“X-Ray Probing of Atomic and Molecular Dynamics in the Attosecond Limit”

Produce high order harmonics (soft x-rays) and use them for ultrafast time-resolved femtosecond dynamics experiments and attosecond dynamics - Electron Dynamics

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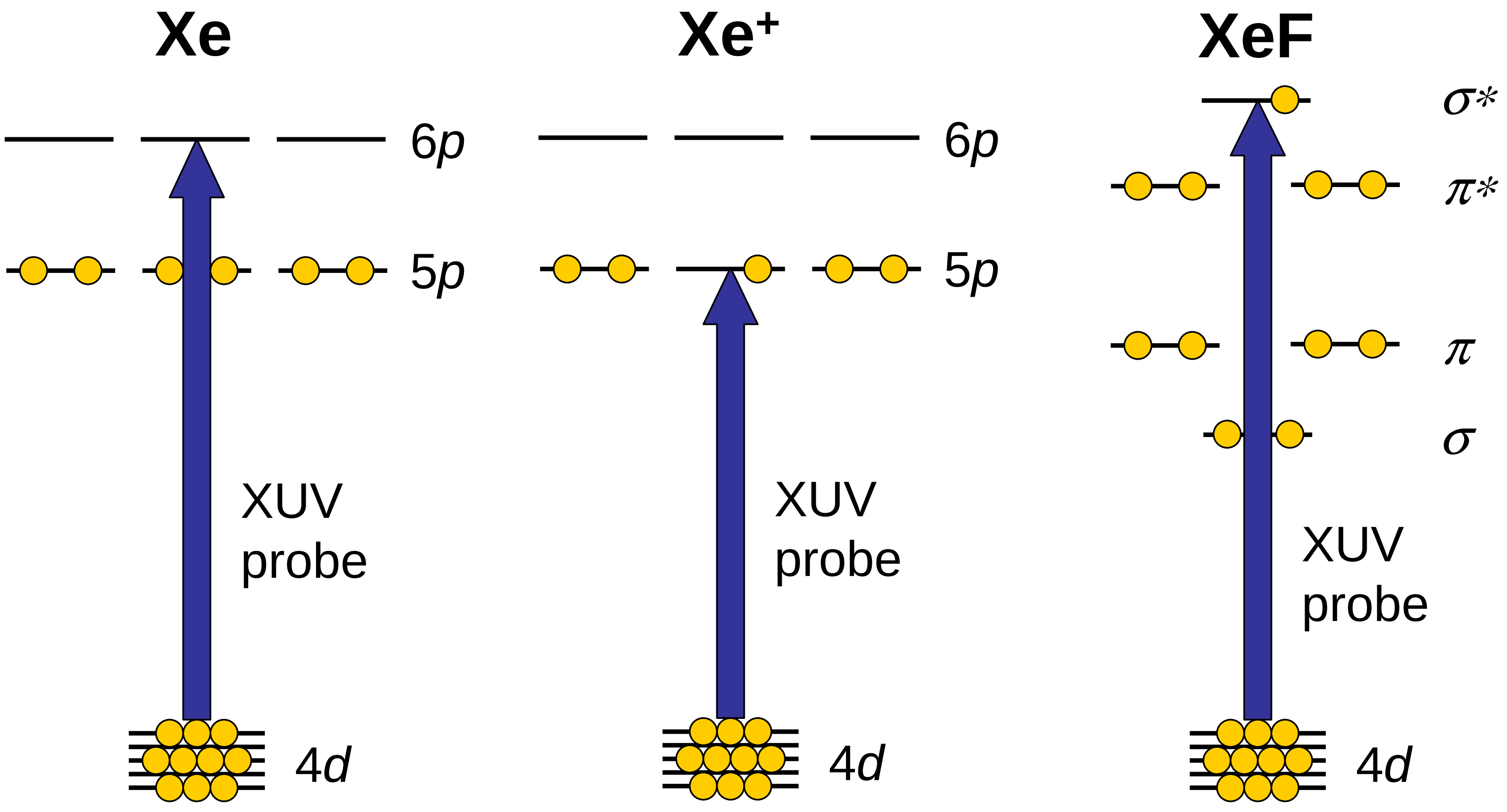
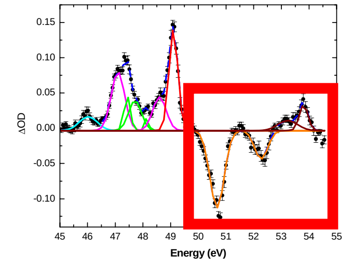
AFOSR, NSF, DOE

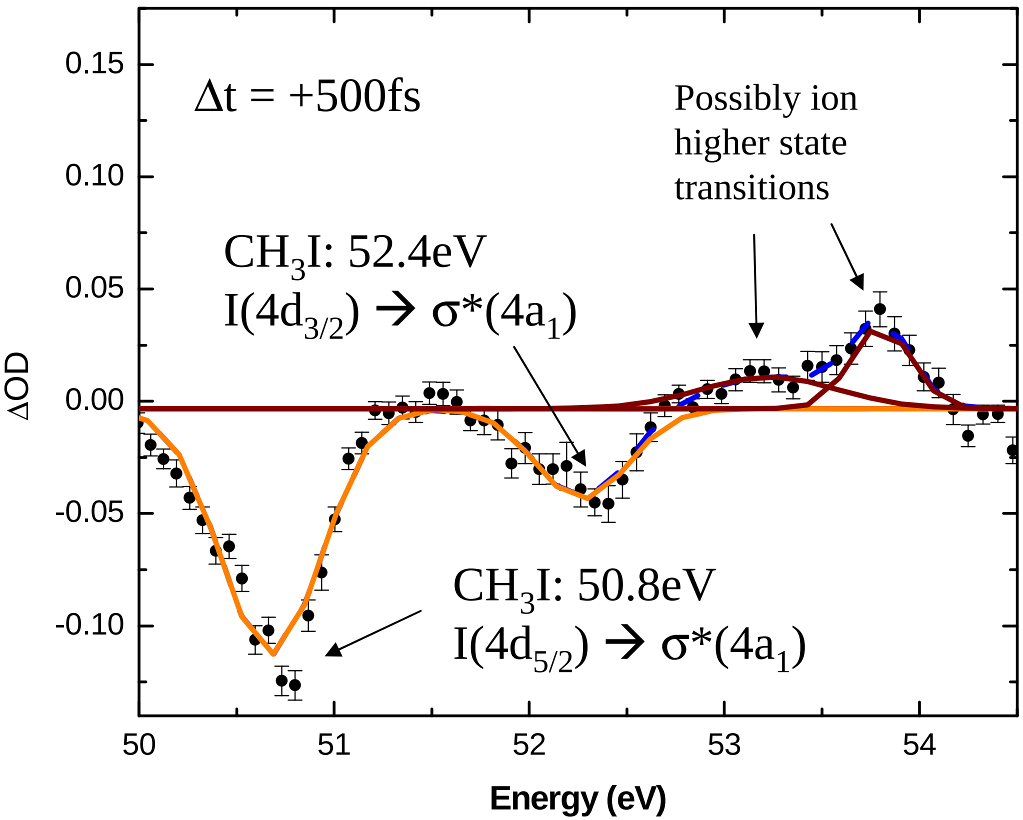
XUV absorption spectroscopy: probe of local electronic structure



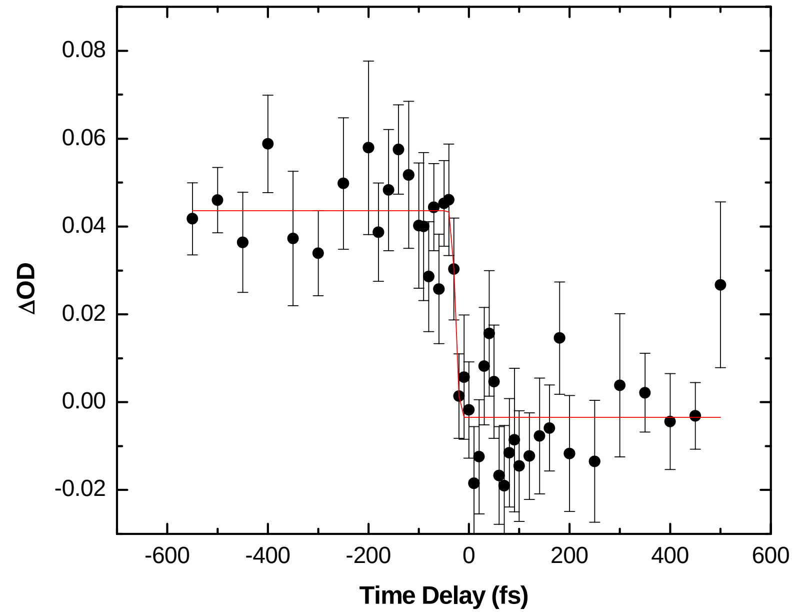
Probe of oxidation states and chemical bonding

Transient Absorption Spectrum of Methyl Iodide





$$\Delta OD = -\log\left(\frac{I(E,\Delta t)}{I(E,-500\,fs)}\right)$$

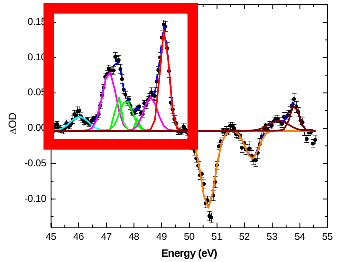


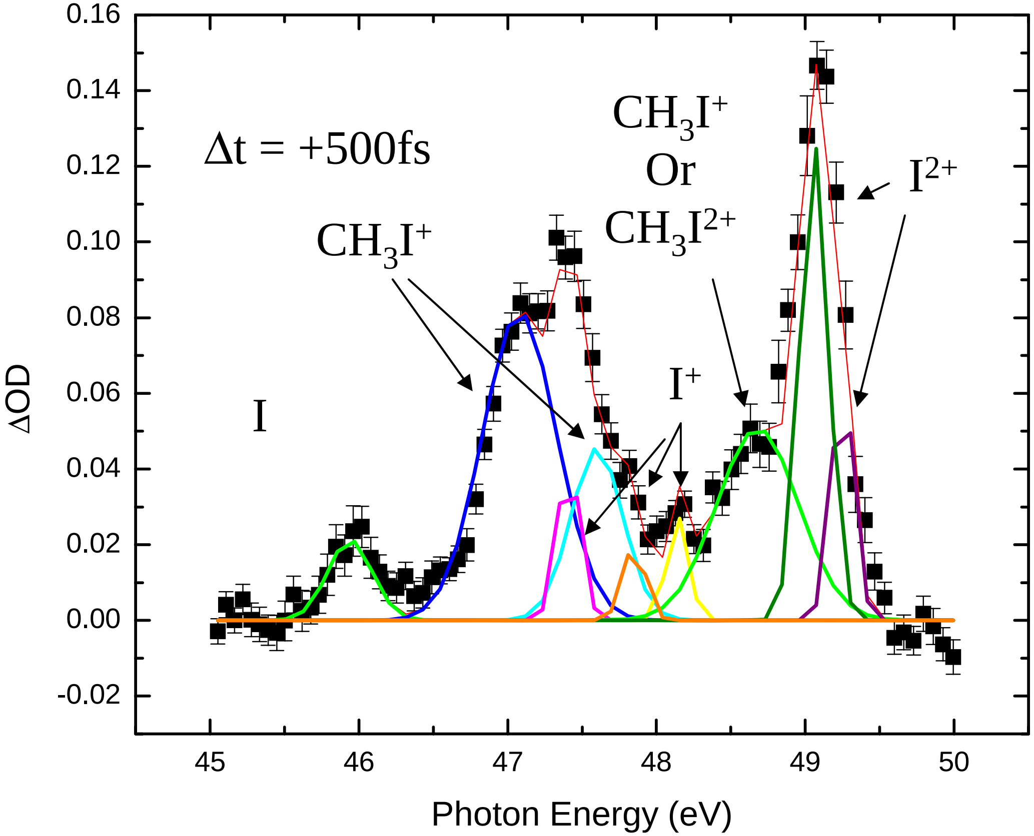
The decay of CH$_3$I dictates the combined ionization and instrument response for the system:

Instrument Response: 25 fs

T.N. Olney. Chem. Phys. 232. 211-237. 1998.

Transient Absorption
Methyl Iodide





Probed I 4d Transitions:

For I: $^2P_{3/2} \rightarrow ^2D_{5/2}$ **46.0eV**

For I^+: $^3P_2 \rightarrow ^3D_3$ **47.4eV**
$^3P_1 \rightarrow ^3D_2$ **47.6eV**
$^3P_2 \rightarrow ^3D_2$ **48.1eV**

For I^{2+}: $^4S_{3/2} \rightarrow (^3P)\ ^4P_{5/2}$ **49.0eV**

For CH_3I^+: $I(4d_{5/2}) \rightarrow$ SOMO **47.0eV**
$I(4d_{3/2}) \rightarrow$ SOMO **48.6eV**

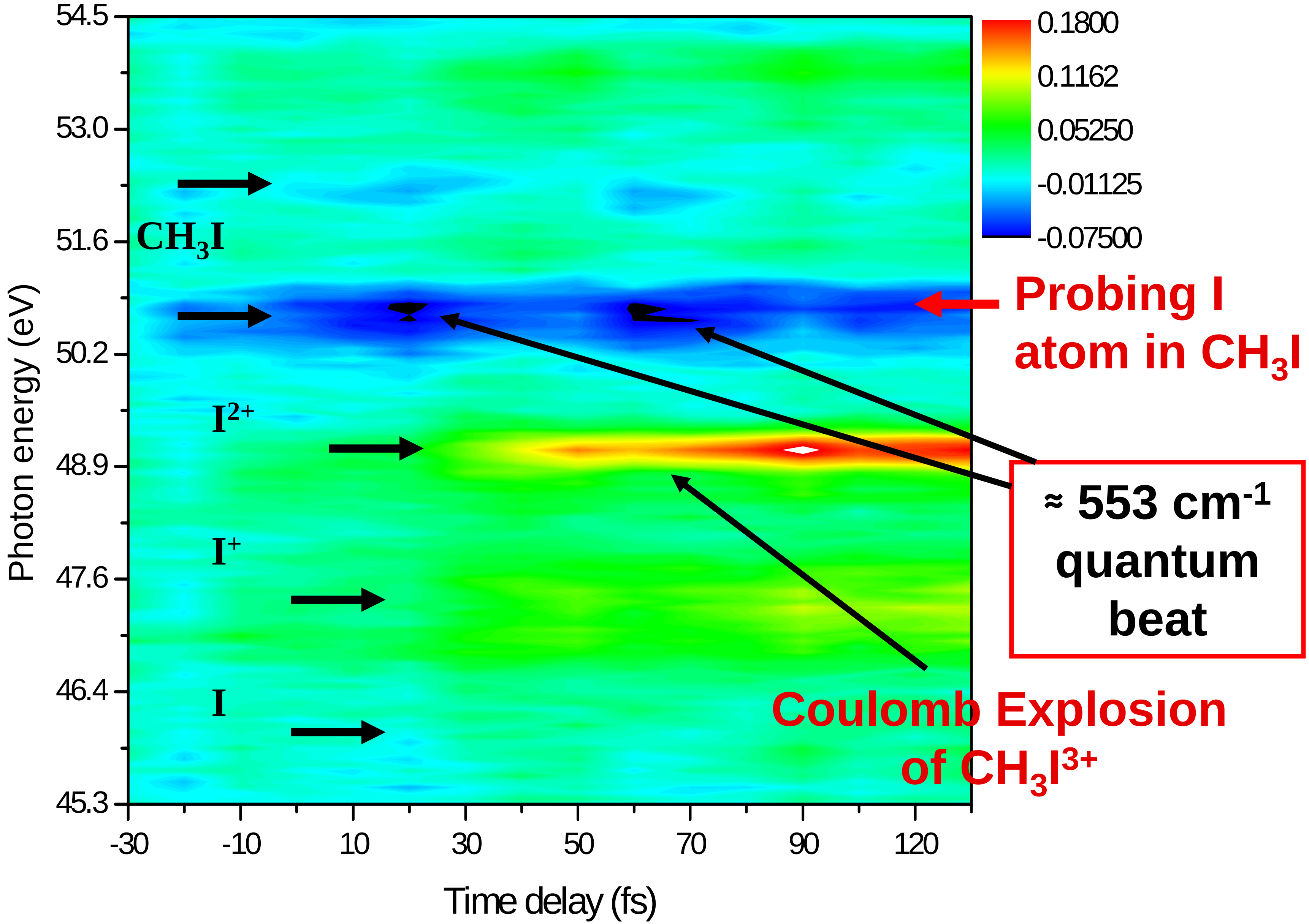
Dissociation Pathways:

