

Attosecond Time-Resolved Molecular Electron Dynamics



Marc Vrakking

Max-Born-Institut (MBI), Berlin, DE

Santa Barbara
26-8-2014

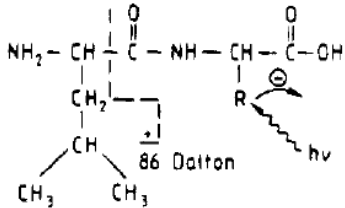
Application of Attosecond Pulses to Molecular Science

Question: why should we care?

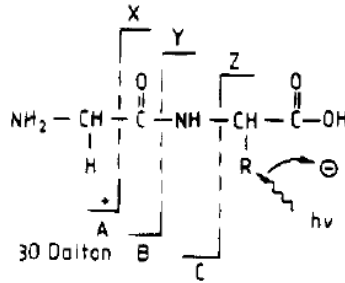
1. Any light-induced photo-chemical process starts with an electronic interaction; atomic motion sets in because of **coupling of electronic and nuclear degrees of freedom**
2. Many light-induced interactions involve multiple electrons – when is **coupling of electronic degrees** of freedom important?
3. By studying molecular dynamics on attosecond to few-femtosecond timescales we may uncover **new pathways towards control at the molecular level**

Attosecond molecular electron dynamics

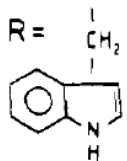
Leu-Y



Gly-Y



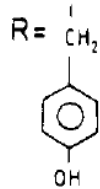
Tryptophan



IP ~ 7.5 eV

$\lambda_{OPT} = 286.7 \text{ nm}$

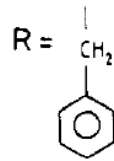
Tyrosine



IP ~ 8.0 eV

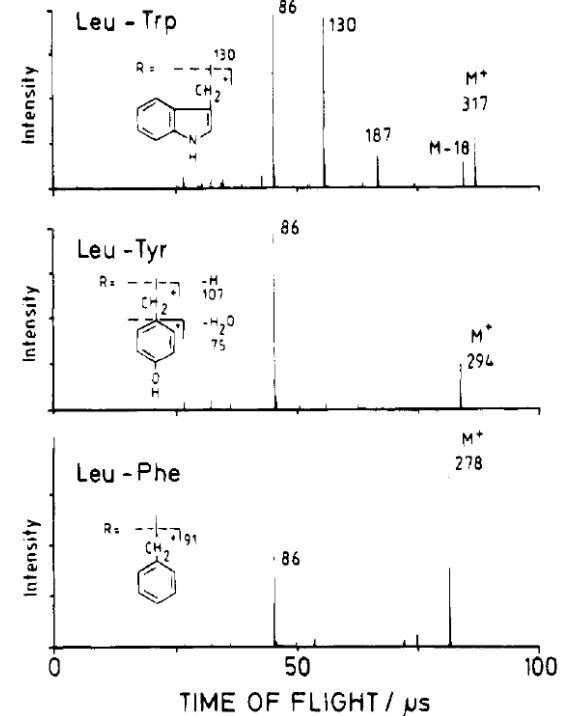
$\lambda_{OPT} = 281.7 \text{ nm}$

Phenylalanine



IP ~ 8.4 eV

$\lambda_{OPT} = 266.4 \text{ nm}$



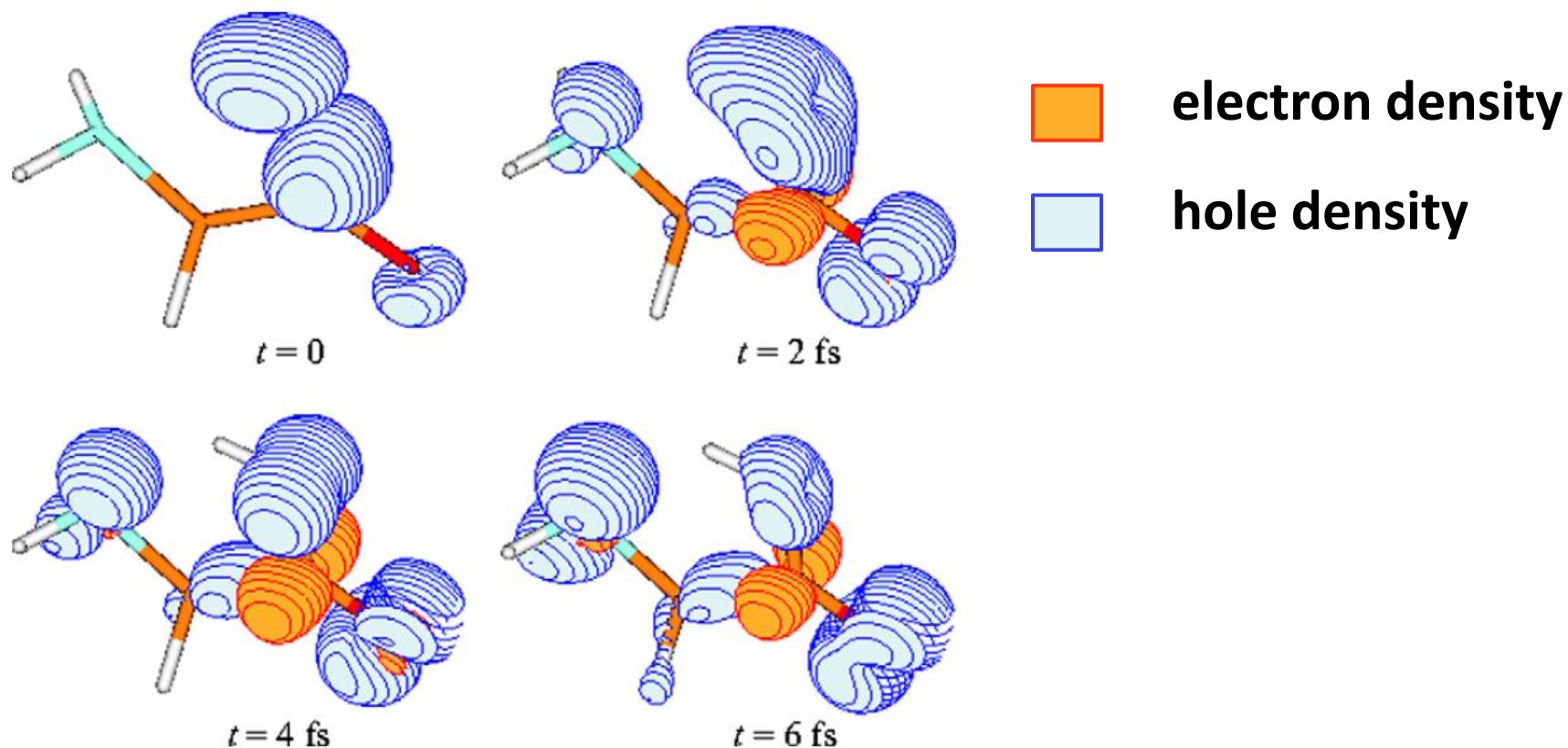
After selectively ionizing a chromophore on the C-terminal end of the peptide ionic fragmentation patterns resulting from additional UV absorption were dominated by ionic species related to the N-terminal end of the peptide

Interpreted in terms of efficient *charge migration* (i.e purely electronic motion, not involving the nuclei) from the N-terminal end of the peptide to the chromophore

Weinkauff et al., *J. Phys. Chem.* **99**, 11255 (1995)

Attosecond molecular electron dynamics

Charge migration upon sudden ionization (Glycine II):



Coherent preparation of ionic states

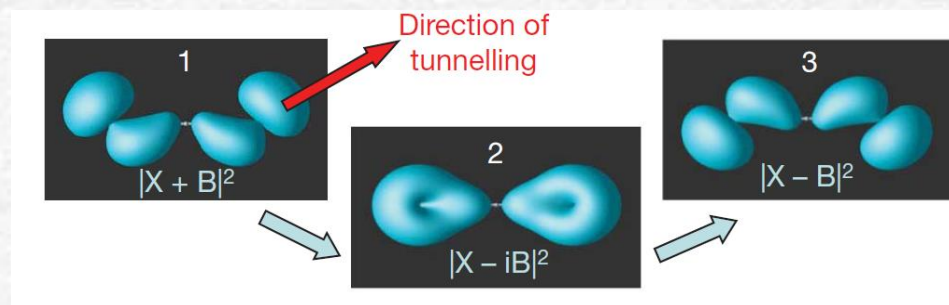
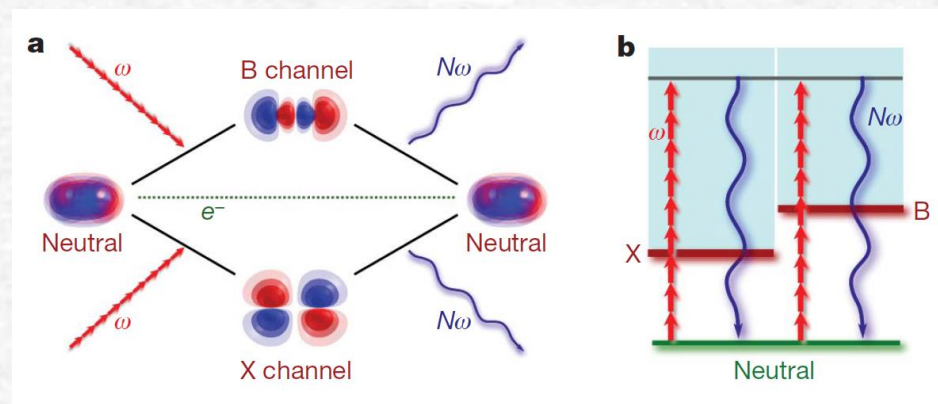
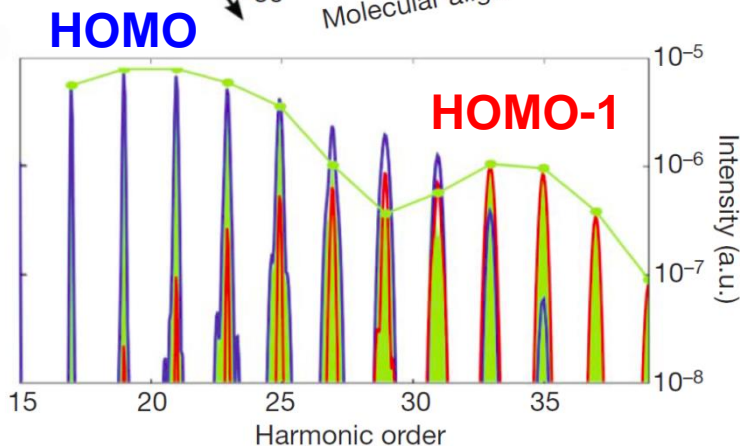
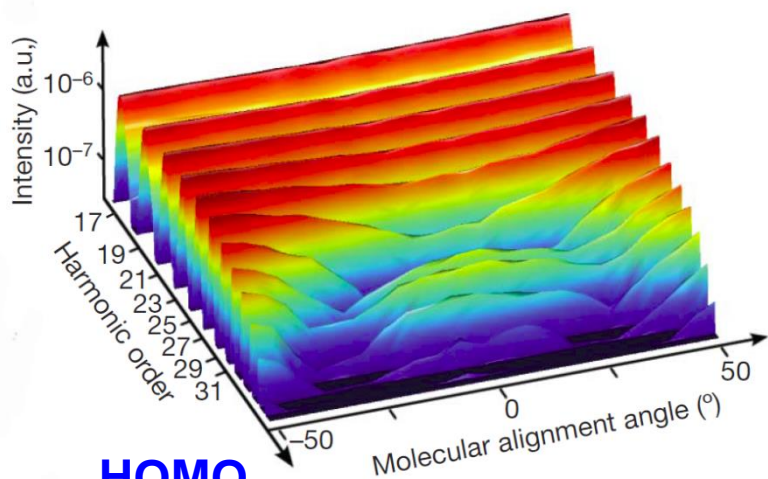
Kuleff & Cederbaum, Chem Phys 338, 320 (2007)

Questions I will try to address today

1. Can **charge migration** only be induced by attosecond pulses or are there other ways?
2. Can we use attosecond pulses to **probe time-dependent electron dynamics** in molecules?
3. Under which conditions does **correlation between a molecular ion and the ejected photoelectron** play a role?
4. Time permitting: **an alternative look at photoionization time delays**

Can we use strong-field ionization to induce charge migration?

Is the single active electron approximation valid in strong field ionization?

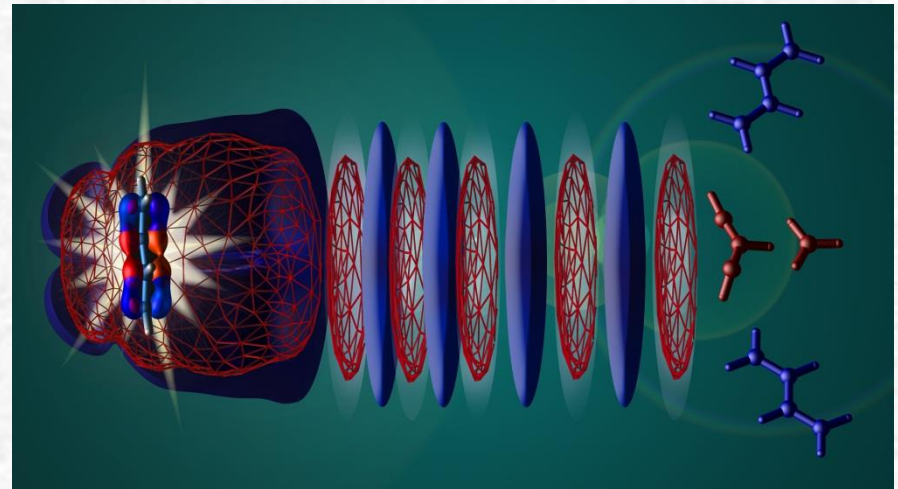


Can we use strong-field ionization to induce charge migration?

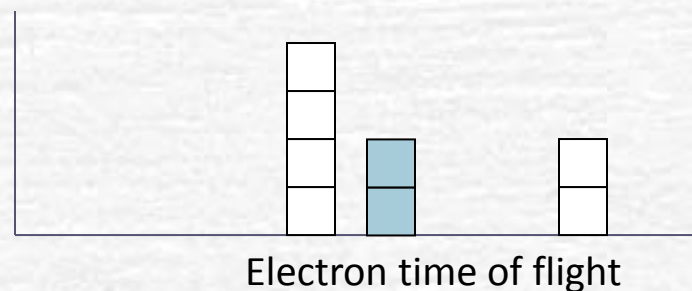
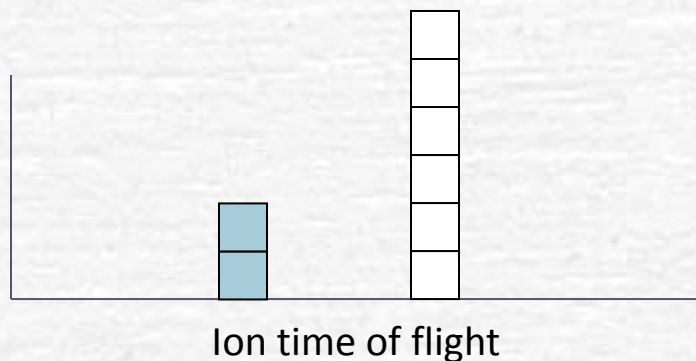
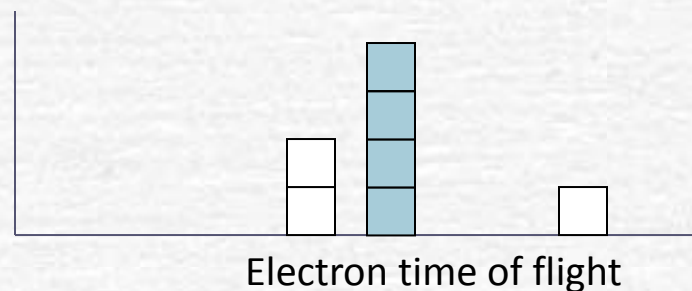
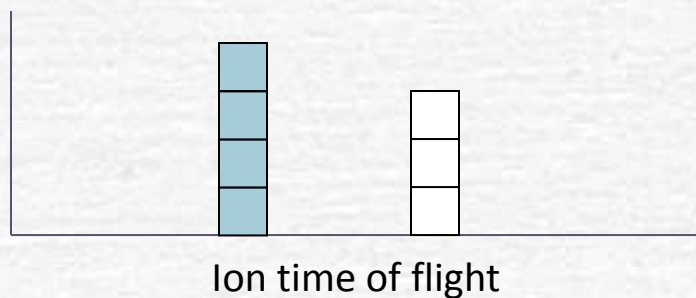
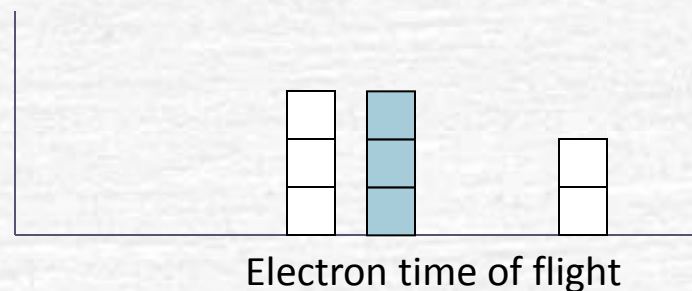
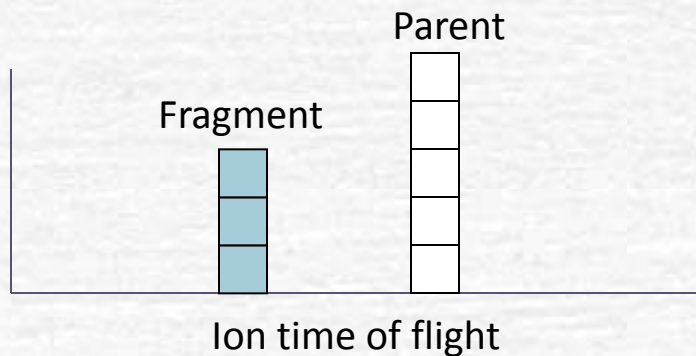
Is the single active electron approximation valid in strong field ionization?

