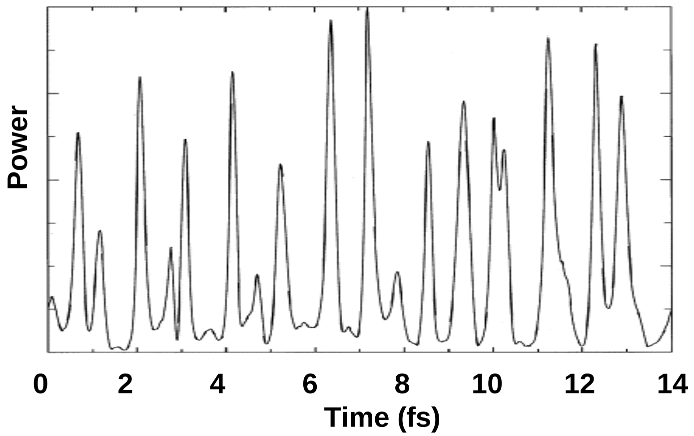
P. Emma et al. / Proceedings of the 2004 FEL Conference, 333-338

Many future ideas to shorten the pulses

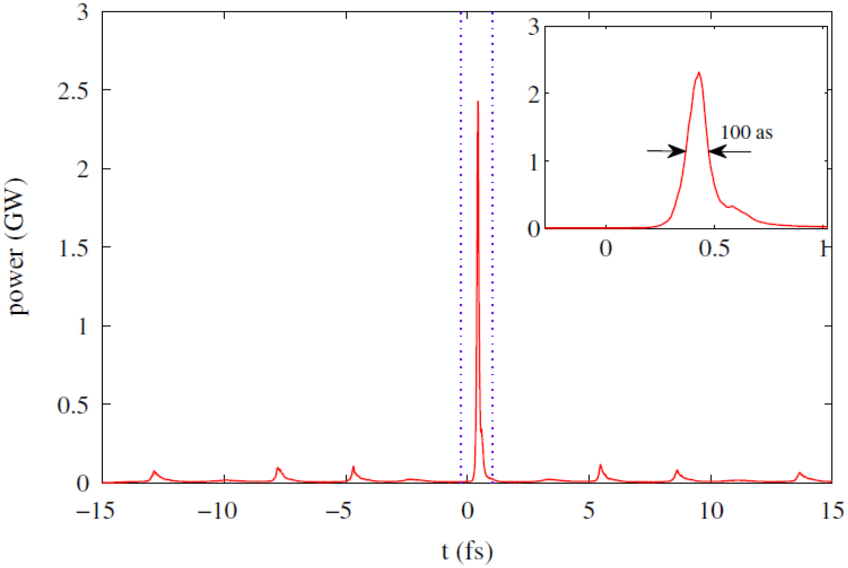
Laser pre-modulated electrons tame SASE



Typical SASE:



Single spike SASE:



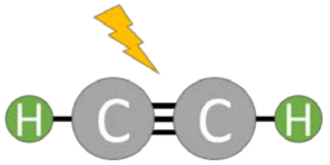
Ding, Y., PRST 12, (2009).

Three x-ray probe experiments

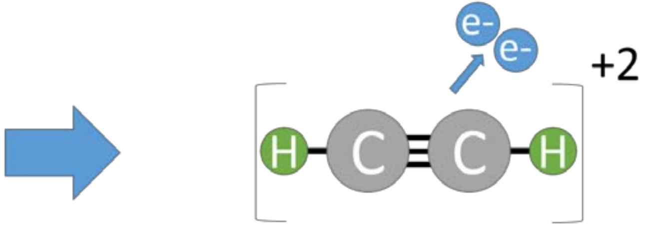
- **Photoionization/Auger-induced motion:**
  - **Acetylene to vinylidene.[In review. Conference proceedings: P. H.B., C. Liekhus-Schmaltz, et al. [Ultrafast Phenomena doi:10.1364/UP.2014.11.Fri.B.6]**
- **X-ray probe of UV-induced motion**
  - **Transient Auger spectroscopy in thymine [McFarland, …Guehr et al. Nature Comm. 5, 4235 (2014)]**
- **X-ray probe of conical intersections**
  - **CHD isomerization [Petrovic et al. PRL 108 2012 253006.]**

X-ray absorption can lead to internal motion.

Acetylene: The smallest organic molecule that can isomerize.

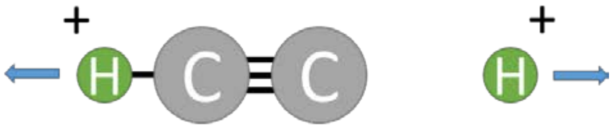


(1) 400 eV x-ray absorption



(2) Auger decay

(3-A) Break the C-C bond



(3-P) Break the C-H bond

(3-V) Isomerize to vinylidene and then fragment.

X-ray-induced proton migration in acetylene

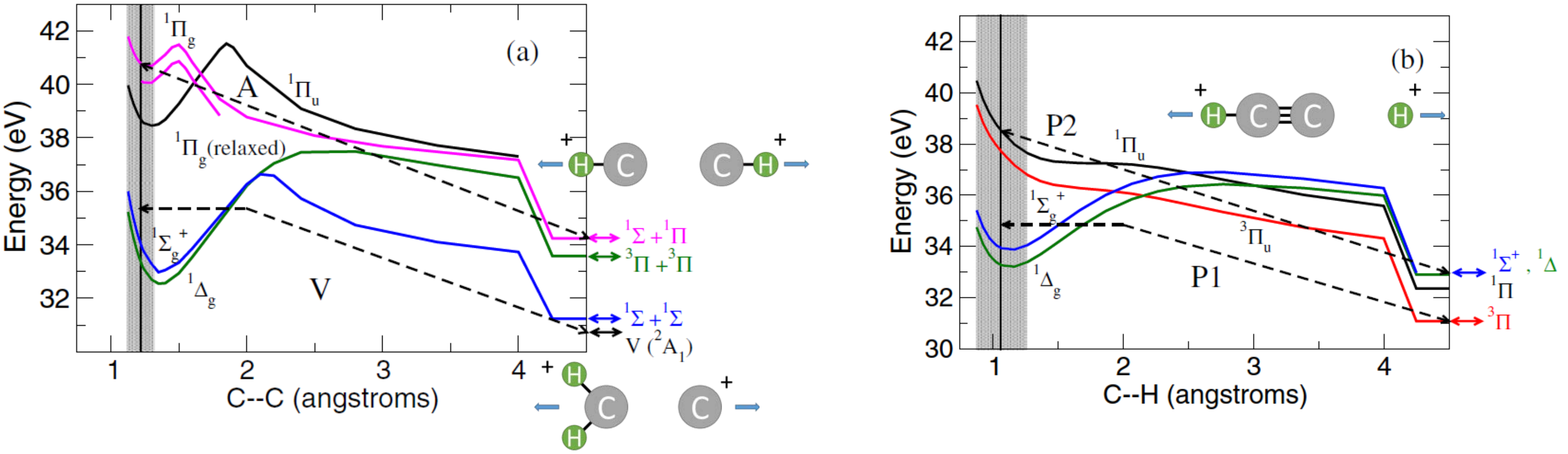
- **Proton migration in acetylene leads to vinylidene.**

H-C≡C-H $H_2C=C:$

- **Acetylene dication is simple enough to model, extensively studied.**

<60 fs for isomerization

[T. Osipov et al., Physical Review Letters 90, 233002 (2003).]



[T. Osipov et al. J Phys B 2008 41 091001]

AMO75113: “Initiating New Chemistry with Short X-ray Pulses: Multi-configuration Wavepackets

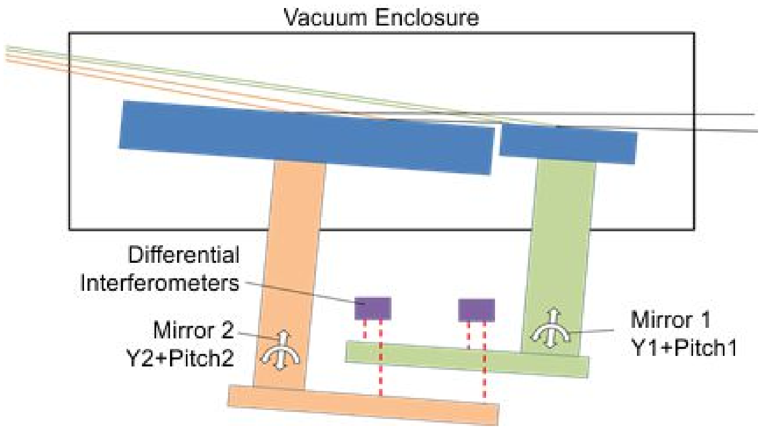
Vladimir S. Petrovic[1,2] (sp.)
Philip H. Bucksbaum[1,2,4]
James M. Glownia[2,4]
Brian K. McFarland[2,4]
Adi Natan[2]
Ian Tenney[2]
Shungo Miyabe[2,9]
Chelsea Liekhus-Schmaltz[1,2]
Limor Spector[1,2]
Julien Devin[1,2]
Song Wang[1,2]
Li Heng[2]
Alvaro Sanchez[3]
Daniel Walke[3]
Andrei Kamalov[2]

Todd Martinez[2,9]
Markus Guehr[2]
Nora Berrah[5]
Brendan Murphy[5]
Timur Osipov[5]
Li Fang[5]
Jonathan P. Marangos[3]
Marco Siano[3]
Emma Simpson[3]
Robert W. Field[8]
Lutz Foucar[12]

Ali Belkacem[10]
Thorsten Webber[10]
Christoph Bostedt[6]
John D. Bozek[6]
Ken Ferguson[6]
Sebastian Carron[6]
Michelle Swiggers[6]
Ryan Coffee[6]
Jacek Krzywinski[6]
Artem Rudenko[11]
Daniel Rolles[7]
Cedric Bomme[7]
Rebecca Boll[7]
Benjamin Erk[7]

[1]Stanford University, Department of Physics, Stanford, CA
[2]The PULSE Institute, SLAC, Menlo Park, CA
[3]Department of Physics, Imperial College London, UK
[4]Stanford University, Department of Applied Physics, Stanford, CA
[5]Physics Department, University of Connecticut, CT
[6]LCLS at SLAC National Accelerator Laboratory, Laser group, Menlo Park, CA
[7]DESY, Hamburg, Germany
[8]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA
[9]Stanford University, Department of Chemistry, Stanford, CA
[10]Advanced Light Source, LBNL, Berkeley, CA
[11]Department of Physics, Kansas State University, Manhattan, KS
[12] Max Planck Center for Medical Research, Munich, Germany

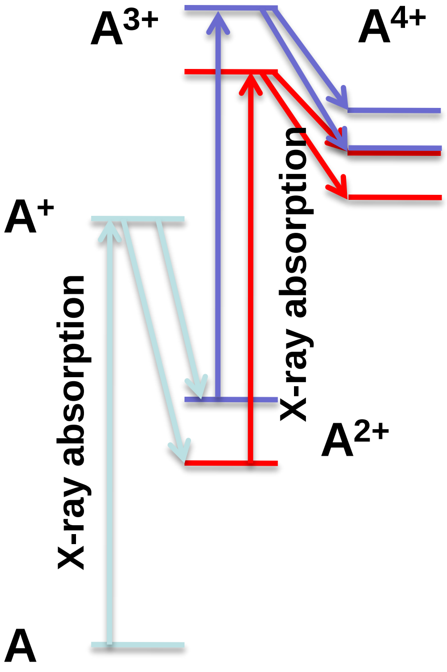
X-ray-induced processes can be probed by a second time-delayed x-ray pulse



B. Murphy, et al.
J. Phys. Conf. 388 (2012) 142003.

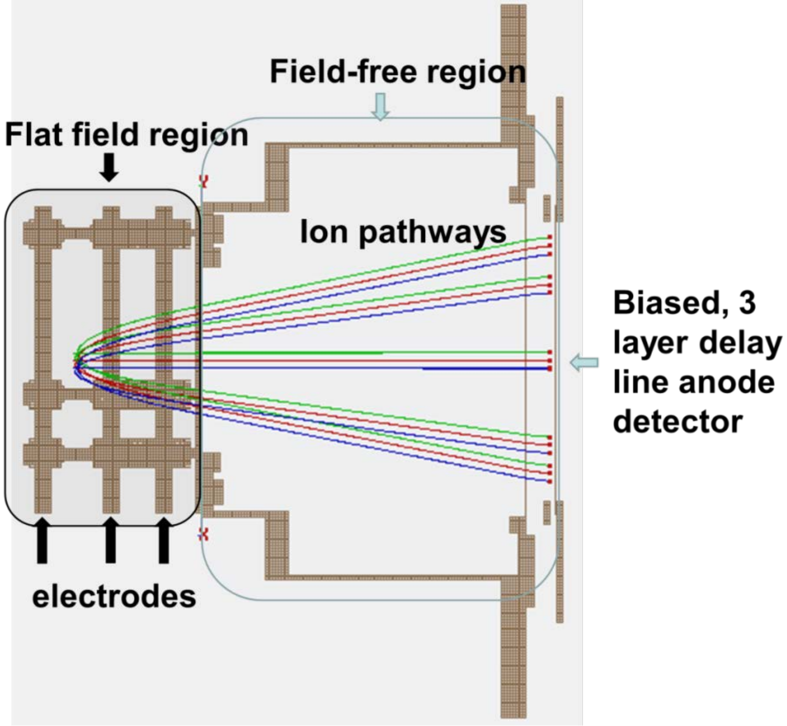
Split-and-delay apparatus

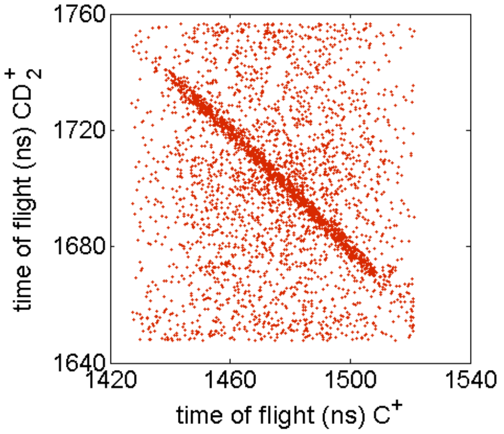
Recorded the following delays:
C_2H_2: 0, 30, 50, 100 fs
C_2D_2: 0, 12, 25, 50, 100 fs
OCS: 0, 20, 30, 40, 60, 100 fs
CO: 0, 150 fs