$CH_3I^{3+} \rightarrow CH_3^+ + I^{2+}\ (^4S_{3/2})$
$CH_3I^{2+} \rightarrow CH_3^+ + I^+\ (^3P_2$ and $^3P_1)$
$CH_3I^+\ (X\ ^2E_{(3/2, 1/2)}) \rightarrow CH_3^+ + I\ (^2P_{3/2})$
$CH_3 + I^+\ (^3P_2, ^3P_1)$

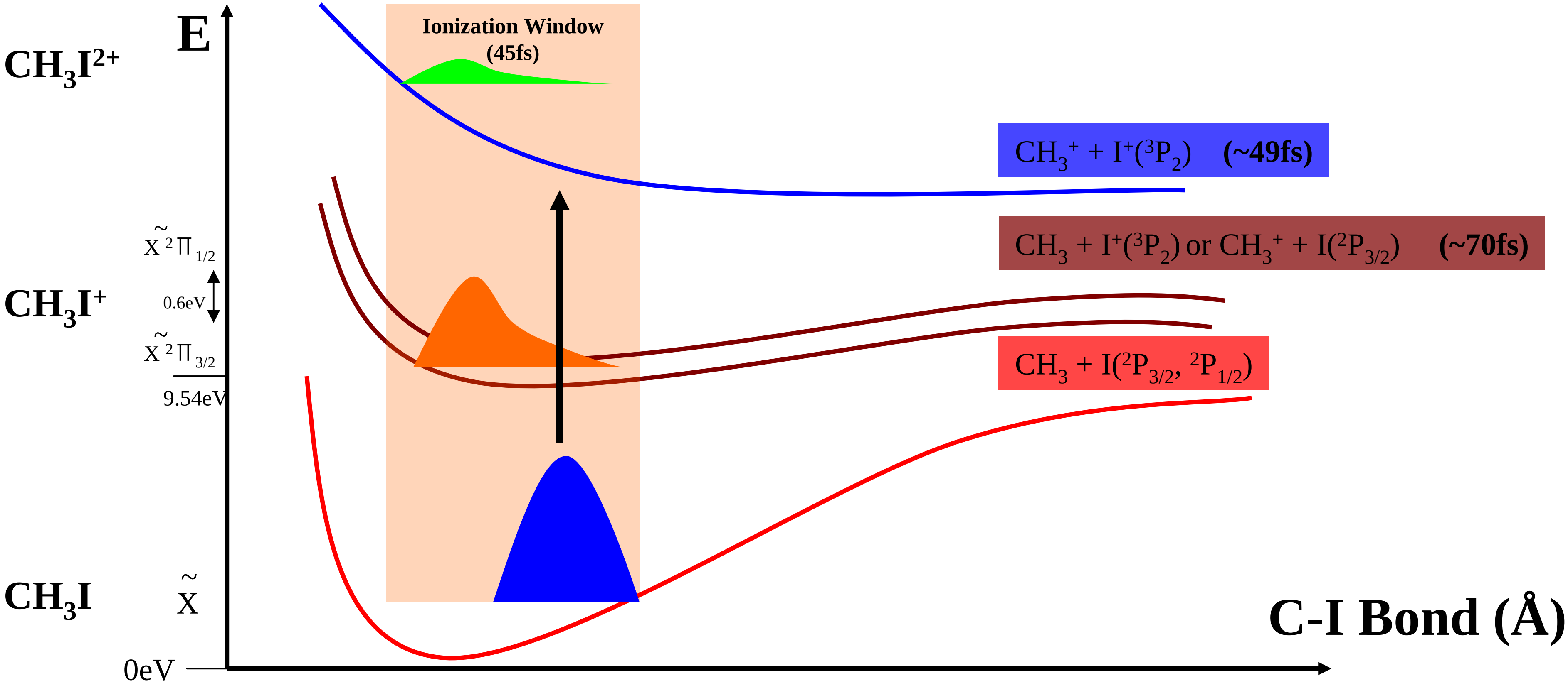
O'Sullivan, et al. Phys. Rev. A. 53, (5). 1996.
Liu, et al. J. Chem. Phys. 126. 044316. 2005.

SOMO = singly occupied molecular orbital

Wave packet in C-I bond of methyl iodide formed by high field ionization and probed via core level transitions!



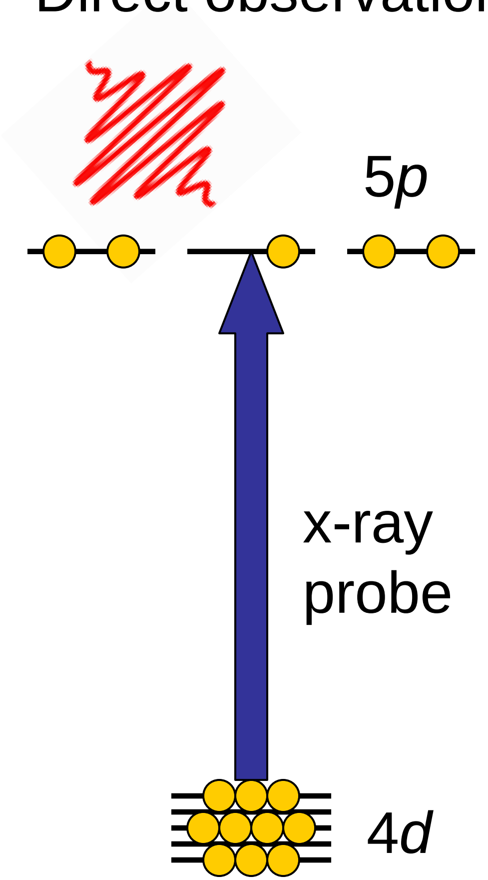
Lochfrass Electronic Ground State Wave Packet

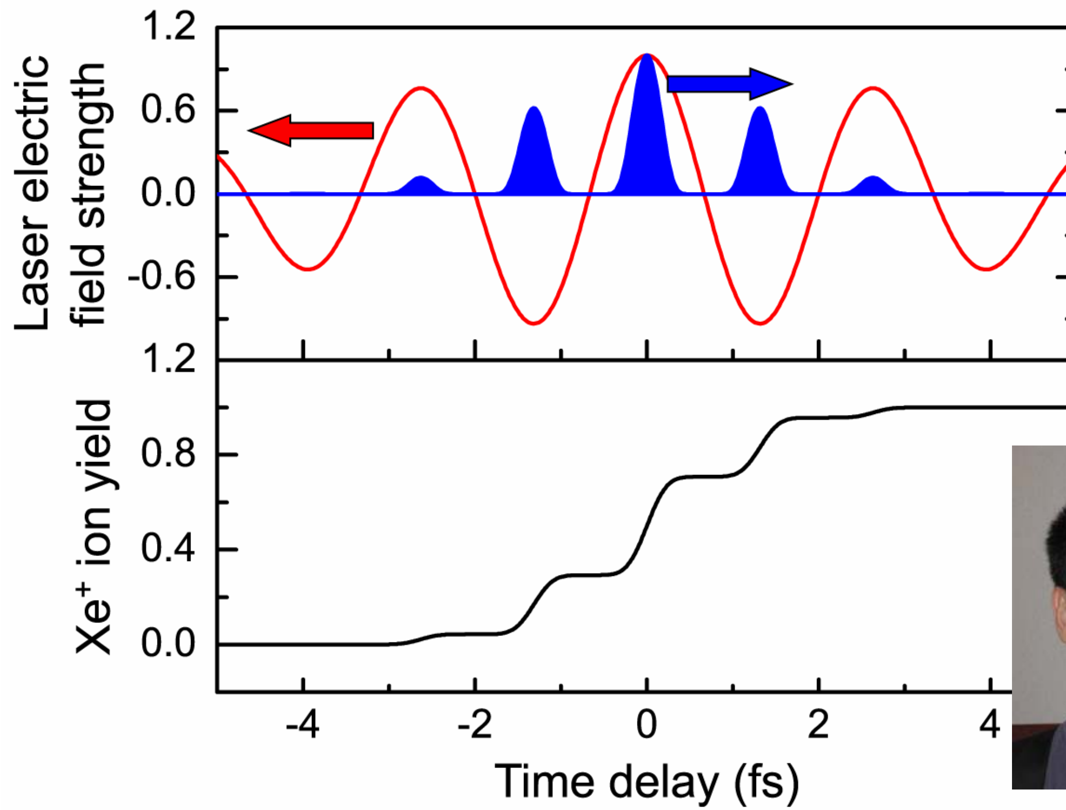


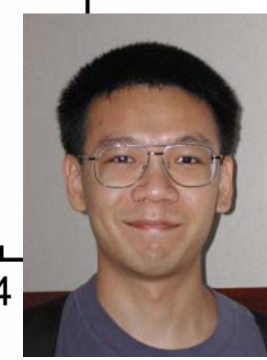
High field ionization allows for the formation of an Electronic Ground State wave packet in CH_3I by deformation of $\Psi(R,t)$ in the pump field, but also simultaneously forms wave packets on the ion states of the molecule as the pump pulse eats away the ground state wave function (Lochfrass), yielding an oscillation in the signal of CH_3I and possibly in some of the ions.

Sub-cycle-resolved strong-field ionization - collaboration with Ferenc Krausz' group

Direct observation of tunneling on the sub-cycle timescale:

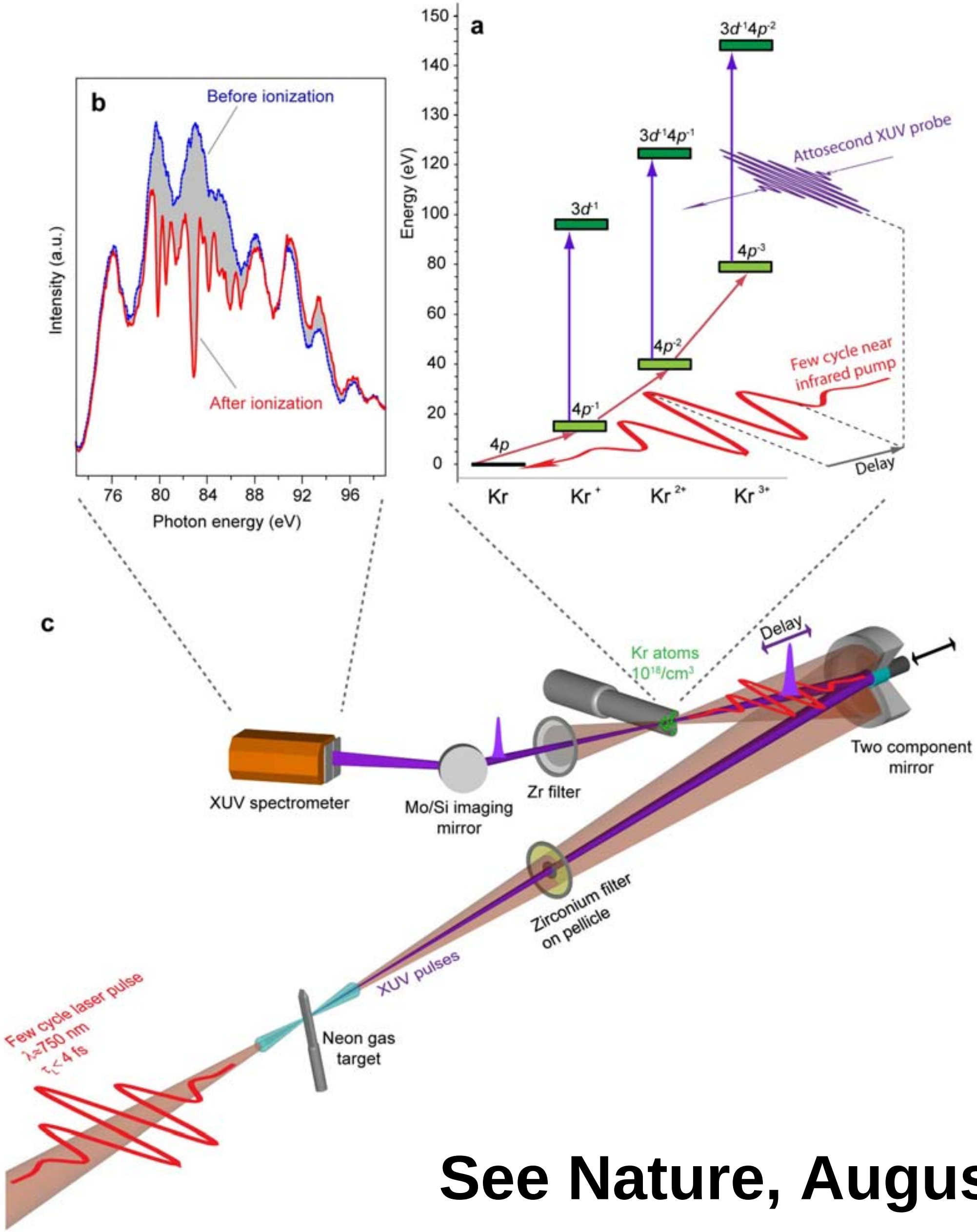






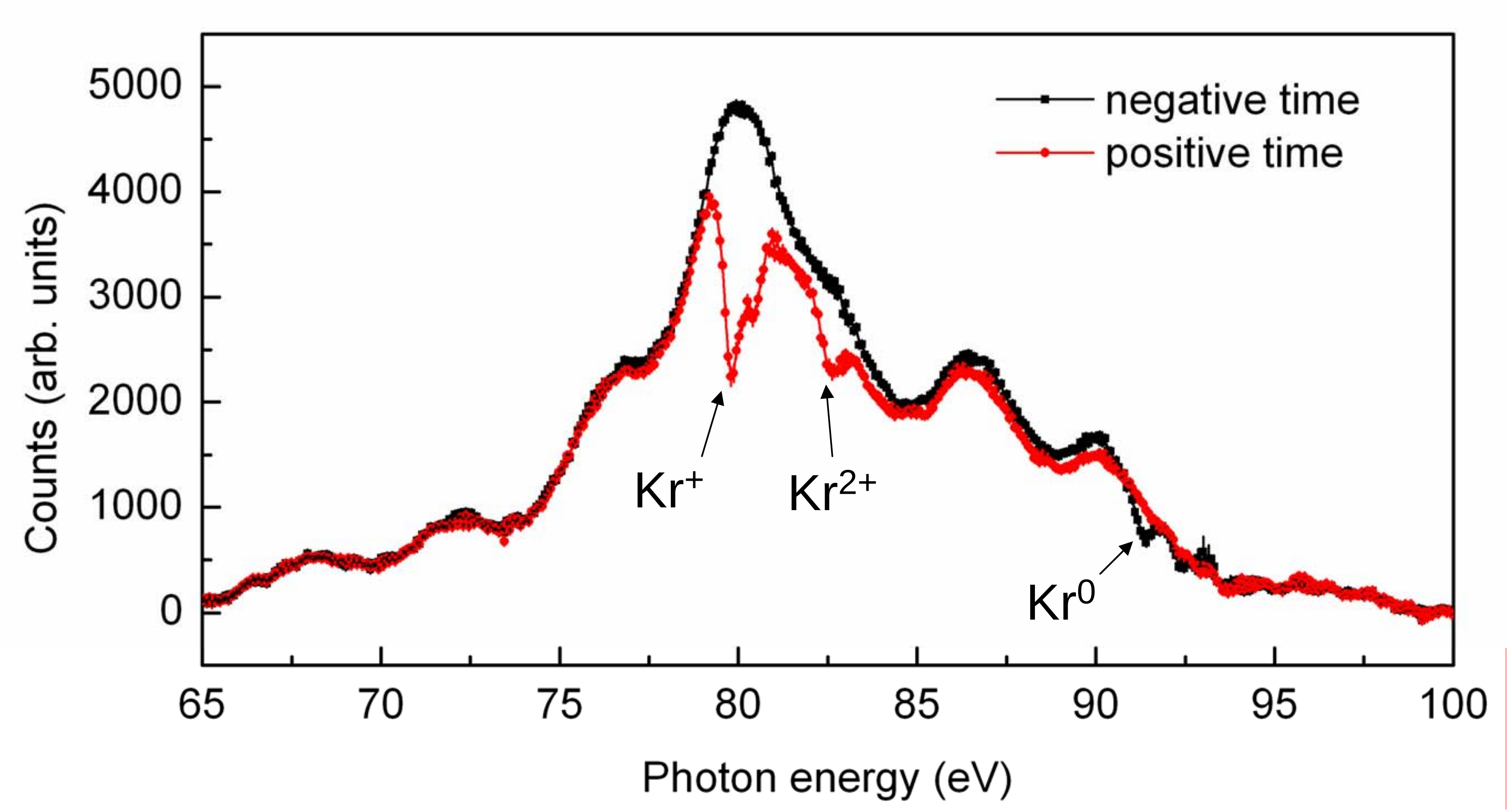
Temporal response is a direct measure of non-adiabaticity in optical strong-field ionization.

In Krausz' Lab



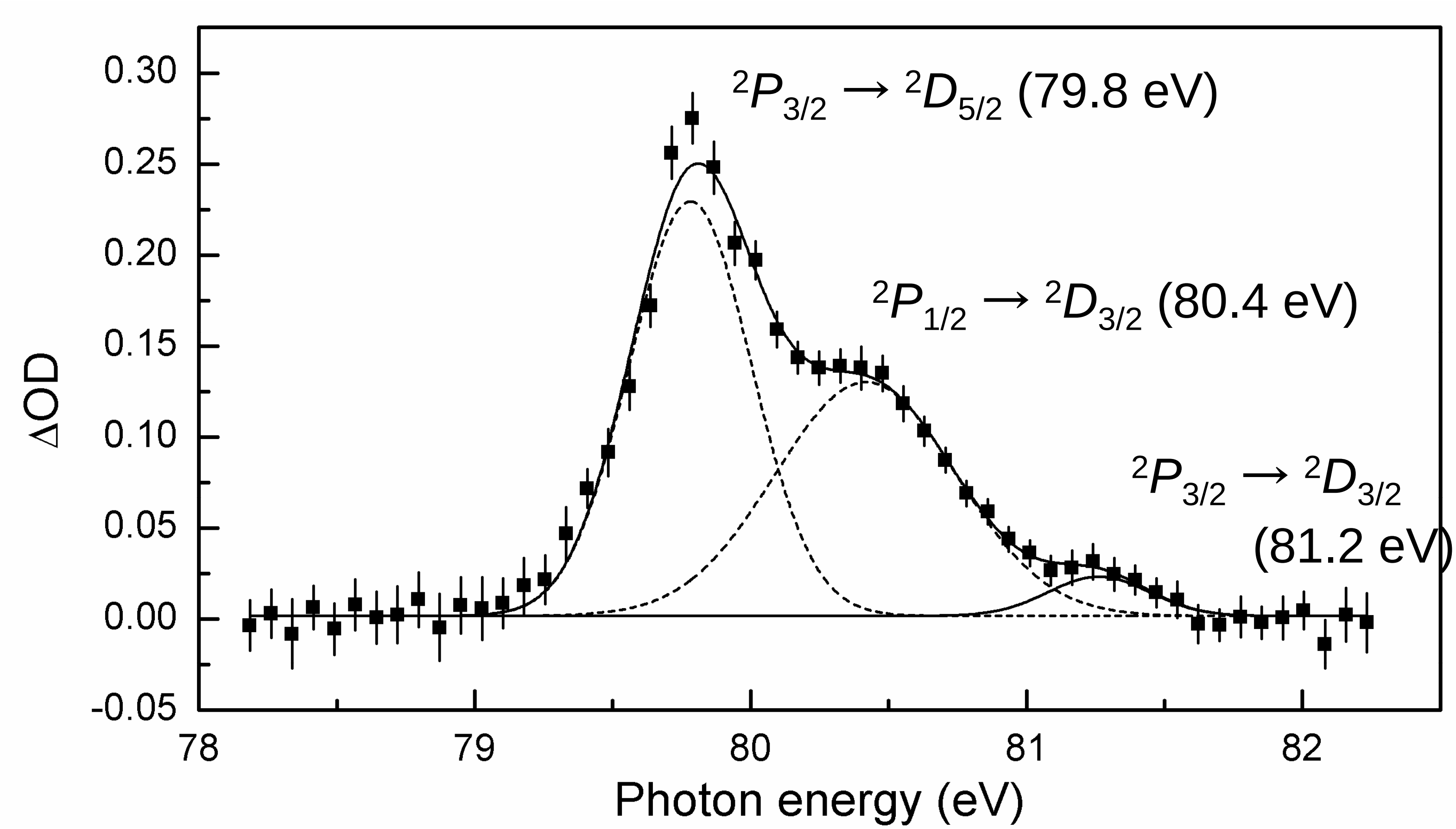
See Nature, August 5th, 2010

Strong-field ionization of Kr observed by high-order harmonic absorption



20 sec integration time per HH spectrum per set, average over 20 sets

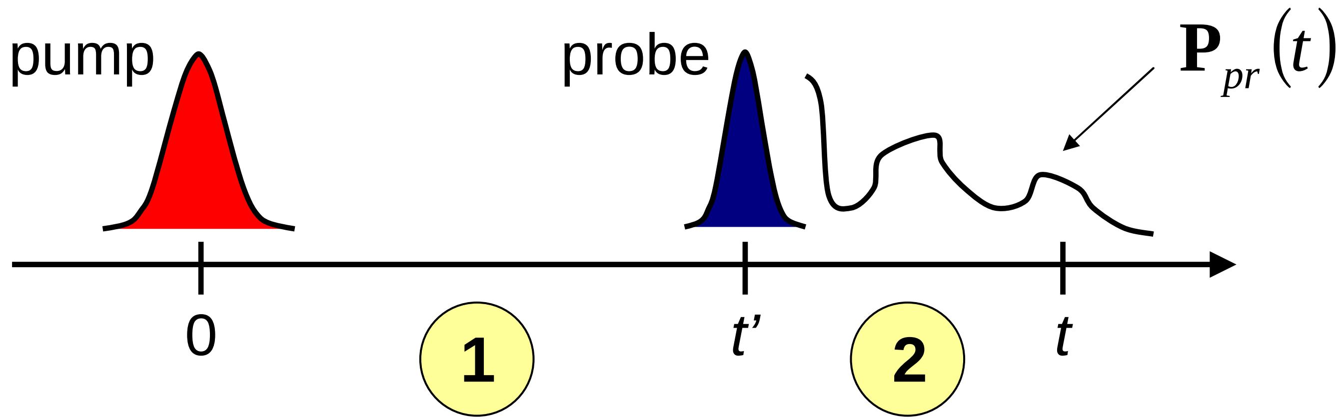
Quantum state-resolved probing of Kr^+



How does strong-field ionization of Kr^0 with a few-cycle pulse (4 fs) differ from that with a many-cycle pulse (50 fs)?

Violation of uncertainty principle?

Does spectrally-dispersed transient absorption spectroscopy with attosecond time resolution violate the uncertainty principle?



- Time resolution $\Delta t1$ determined by pump-probe cross-correlation
- Spectral resolution $\Delta E2$ determined by spectrometer configuration

$\Delta E2 \bullet \Delta t1$ can take on any arbitrary value!

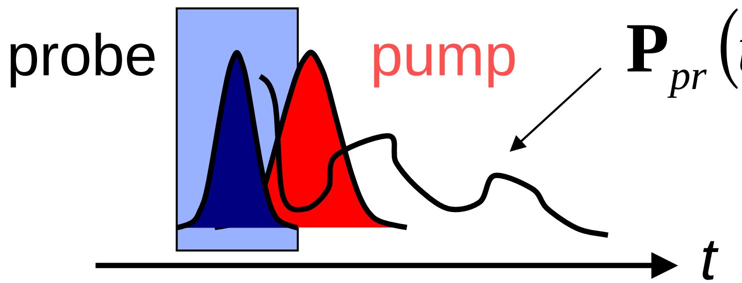
Mathies & friends, J. Chem. Phys. **92**, 4012 (1990); Annu. Rev. Phys. Chem. **43**, 497 (1992).

But there is a problem …

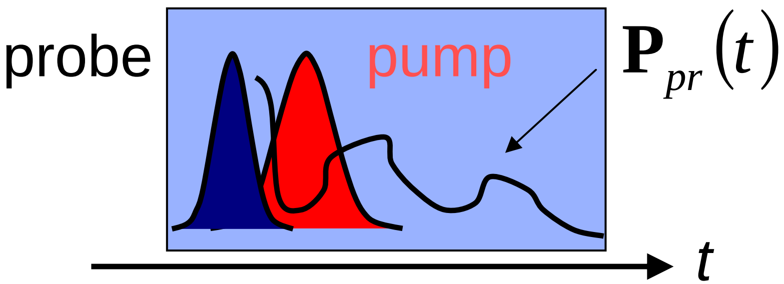
1) Broadband probe pulse induces a polarization.

2) Electric field emitted by polarization is picked up by the detector. When the pump pulse overlaps in time with the XUV probe-induced polarization:

Ideal case (local):



In reality (nonlocal):



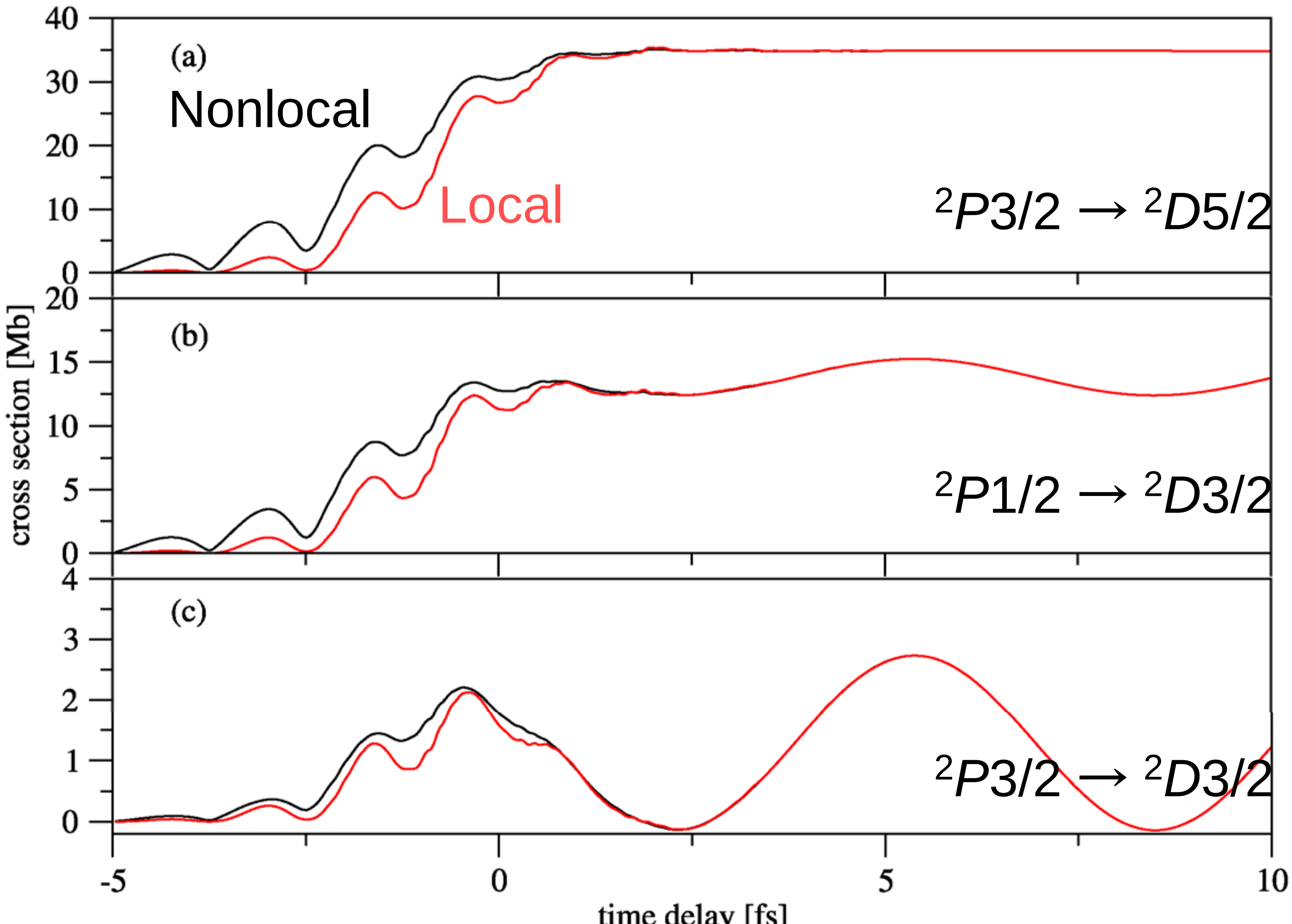
(note that: $\tau_{pr} = 1/\Gamma_c$)

Temporal nonlocality: XUV probe-induced polarization samples the time-varying amplitude coefficients even after XUV probe pulse has passed through the sample!