- ❖ Look at the formation of fragment ions – hints at excited state formation, but **mechanism can also be sequential**
- ❖ Look at the formation of shifted ATI combs – hints at excited state formation, but **may also reflect Freeman resonances**
- ❖ Solution: look at the formation of fragment ions and shifted ATI combs **in coincidence or using covariance**

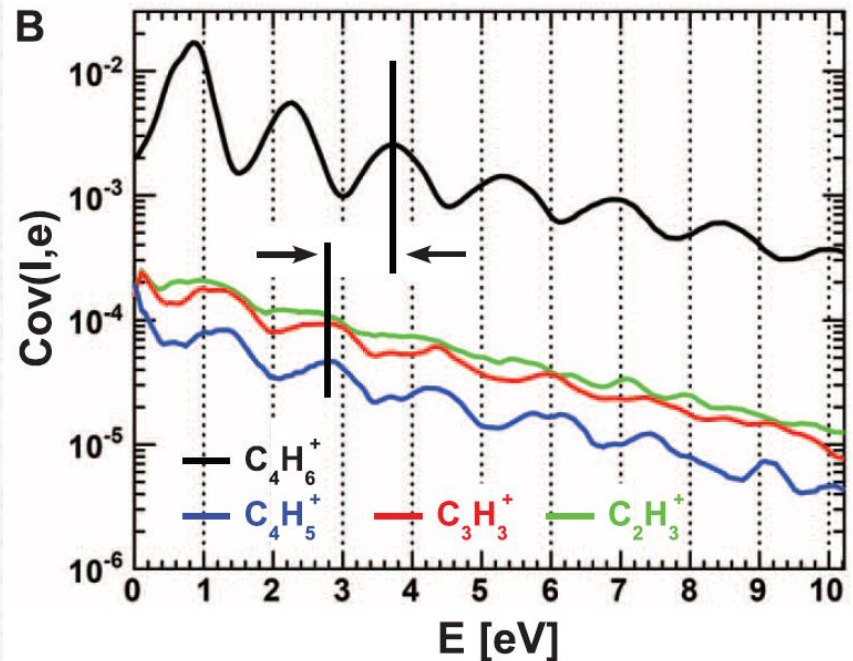
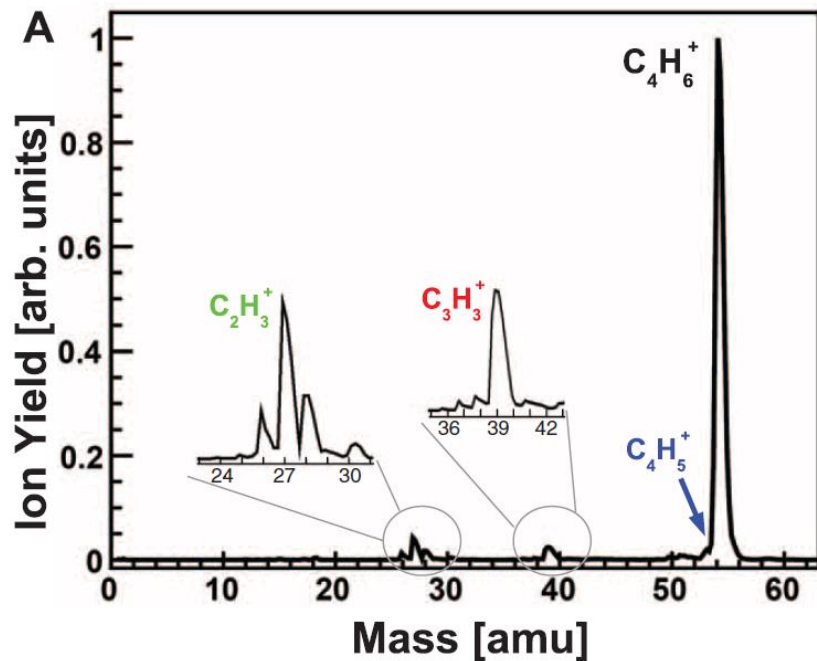
A.E. Boguslavskiy et al., *Science* 335, 1336 (2012)



Covariance detection of ATI spectra and parent/fragment ion yields



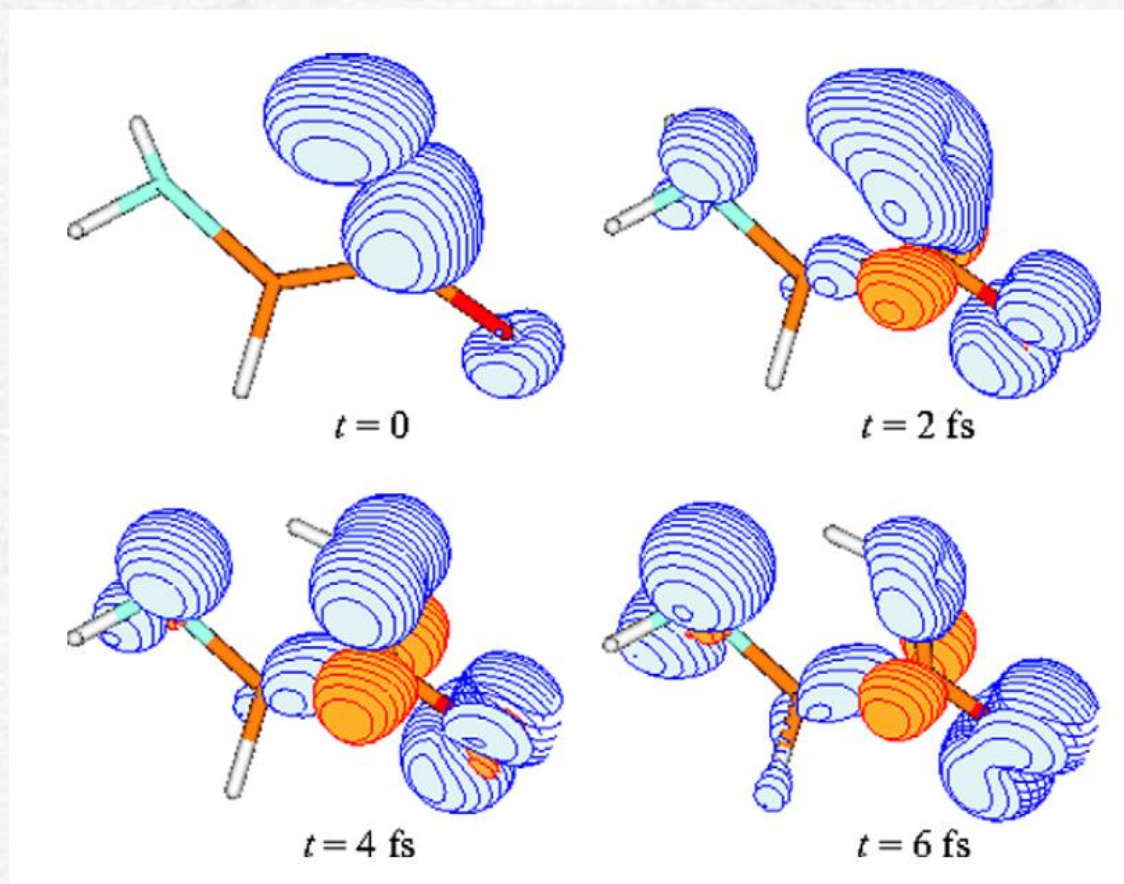
The breakdown of the single active electron approximation in strong field laser ionization



Direct evidence for the direct population of excited ionic states in strong-field ionization – multi-electron dynamics on attosecond timescale

Attosecond molecular electron dynamics

Charge migration upon sudden ionization (Glycine II):



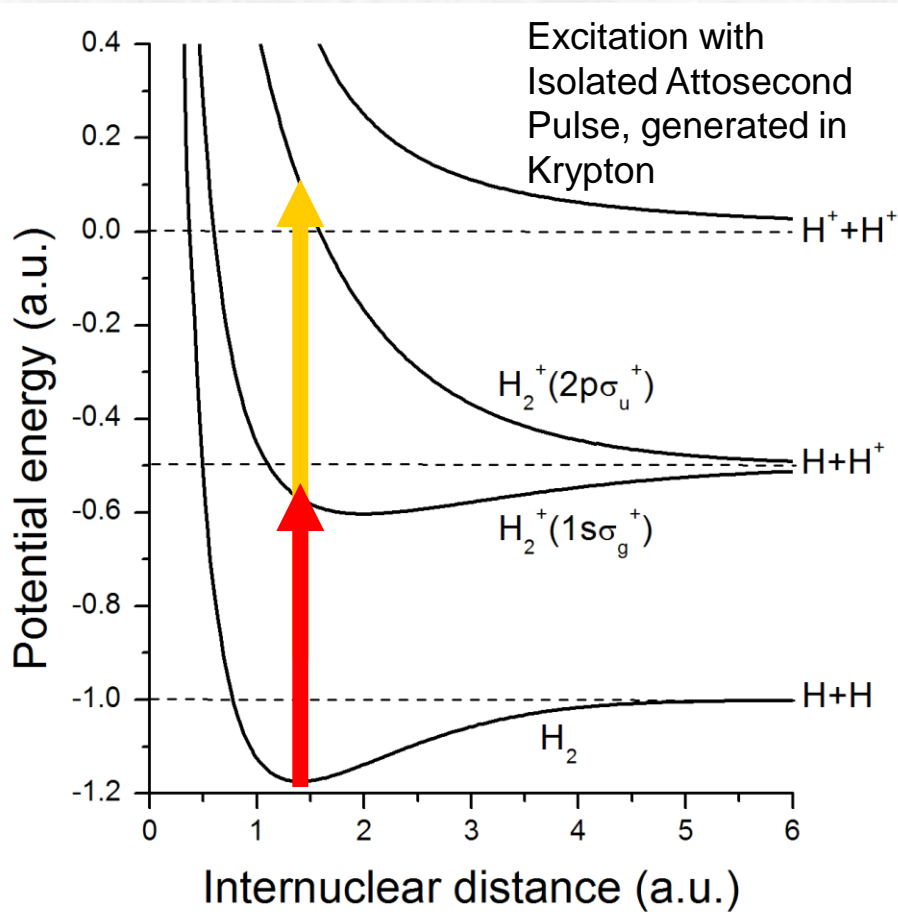
■ electron density
■ hole density

Possible observation
in IR pump-XUV
probe experiment

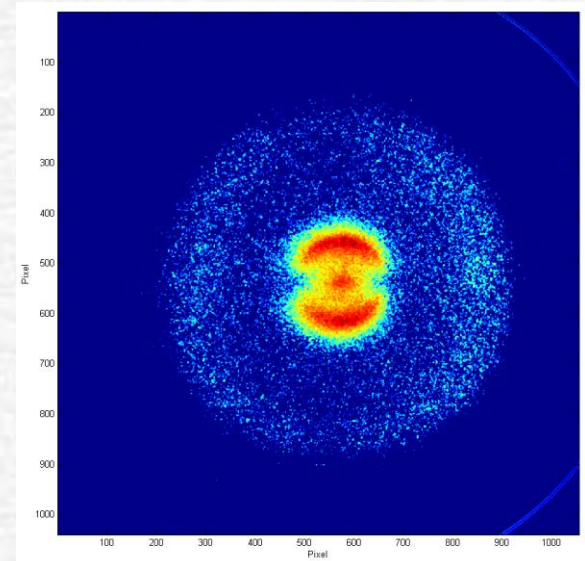
Coherent preparation of ionic states

Kuleff & Cederbaum, Chem Phys 338, 320 (2007)

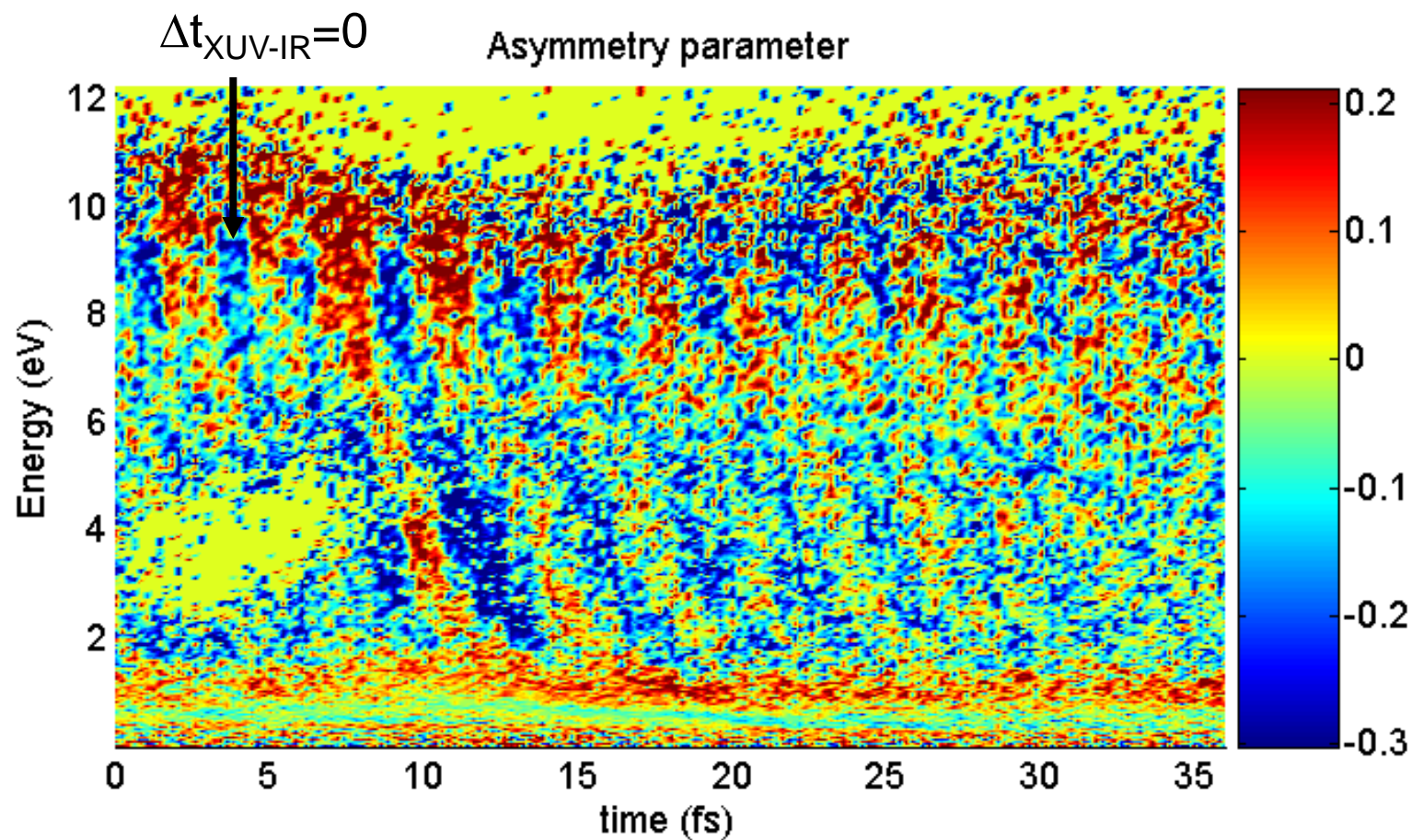
XUV-IR Pump-probe experiments on H_2 and D_2



Use isolated attosecond pulse generated in Krypton to launch a wavepacket on the $2p\sigma_u^+$ state or the $1s\sigma_g^+$ state and investigate the subsequent IR interaction



Electron localization in XUV-IR dissociative ionization of H₂ and D₂



Localized States of H_2^+

The $2p\sigma_u^+$ and $1s\sigma_g^+$ states can be viewed as bonding and anti-bonding combinations of $1s$ atomic orbitals

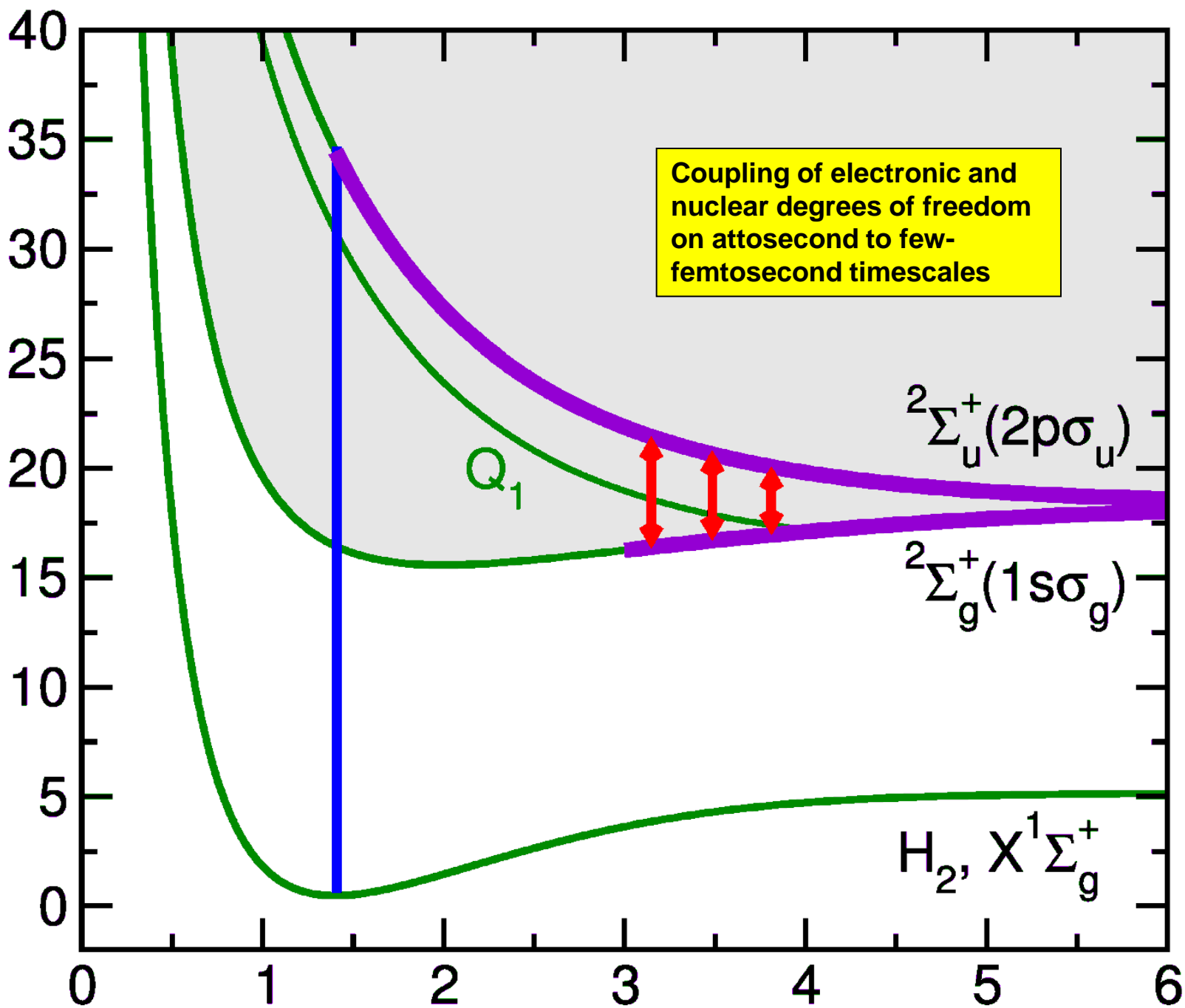
$$\begin{aligned}|g\rangle &= \frac{1}{\sqrt{2}} (|1s_{left}\rangle + |1s_{right}\rangle) \\ |u\rangle &= \frac{1}{\sqrt{2}} (|1s_{left}\rangle - |1s_{right}\rangle)\end{aligned}$$

Therefore, the nuclear wave function can also be expressed on a basis of localized states

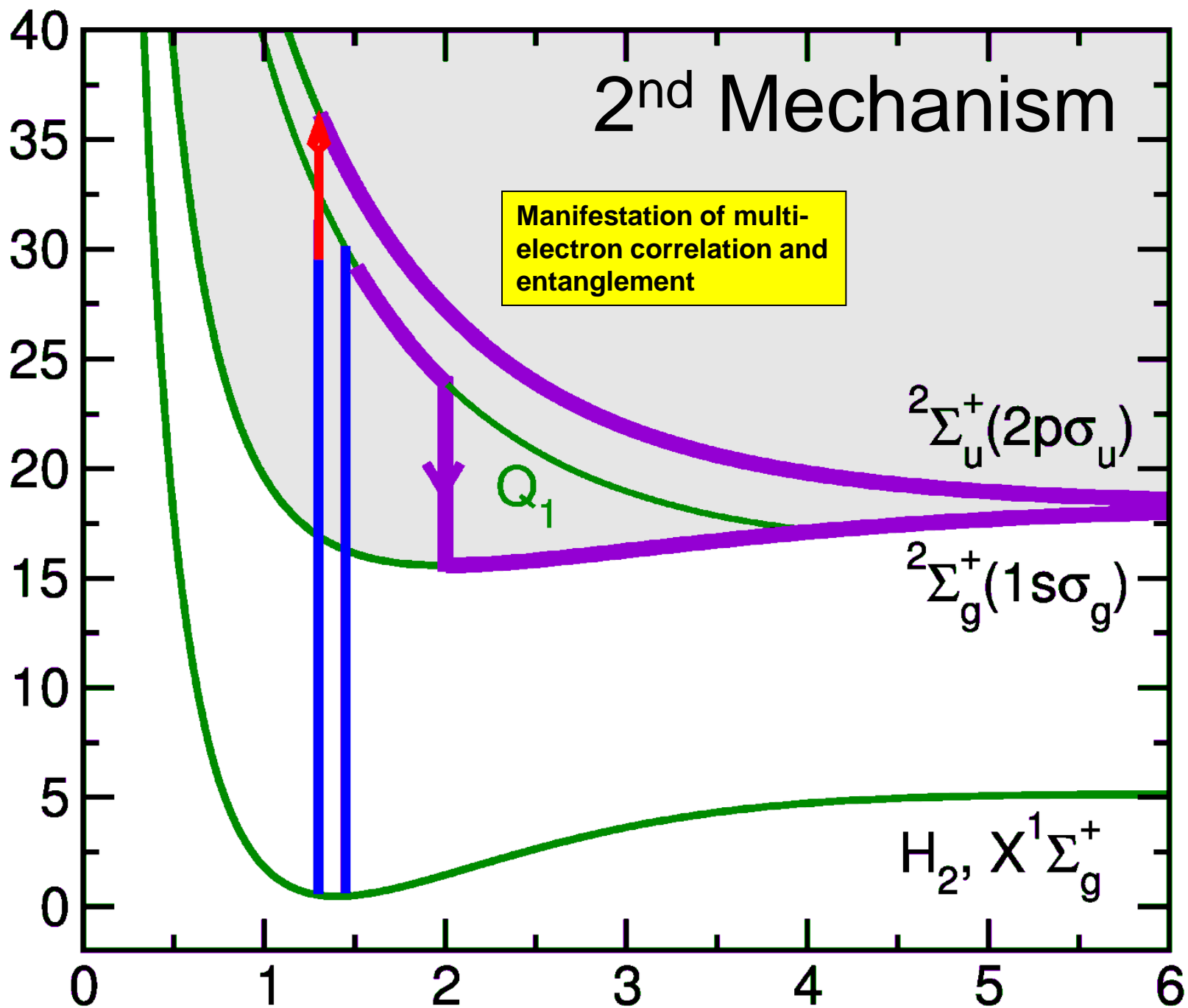
$$\begin{aligned}|l\rangle &= \frac{1}{\sqrt{2}} (|g\rangle + |u\rangle) \\ |r\rangle &= \frac{1}{\sqrt{2}} (|g\rangle - |u\rangle)\end{aligned}$$