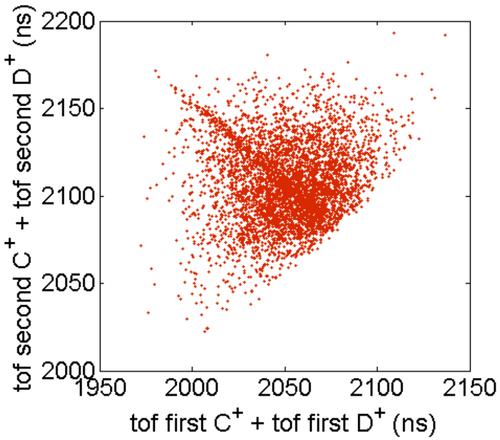


X-rays: 400 eV

Ion fragmentation momentum







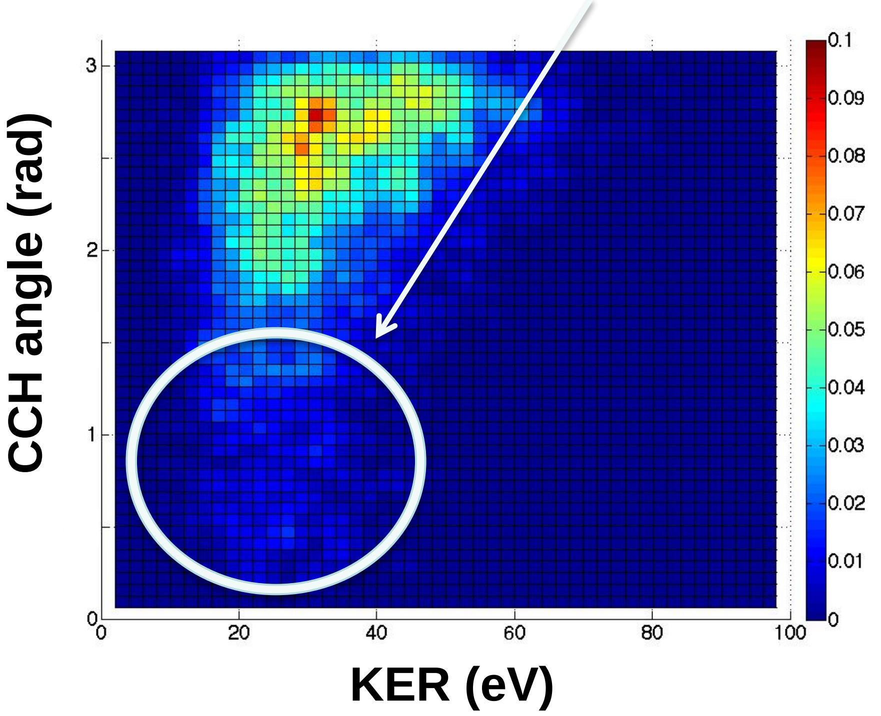
Full momentum recovery for all four fragments using delay line anode detector.

Permits recovering information about the geometry.

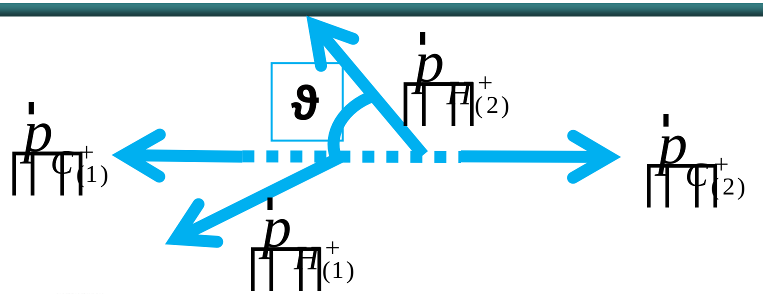
Vinylidene and Acetylene Channels also Have Different KER Distributions

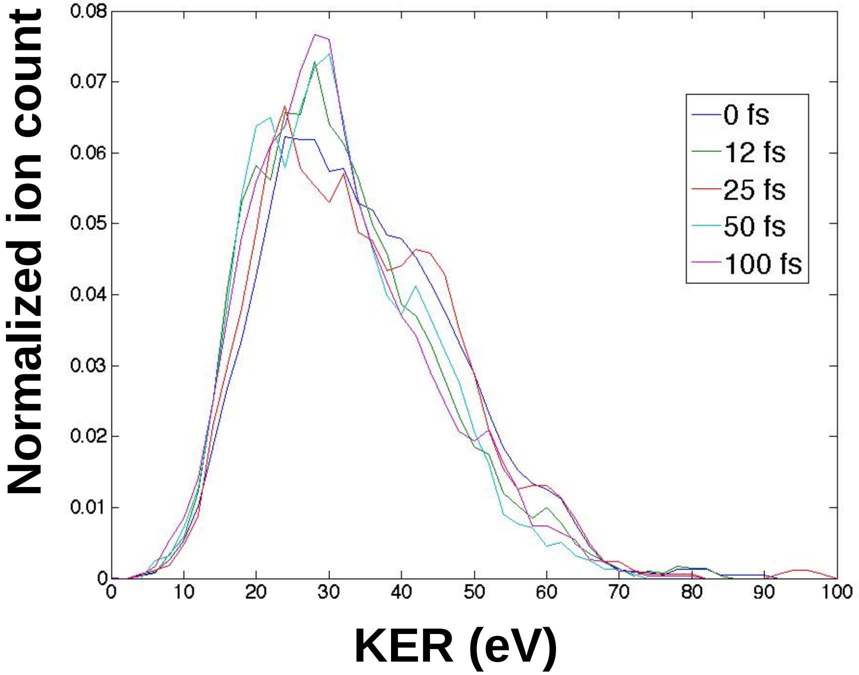
$C^+/C^+/D^+/D^+$ channel

Vinylidene-like



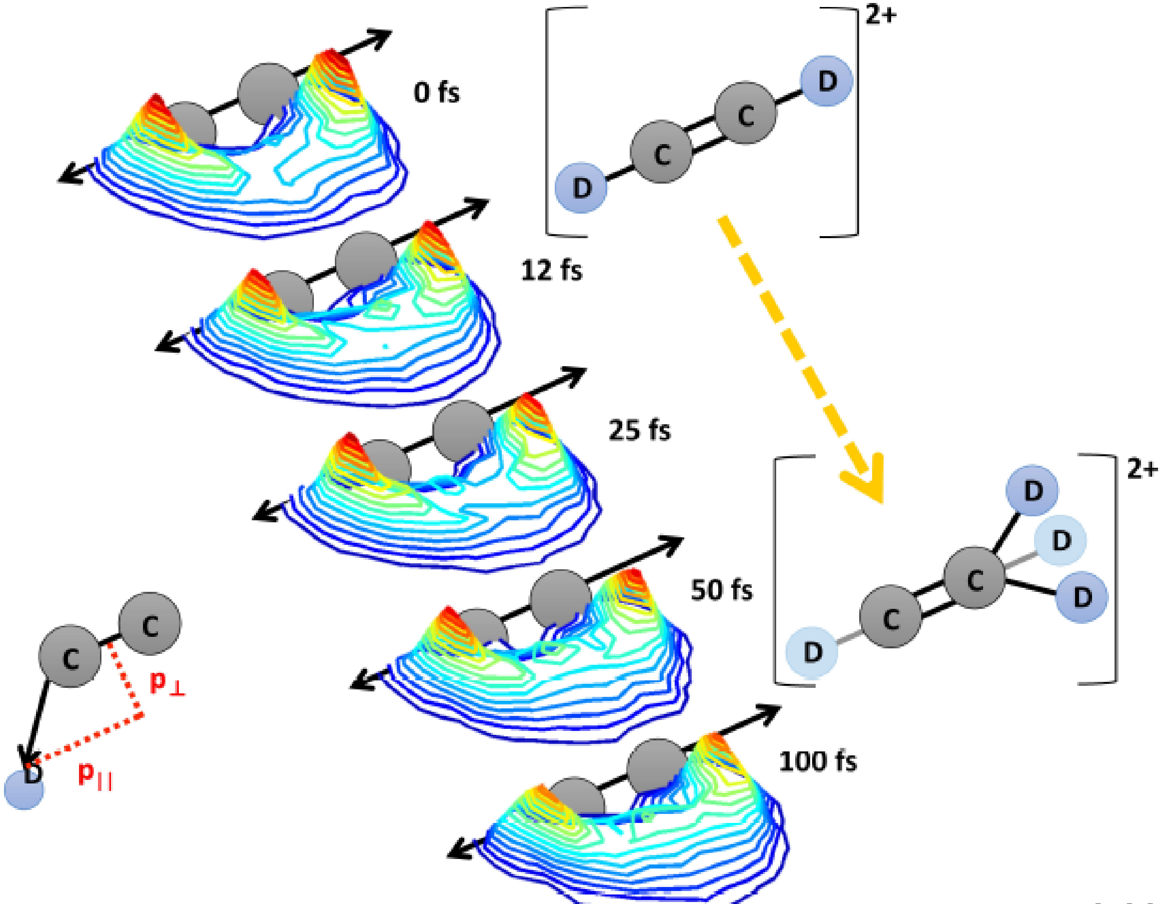
Dependence of KER distribution on proton ejection angle





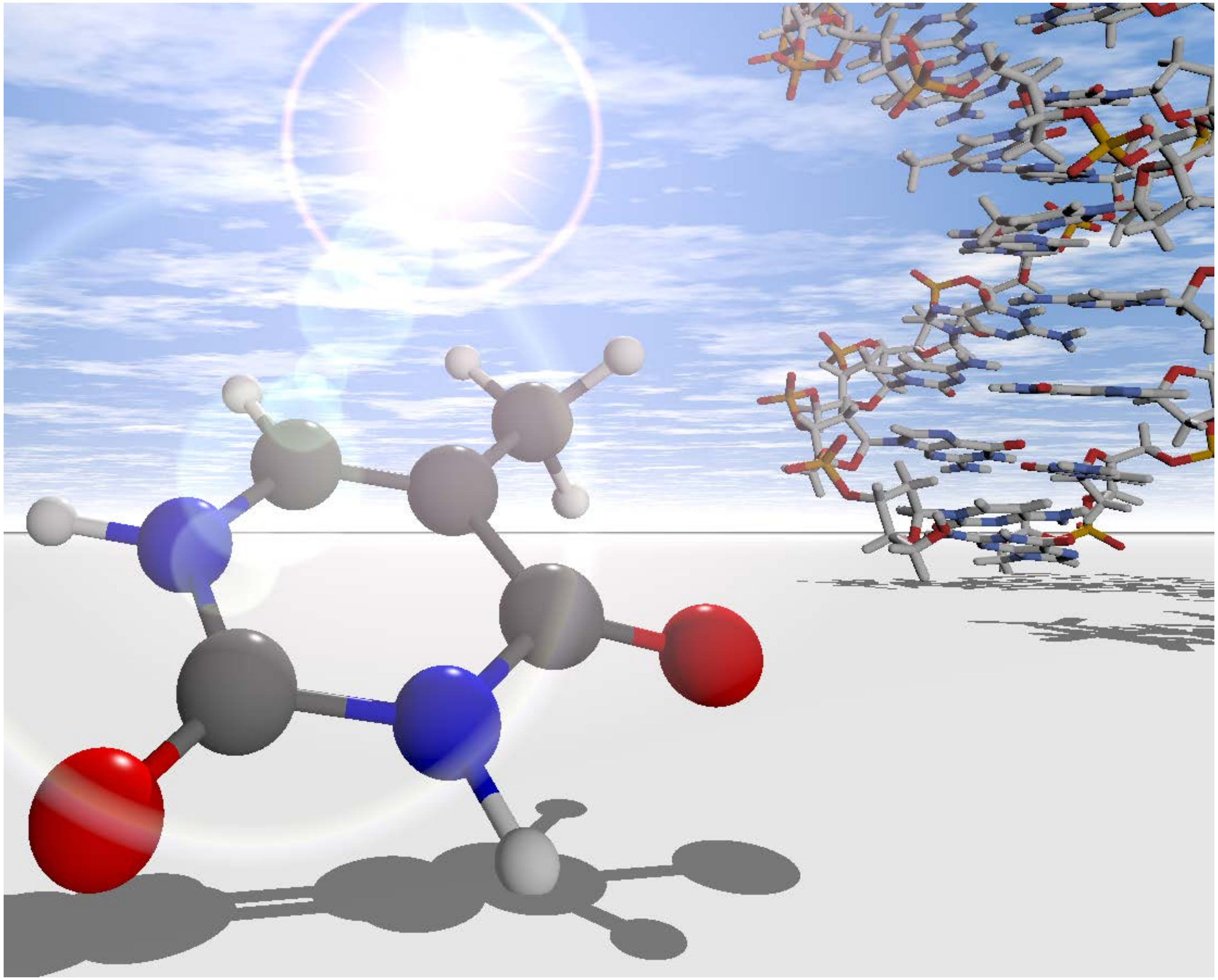
Evolution of KER distribution on x-ray pump x-ray probe time delay