(R. Santra)

Effect of temporal nonlocality

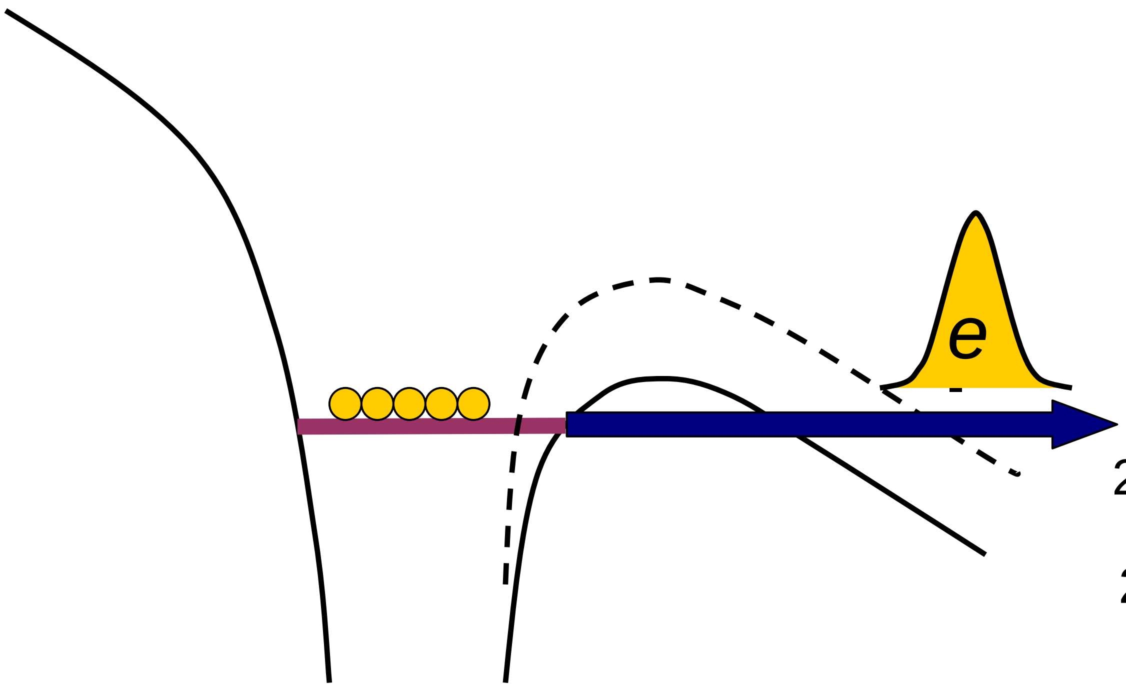
Example: Kr^+ resonances



(R. Santra)

Formation of electronic coherence by strong-field ionization

Two open channels in the strong-field ionization of Kr:



$^2P1/2$ (14.67 eV)

$^2P3/2$ (14.00 eV)

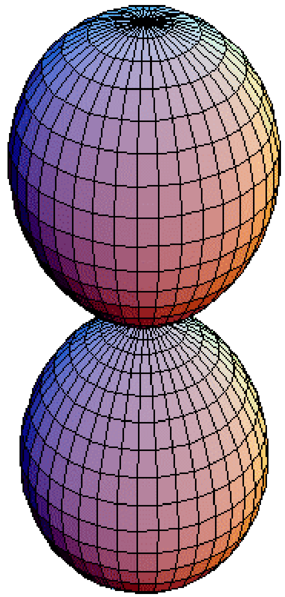
Can strong-field ionization lead to the coherent excitation of the Kr^+ $^2P3/2$ and $^2P1/2$ spin-orbit states?

Santra *et al*., Phys. Rev. A **74**, 043403 (2006).

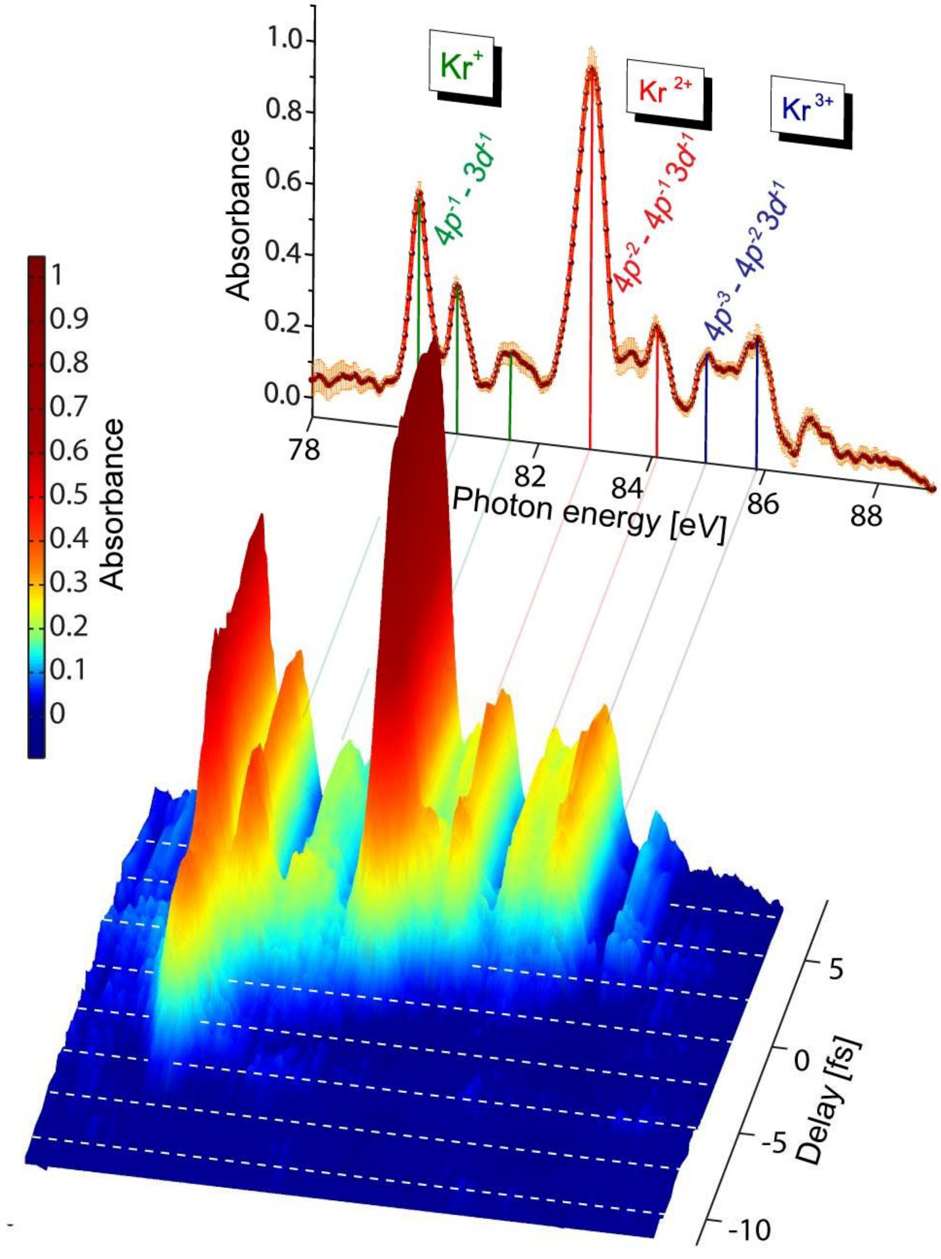
End result: possible real-time observation of electron motion

Time-evolution of hole density after laser pulse:

$$\left|\psi(t_0+t)\right\rangle = c_{3/2}e^{-i\omega_{3/2}(t_0+t)}\left|{}^2P_{3/2}\right\rangle + c_{1/2}e^{-i\omega_{3/2}(t_0+t)}\left|{}^2P_{1/2}\right\rangle$$



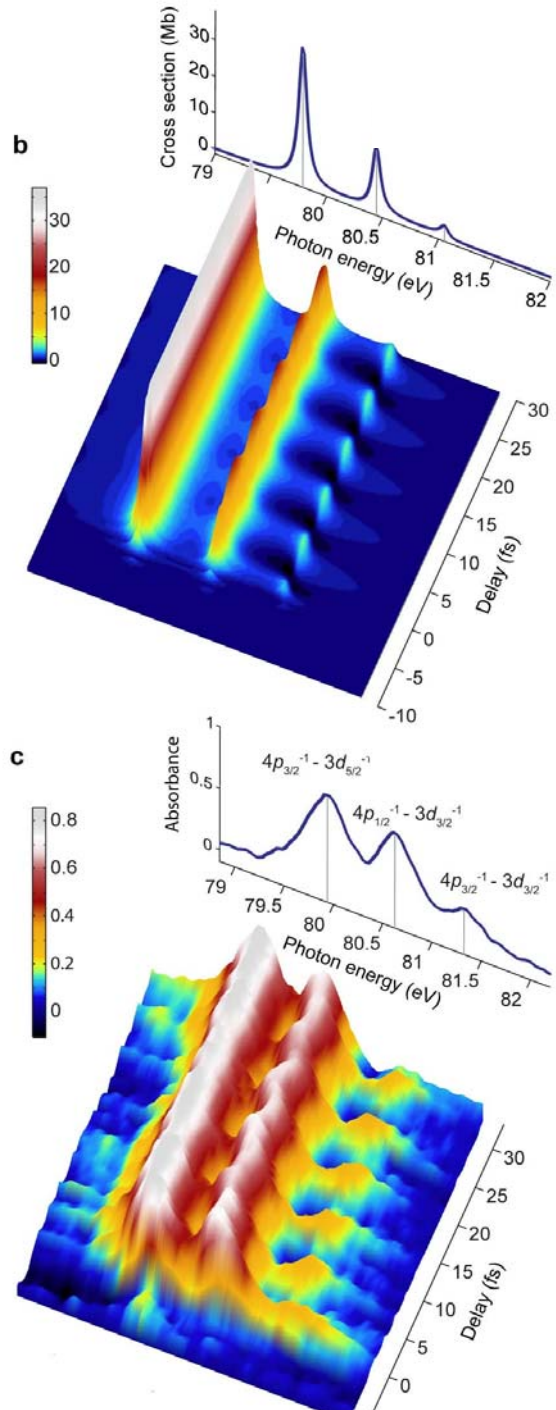
$\hat{\varepsilon}_{NIR}$



Kr+
Kr 2+
Kr 3+
$4p^{-1}$ - $3d^{-1}$
$4p^{-2}$ - $4p^{-1}3d^{-1}$
$4p^{-3}$ - $4p^{-2}3d^{-1}$
Absorbance
Photon energy [eV]
Delay [fs]

Kr$^+$ region

Theory



Experiment

Quantum beat wave packet between spin orbit states

Energy shifts expected based on interplay between dispersion and absorption

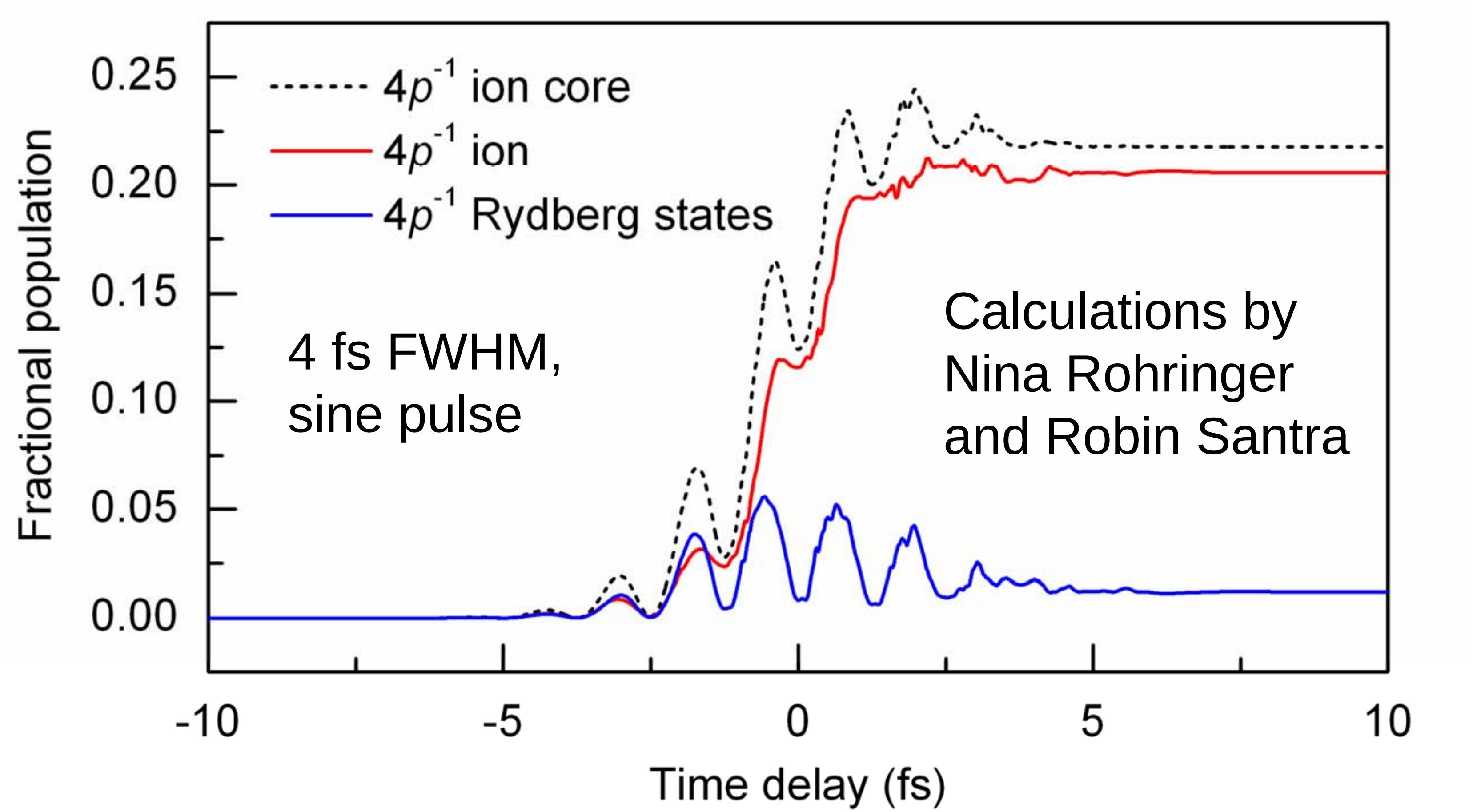
Quantum state distribution: few-cycle vs. many-cycle pulse