By projecting onto these states the fraction of the wave function that is on the left or right side of the molecule can be determined

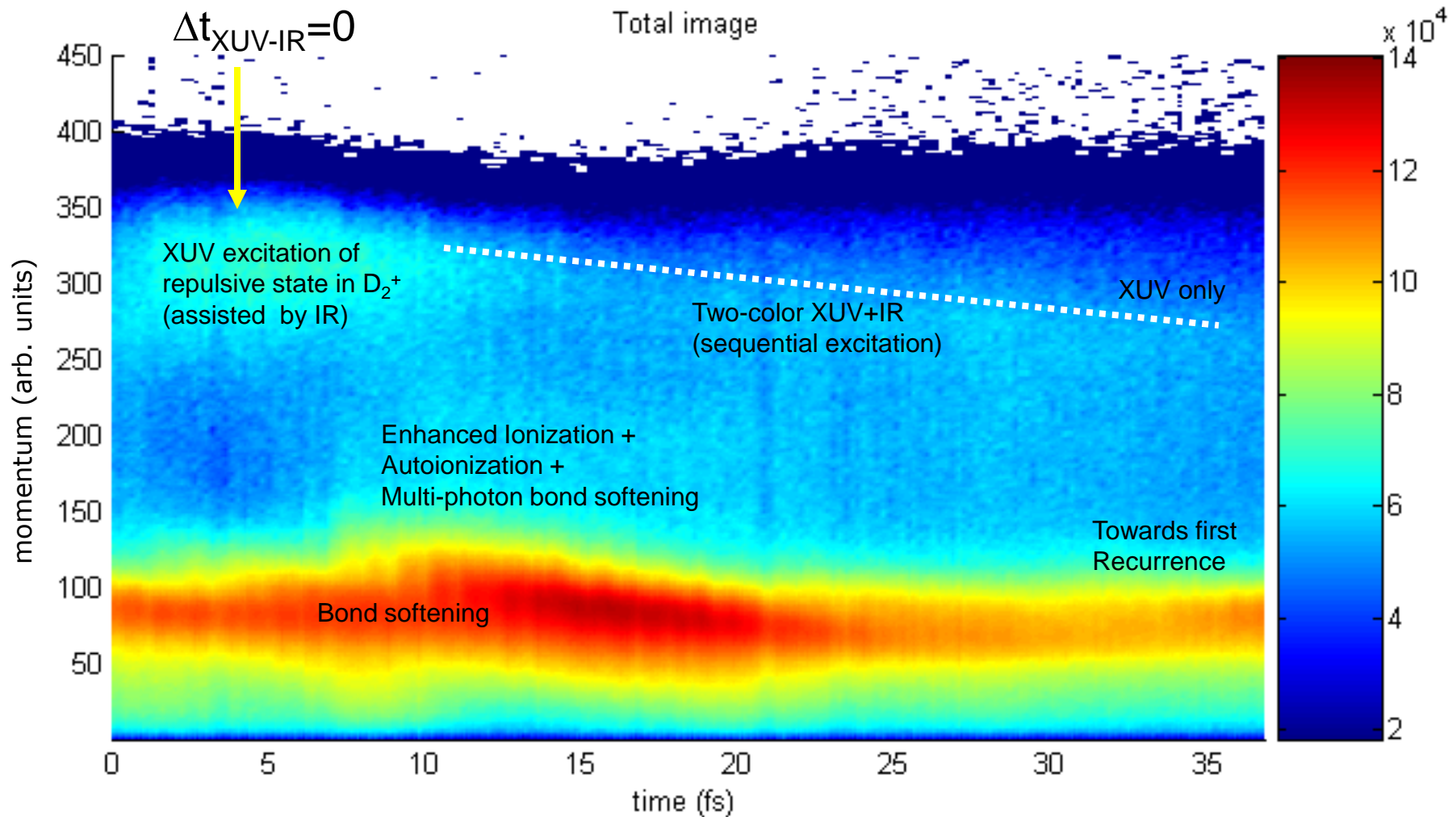
Energy (eV)



Energy (eV)

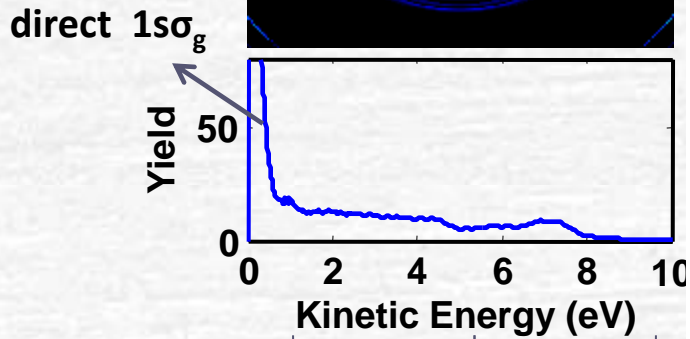
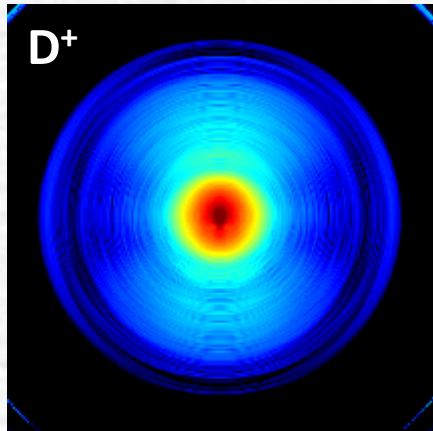


Can we use attosecond pulses for probing of ultrafast electron dynamics?



IR-XUV Pump-probe experiments H_2/D_2

APT only

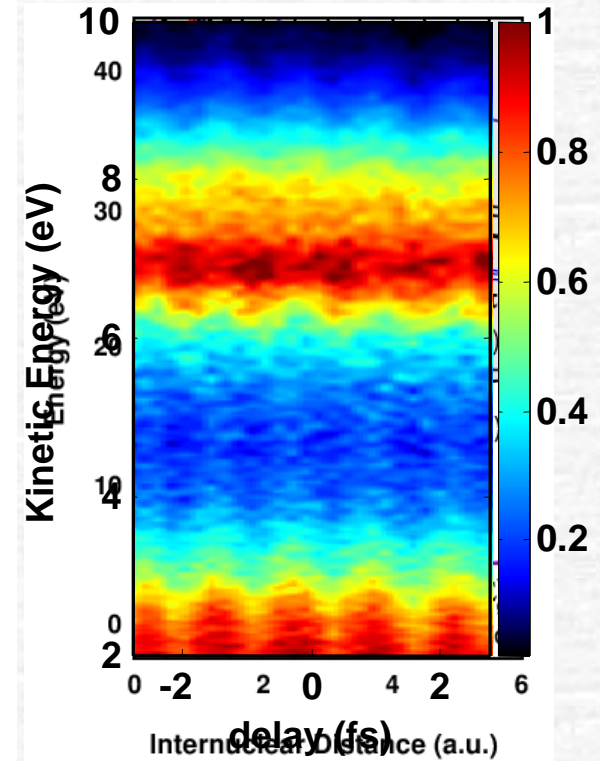


autoionization

autoionization & direct $2p\sigma_u$

Two arrows point from the x-axis labels to the plot. One arrow points to the region from 0 to 2 eV, labeled "autoionization". Another arrow points to the region from 2 to 10 eV, labeled "autoionization & direct $2p\sigma_u$ ".

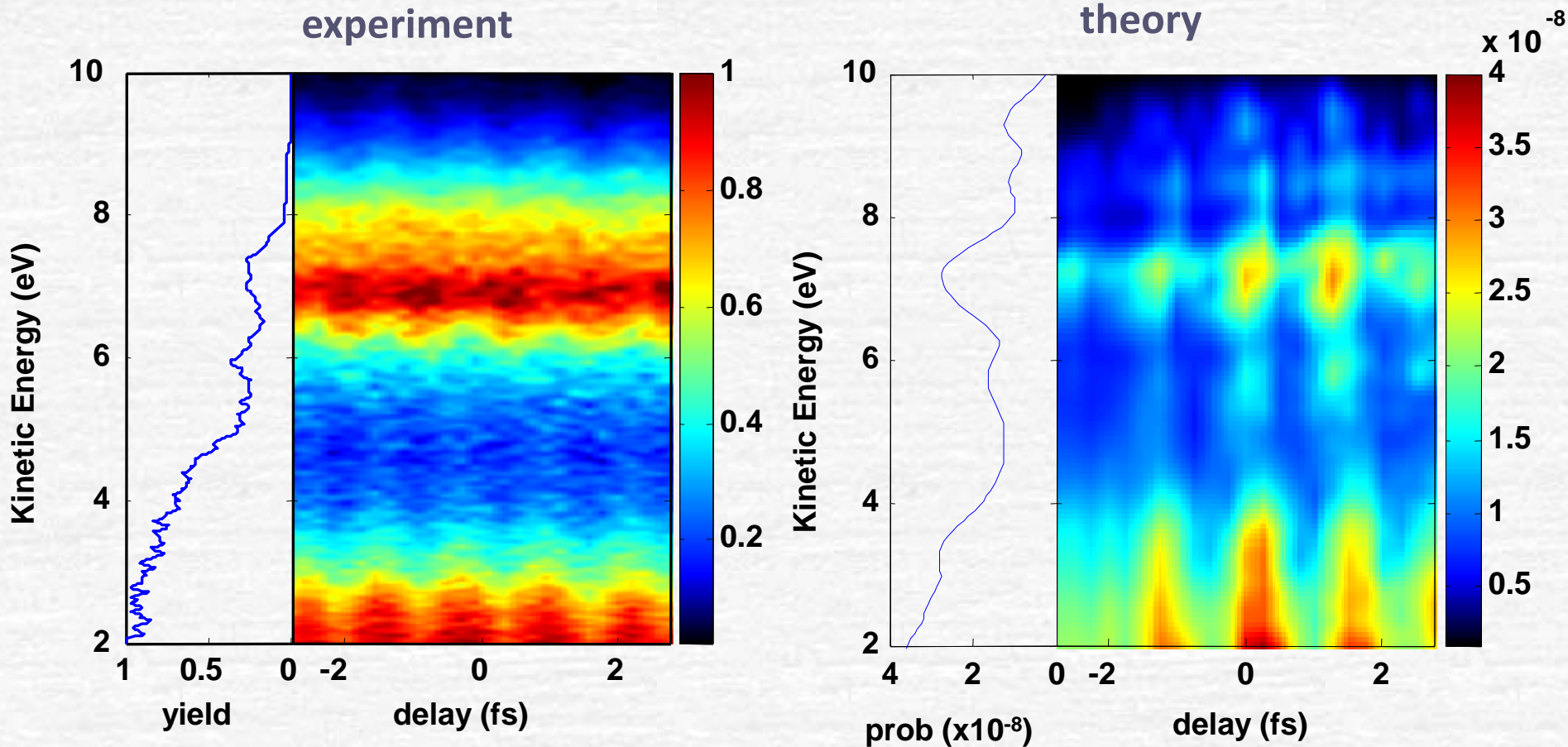
Bond Softening



focus of this work

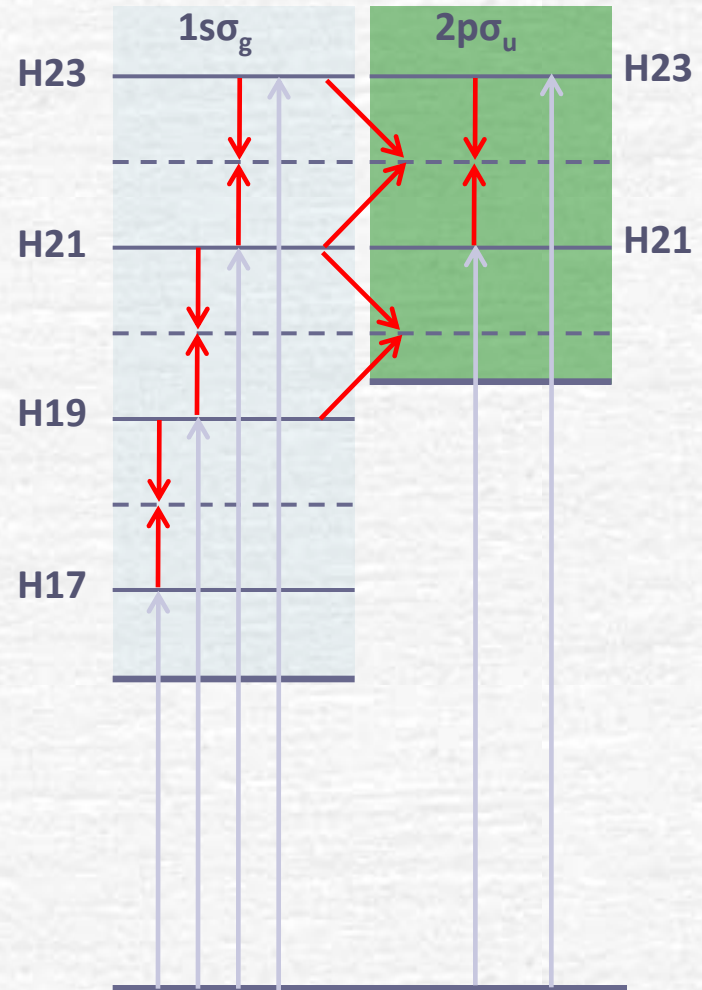
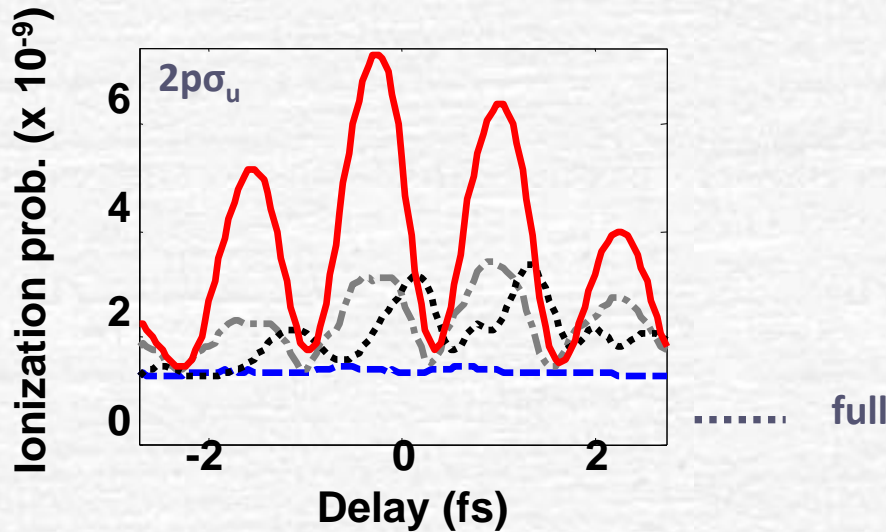
An arrow points from the text "focus of this work" to the heatmap, indicating the region of interest in the experiment.

Theory and experiment agree well



→ What is the role of electron dynamics in the experiment?

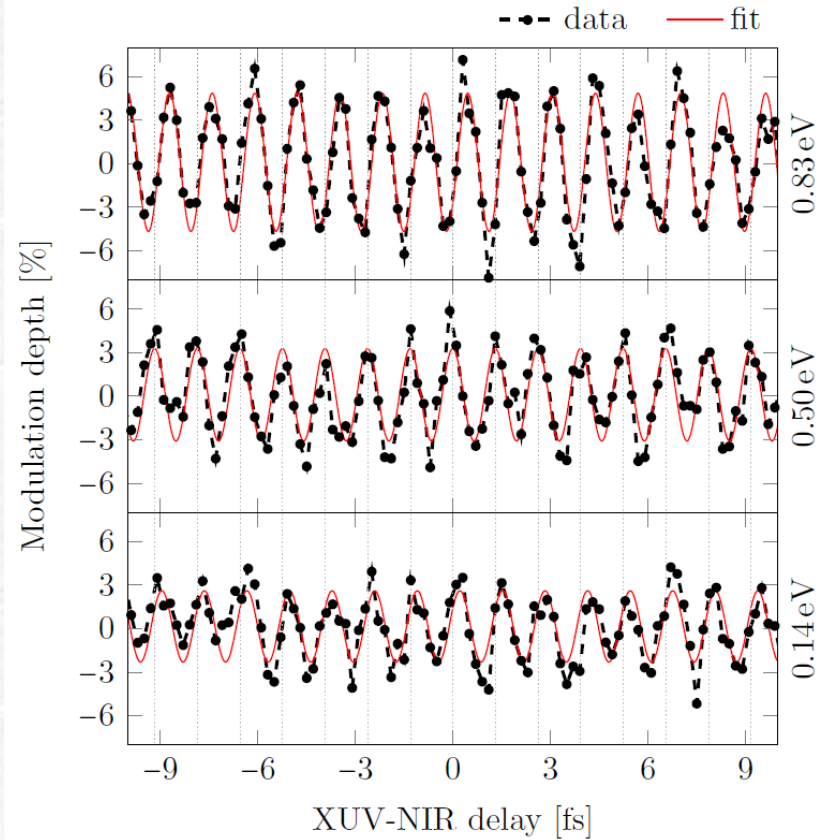
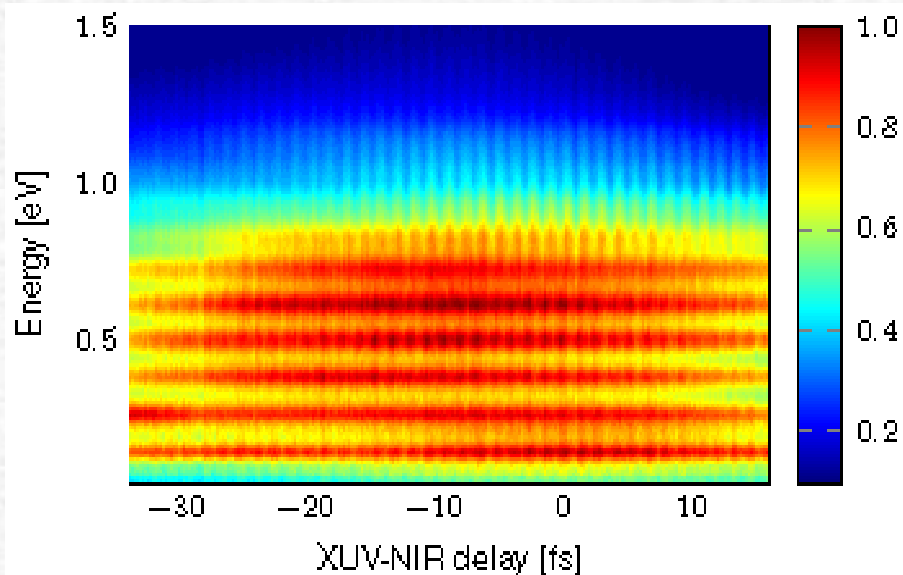
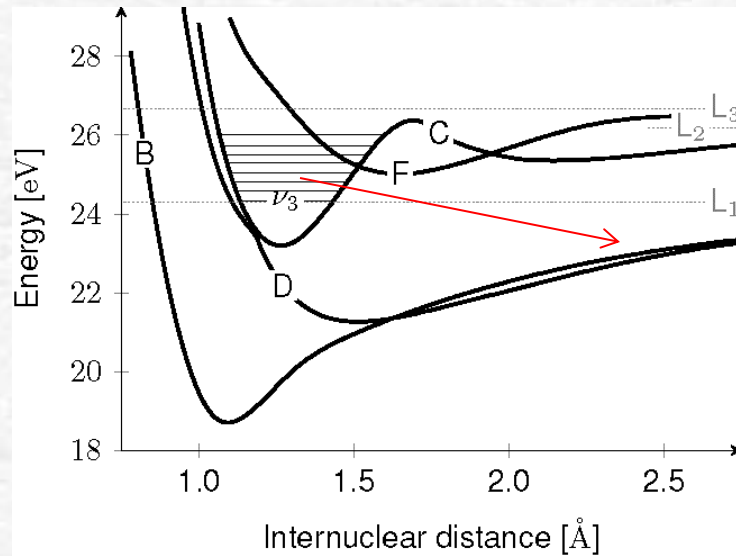
Simple Fixed Nuclei Approximation model