Molecular movie

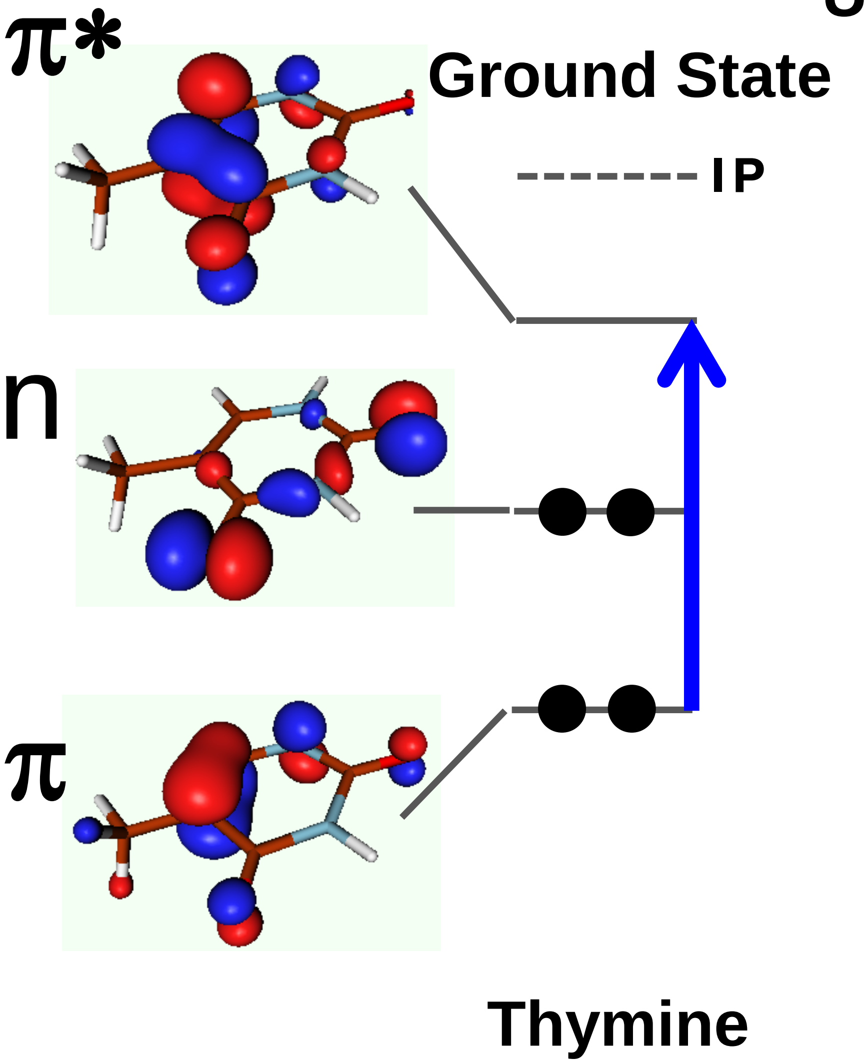


P. H.B., C. Liekhus-Schmaltz, et al.
Ultrafast Phenomena
doi:10.1364/UP.2014.11.Fri.B.6

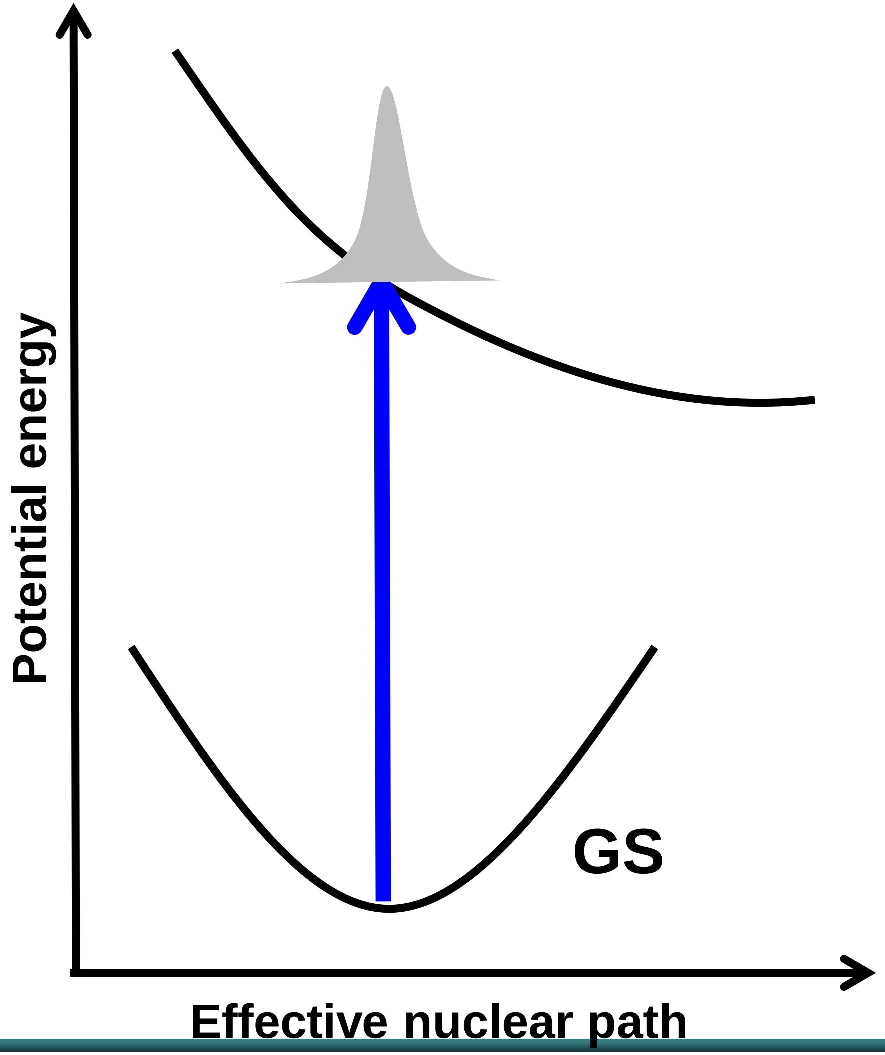
Transient Auger probe of electron dynamics



Ultrafast electron dynamics: Nucleobase photoprotection



UV excitation: π →π*



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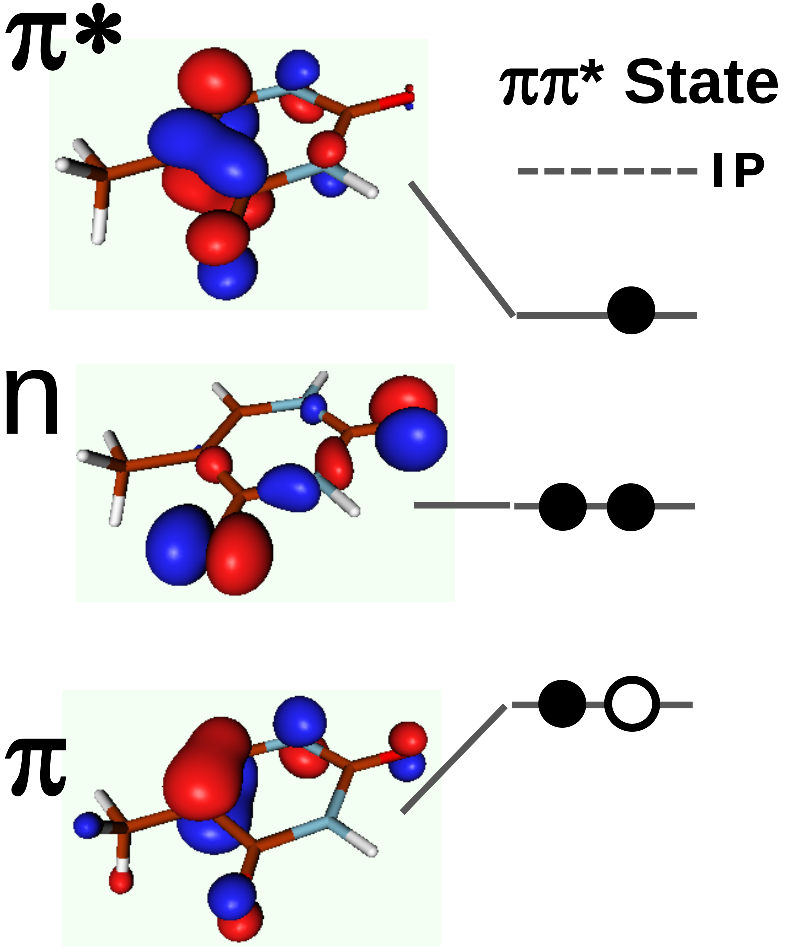
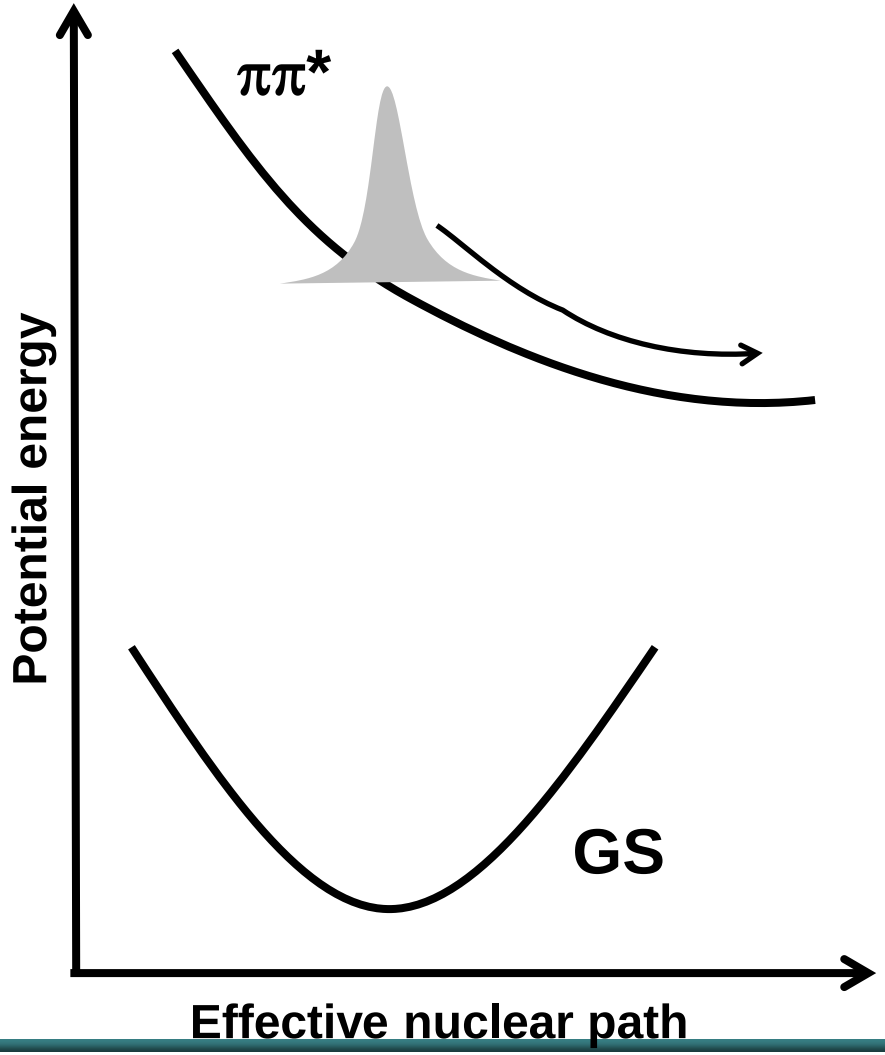
Ultrafast electron dynamics: Nucleobase photoprotection