Quantum state dist., $\rho_{j,m}$	Many-cycle (50 fs) [1]	Few-cycle (4 fs)	Time-Dep. Schröd. Eq. calc.
$\rho_{3/2,1/2}$	59 ± 6	42 ± 10	68
$\rho_{3/2,3/2}$	6 ± 6	23 ± 8	6
$\rho_{1/2,1/2}$	35 ± 4	35 ± 3	26
Degree of coherence	---	g=0.67 ± 0.17	g = 0.6

g = 1 is max

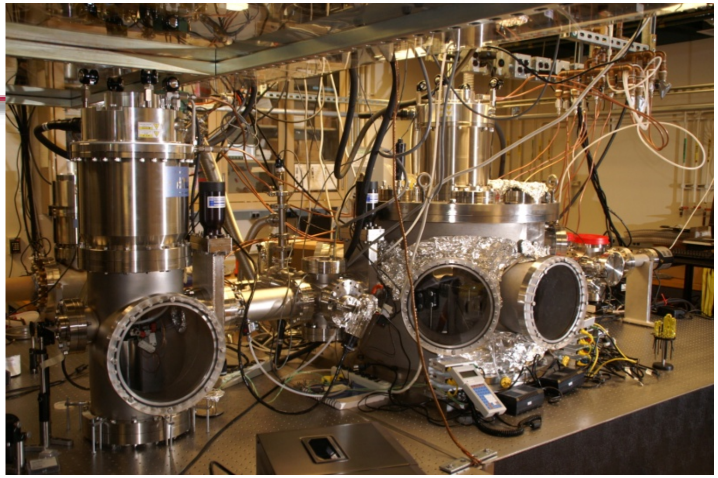
[1] L. Young et al., Phys. Rev. A **76**, 043421 (2007).

Calculation: Transient population of Kr^0 Rydberg states



Laser field induces a transient population and depopulation of the neutral Kr Rydberg states.

The Leone/Neumark Team for Attosecond Dynamics



Current team members

Steve

Dan

Hiroki

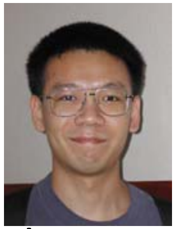
Annelise

Mark

Phil

Justine

Allison



Zhi-Heng

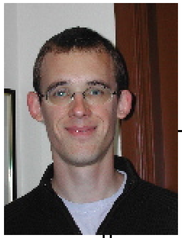
& Colby (undergrad)

Former team members

Thomas

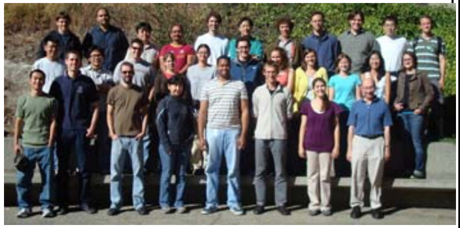
Lukas

Aurélie



Willem

Neumark group



Leone group

Collaborations:

Center for X-ray optics (CXRO)
Andrew Aquila
Yanwei Liu
David Attwood

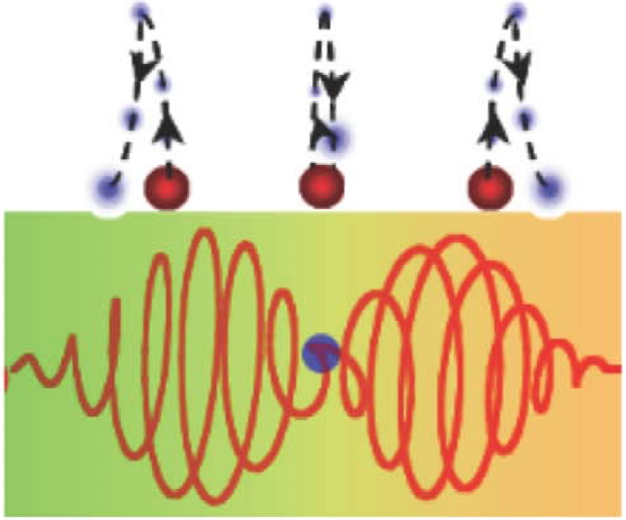
JILA, Boulder
Jason Jones
Jun Ye

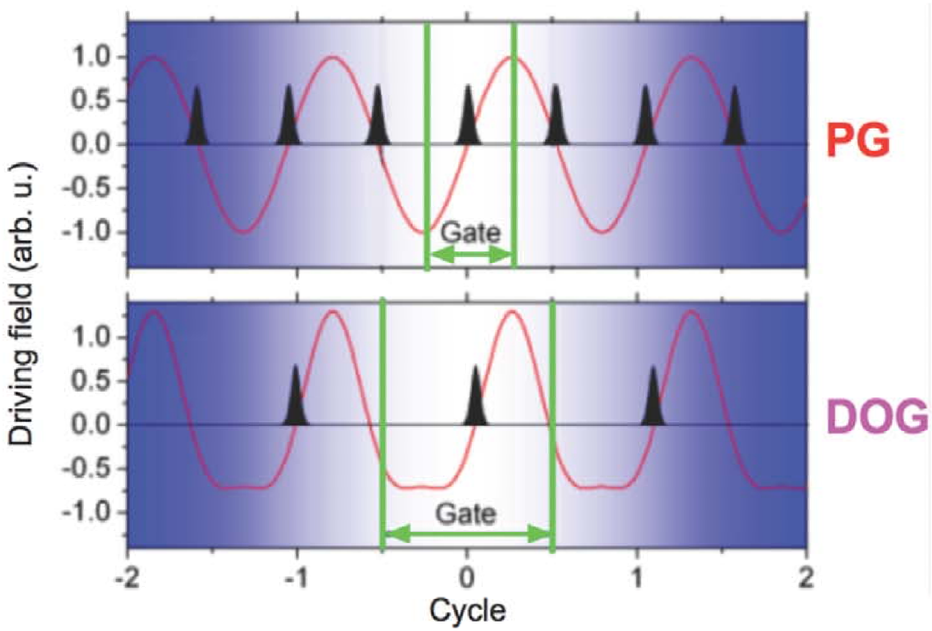
Financial support:

MURI-AFOSR provided initial support, DOE, NSF

Double Optical Gating (DOG) to Produce Continuum Harmonic Spectra

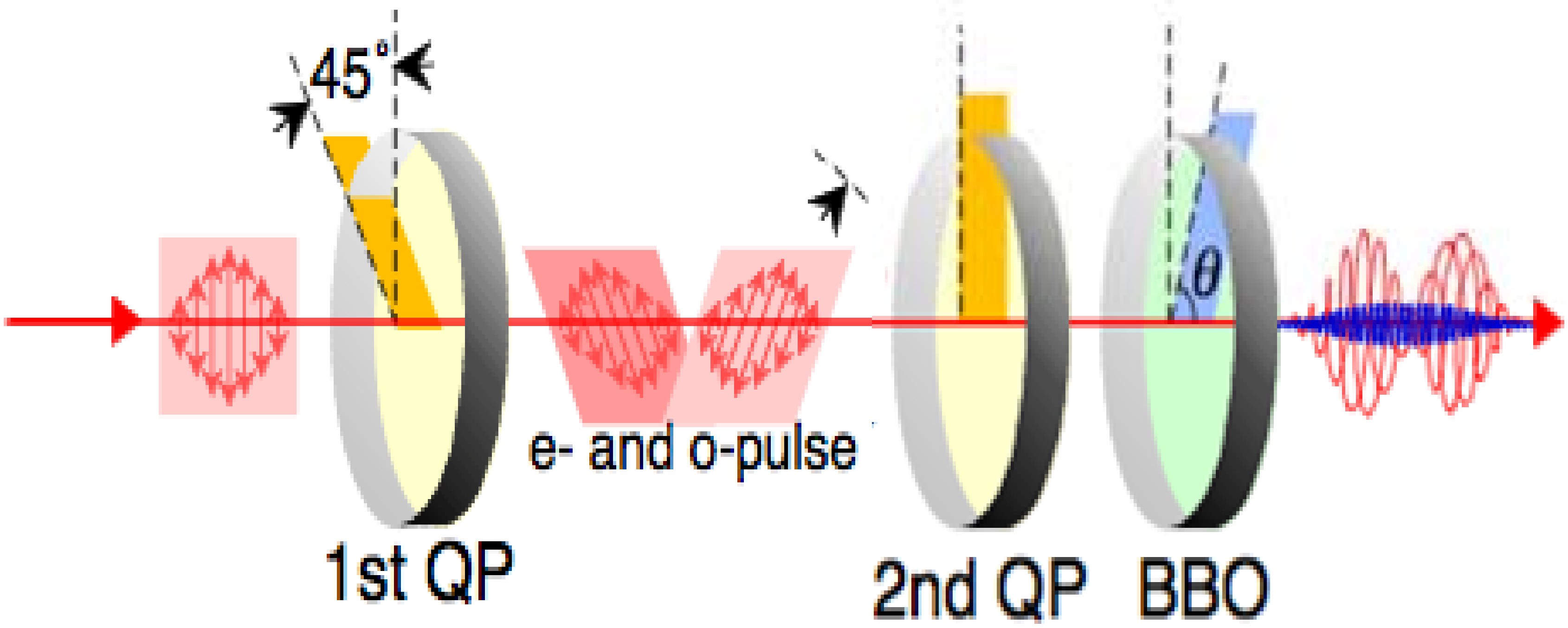
Double optical gating =
Polarization gating + Two color gating


Ellipticity dependent pulse



H. Mashiko et. al., Phys. Rev. Lett. 100, 103906 (2008).

Optics for DOG

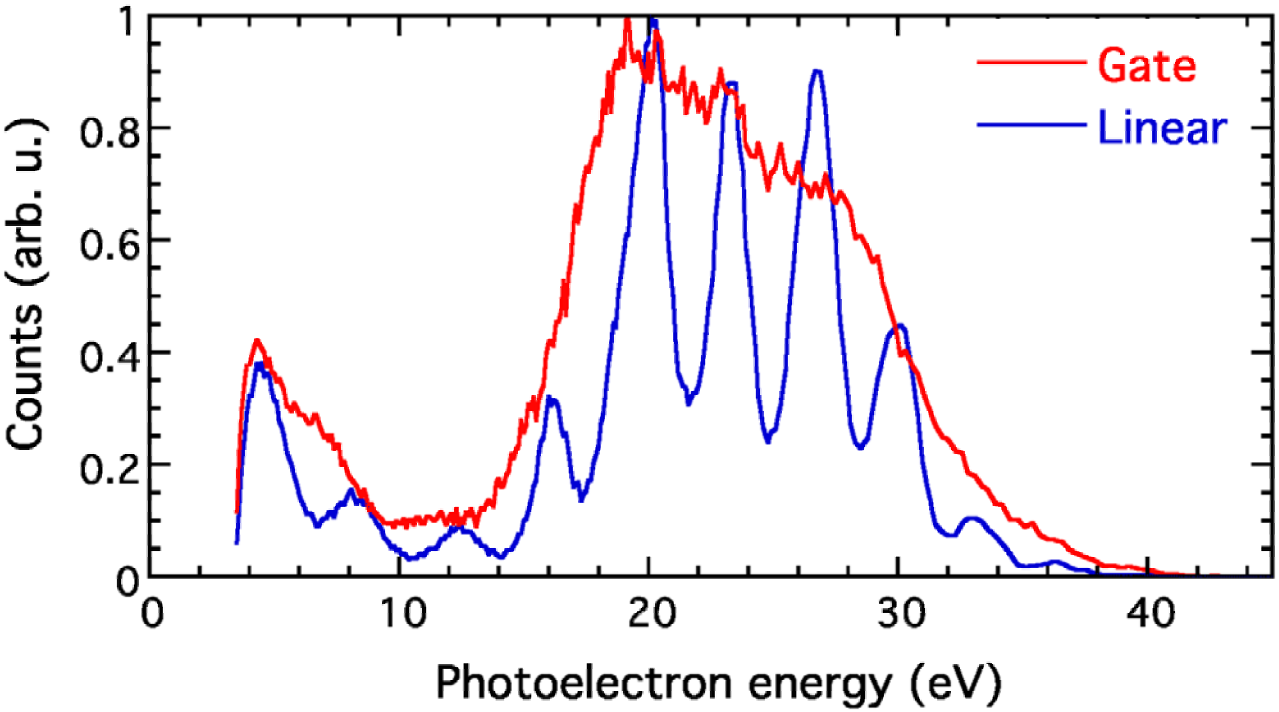


H. Mashiko et al. Opt Lett, 34, 3337 (2009).

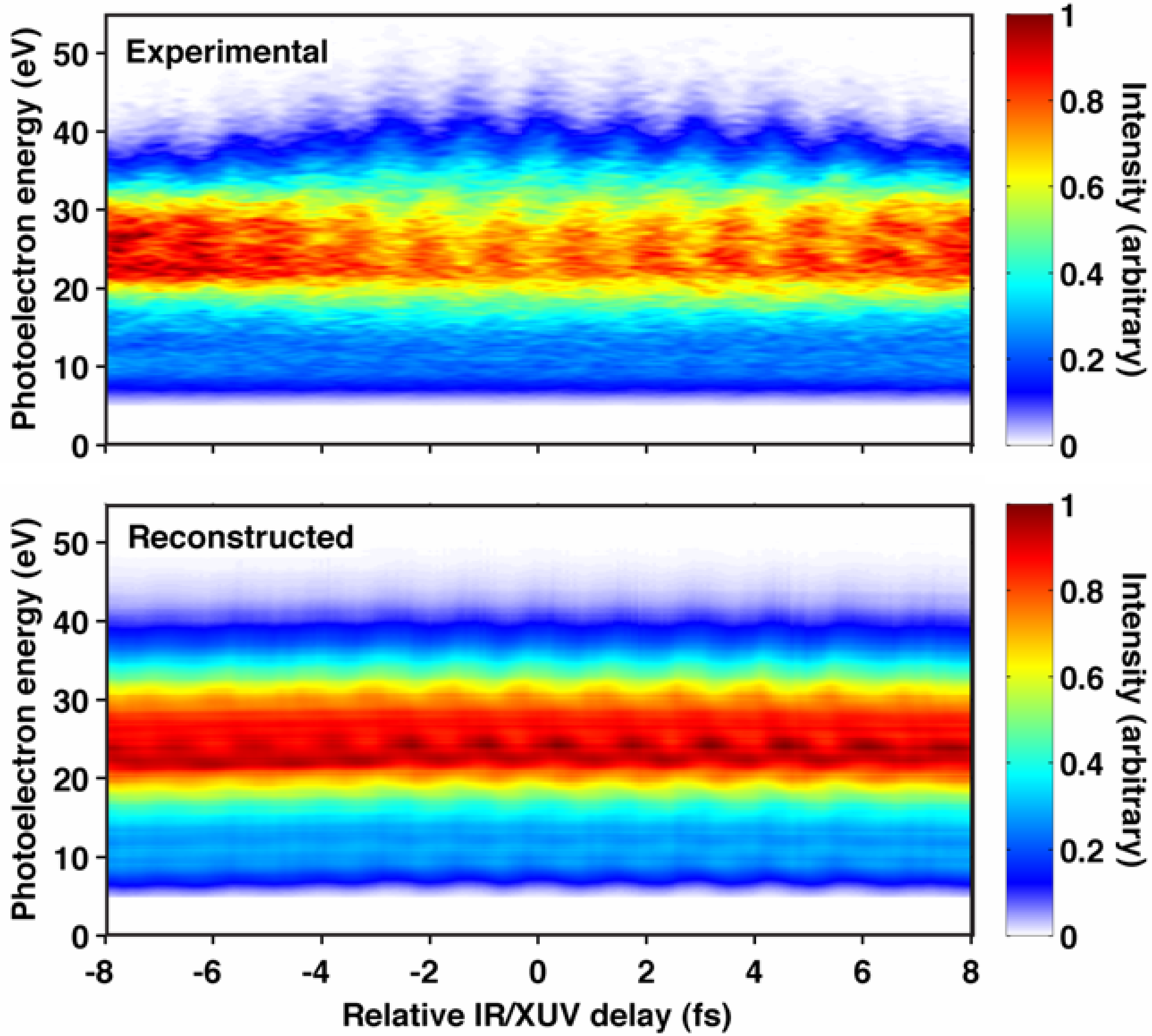
Photoelectron Spectrum from Gate and Linear Pulses