→ 1σ_g-2pσ_u coupling leads to IR induced polarization of the molecules
→ attosecond ionization is sensitive to this charge dynamics

→ No role of attosecond electron dynamics in the neutral molecule

IR-XUV Pump-probe experiments N_2



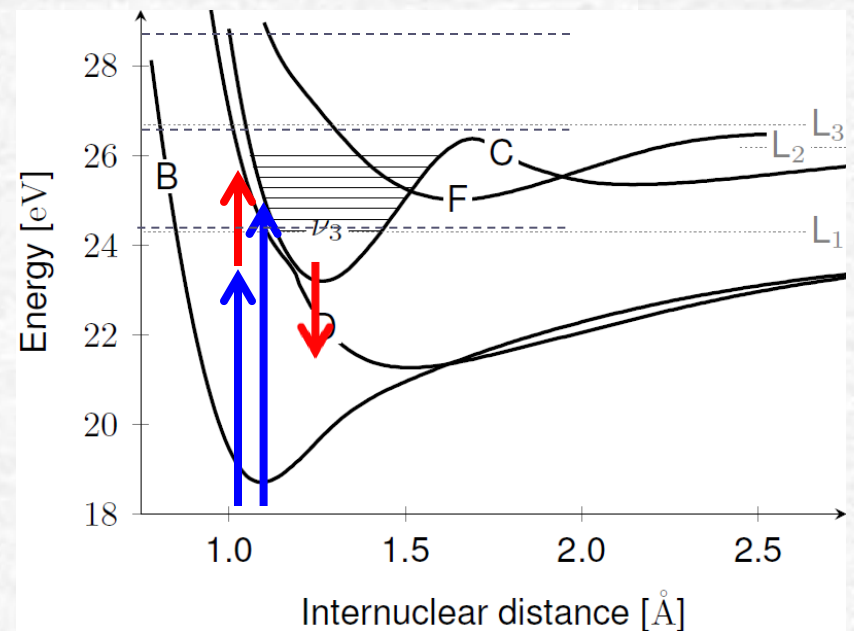
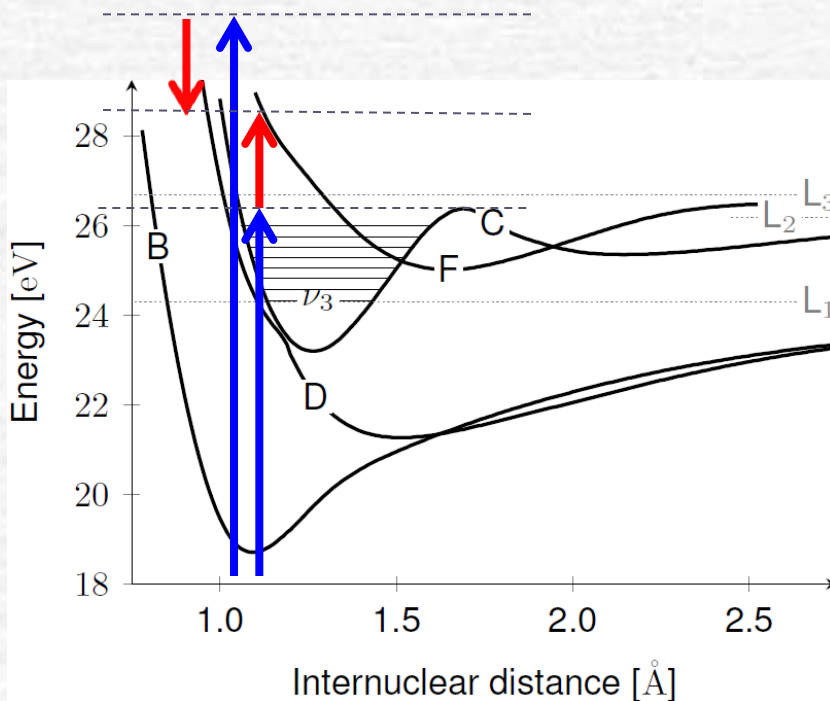
- Phase shifts cannot be explained by RABBITT-like mechanism (H_2)
- Largest contrast in fringes away from optimal time overlap

IR-XUV Pump-probe experiments N₂

Tentative explanation: Two mechanisms causing the XUV-IR time dependence:

1) RABBITT-like mechanism :
interference of XUV+IR and XUV-IR
ionization in the production of specific
final vibrational states of the C-state

2) Interference between direct and
delayed production of population on D-
state – made possible by ca. 30 fs long
IR pulse → attosecond control of
femtosecond timescale dynamics



IR-XUV Pump-probe experiments N_2

Mechanism 2: the observed interferences are affected both by N_2^+ **vibrational dynamics** and by the **initial coherence** between the C- and D-state resulting from the ionization by the attosecond pulse

$$|\Psi(t)\rangle = \sum_i |i\rangle |\chi_i(t)\rangle |\phi_i(t)\rangle$$

Electronic state
Photoelectron wavepacket

Vibrational wavepacket

Important: The measurement basis is generally different from the initial molecular basis where the photo-excitation occurs → enables interferences

$$|\Psi(t)\rangle = |n\rangle |\chi(t)\rangle |\phi(t)\rangle$$

Electronic state
(often not measured)
Photoelectron wavepacket
(often not measured)

Continuum momentum wavepacket

IR-XUV Pump-probe experiments N₂

$$W_n(\chi) = \int d\phi |\langle n | \langle \phi | \langle \chi | \Psi \rangle|^2 =$$

$$= \sum_i |\langle i | n \rangle|^2 |\langle \chi_i(t) | \chi \rangle|^2 +$$

$$+ \sum_{i \neq j} \langle j | n \rangle \langle n | i \rangle \times \langle \chi_j(t) | \chi \rangle \langle \chi | \chi_i(t) \rangle \times \langle \phi_j(t) | \phi_i(t) \rangle$$

Measurement: momentum-resolved N⁺ measurement without measuring N⁺ electronic state or photoelectron properties

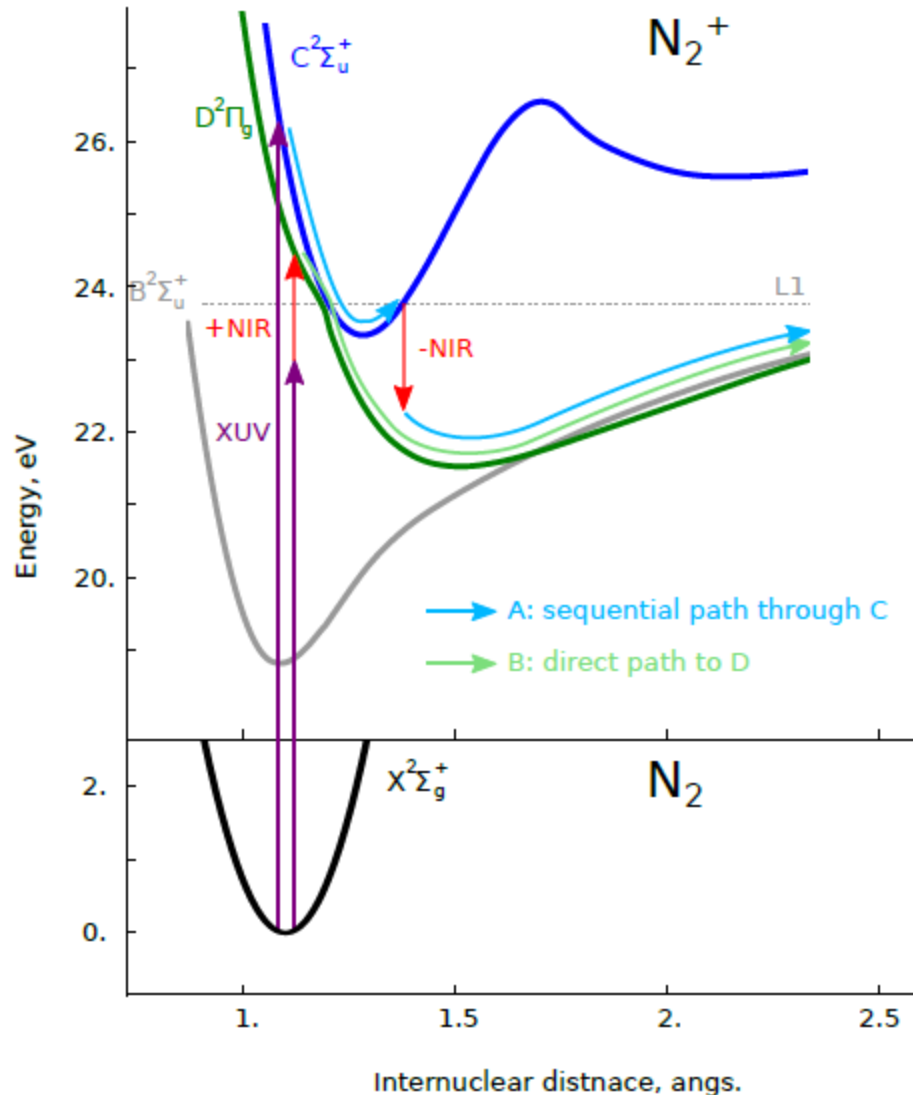
Interference term

Vibrational propagation

Overlap of accompanying photoelectron wavepackets

Mechanism 2: the observed interferences are affected both by N₂⁺ vibrational dynamics and by the initial coherence between the C- and D-state resulting from the ionization by the attosecond pulse

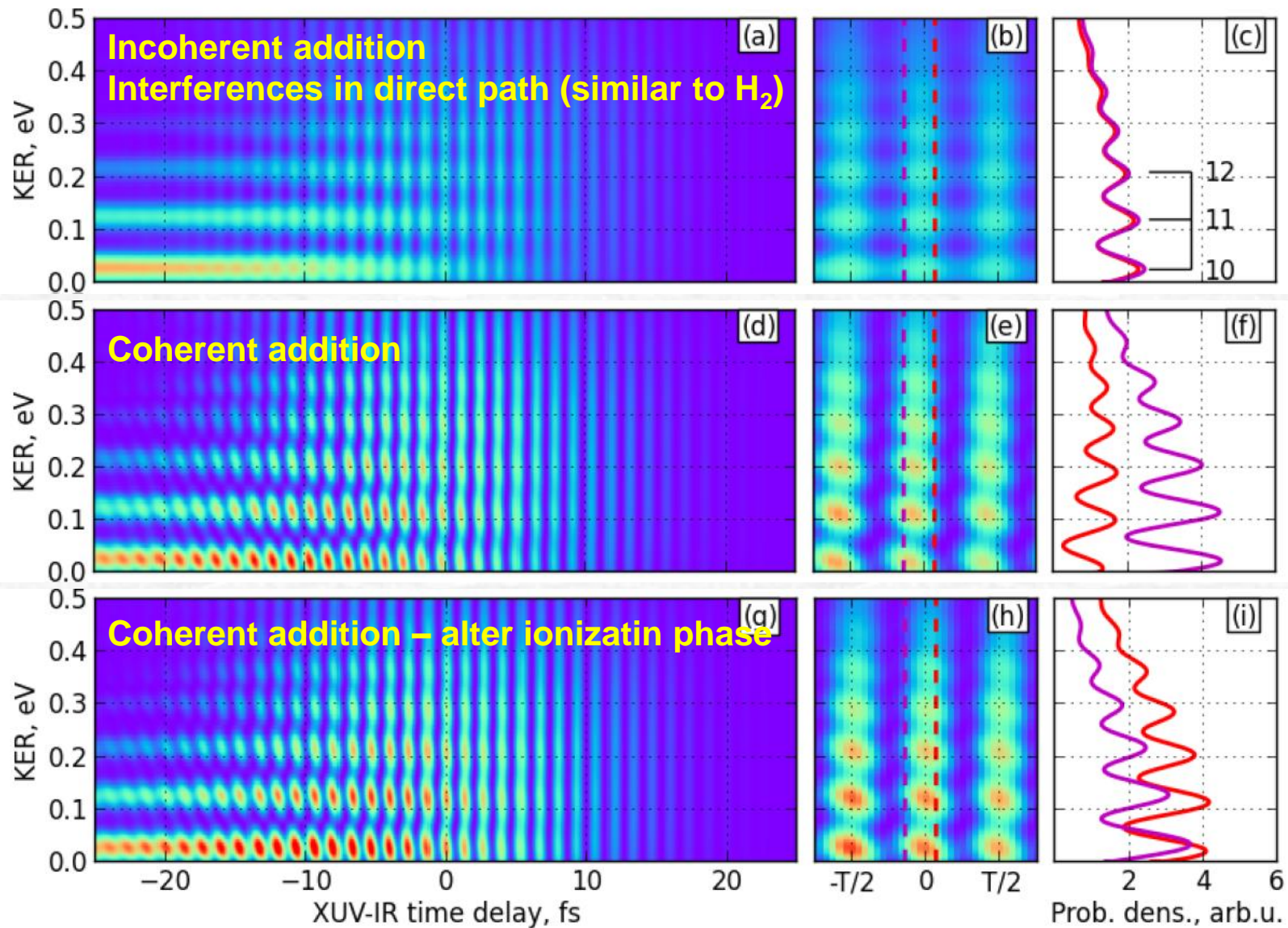
IR-XUV Pump-probe experiments N_2



Calculation: consider 2-color dissociative ionization of N_2 by an attosecond pulse and a co-propagating IR pulse

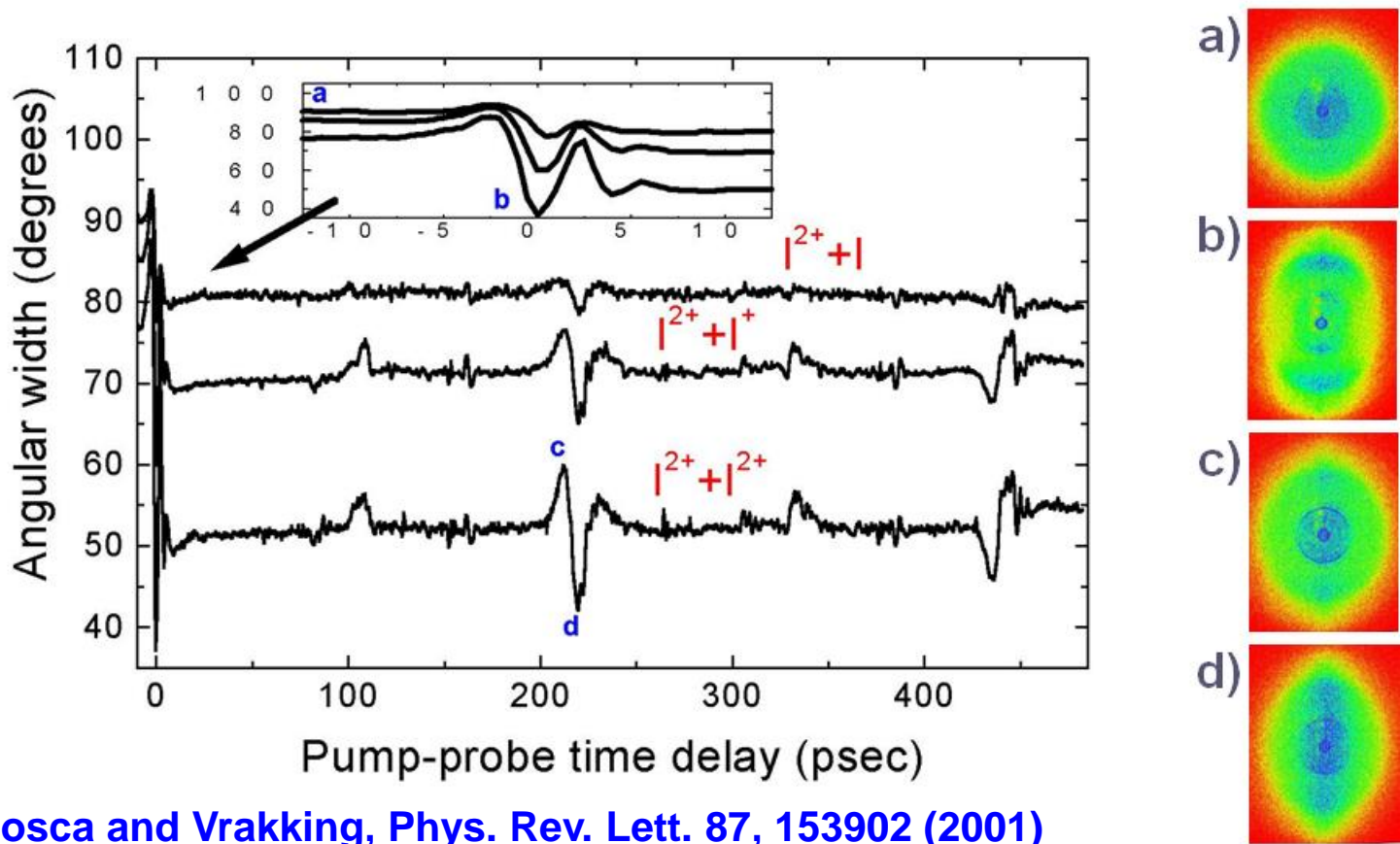
Pathway 1: direct two-color population of D-state (B-state acts as intermediate)

Pathway 2: XUV-induced population of C-state followed by de-excitation to D-state by IR probe



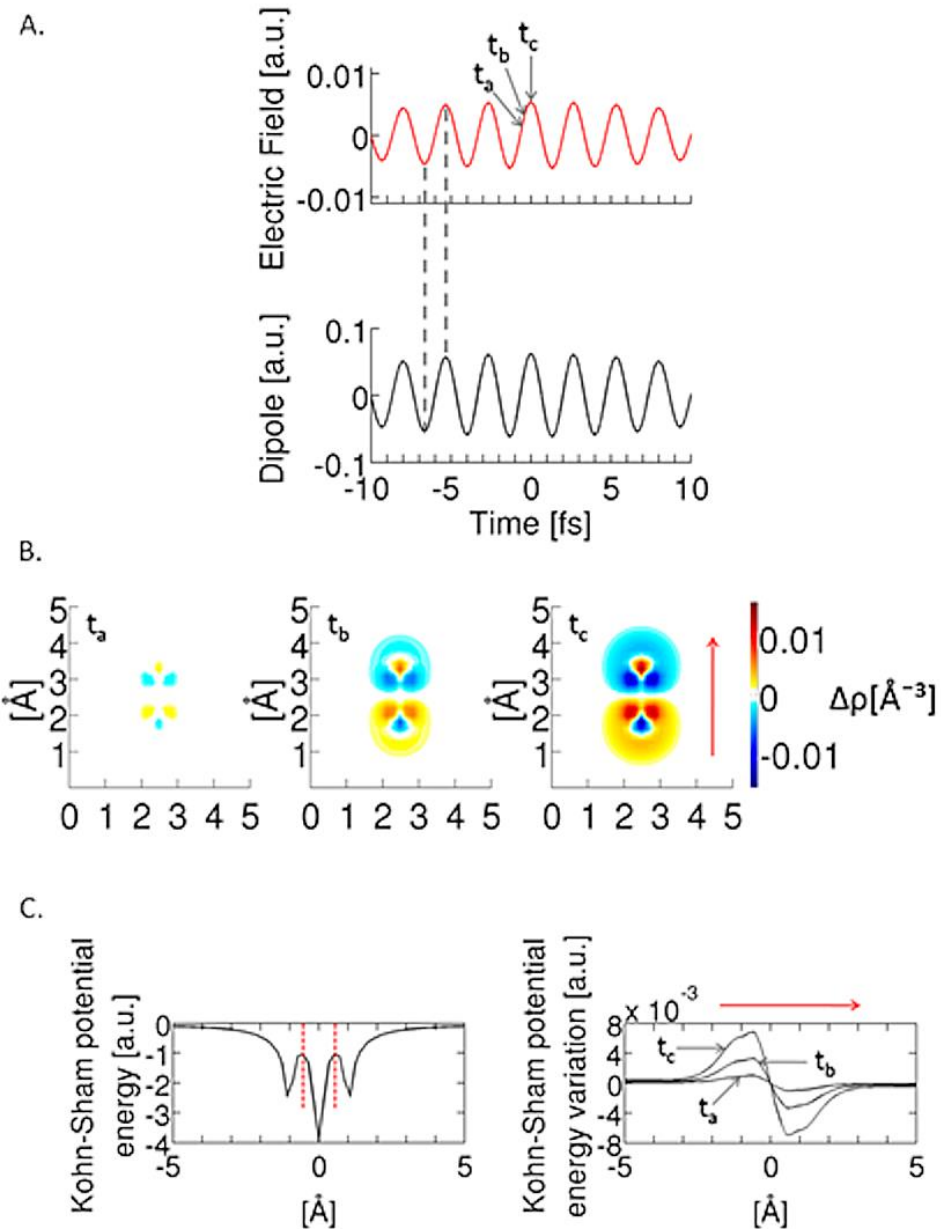
Can we use attosecond pulses for probing of ultrafast electron dynamics?