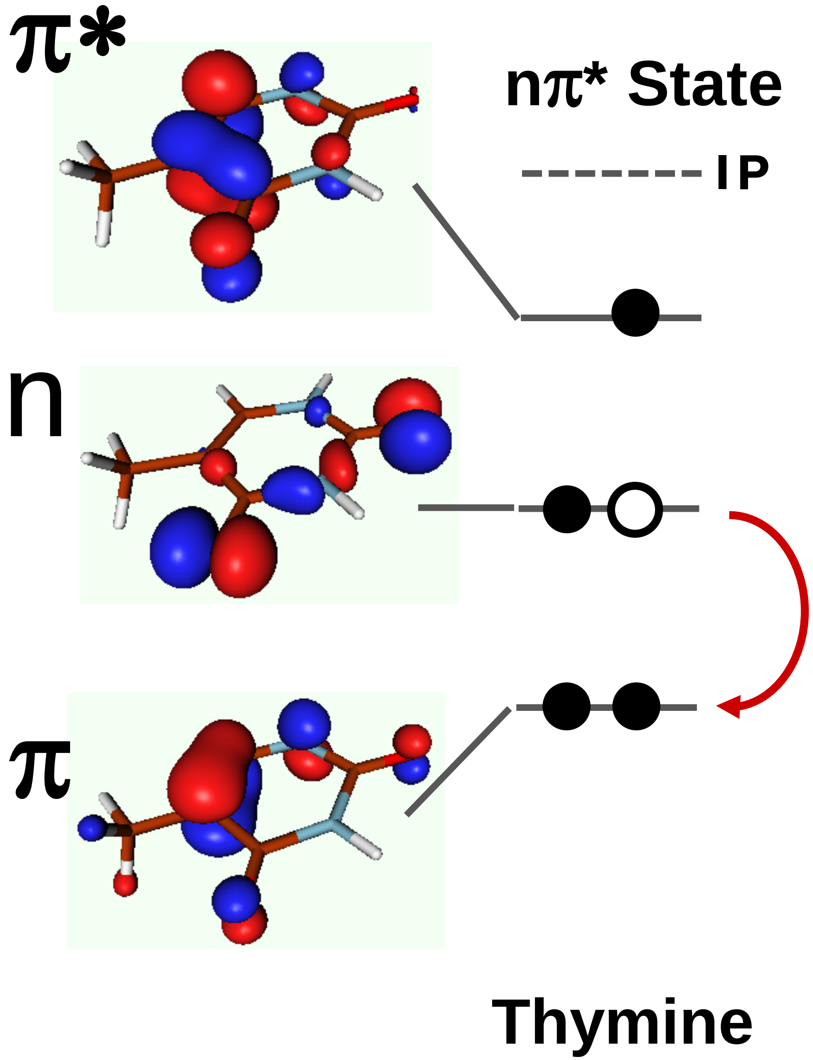


Thymine

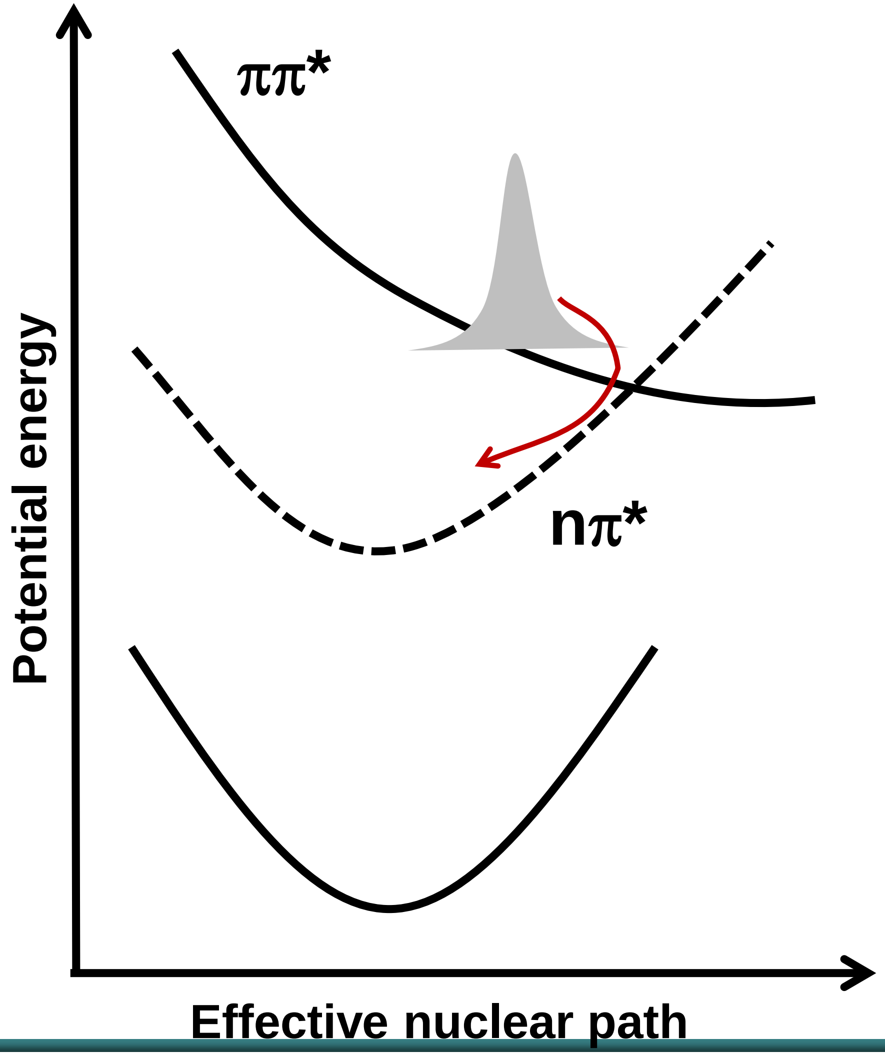
UV excitation: π →π*



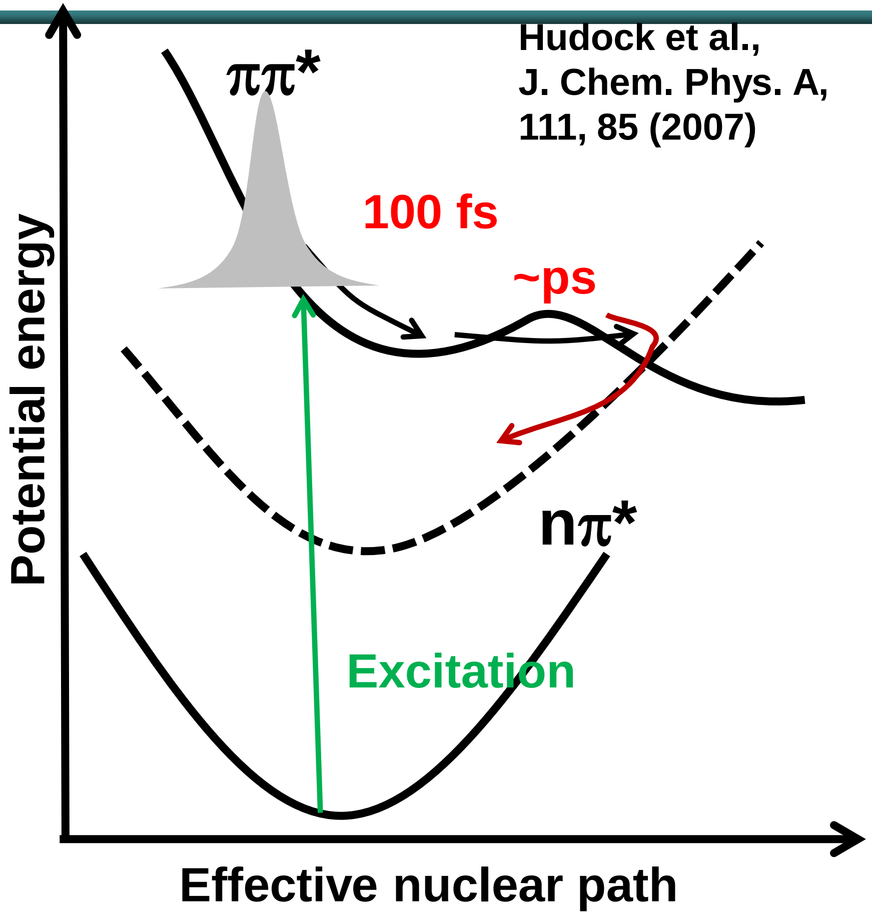
Non-Born-Oppenheimer



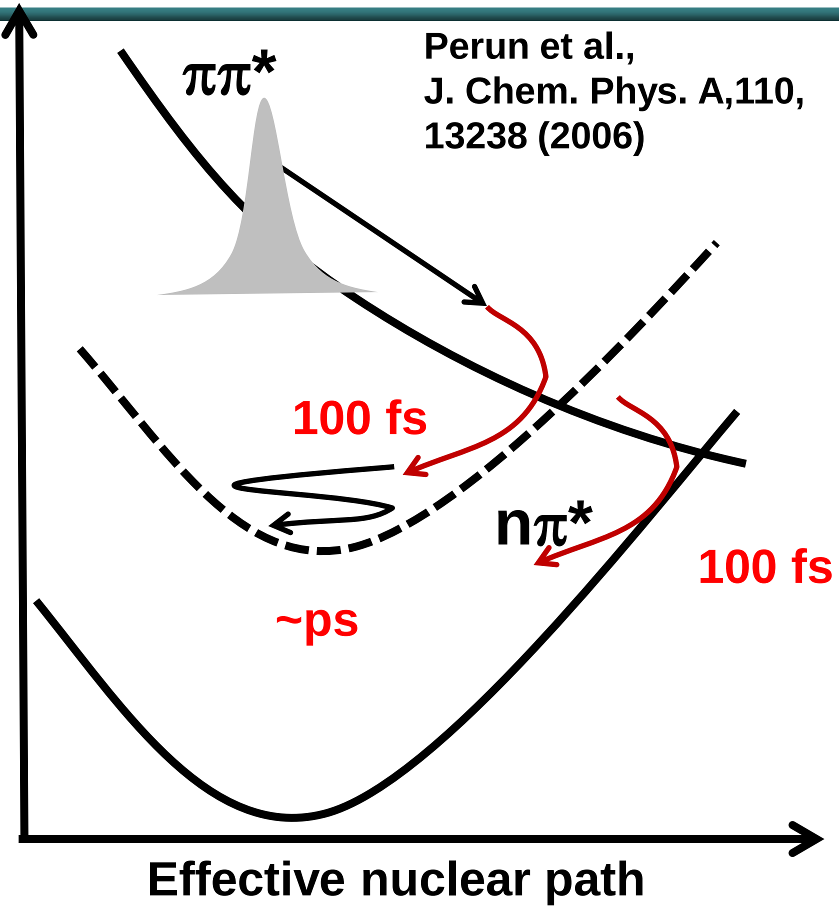
Non-BOA dynamics: n →π



DNA photoprotection (thymine)



Hudock et al.,
J. Chem. Phys. A,
111, 85 (2007)



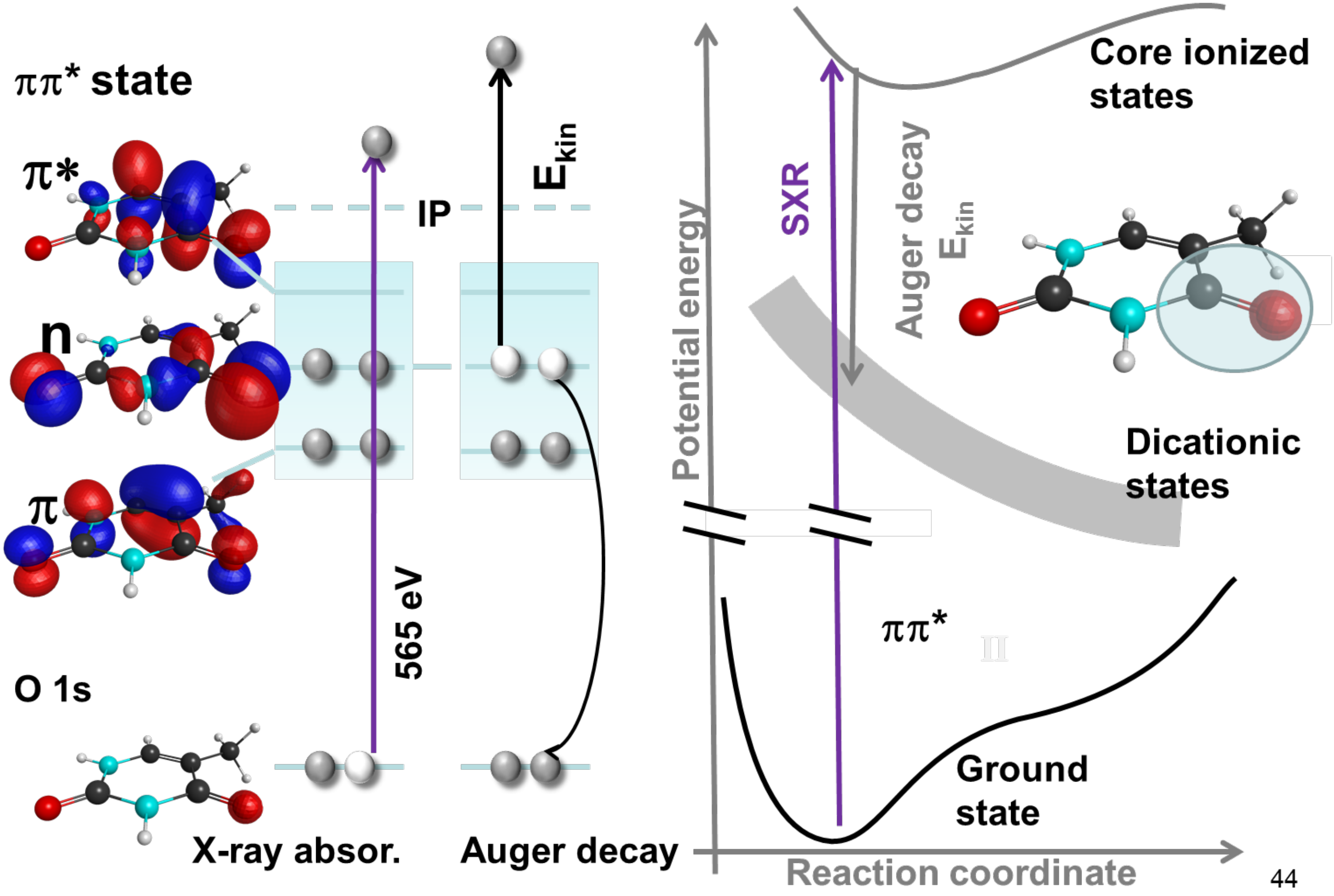
Perun et al.,
J. Chem. Phys. A,110,
13238 (2006)

Fast: 100 fs – relaxation from FC to minimum
Medium: ~ ps – tunneling through barrier

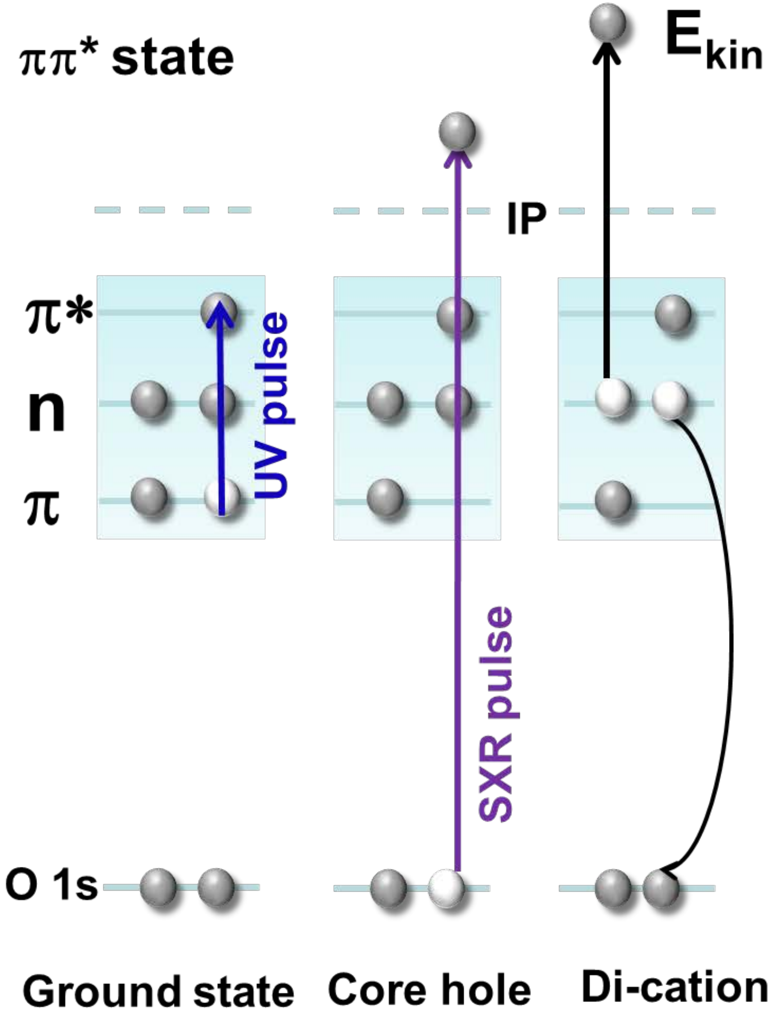
Fast: 100 fs – non-BOA dynamics
Medium: ~ ps – vibrational relaxation

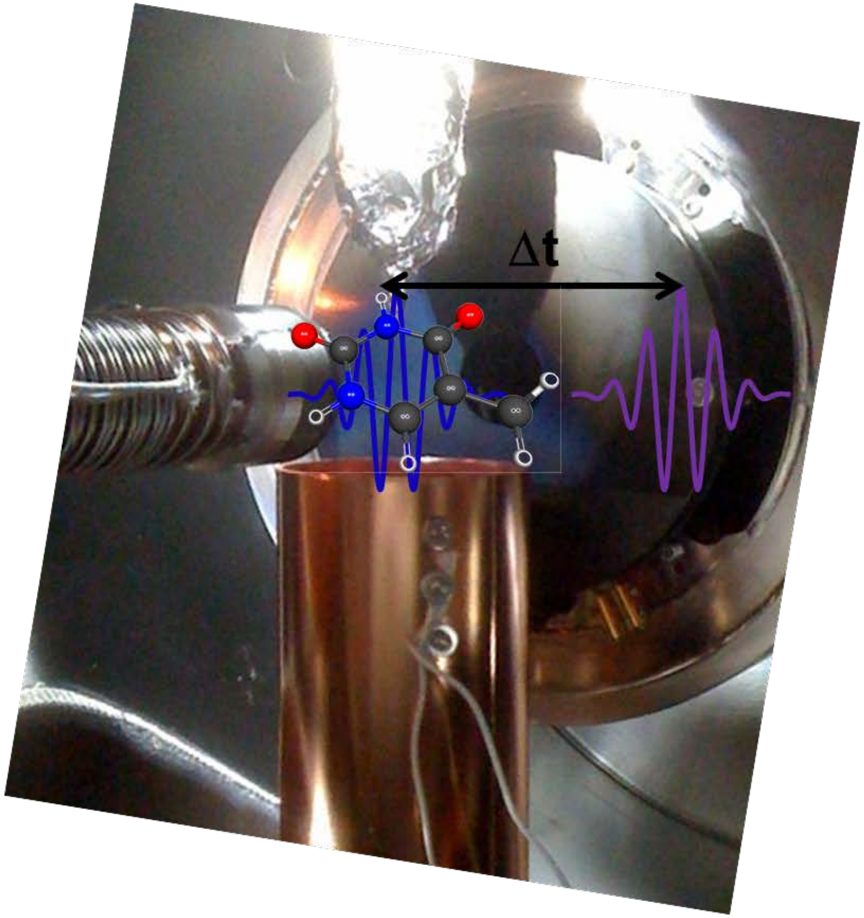
McFarland, …Guehr et al. Nature Comm. 5, 4235 (2014)

Auger decay creates valence vacancies at oxygen.