Harmonics from Ar gas

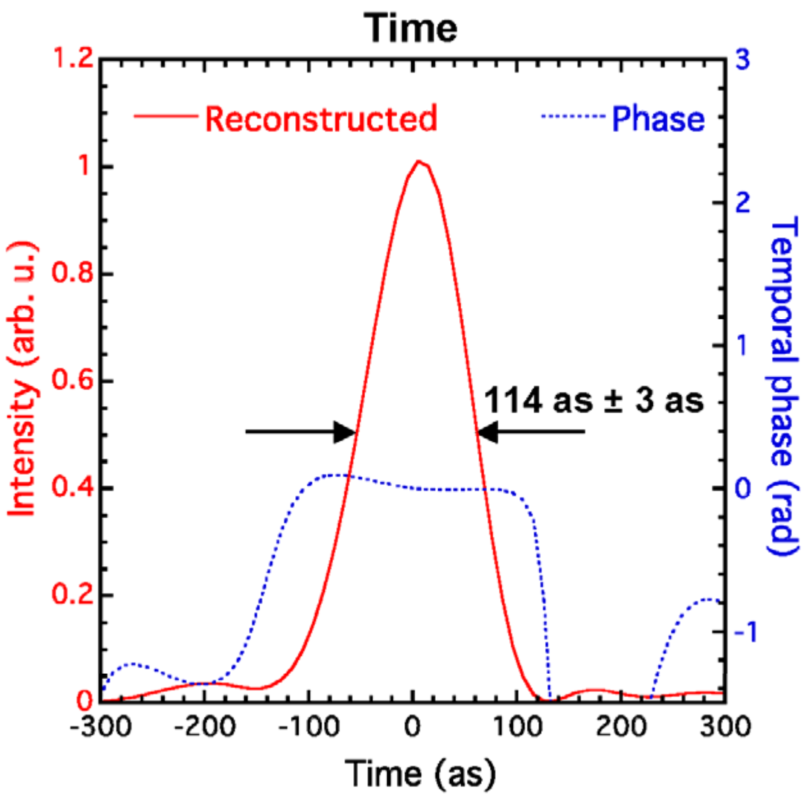
Photoelectron from Ne gas (I_p=21.6 eV)

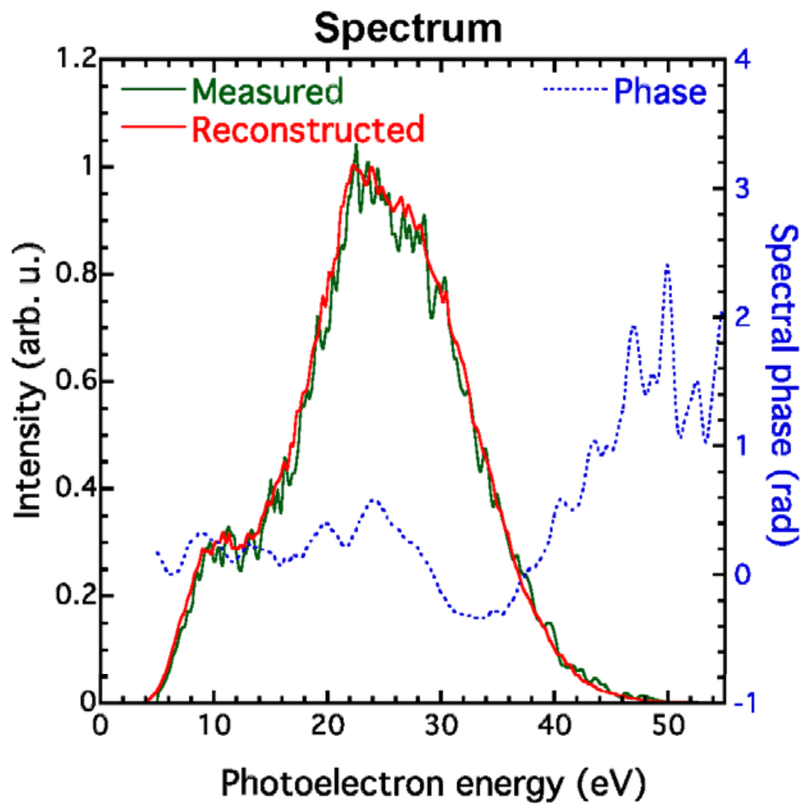


Photoelectron Streak Field & FROGCRAB

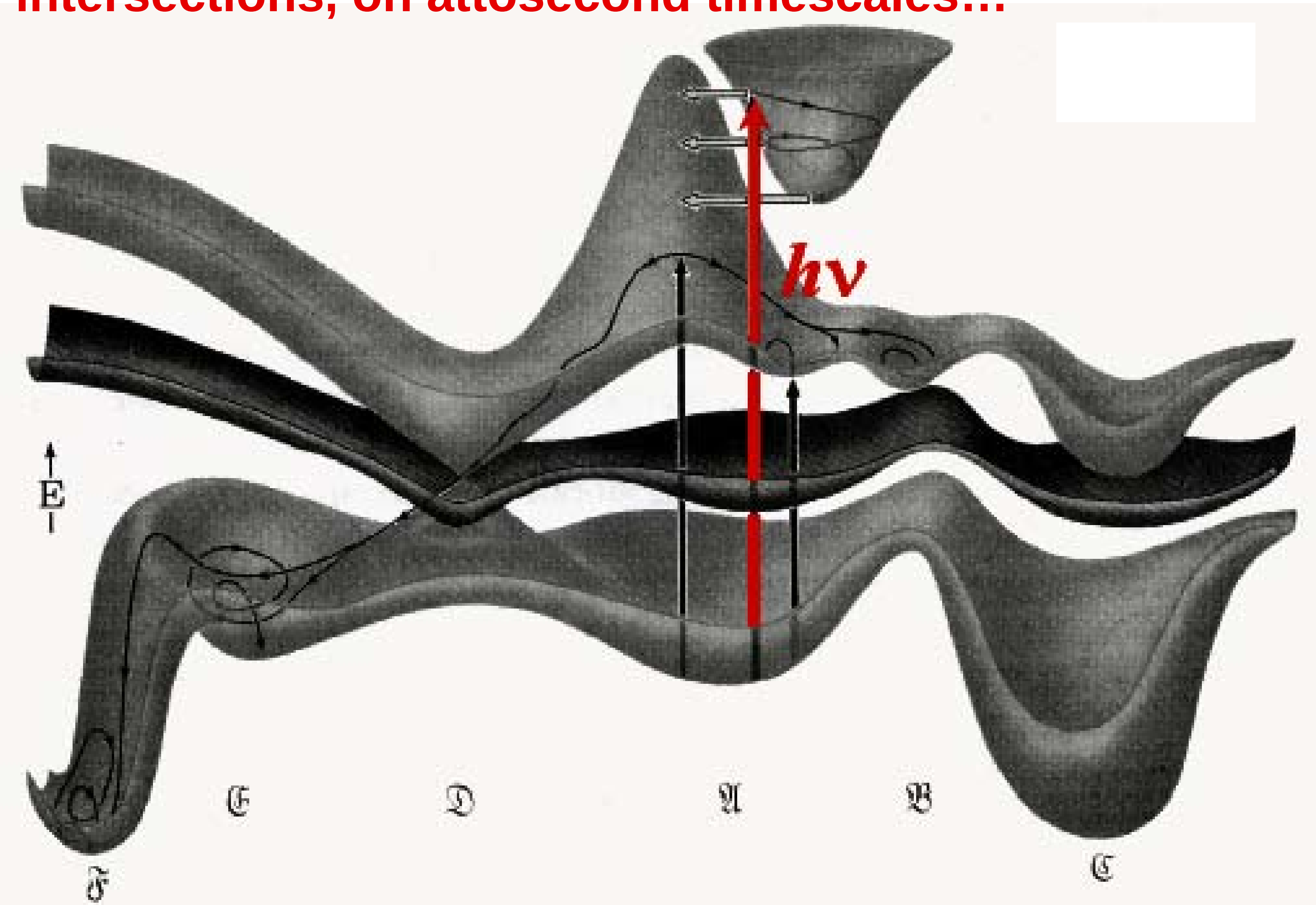


Temporal and Spectral Characterization



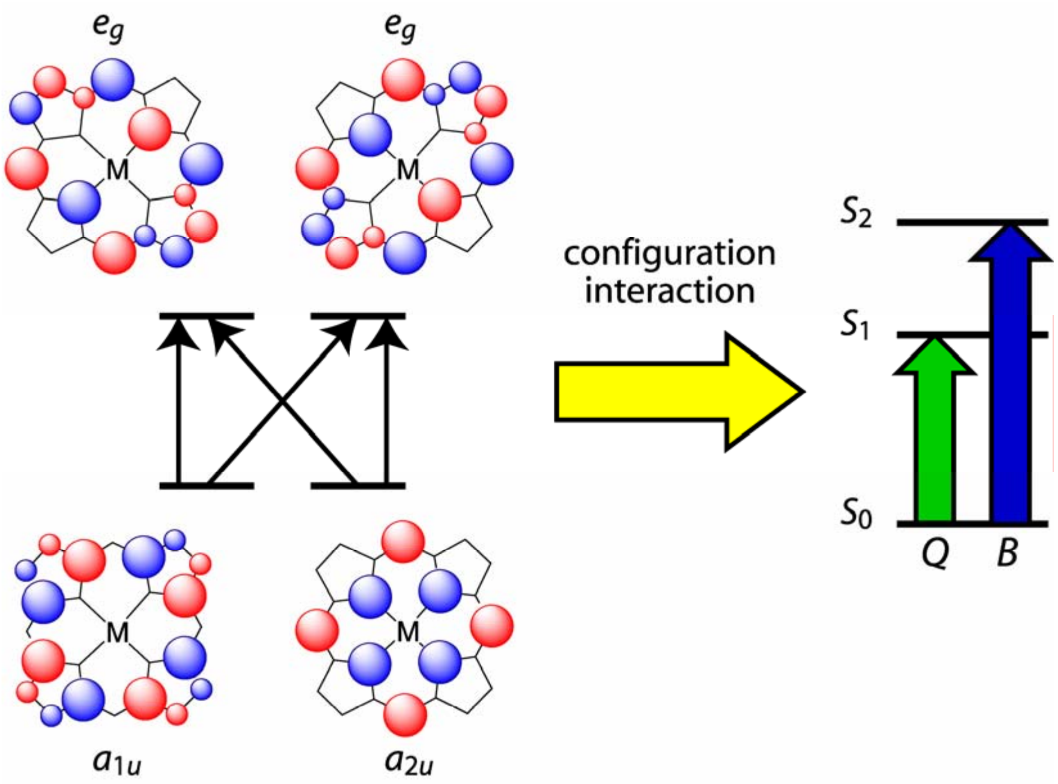


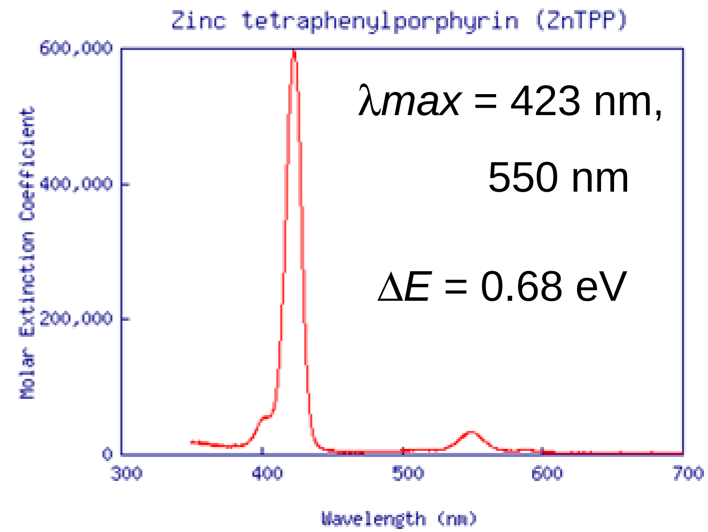
The dream: Follow every feature of electronic pathways in a complex molecule, through conical intersections, on attosecond timescales…



Towards ultrabroadband single-photon coherent excitation

Metalloporphyrins frontier orbitals:



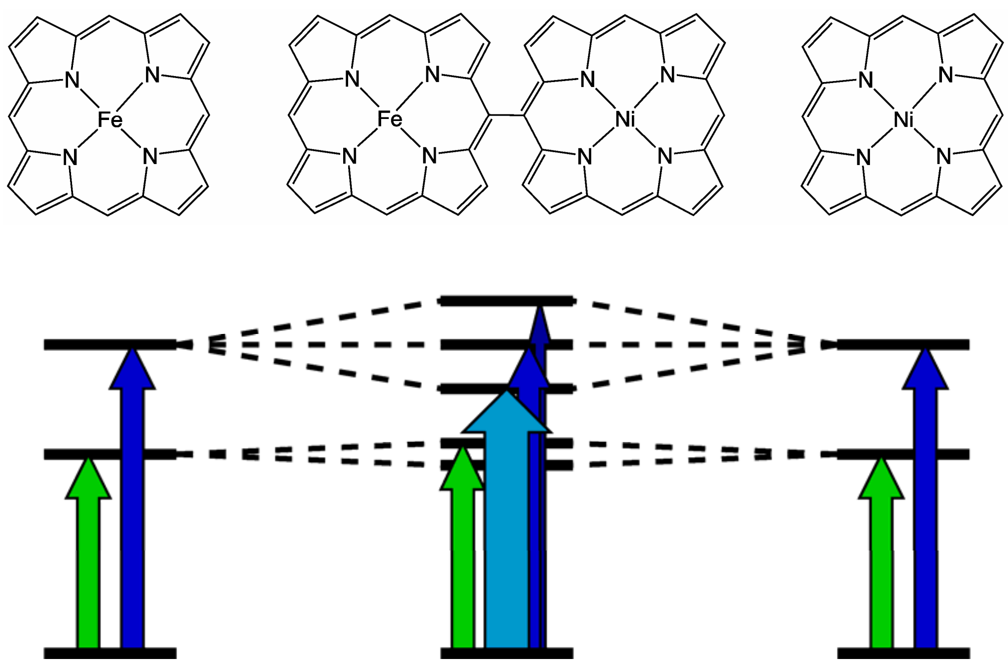


(PhotochemCAD database)

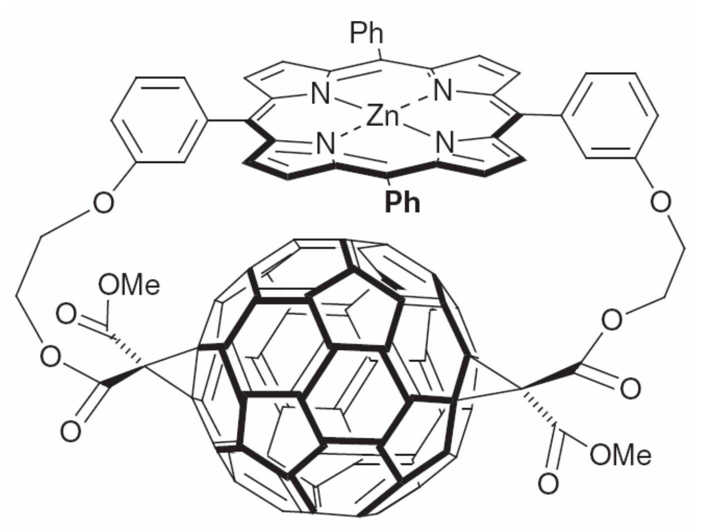
How does electronic coherence influence photophysics?

Electronic coherences produced by ultrabroadband single-photon excitation

Metalloporphyrins dimer and multichromophoric arrays:



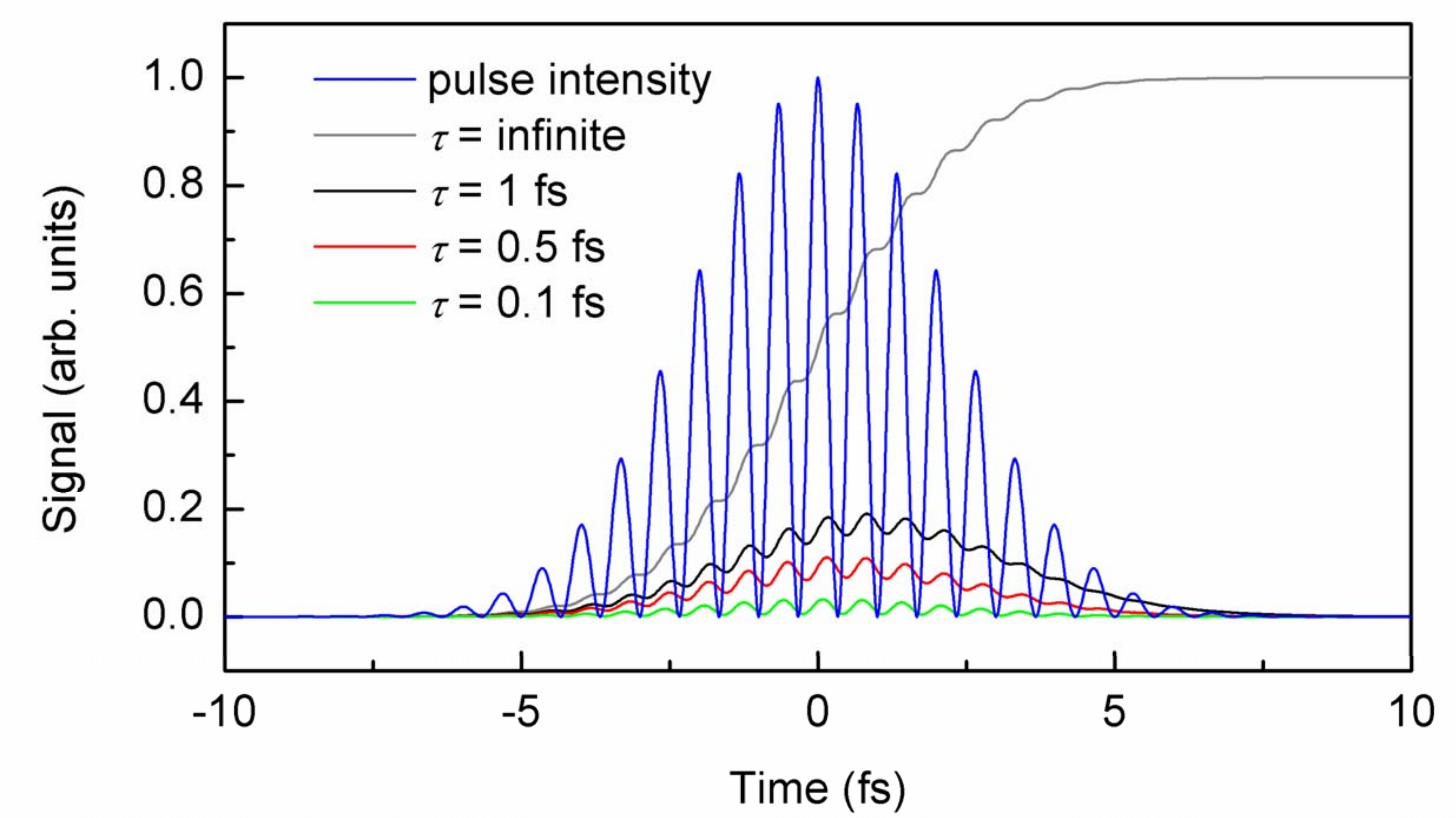
• Control of electron (de)localization?



• Coherent excitation of chromophores?

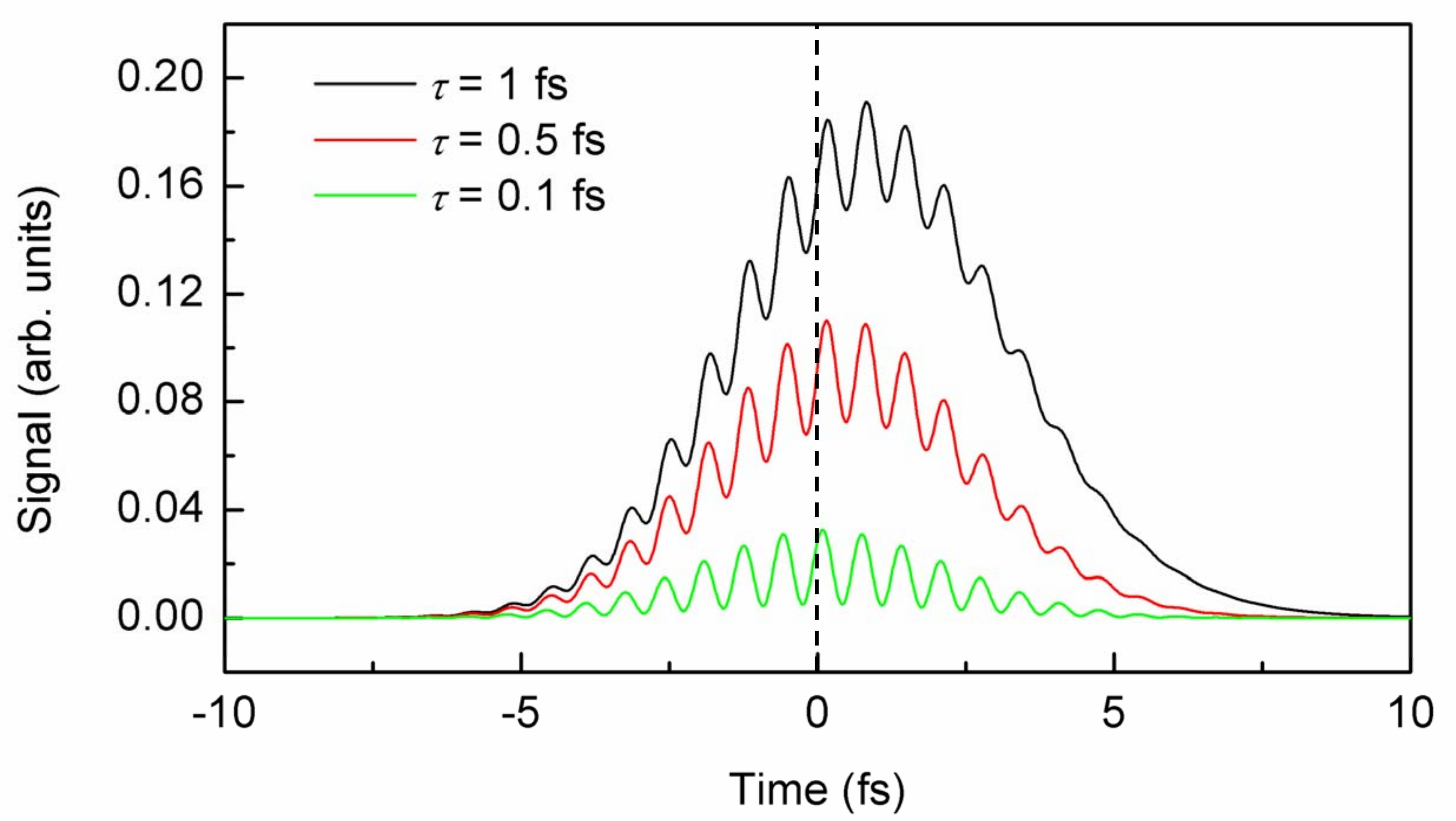
• Gating of photochemistry or electron/energy transfer?

Single-photon excitation @ 400 nm



Individual intensity spikes can be used as pump pulse in single-photon excitation, with τ_{FWHM} = 0.3 fs for each spike.

Single-photon excitation @ 400 nm



Decay lifetimes from sub-fs dynamics can be retrieved from shift in maximum from time-zero and modulation amplitude.

Methods to measure attosecond processes

Harmonic generation by electron recollision - Corkum

Streaking – determining the birth of an electron - Krausz

Tunnel ionization - Krausz

Field manipulation of ion channels– Neumark/Leone

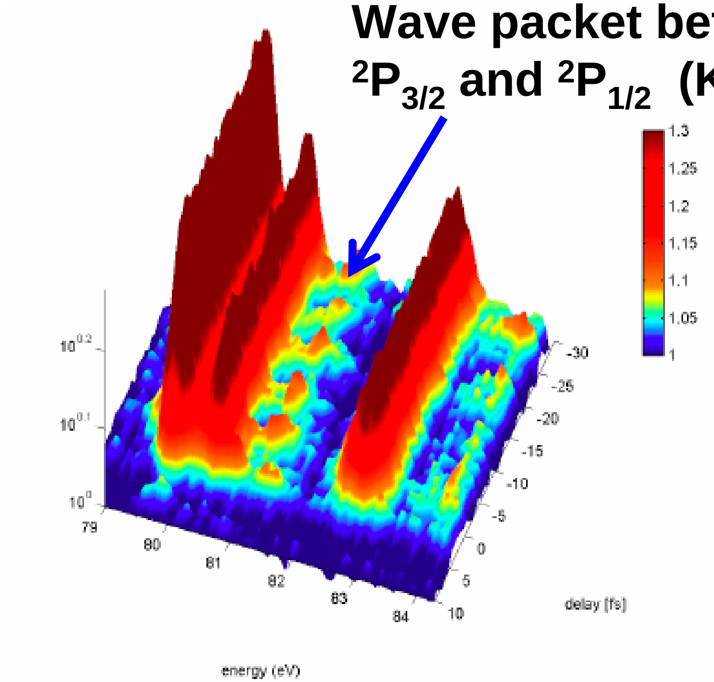
Transient absorption – Leone/Krausz

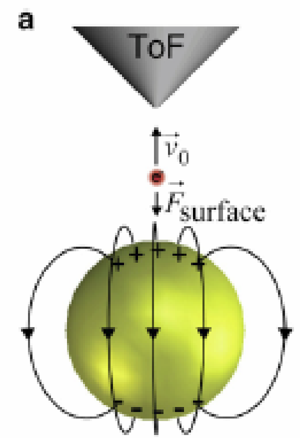
Plasmon enhanced streaking – surfaces

Transient reflectivity – solid state and nano materials

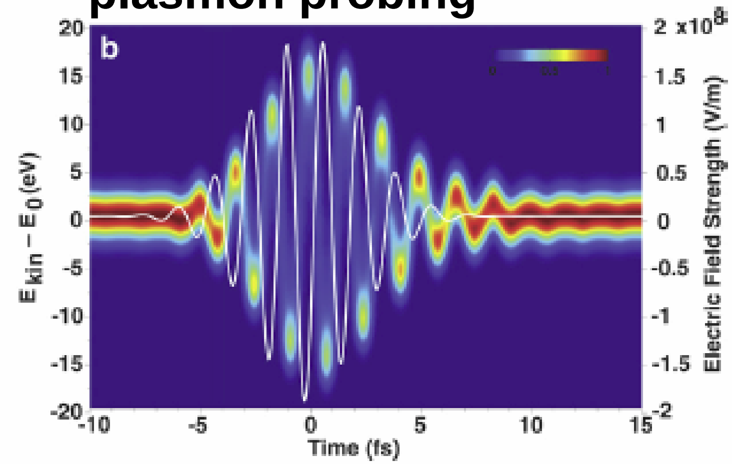
Transient dispersion

Wave packet between $^2P_{3/2}$ and $^2P_{1/2}$ (Kr^+)