Can we use attosecond pulse to measure the polarization that is induced in a molecule by an IR field?

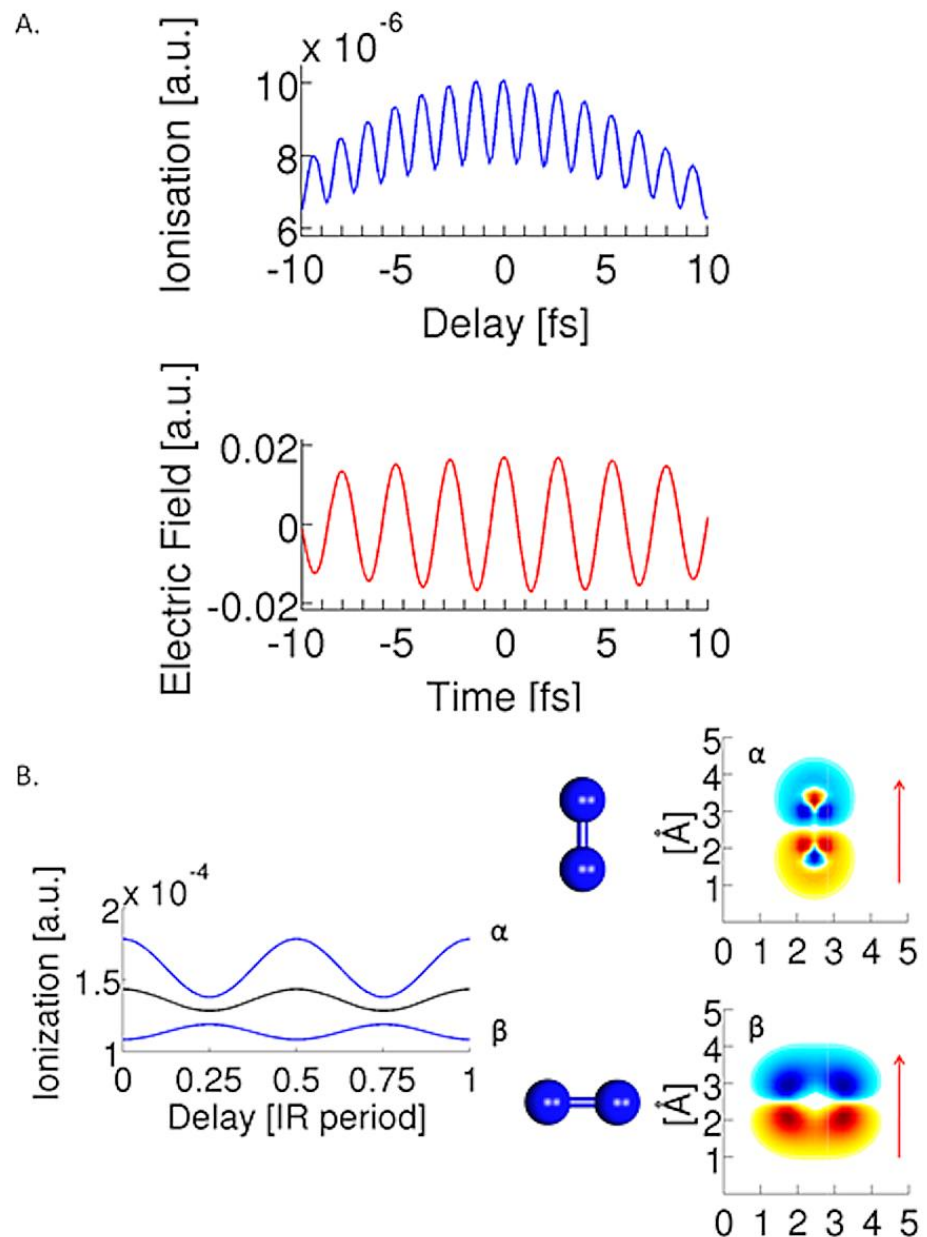


Rosca and Vrakking, *Phys. Rev. Lett.* 87, 153902 (2001)

Calculate induced dipole in N_2 under the influence of a moderately strong IR field (F. Lépine)



Calculate the impact of this induced dipole on the time dependence of XUV ionization (F. Lépine)

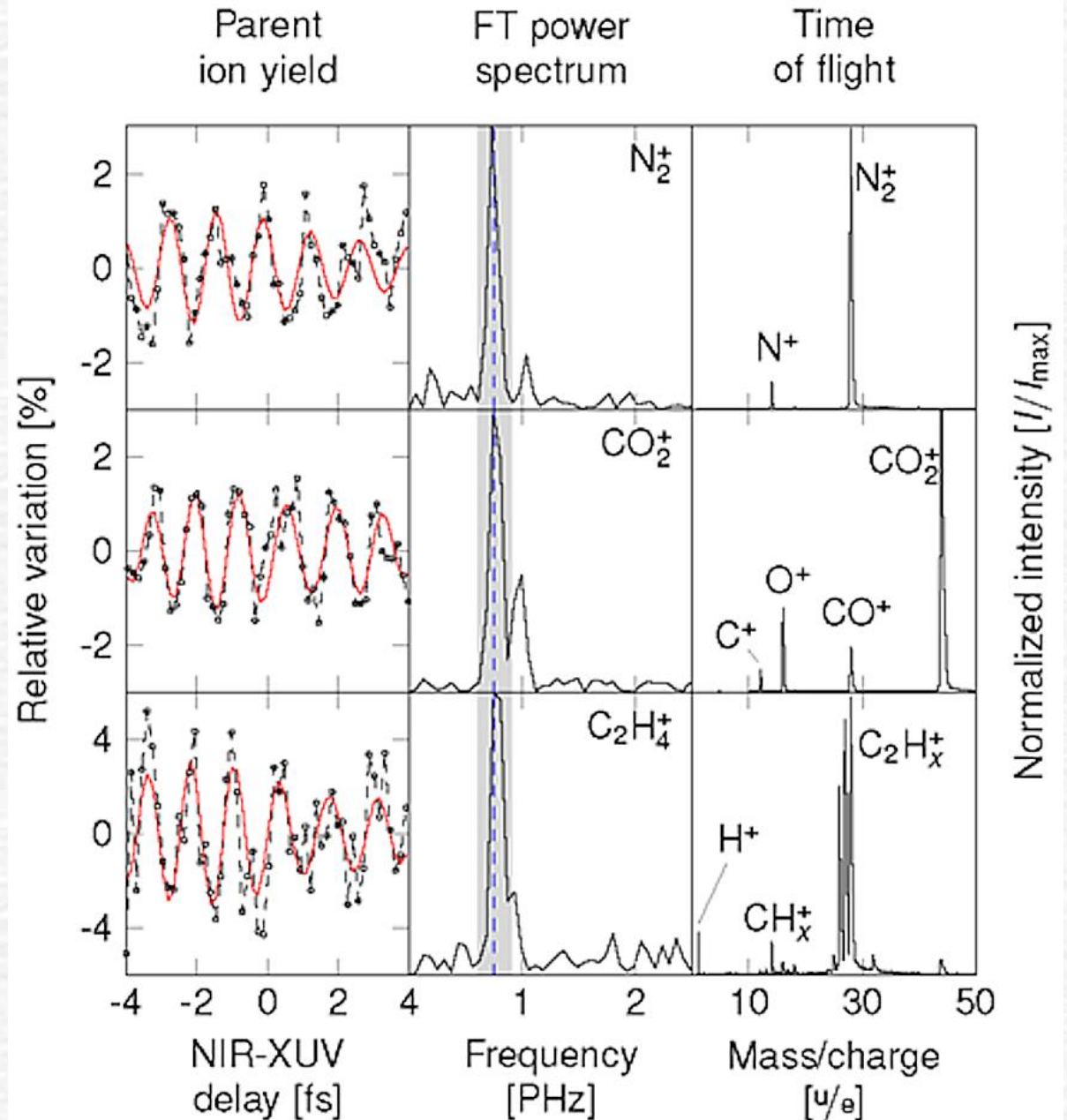


Observation of electron dynamics in neutral N_2 , CO_2 and C_2H_4 molecules

C. Neidel et al.,
Physical Review Letters 111,
033001 (2013).

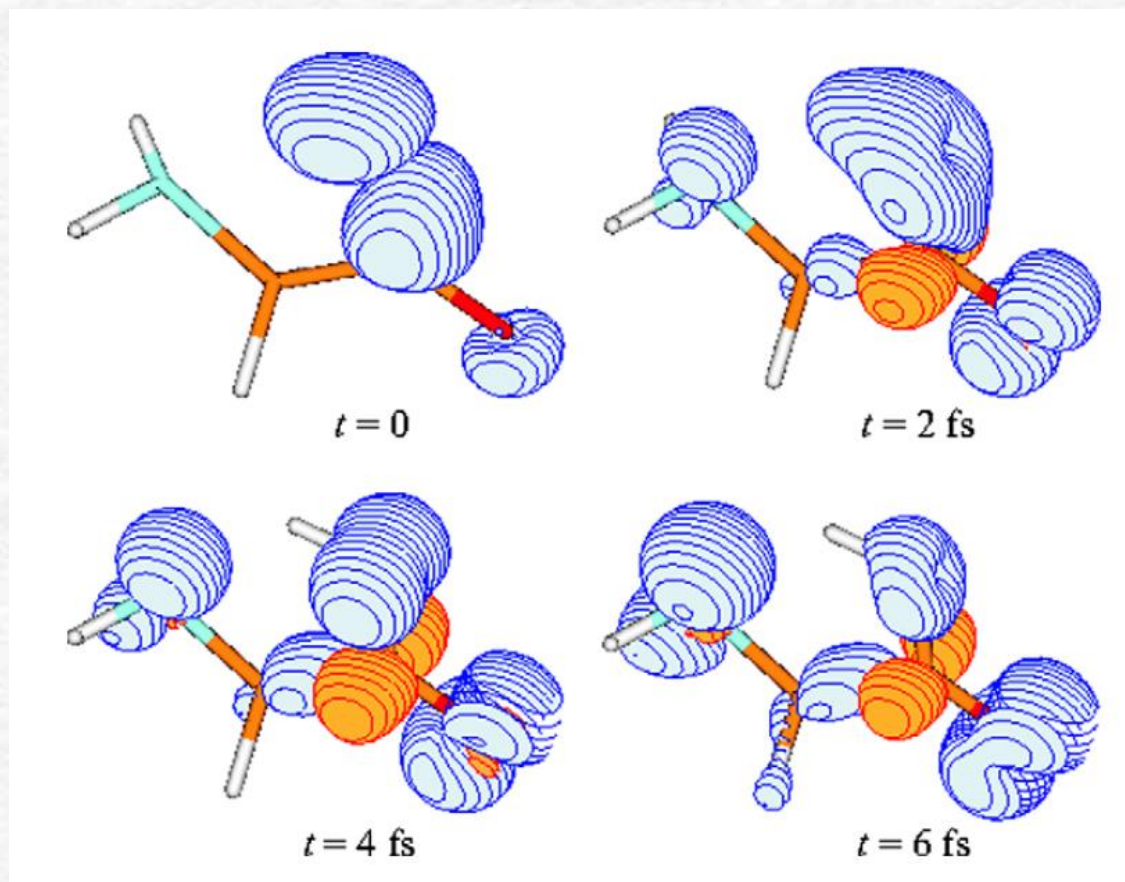


Max-Born-Institut



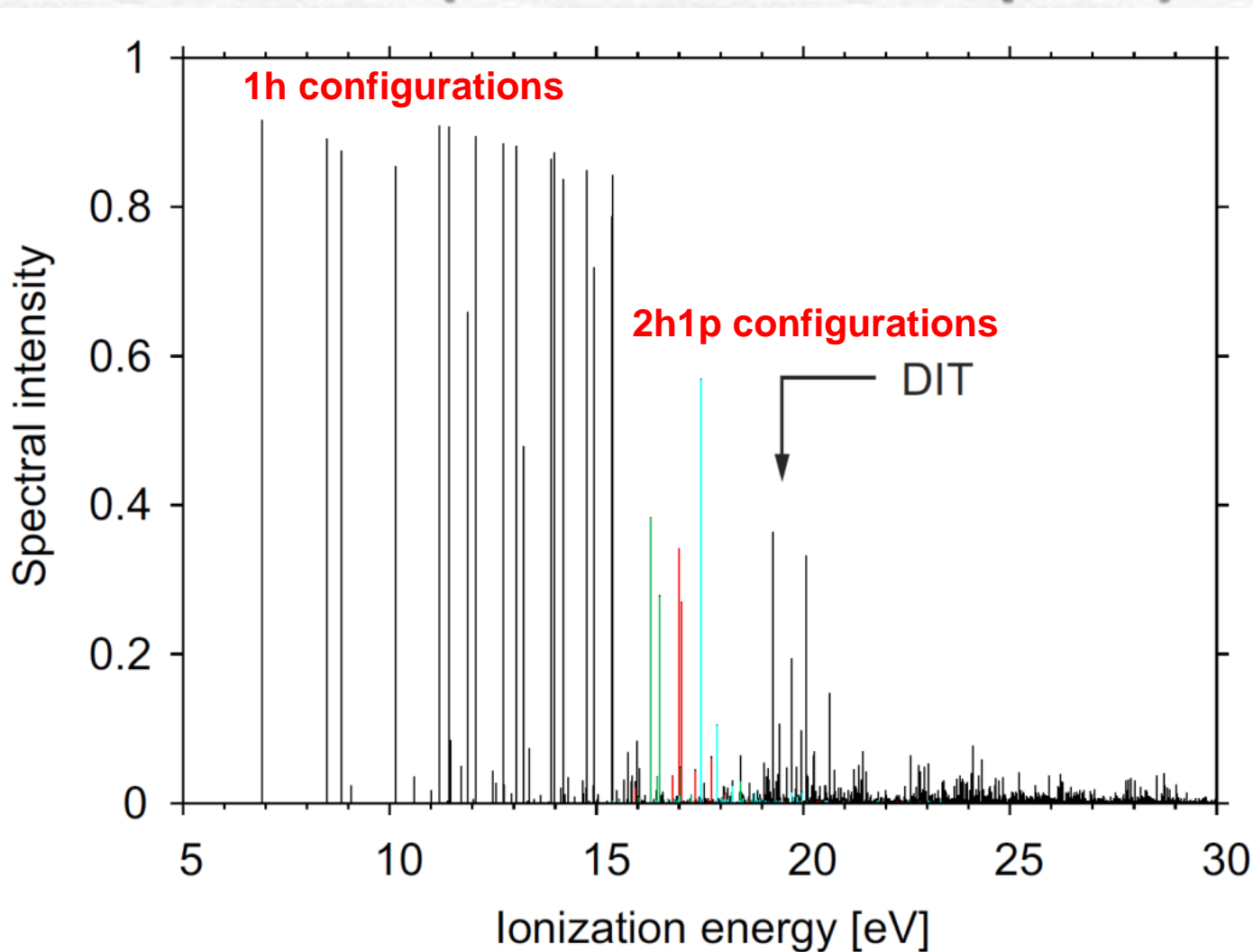
Use of attosecond pulses in pump-probe spectroscopy

Charge migration upon sudden ionization (Glycine II):



 electron density
 hole density

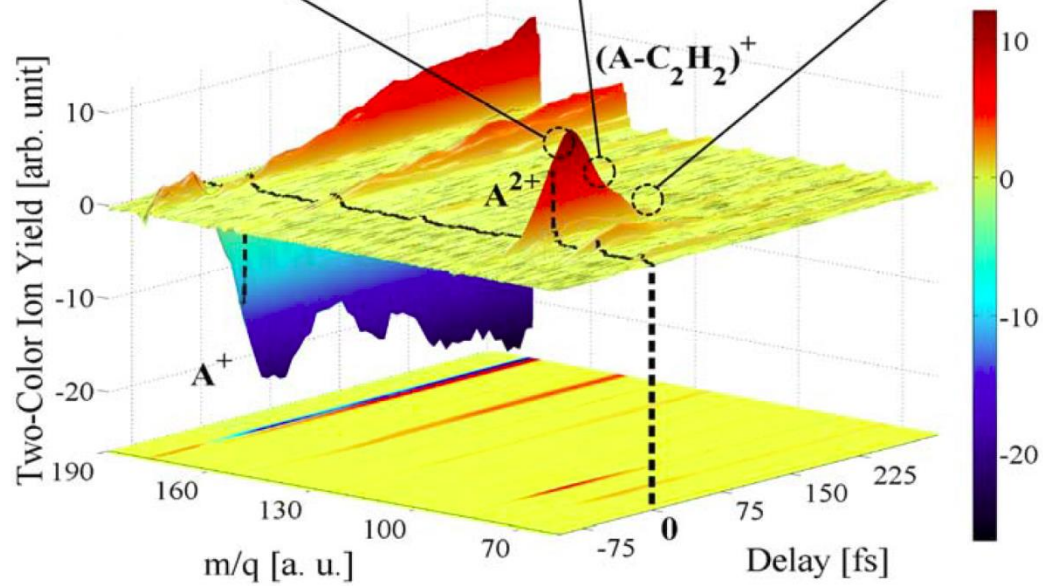
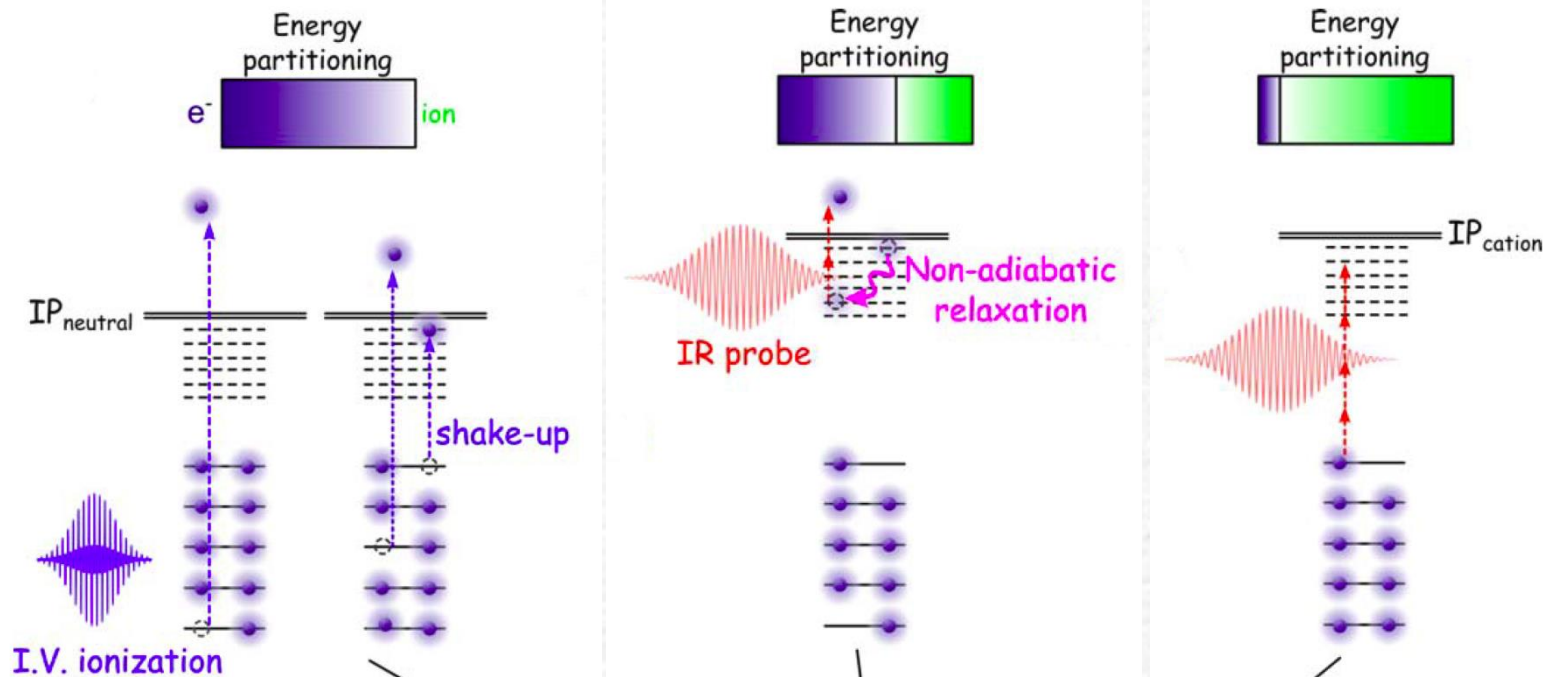
Experiments on Polycyclic Aromatic Hydrocarbons (with Franck Lépine)