Pump probe scheme and setup.





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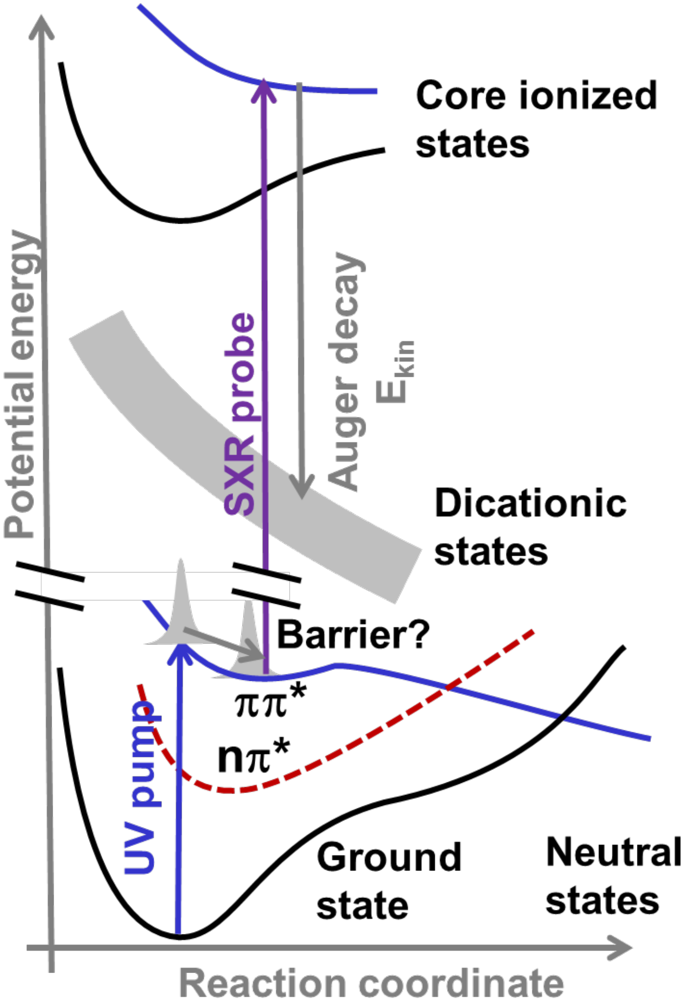
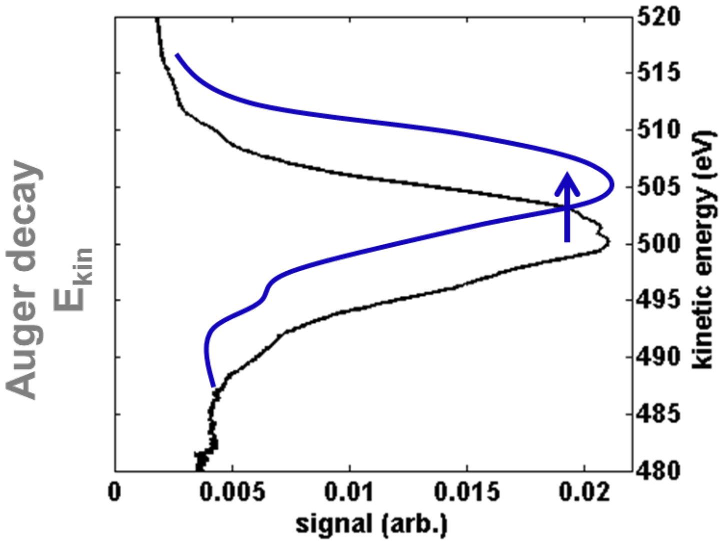
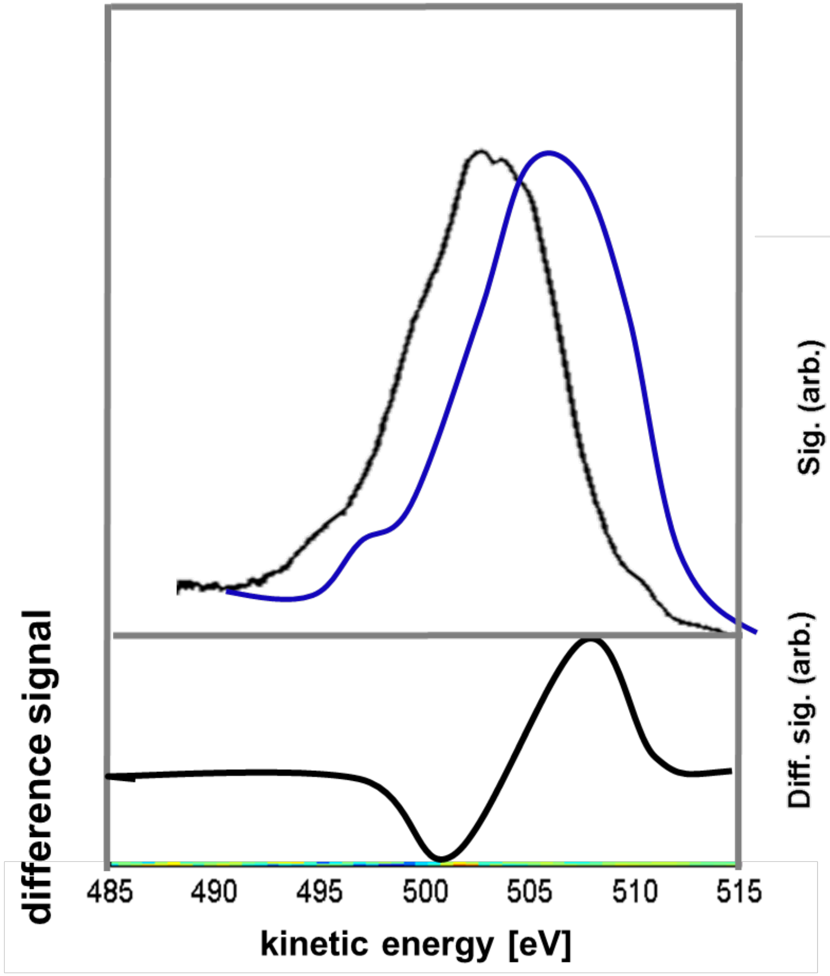
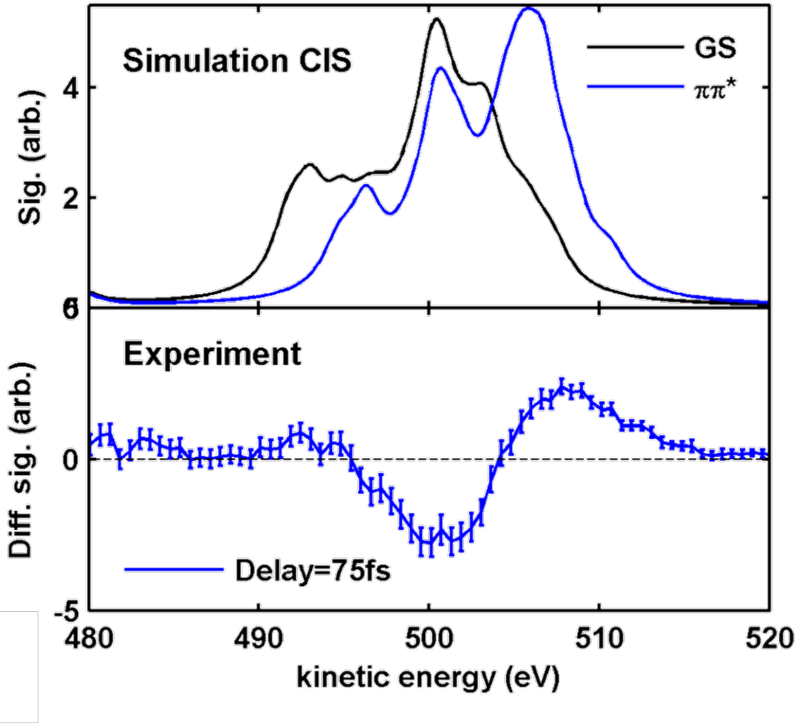

Core ionized states
Potential energy
SXR probe
Auger decay E_{kin}
Dicationic states
Barrier?
$\pi\pi^*$
$n\pi^*$
UV pump
Ground state
Neutral states
Reaction coordinate


Auger decay E_{kin}
kinetic energy (eV)
520
515
510
505
500
495
490
485
480
0
0.005
0.01
0.015
0.02
signal (arb.)

The the shift due to C-O expansion is visible.



Just after UV excitation



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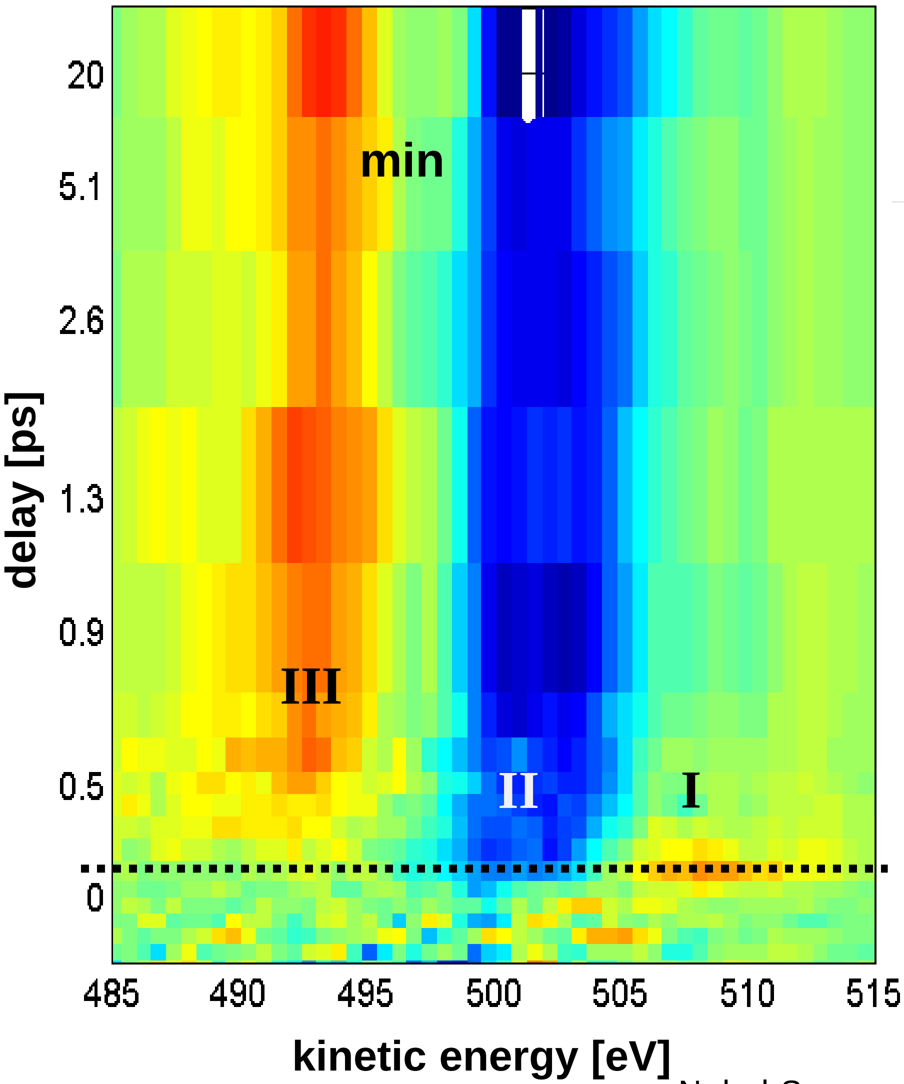
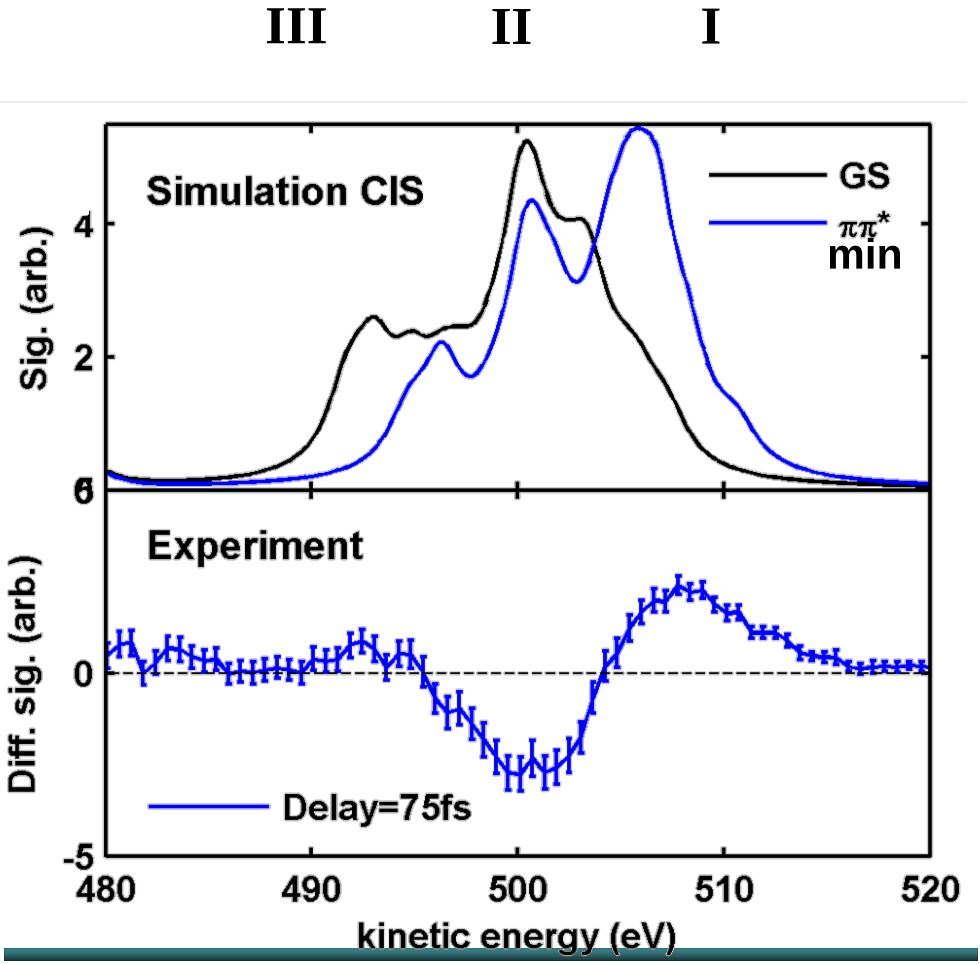
There is no barrier on the $\pi\pi^*$ state