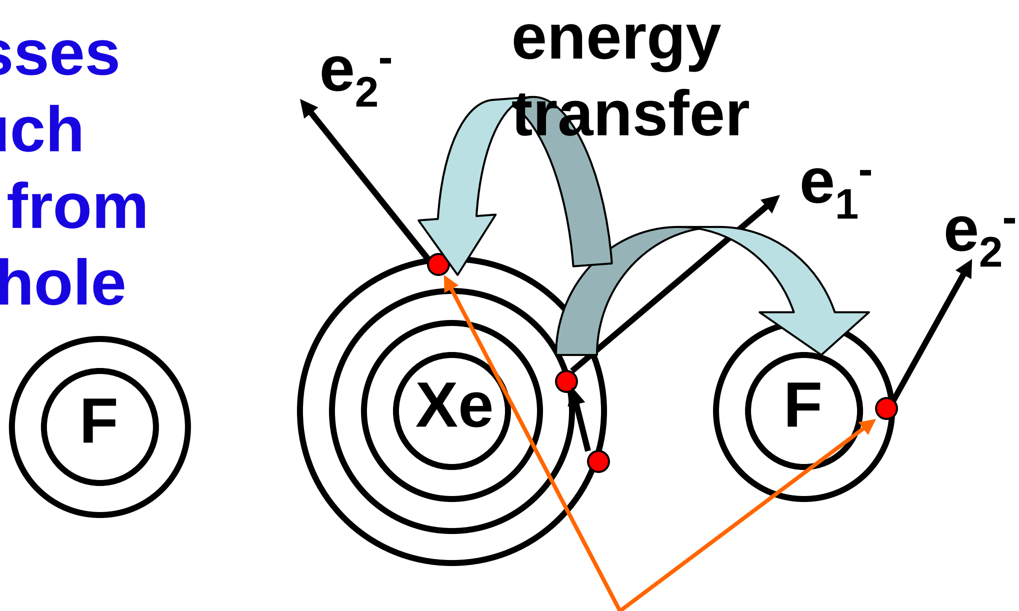


Simulation gold particle plasmon probing



Electron withdrawal by the fluorines slows Auger decay time - but in fact the Auger decay time speeds up

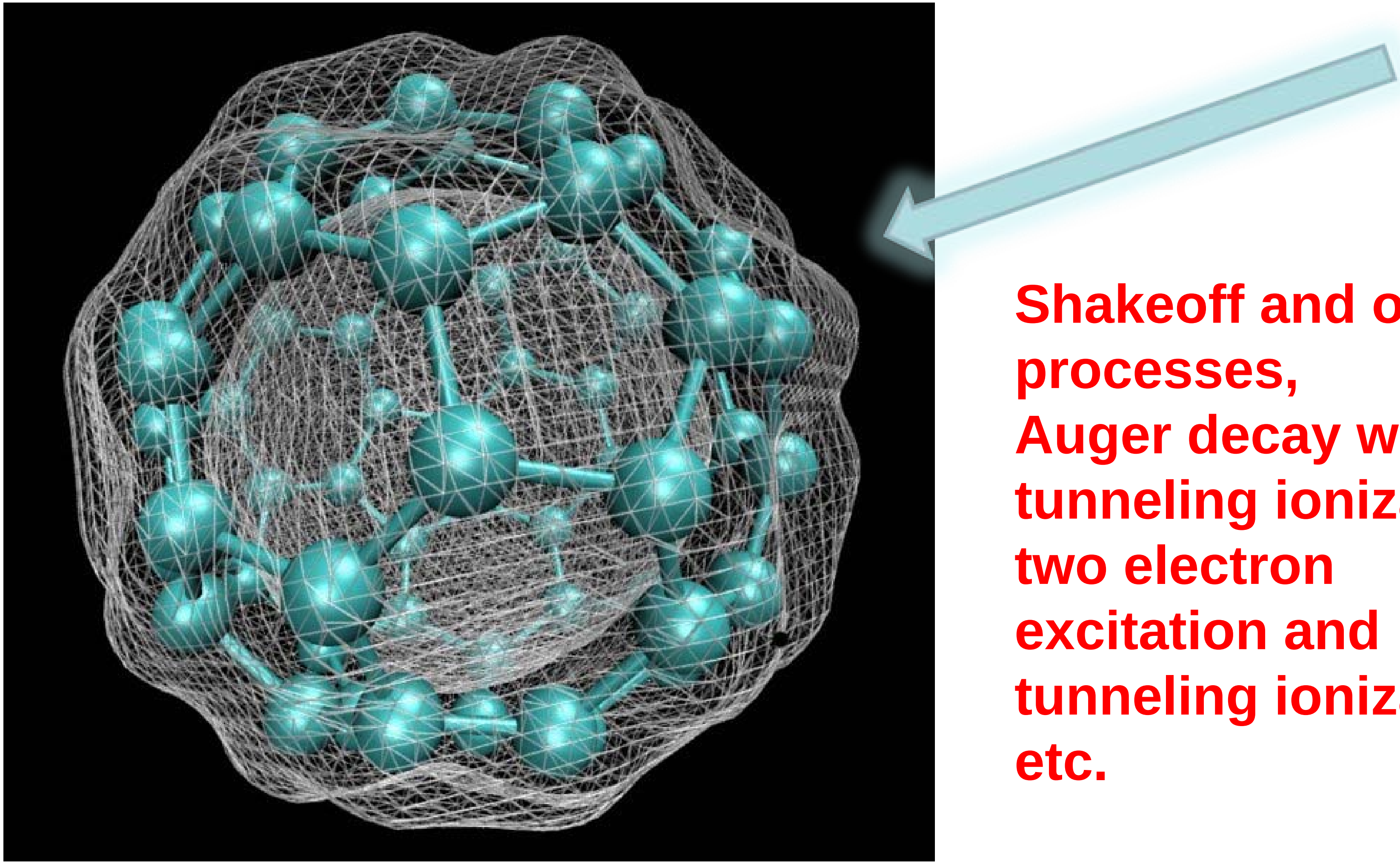
Other processes can occur such as electrons from fluorines fill hole



Competition between normal intra-atomic Auger decay and interatomic Coulombic decay

Buth, Santra, Cederbaum calculate that ICD contributes substantially - - $Fe(CO)_5$ how fast are the iron core level transitions affected by UV excitation that moves electron density from Fe to the antibonding orbital of CO?

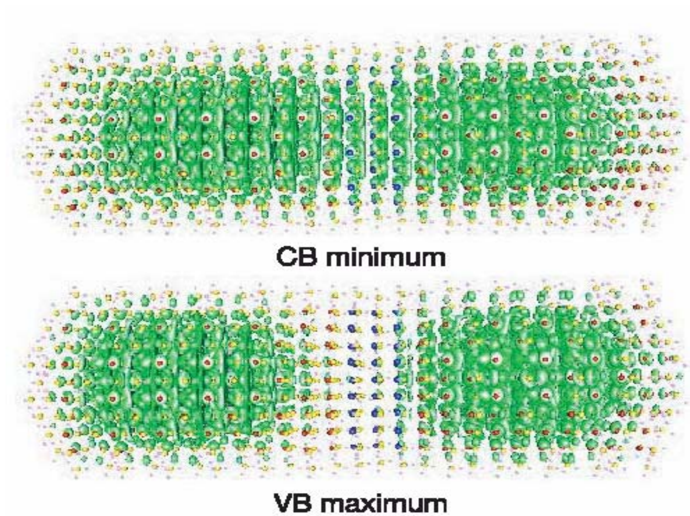
Attosecond Photoelectron Spectroscopy: C_{60} Ionization



Shakeoff and other processes,
Auger decay with tunneling ionization,
two electron excitation and tunneling ionization,
etc.

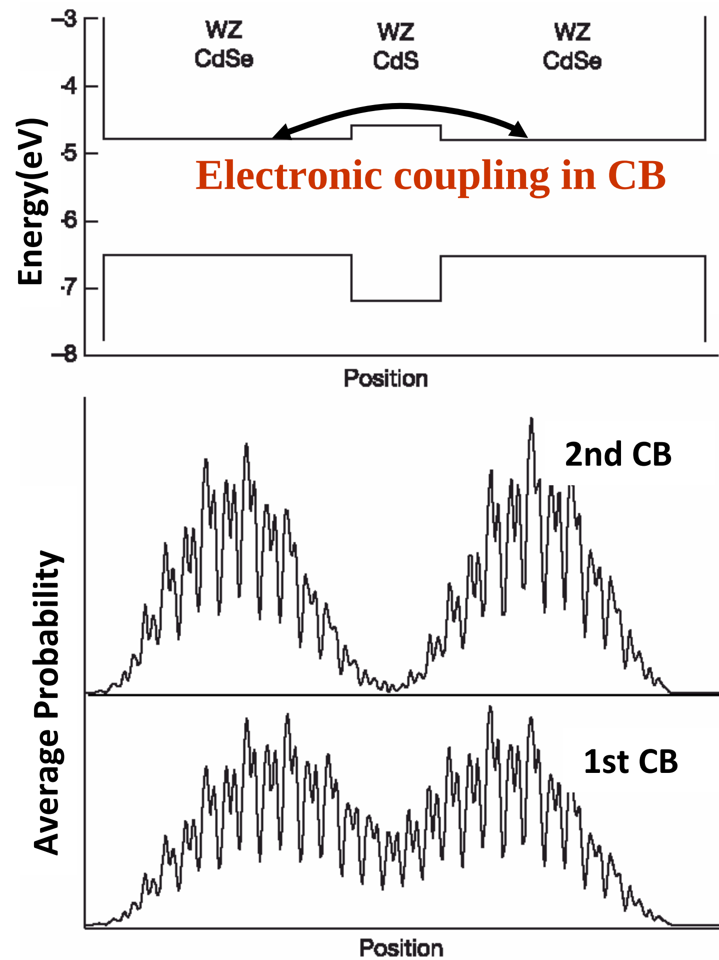
Electronic structure of coupled semiconductor nanorod
Wave packet dynamics

Electron density of CB and VB in CdSe/CdS/CdSe coupled nanorod



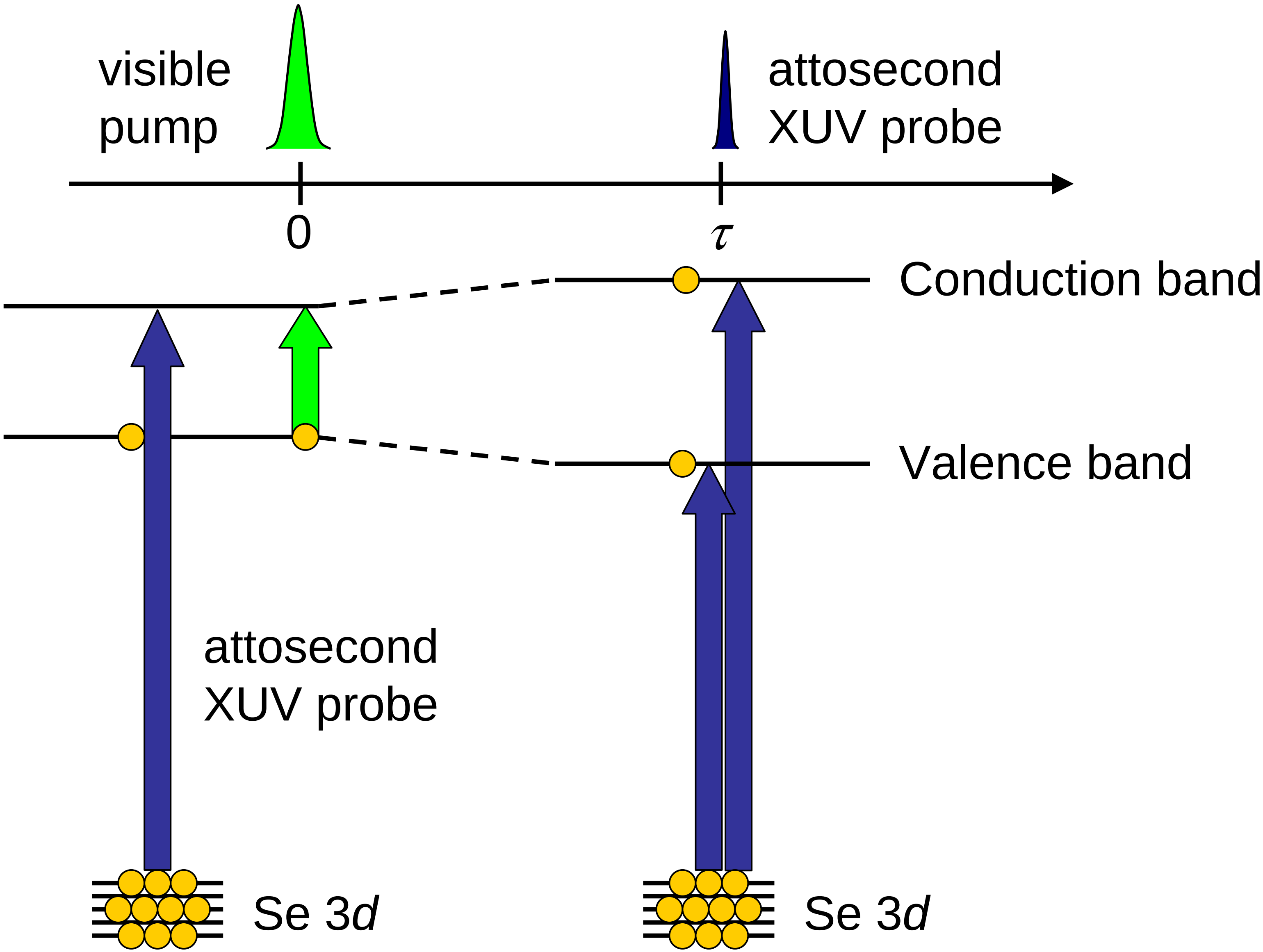
Conduction band of the coupled CdSe/CdS/CdSe nanorod shows a strong electronic coupling, with significant electron density in CdS region

Electron density of the first two CB states in coupled nanorod



D. Milliron et al, *Nature*, 430, 190 (2004)

Nanocrystal core level time resolved investigations



In nanomaterials, such as CdSe, CdSe/CdS, ZnO, nanocrystals and nanowires, core level transitions can probe

Cd 64 eV
Se 55 eV
Zn 89 eV

Probe at the element specific, chemical level

Thus the transfer of an electron charge to or from a nanocrystal can be detected by the chemical changes in the soft x-ray transitions – why it is sensitive: confinement of charges in nanoparticles alters core level transition energies

The attosecond time domain will address important topics on fundamentally new timescales:
Birth of an exciton (association of electron and hole)
Coherent superpositions of exciton states, multiple excitons
Initial dephasing of excitons
Exciton-Exciton interactions at high carrier densities
Electron-hole plasma dynamics at even higher densities

Table-top, femtosecond XUV light sources based on high harmonic generation are already used for transient absorption measurements, as well as photoelectron dynamics.

- Now extended to attosecond transient absorption experiments.
- With FEL facilities, investigations will utilize two color pump-probe pulses that address two different core levels
- Extension to many core level spectroscopies in the time domain
- Can anticipate rapid application to electron transport in molecules, double holes or vacancies, charge transfer dynamics, exciton formation

- **Electron dynamics**