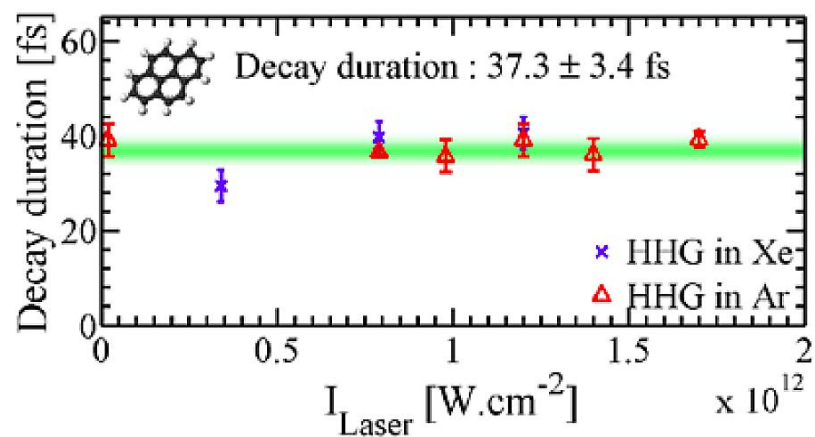
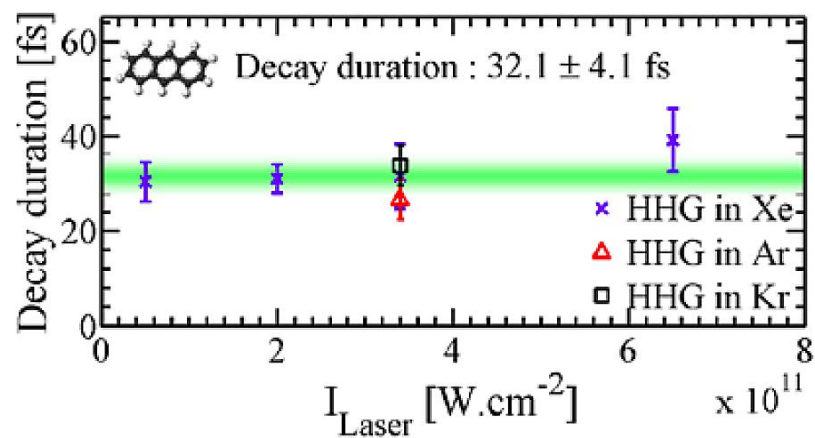
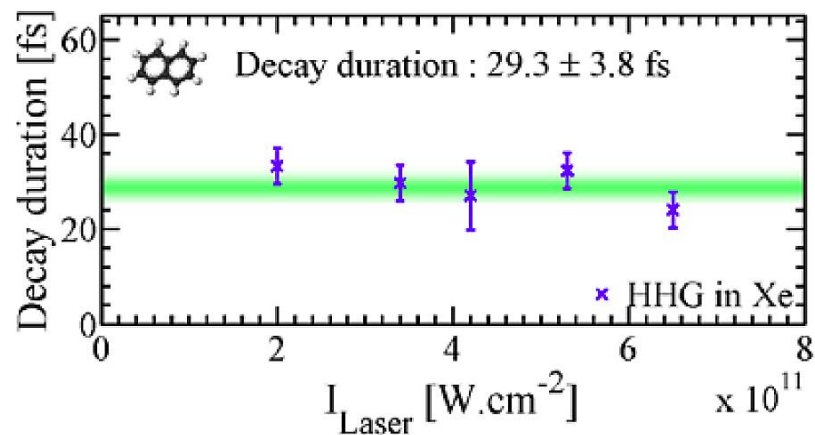
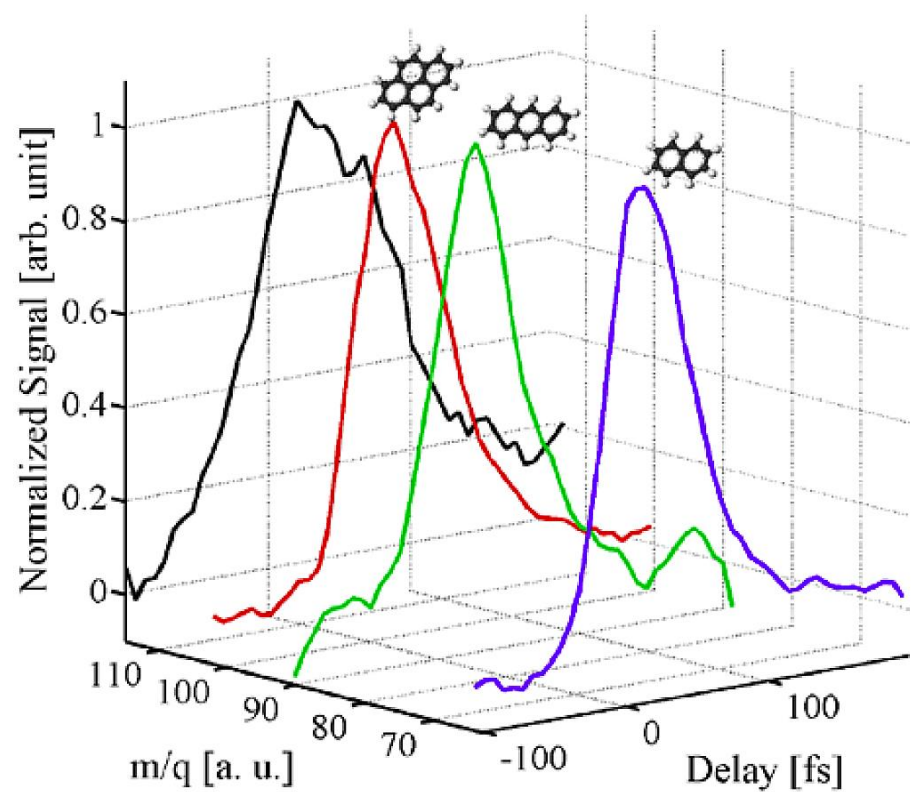
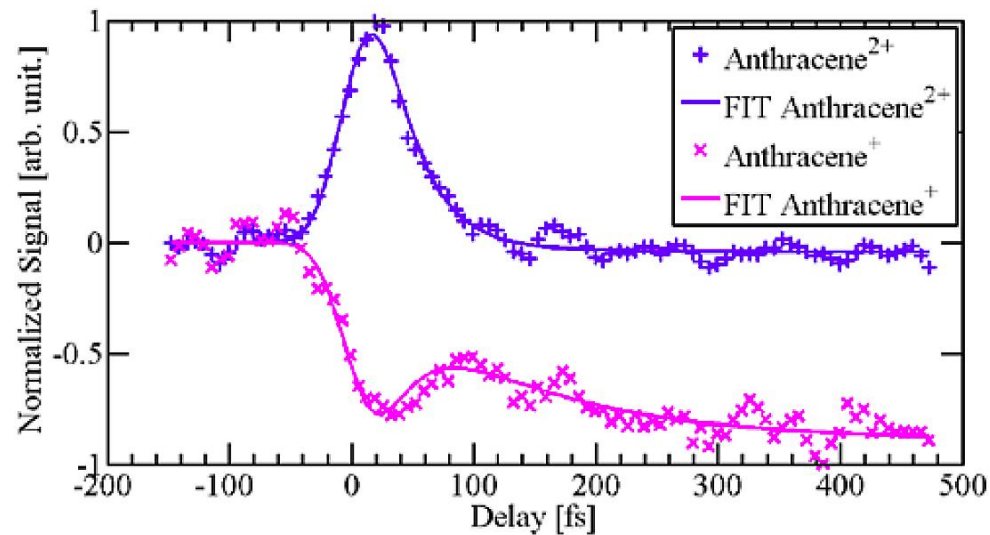


Anthracene

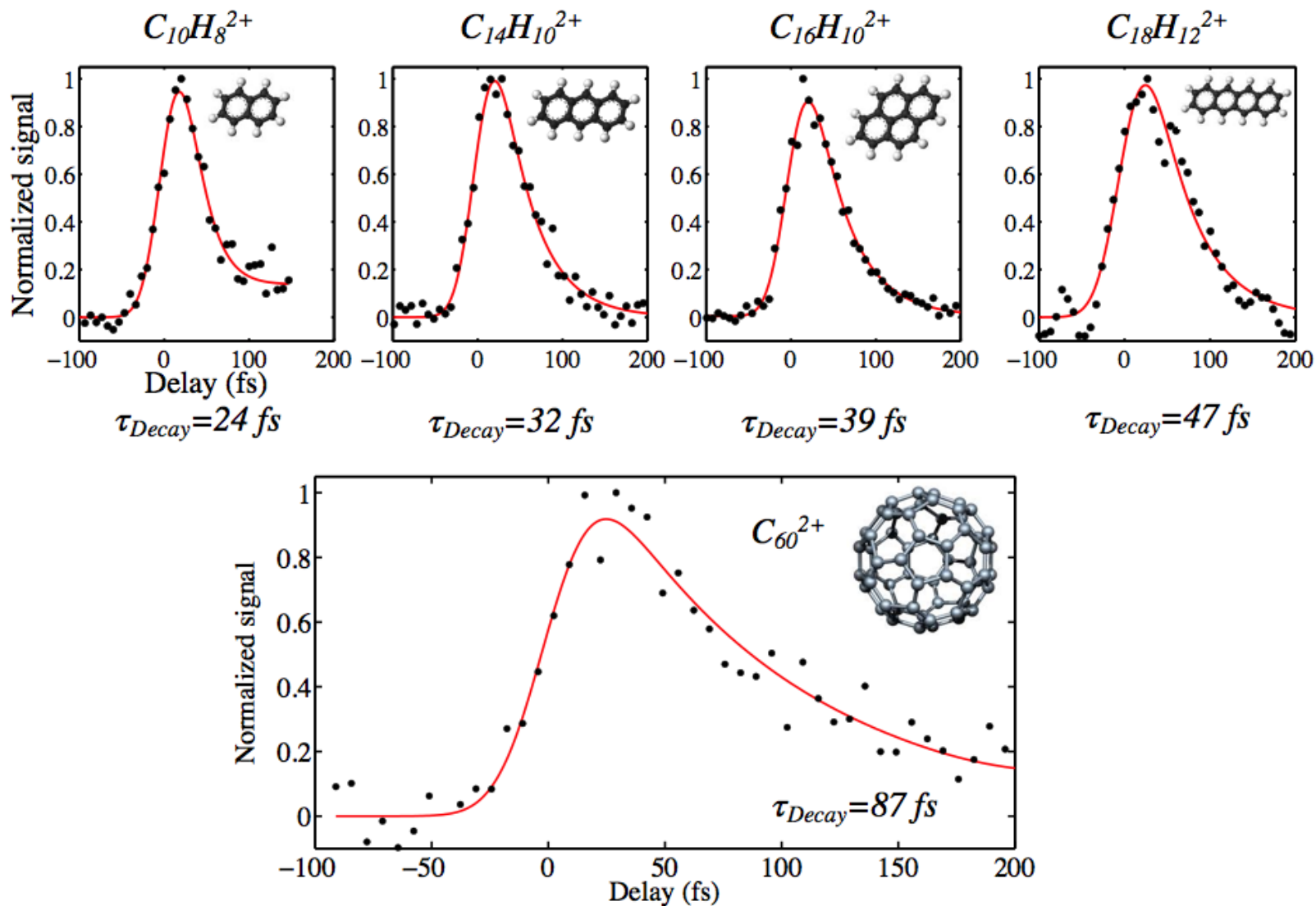
Calculation Alexander Kuleff

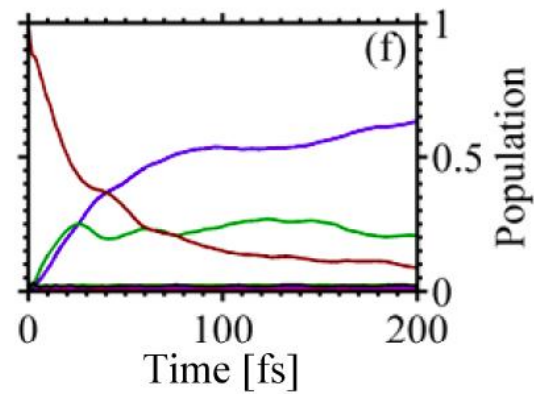
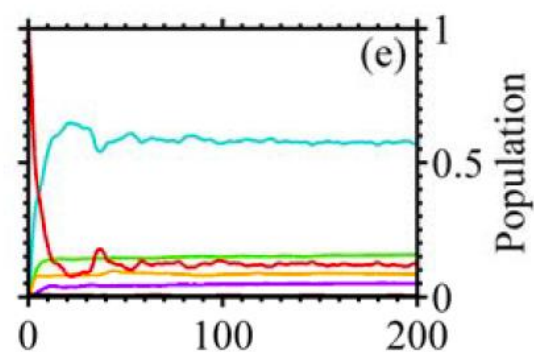
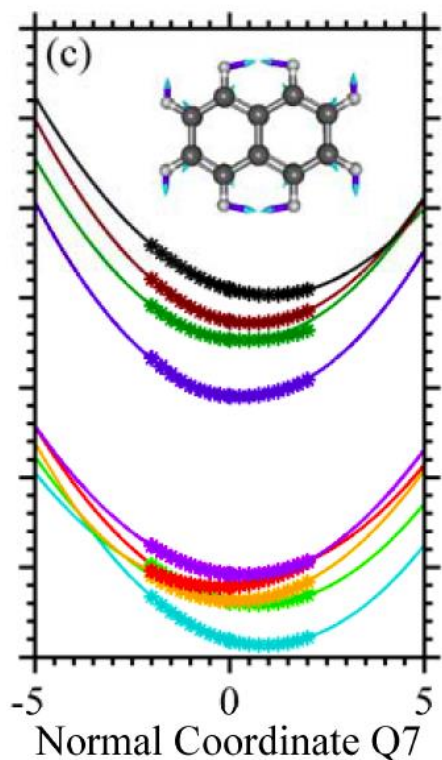
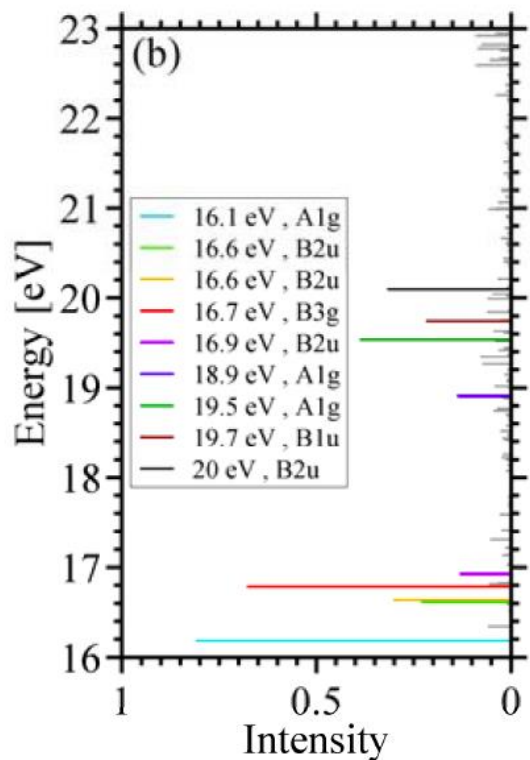
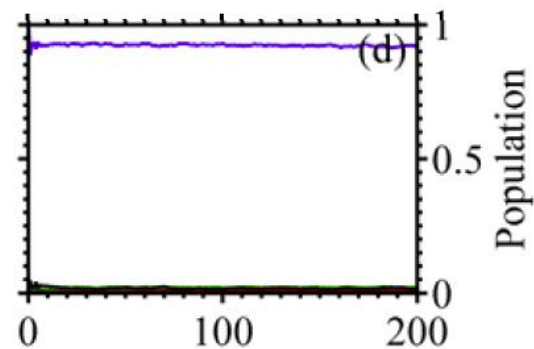
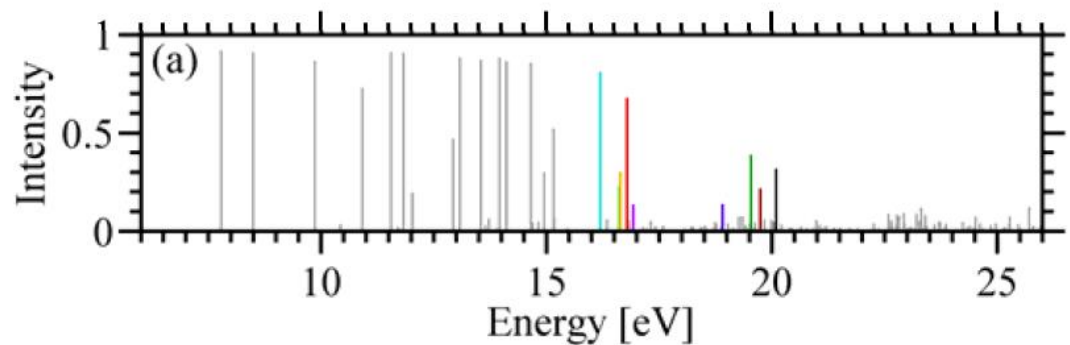
→ Use XUV pump-IR probe experiment





Experiments on Polycyclic Aromatic Hydrocarbons (with Franck Lépine)





Anthracene

Calculation S. Mahapatra

Rapid non-adiabatic dynamics, possibly related to observation of DIBs

Acknowledgements

CRATI measurements: Arjan Gijsbertsen, Jochen Mikosch (NRC, currently MBI), Albert Stolow (NRC)

H₂ Attosecond Pump-Probe: Freek Kelkensberg, Wing Kiu Siu, Giuseppe Sansone (Milano), Mauro Nisoli (Milano), Matthias Kling (MPQ), Franck Lépine (Lyon), Fernando Martin c.s. (Madrid), Misha Ivanov (Imperial, now MBI) & further collaboration partners