McFarland, …Guehr et al.
***Nature Comm.* 5, 4235 (2014)**





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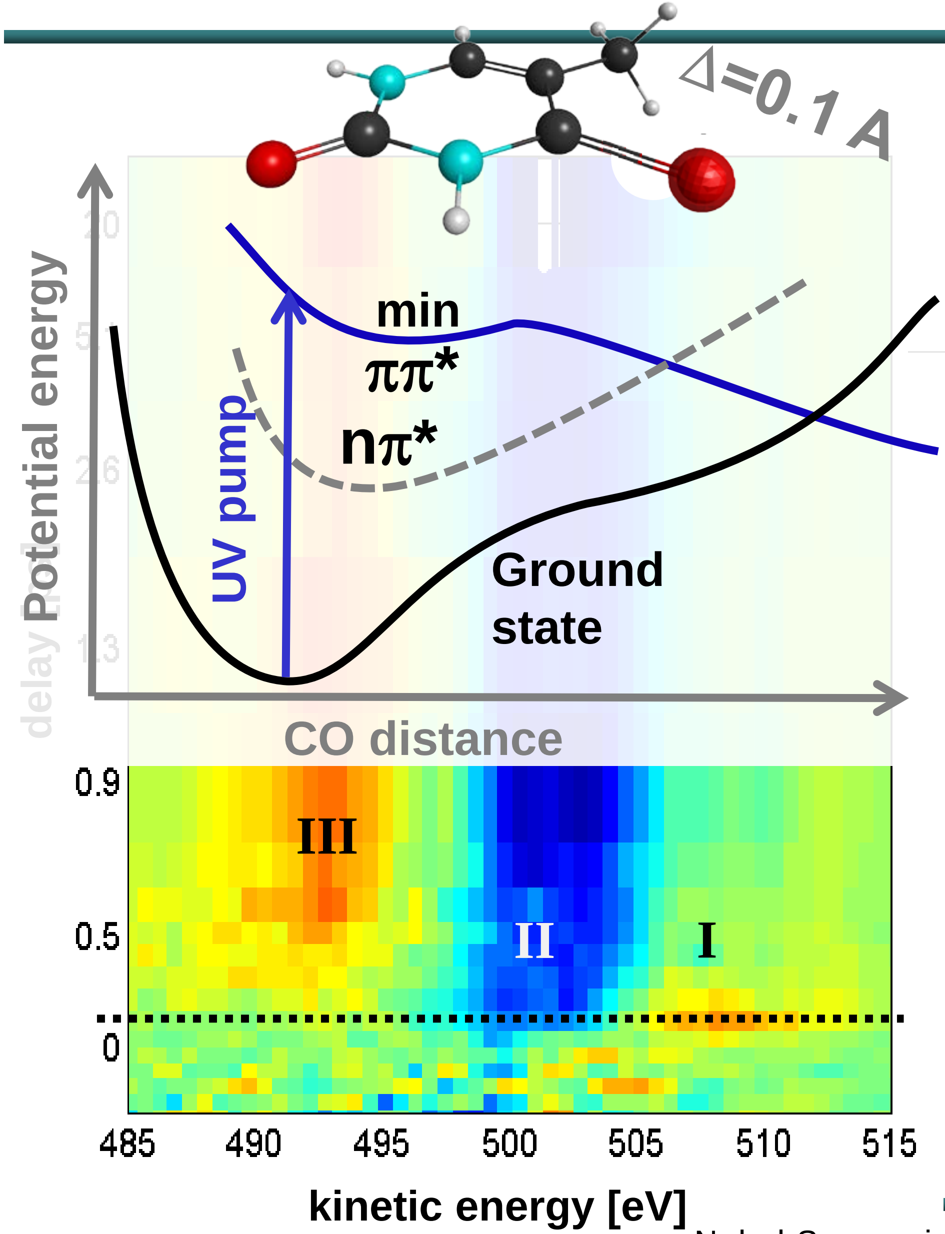
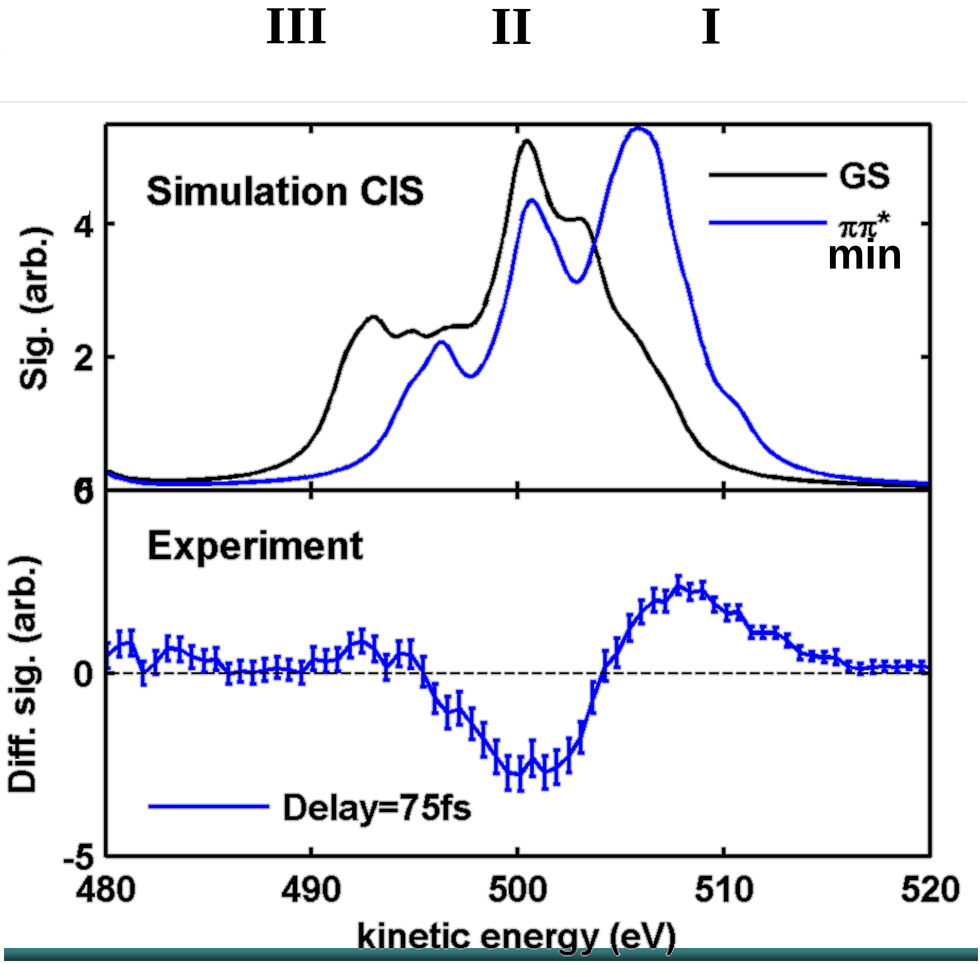
There is no barrier on the *ππ** state

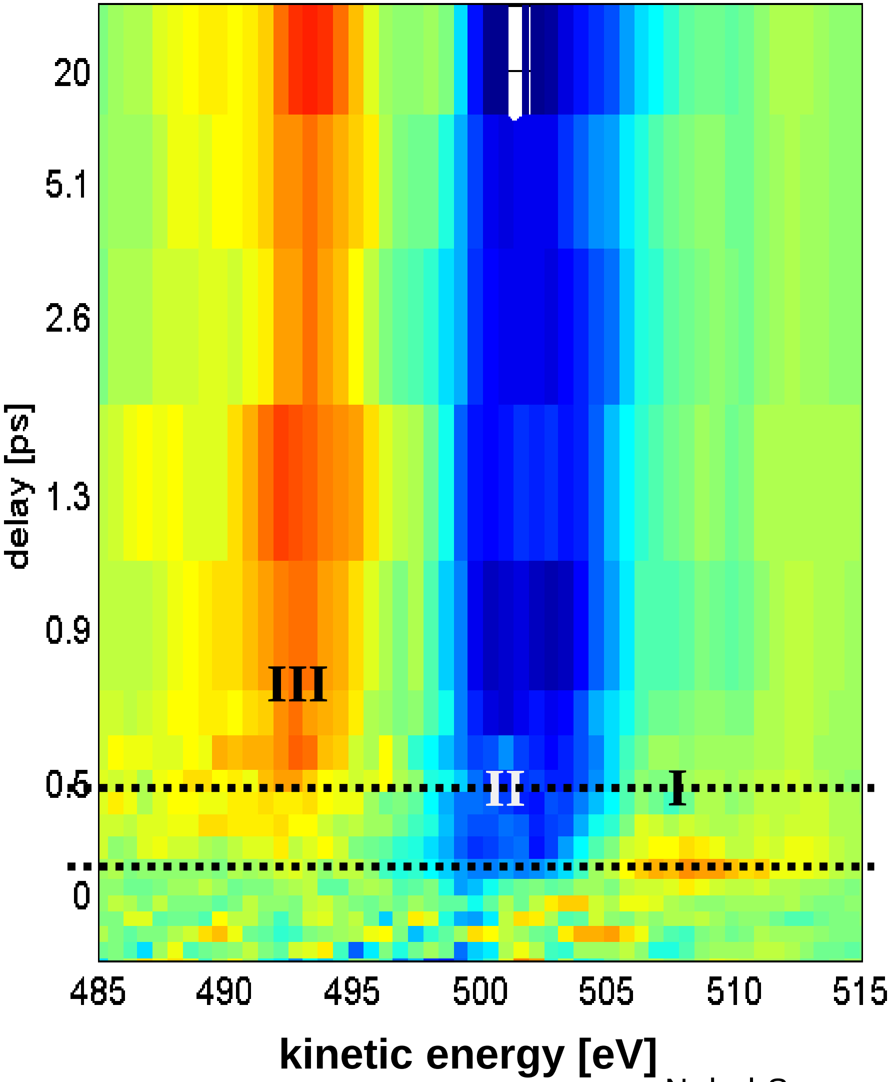


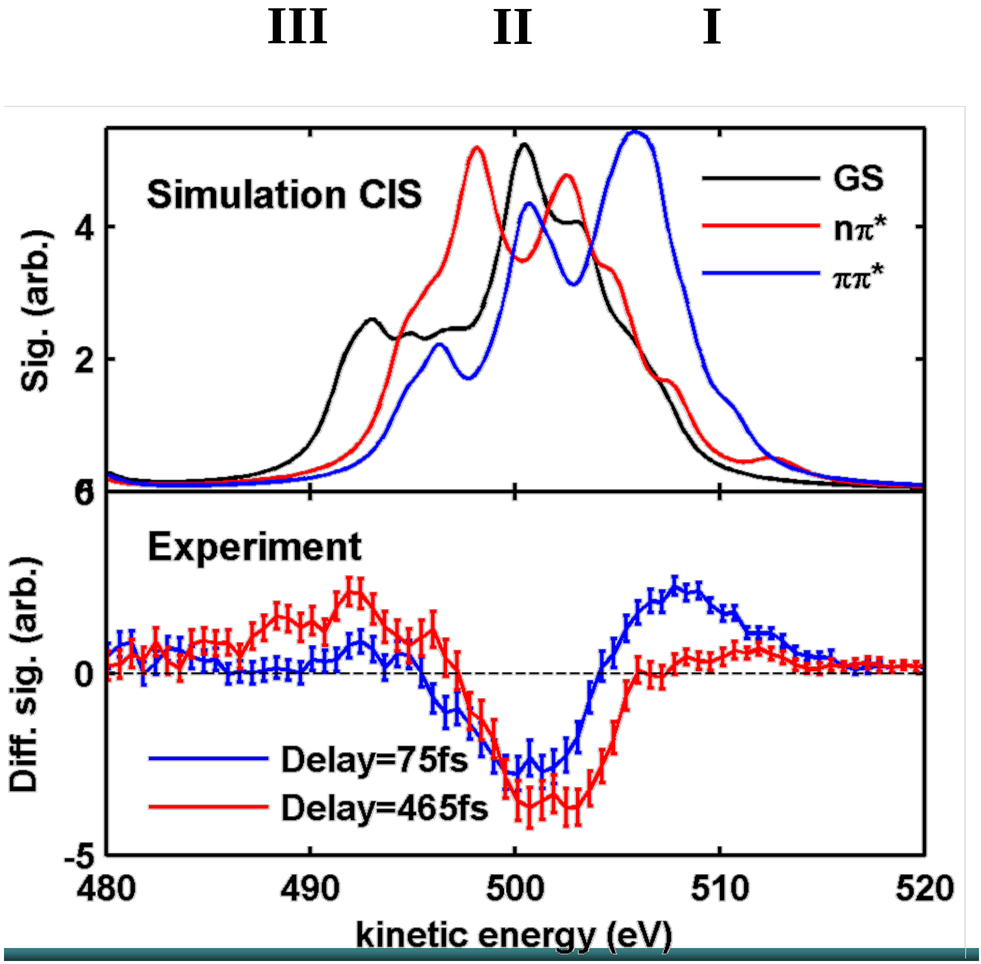
McFarland, ….Guehr, et al.
Nature Comm. **5, 4235 (2014)**



We do not observe a barrier!