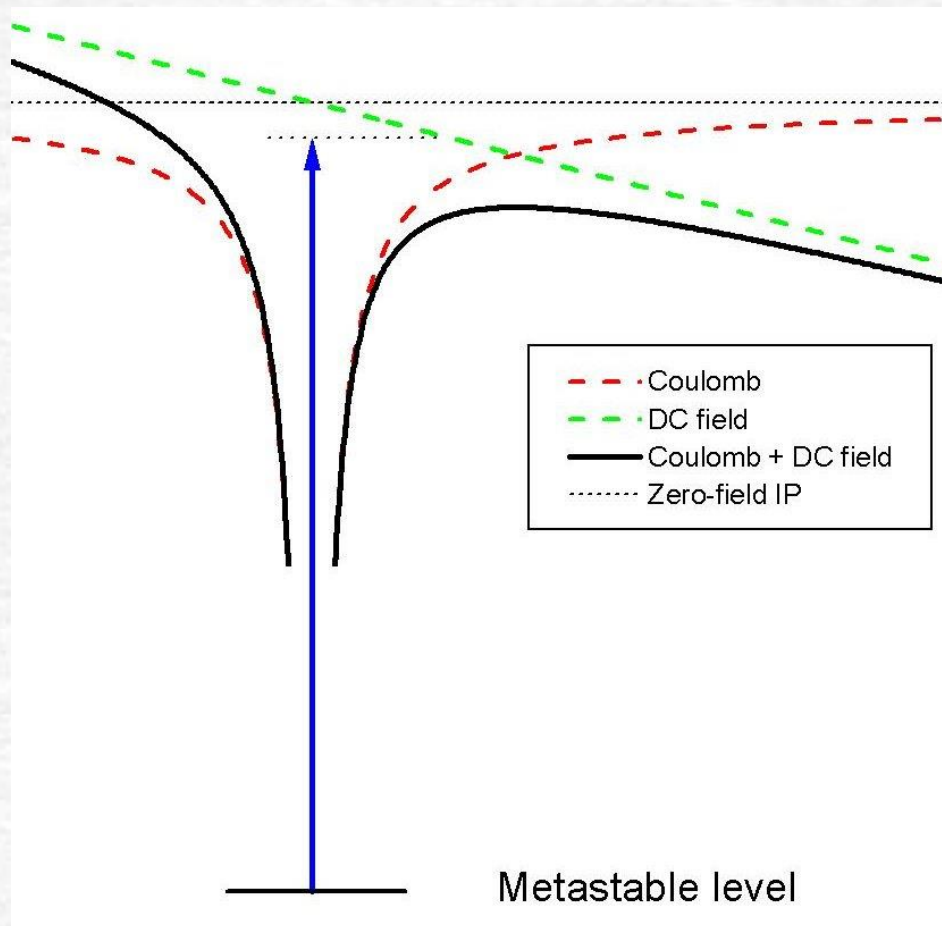
N₂ Attosecond Pump-Probe: Christian Neidel, Jesse Klei, Chung-Hsin Yang, Arnaud Rouzée, Lukas Mediskauskas, Misha Ivanov (MBI), Franck Lépine (Lyon) & further collaboration partners

PAH Pump-Probe: Christian Neidel, Jesse Klei, Chung-Hsin Yang, Arnaud Rouzée, Franck Lépine group (Lyon)

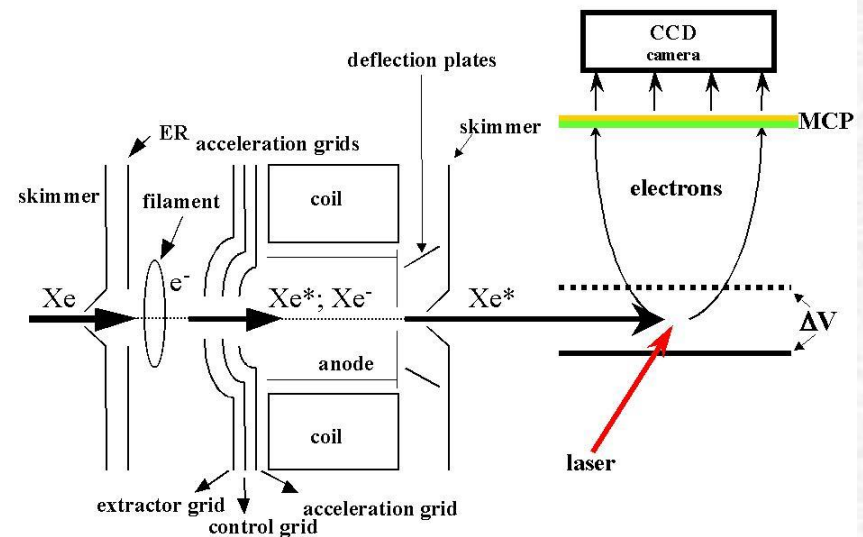
Dessert

An alternative view on
photoionization time delays

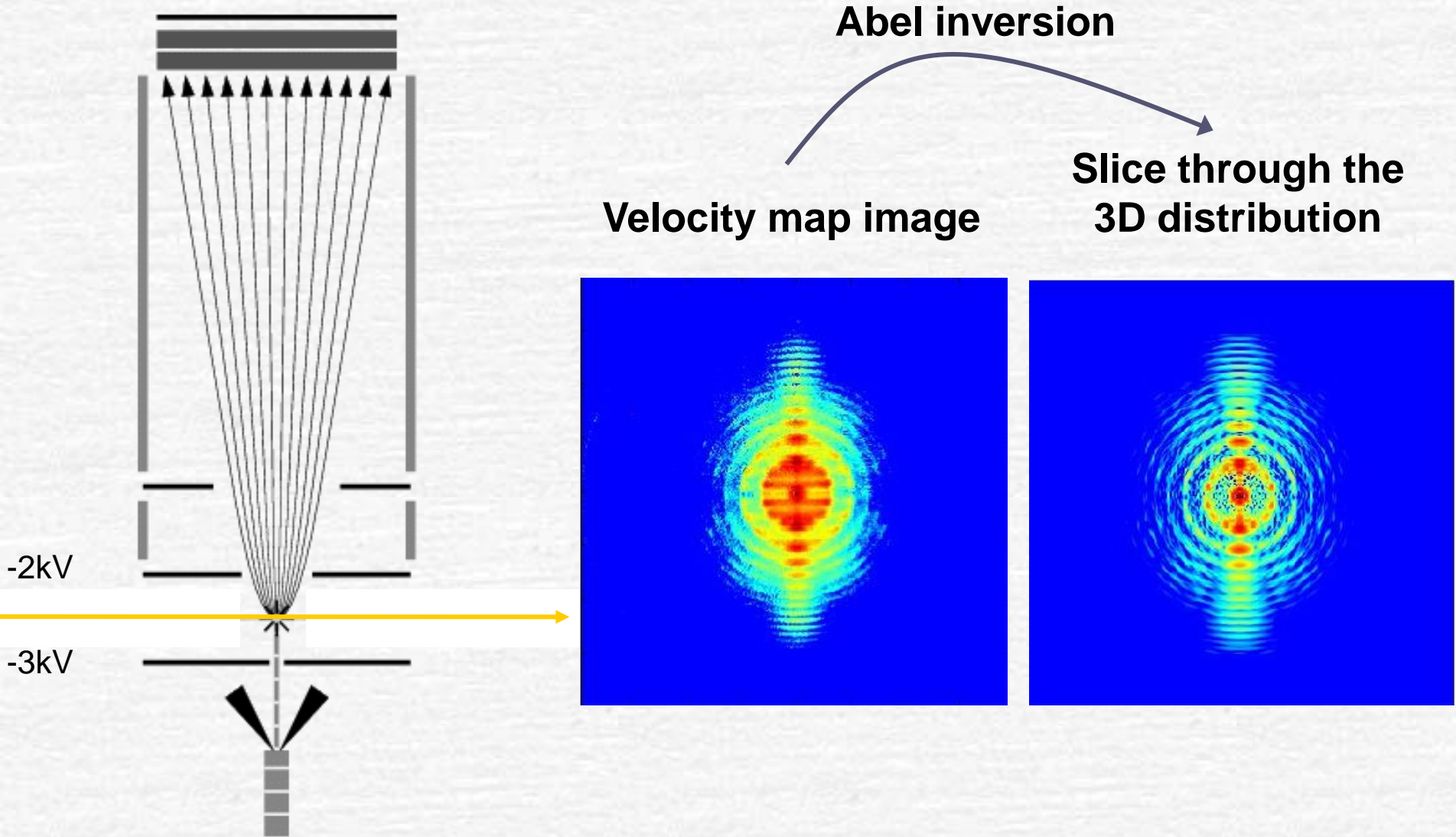
Ionization of metastable Xe atoms with a small excess kinetic energy, using a tunable ns laser



Excitation near the field-free ionisation limit (above the saddle-point in the combined DC field + Coulomb potential)

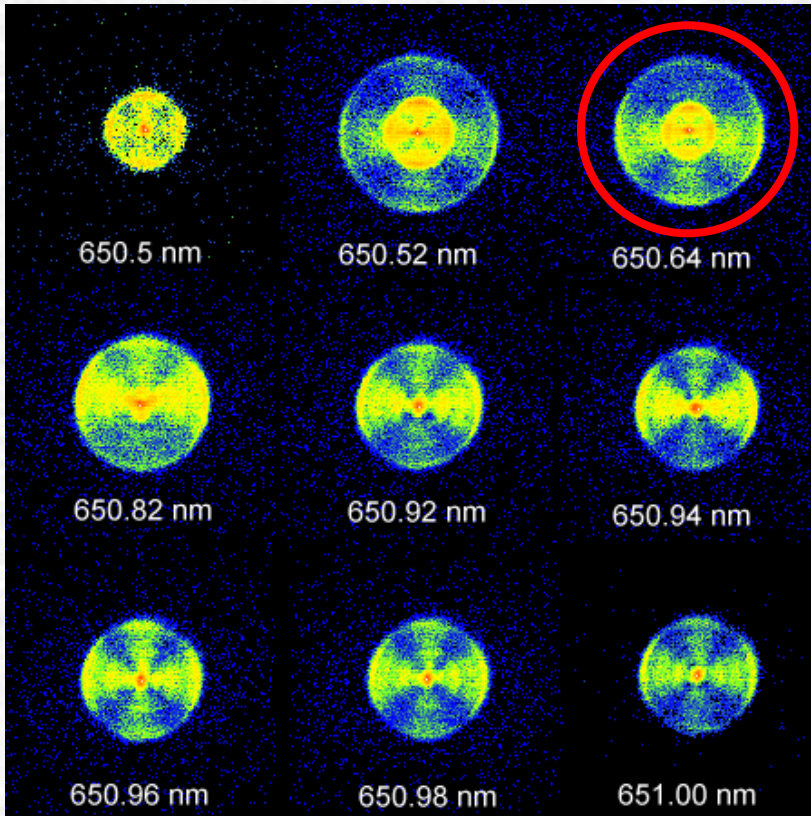


Velocity Map Imaging (VMI) Spectrometry

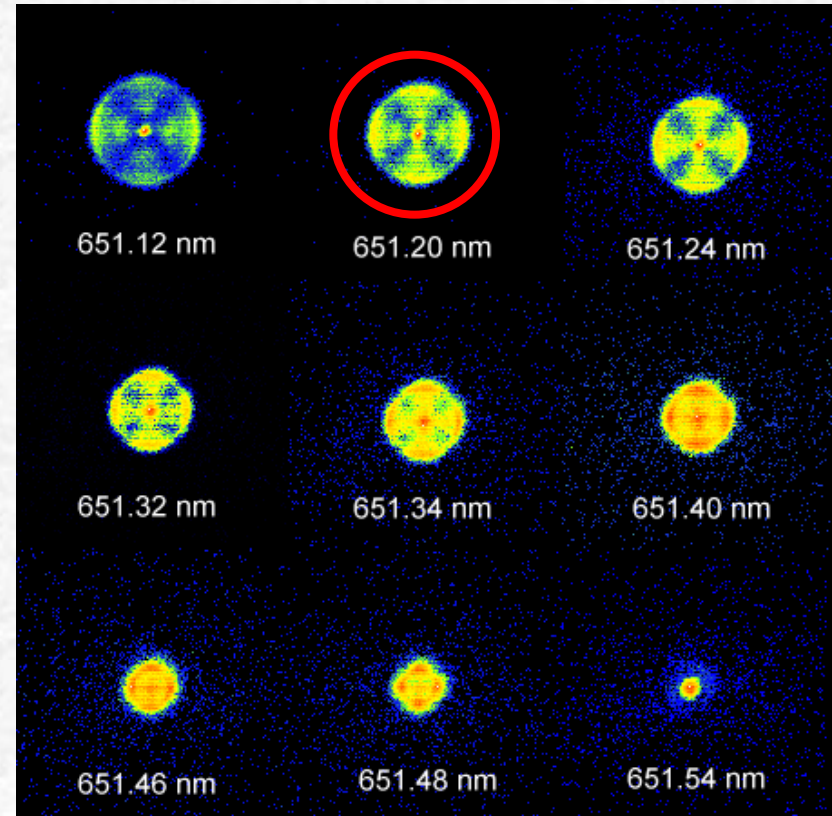


Slow photoelectron imaging

2-photon ionization of $\text{Xe}^*(6s[3/2]_2)$ in a field of 170 V/cm

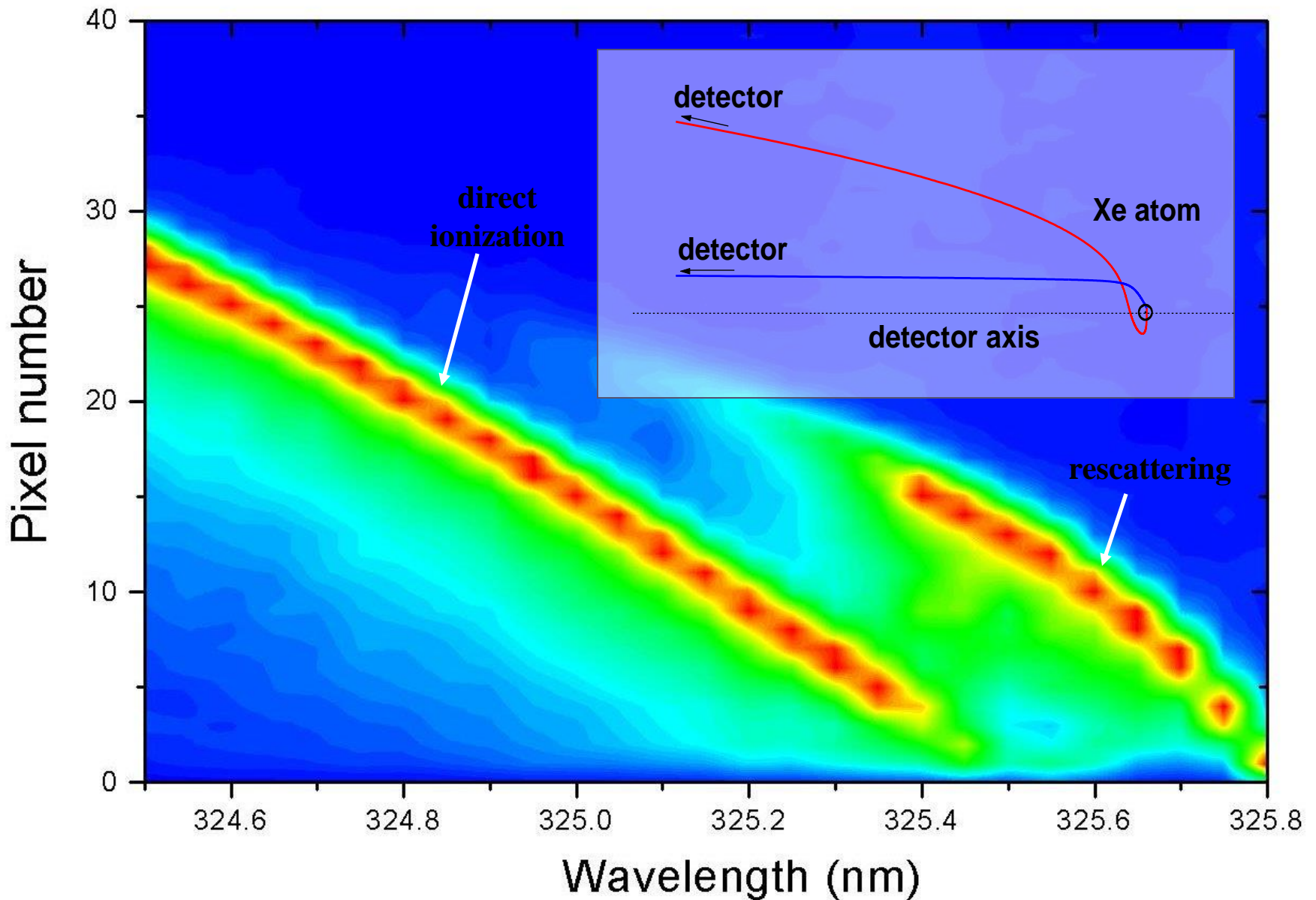


Switching of intensity
from outer to inner ring!!



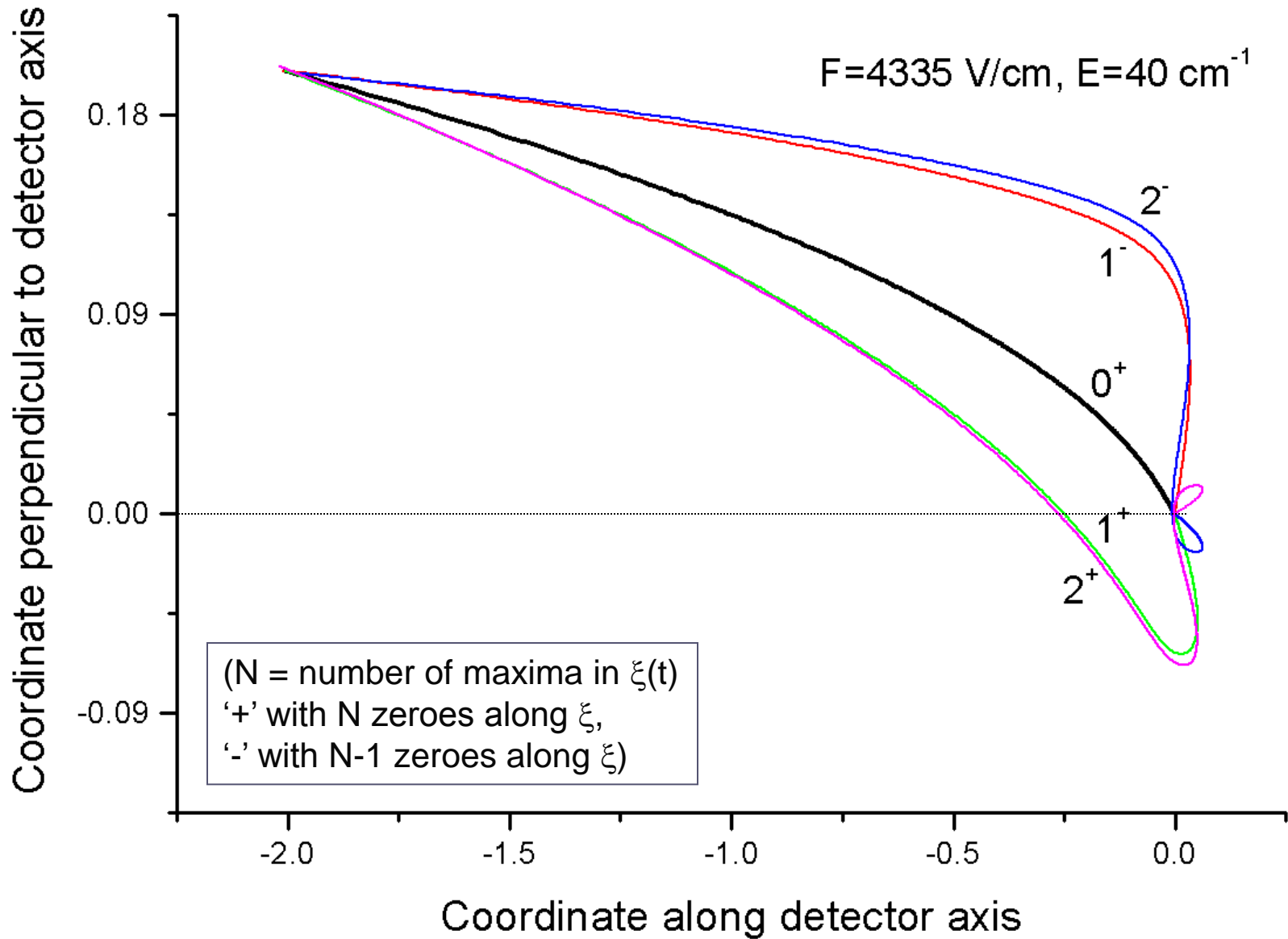
Images are not a single
ring!!