McFarland, Farrell, Miyabe….Guehr, *Nature Comm.* 5, 4235 (2014)





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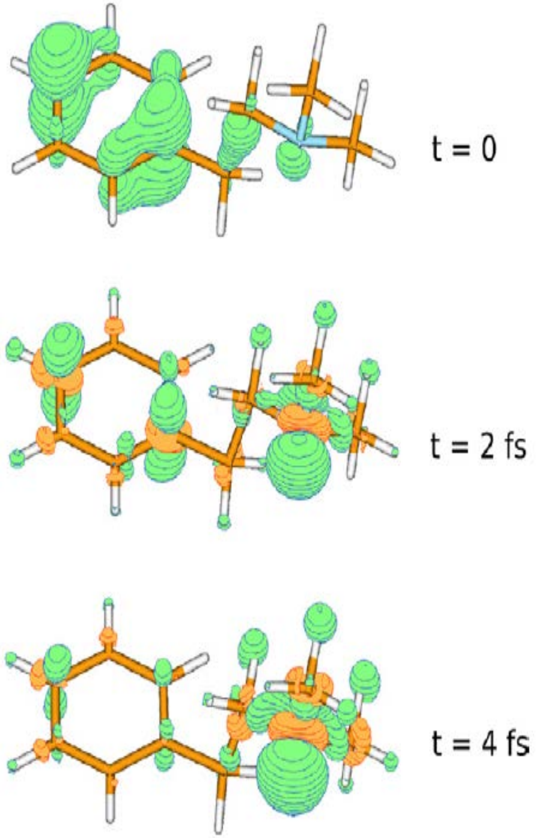
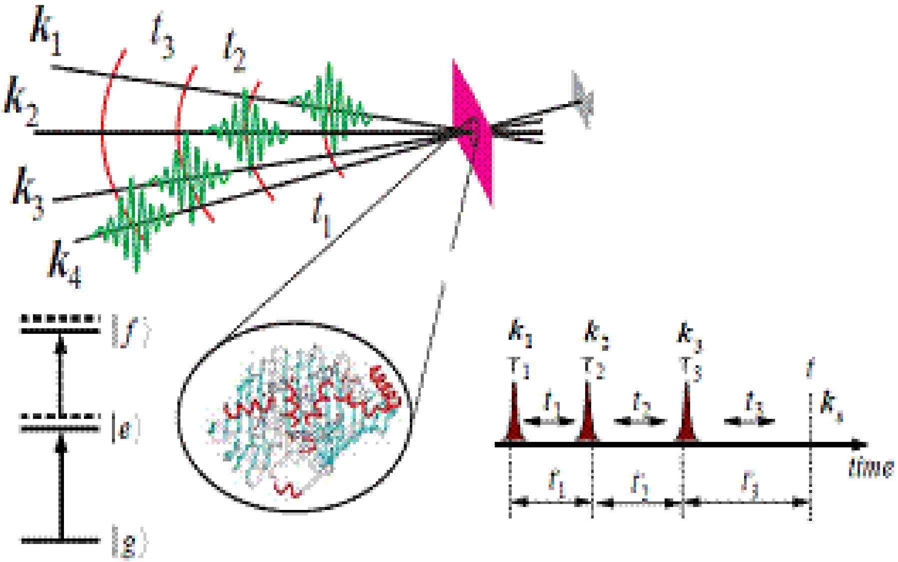
Electronic Raman: Mapping electrons as they cross the molecule in a few femtoseconds

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



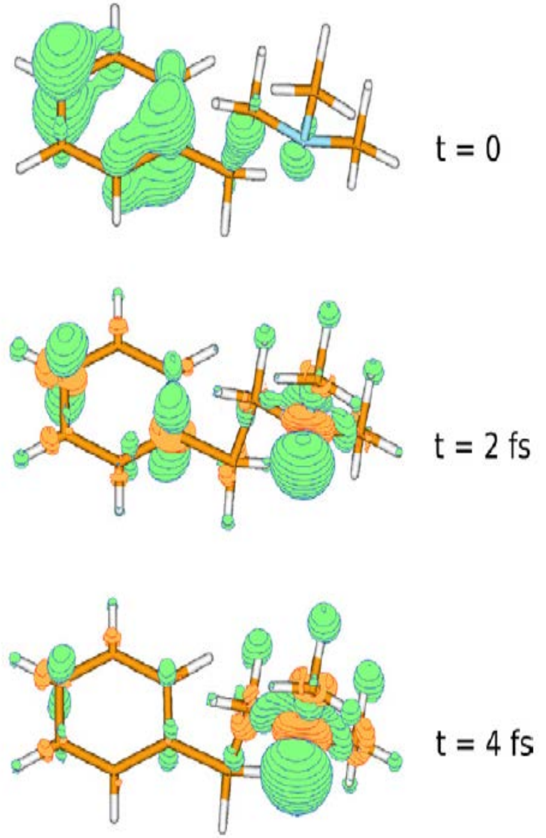
Measured via multi-dimensional spectroscopy. We need to make: Electron wave packets in neutral molecules, created at specific atoms, and then tracked over femtoseconds



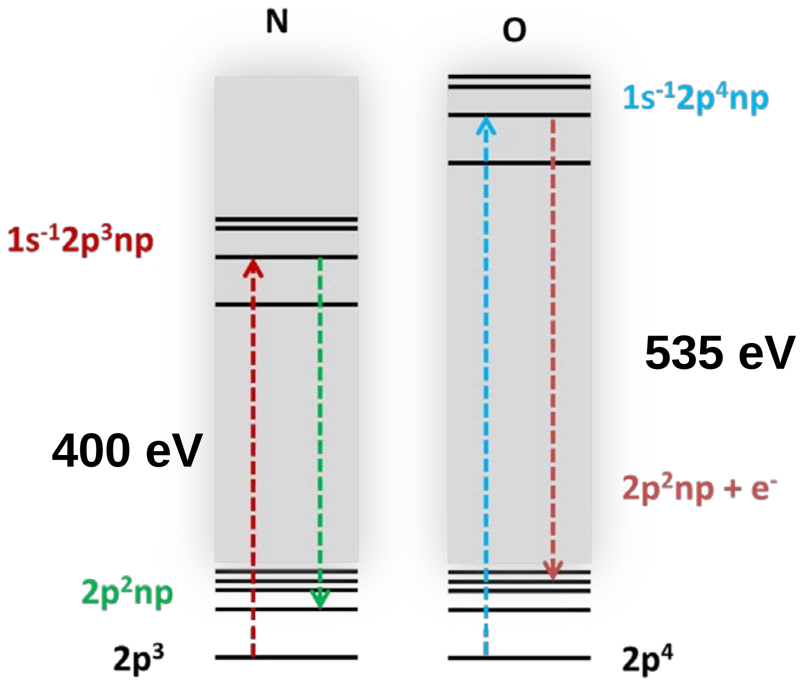
Lunnemann et al., Chem Phys Lett 450 232 (2008); Mukamel et al., Ann Rev. P. Chem. 64, 101 (2013)

Mapping electron dynamics with core excitation

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
Autoionization makes this challenging



Lunnemann et al., Chem Phys Lett 450 232 (2008); Mukamel et al., Ann Rev. P. Chem. 64, 101 (2013)

Stimulated Raman in the impulse limit: A swift kick

- **Kramers Heisenberg**

$$\frac{d\sigma}{d\Omega} = (N+1)\frac{\omega^3\omega'}{c^4}|\vec{\varepsilon}\cdot\alpha_{km}\cdot\vec{\varepsilon}'|^2,$$

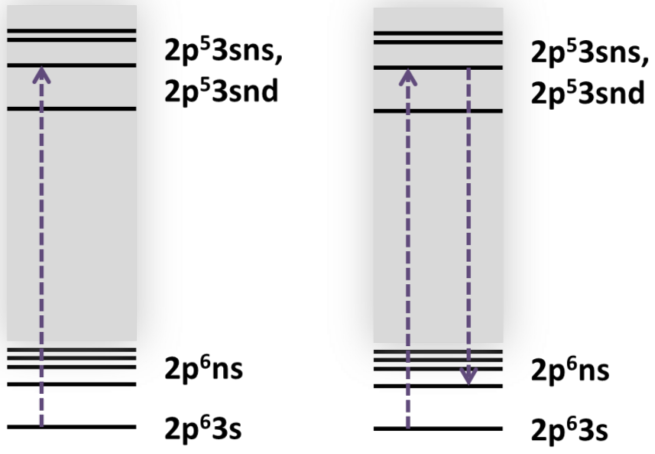
$$(\alpha_{km})_{ij} = \frac{1}{\hbar}\sum_n\left\{-\frac{\mu^i_{nm}\mu^j_{kn}}{\omega-\omega_{nk}-i\Gamma}\right\},$$

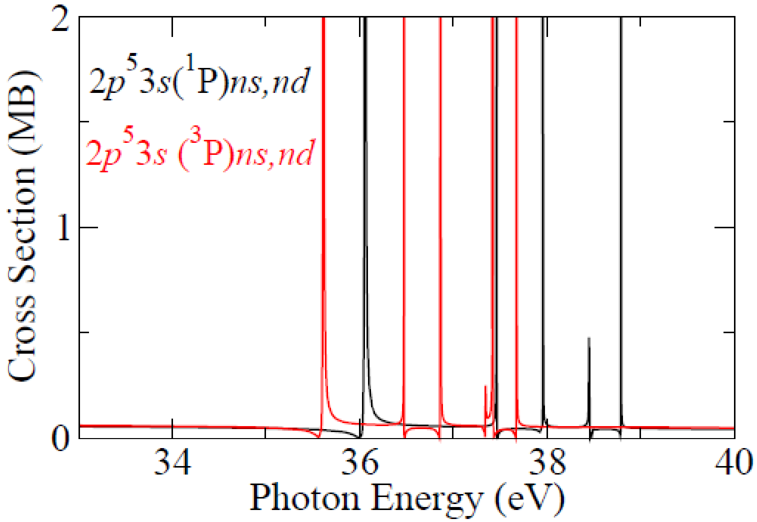
- **Impulse limit:**

$$N = (I_0/\omega^3\alpha), \qquad F_0 = \int dt I_0.$$

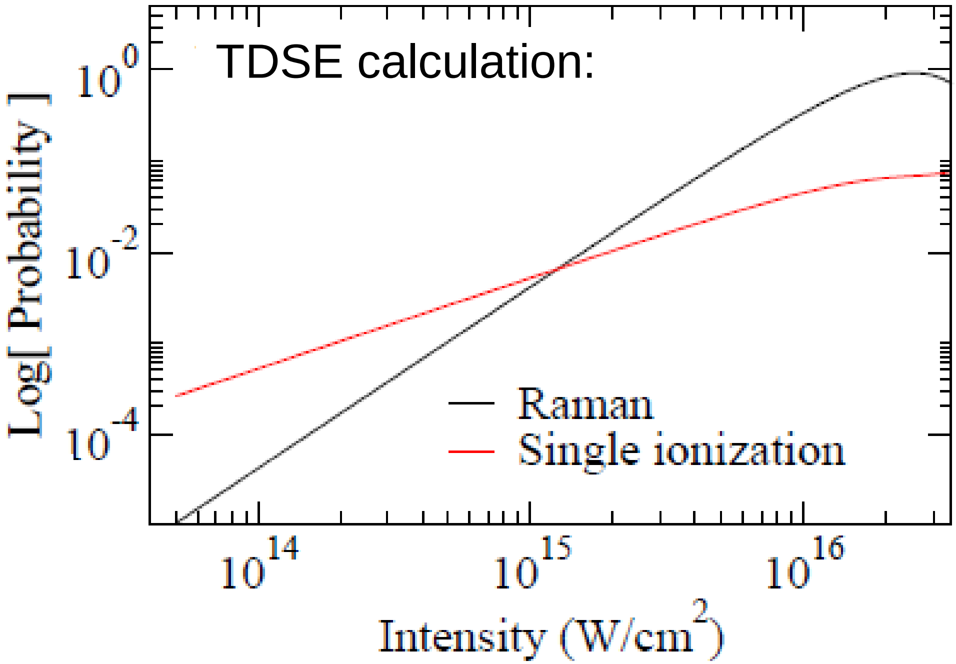
- **Total rate**
  - $P = \int dE(d\sigma/d\Omega)F_0.$
  - I_0^2

HHG example we can study: Impulsive excitation of 2p → ns,nd in Na



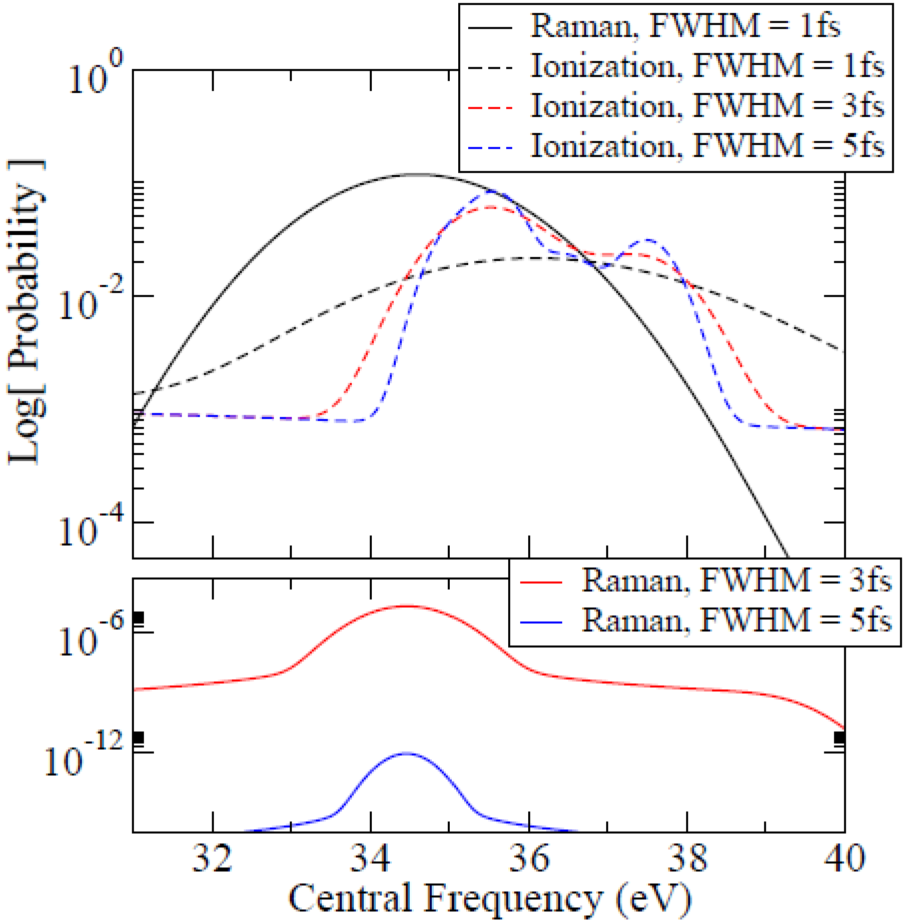


Miyabe and Bucksbaum, PRL 114, 143005 (2015)



- **Strong field regime in the XUV when 2-photon rates exceed 1-photon rates: ~10^{15} W/cm^2**
- **Well below saturation**
- **But it's even better than that…**

Transient Impulsive Giant Electronic Raman (TIGER) redistribution *turns on* for 1fs TL pulses

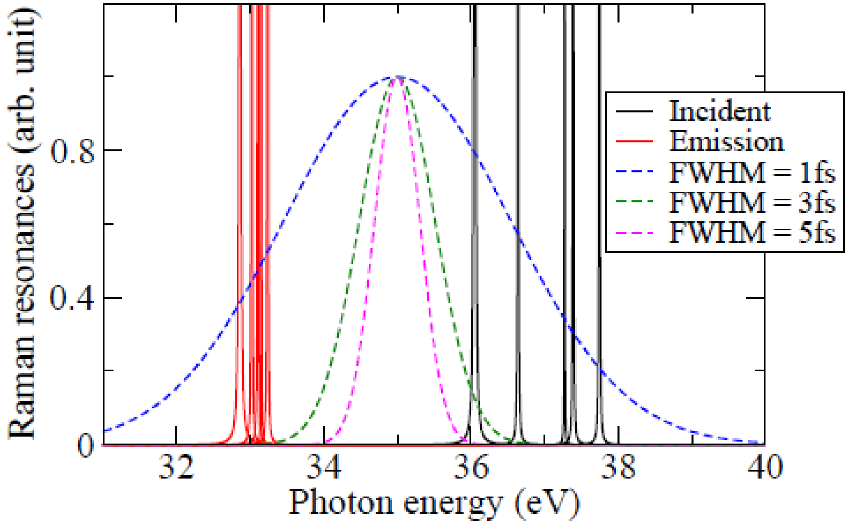


5 microjoule TL pulses

Miyabe and Bucksbaum, PRL 114, 143005 (2015)

How it works:

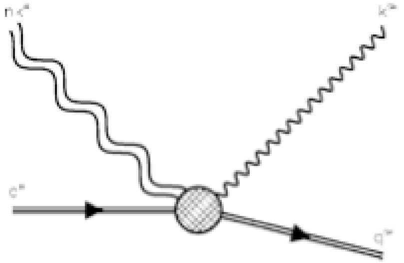
- **Trillion-fold increase in TIGER rate from 5fs to 1fs is due to the coherent spectral broadening:**



- **Coherent femtosecond pulses produce *sub-angstrom* wave packets;**
- **Efficiently suppress ionization and Auger backgrounds;**
- **Has element specificity**

X-ray Nonlinear Compton Scattering

David Reis, Matthias Fuchs, et al. arXiv:1502.00704 [physics.optics]



$$e + n\omega_0 \rightarrow e' + \omega$$

$$\sigma^{(2)} \approx \eta^2 \sigma_0 \propto I$$

$$\eta = \frac{eE_{\text{rms}}}{m\omega} \ll 1$$

Differential cross-section, semi-classical nonlinear QED e.g.
L. S. Brown and T. W. B. Kibble, Phys. Rev. 133, A705 (1964).

Kinematics:

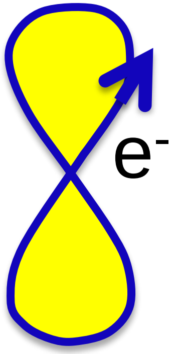
photons from field

$$\omega' = \frac{n\omega}{1 + \frac{n\omega}{m}\left(1 + \frac{U_p}{n\omega}\right)(1 - \cos\theta)}$$

recoil

ponderomotive correction

scattering angle



$$\text{At } \omega = 9 \text{ keV}, I = 10^{20}\text{W}/\text{cm}^2 :$$

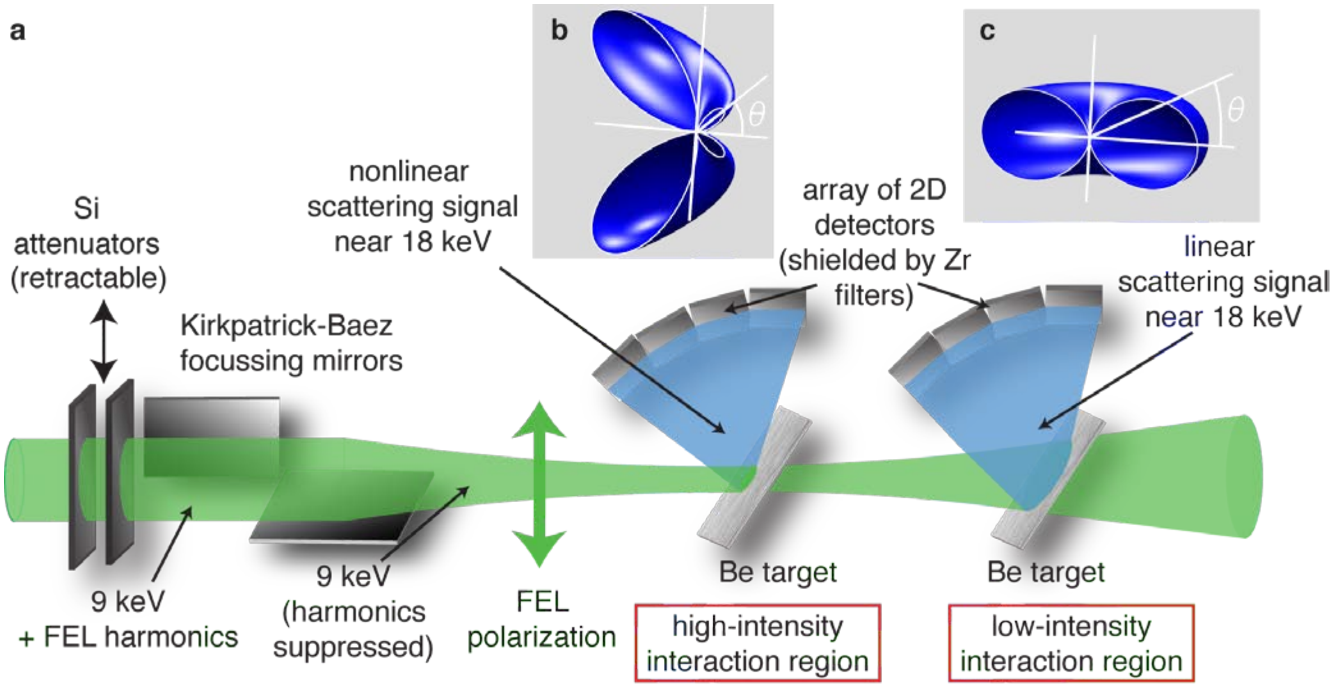
$$E \sim 3\text{keV}/\mathring{A}$$

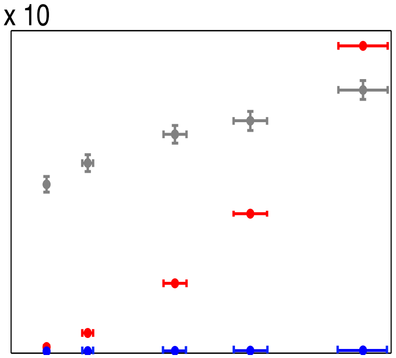
$$\eta \sim 10^{-3}$$

$$U_p = \frac{1}{2}mc^2\eta^2 \sim 0.2\text{eV}$$

$$(x_0 \sim 3 \times 10^{-4}\mathring{A}(\sim 10r_0)$$

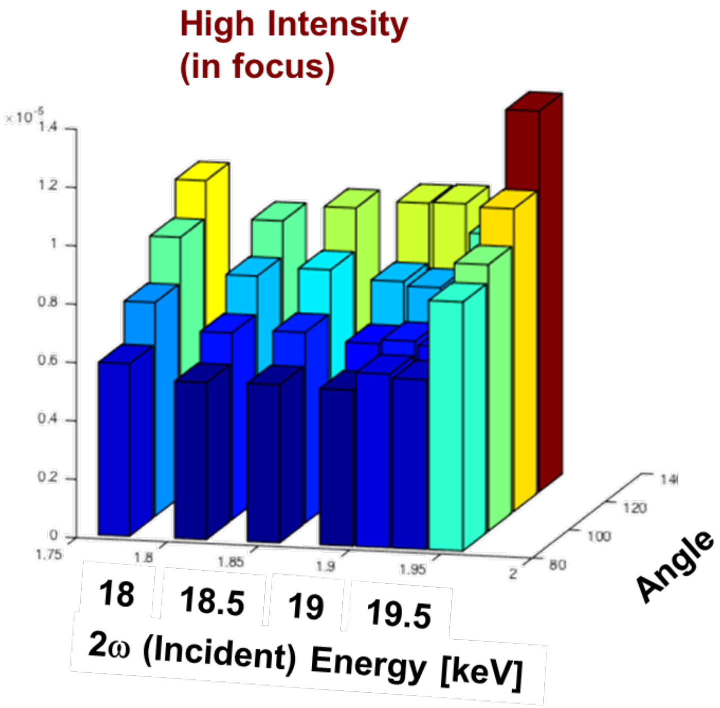
Experimental Setup



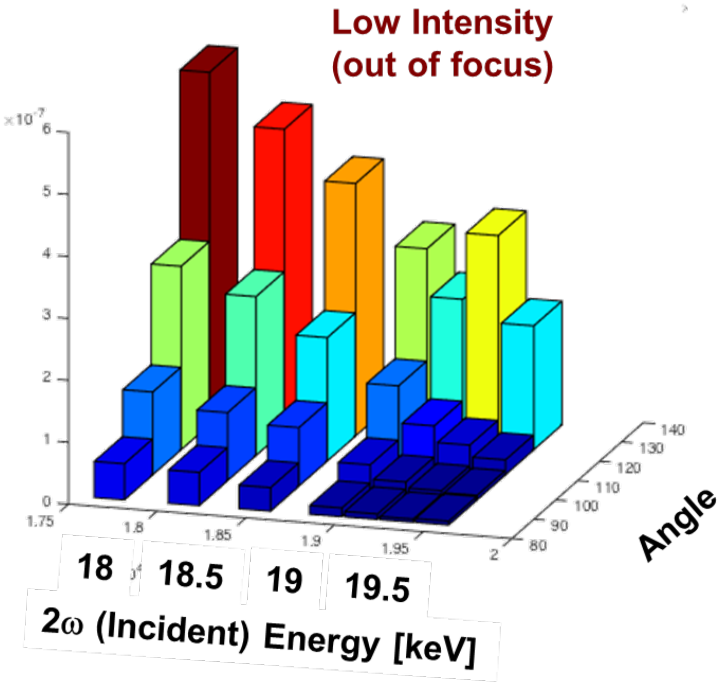


M. Fuchs et al. arXiv:1502.00704

Non free-electron-like behavior

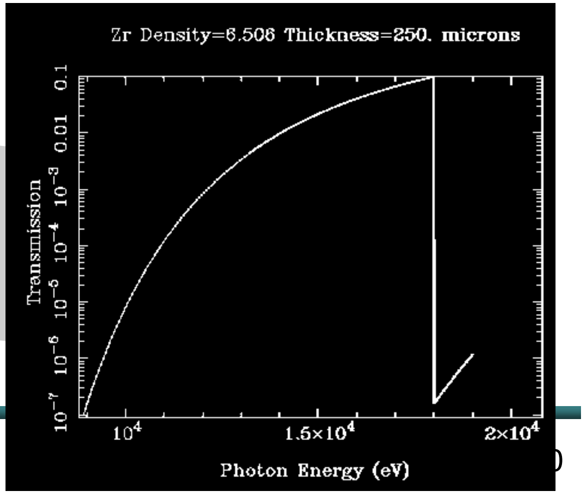


High Intensity
(in focus)



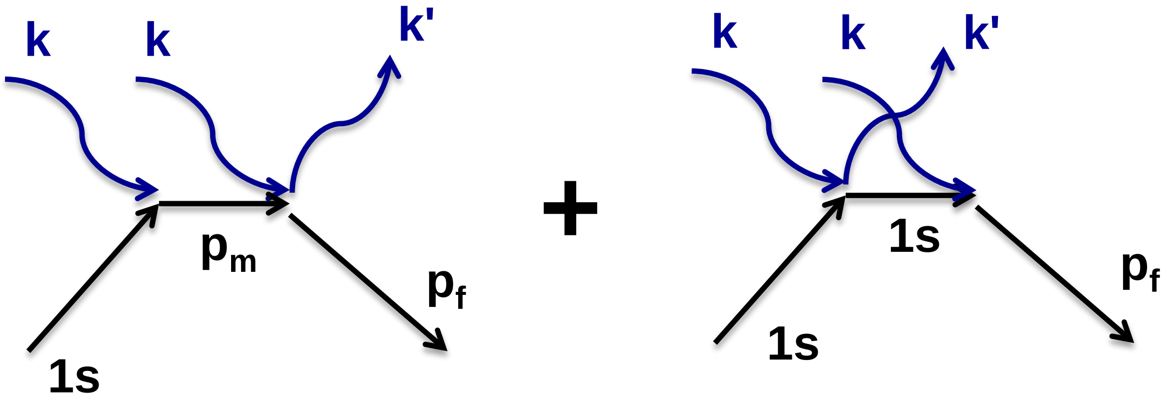
Low Intensity
(out of focus)

NL Compton shows unexpected additional red shift of > 800 eV @ 90º



M. Fuchs et al. arXiv:1502.00704

Bound-state nonlinear-Compton scattering



M. Fuchs et al. arXiv:1502.00704

Nonlinear Compton Collaboration

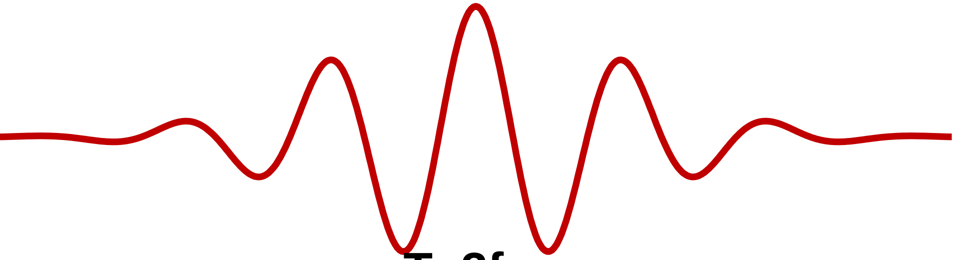
Matthias Fuchs (Nebraska), M. Trigo, J. Chen, S. Ghimire, M. Kozina, M. Jiang, T. Henighan, C. Bray, G. Ndabashimiye, S. Shwartz (Bar Ilan) , Y. Feng, S. Boutet, G. Williams, M. Messerschmidt, M. Seibert, S. Moeller, J.B. Hastings, P. Bucksbaum, David Reis.

Ion takes up extra momentum

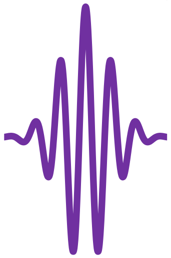
Strong fields and short wavelengths can induce dynamics in molecules

- Molecules are highly interactive multi-particle systems.
- Strong infrared fields couple to the polarizability in molecules, rotations and vibrations.
- Strong optical fields couple to electrons, induce ionization and structural changes, ATI, HHG
- Short wavelengths excite inner electrons, leading to exotic many-electron excited states, Auger relaxation.

Laser Lab: hν=1.5 eV



LCLS: hν=1500 eV



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