Classical interpretation of electron dynamics

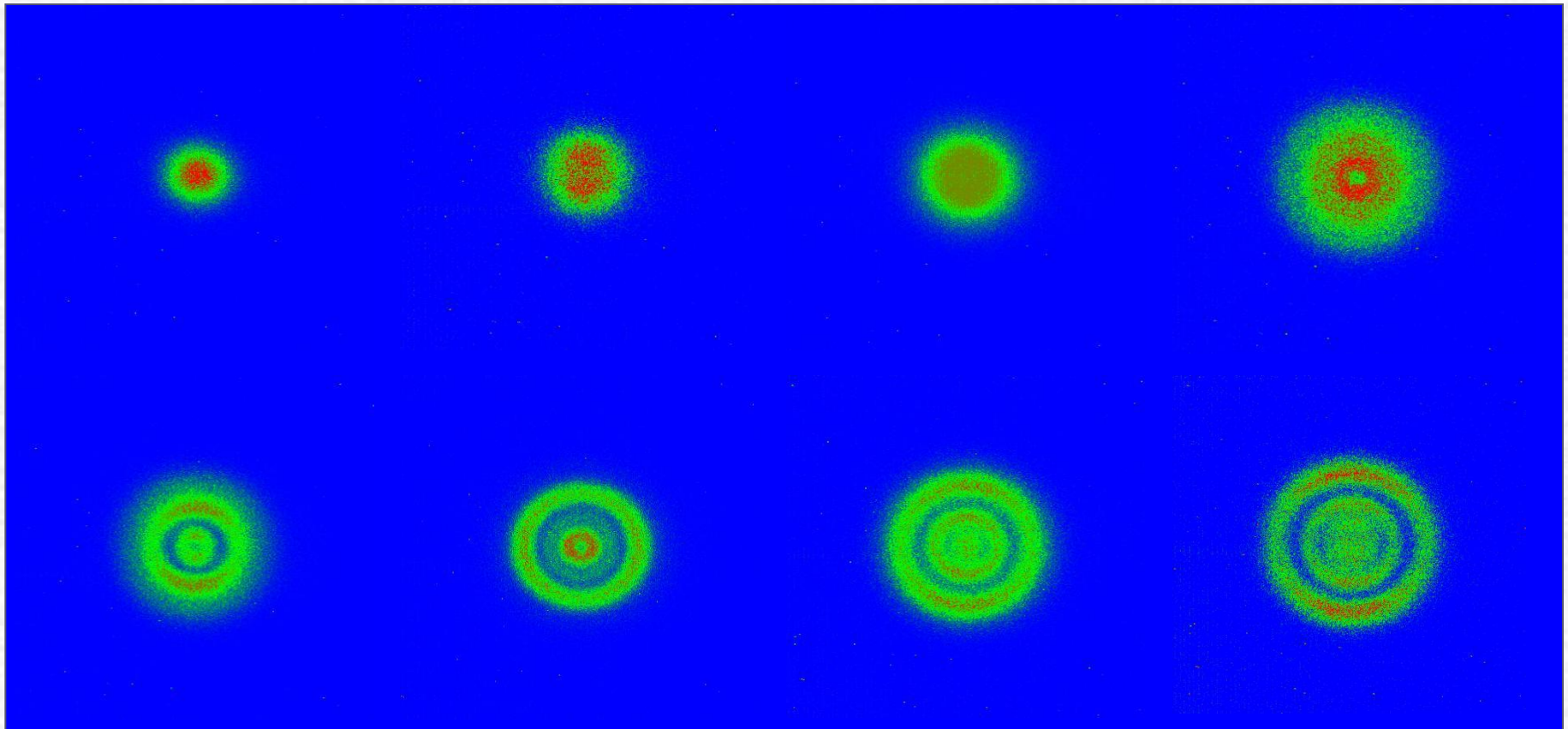


Classification of the trajectories - II

Expect multiple interfering pathways

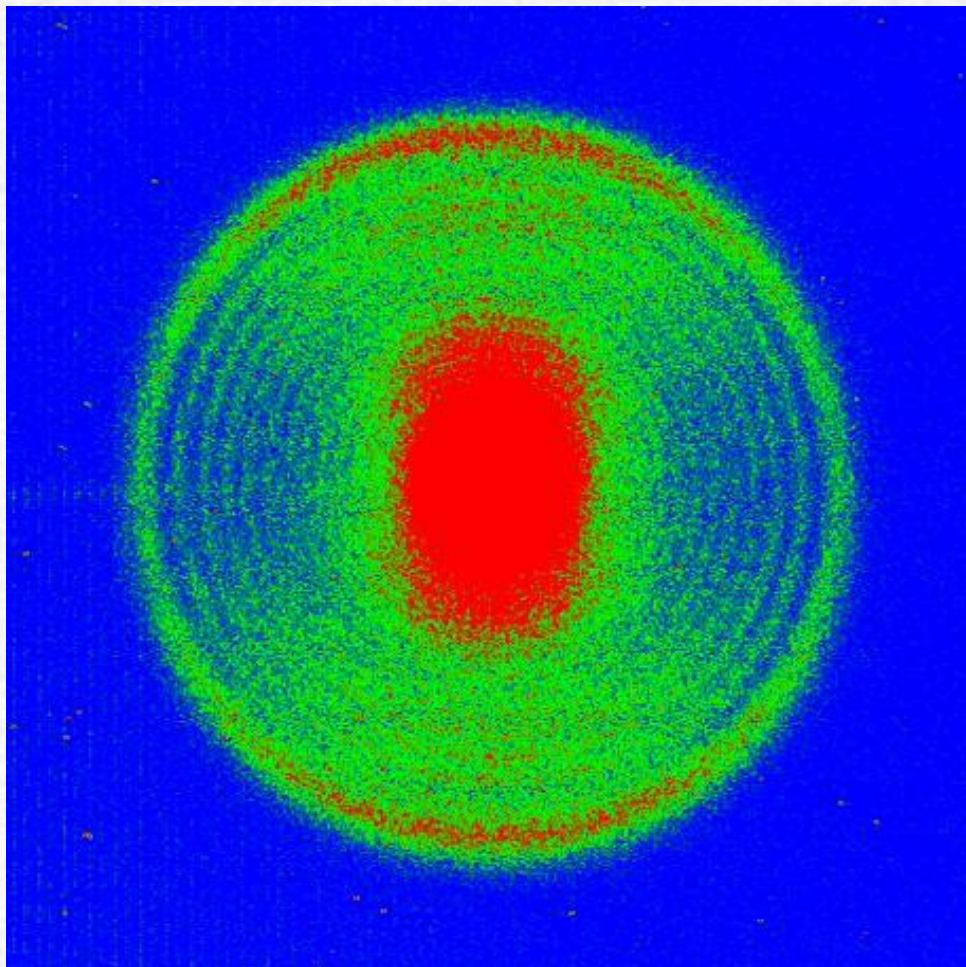


Observation of multi-slit electron interference

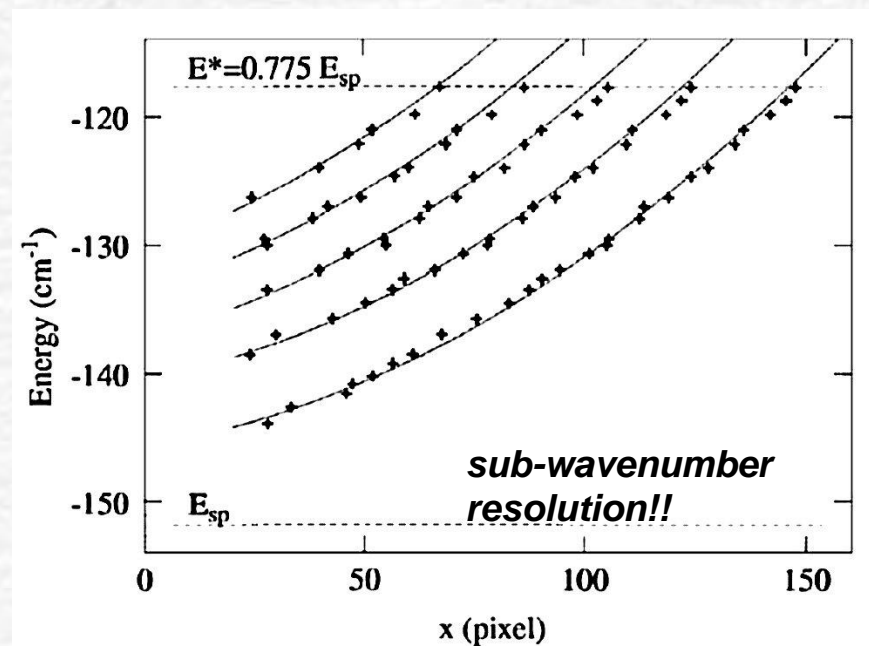


1-photon ionization of $\text{Xe}^*(6s[3/2]_2)$ in a field of 170 V/cm,
Increasing photon energy

Observation of multi-slit electron interference

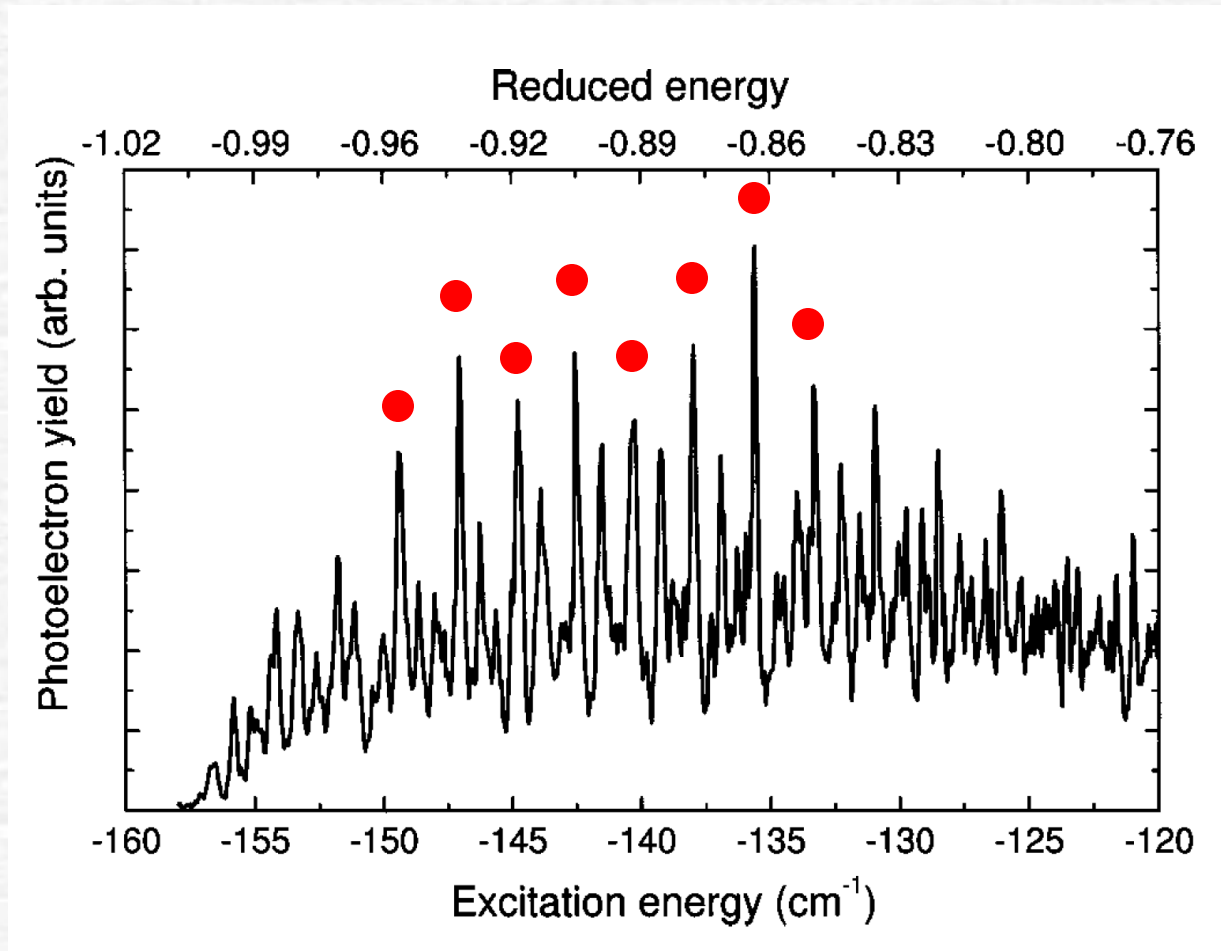


1-photon ionization of $\text{Xe}^*(6s[3/2]_2)$ in a field of 170 V/cm



The number of fringes increases as a function of the energy above the saddlepoint

However, this results was also very disappointing...



Interference patterns in Xe are only governed by photoelectron energy and not at all by nature of Stark state.....

Solution: perform the experiment for H atoms!

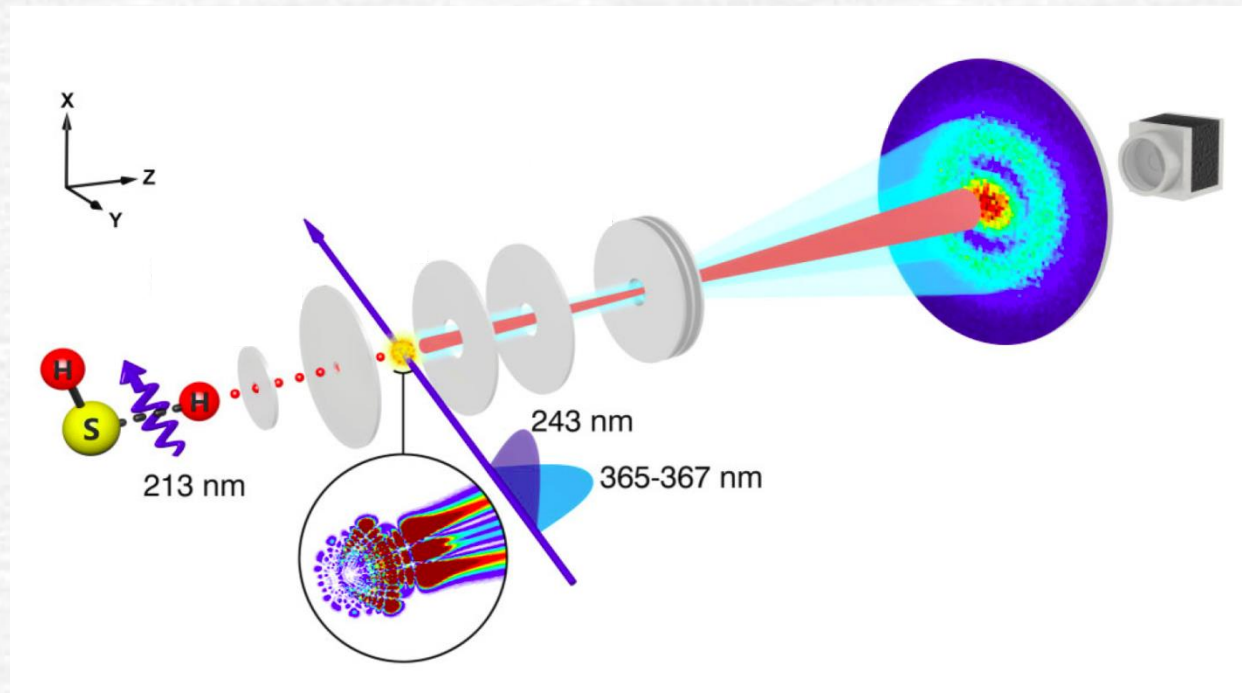
The Stark Hamiltonian is separable in parabolic coordinates:

$$\Psi(\xi, \eta, \varphi) = (2\pi\eta\xi)^{-1/2} \chi_1(\xi)\chi_2(\eta)e^{im\varphi}$$

$$\eta = r - z$$

$$\xi = r + z$$

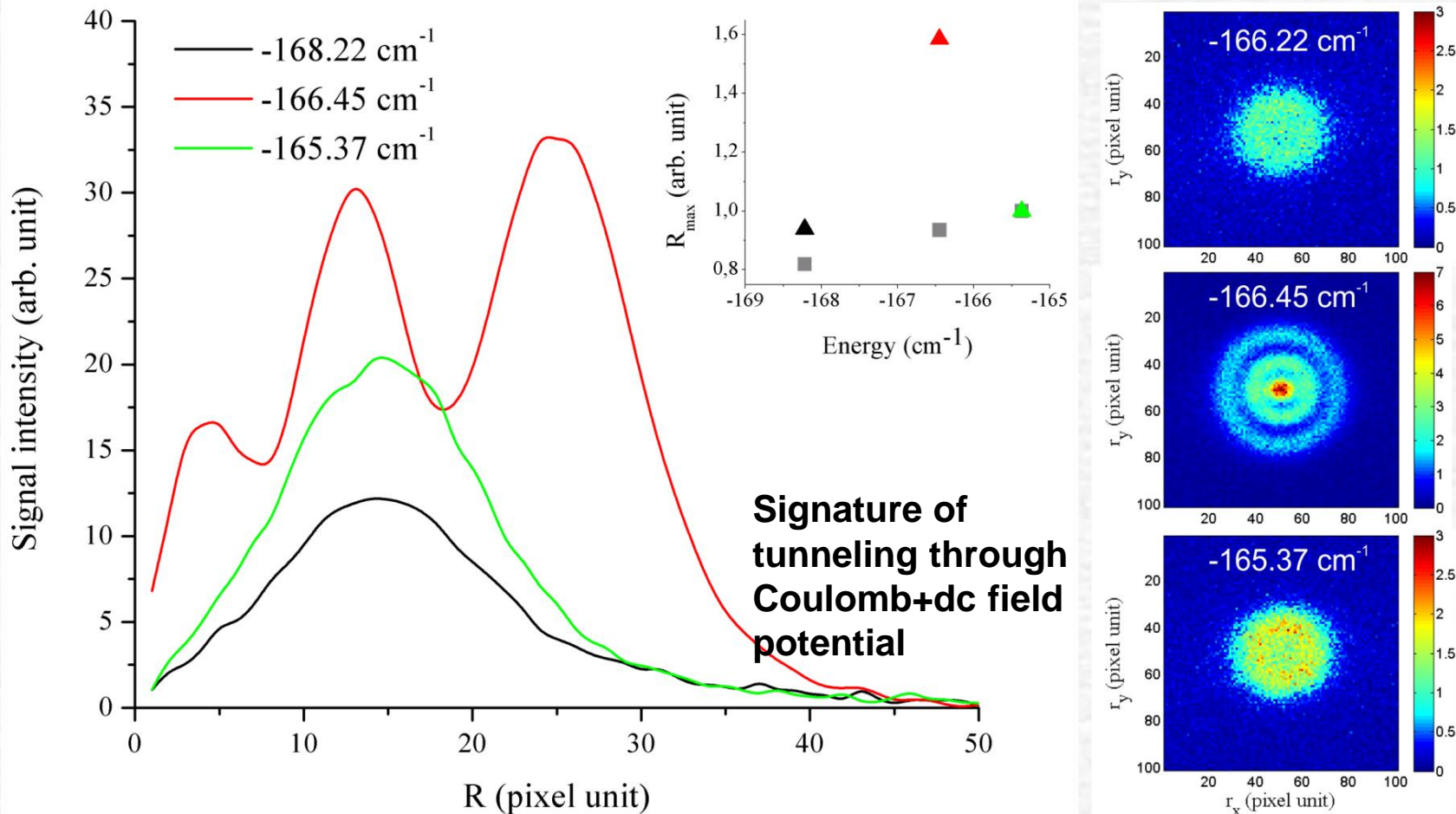
This separation in parabolic coordinates is *independent of the applied electric field*
→ persists from the interaction region ($F \approx 500$ V/cm) to the two-dimensional detector ($F = 0$ V/cm)





Hydrogen Atoms under Magnification: Direct Observation of the Nodal Structure of Stark States

A. S. Stodolna,^{1,*} A. Rouzée,^{1,2} F. Lépine,³ S. Cohen,⁴ F. Robicheaux,⁵
 A. Gijsbertsen,¹ J. H. Jungmann,¹ C. Bordas,³ and M. J. J. Vrakking^{1,2,*}

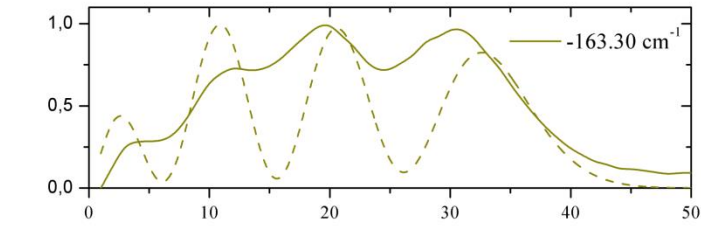
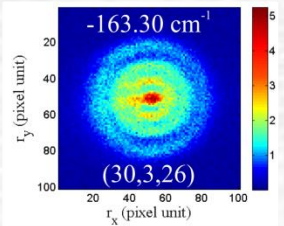
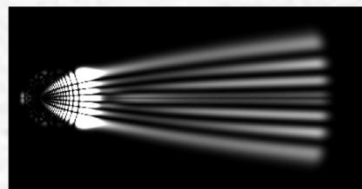
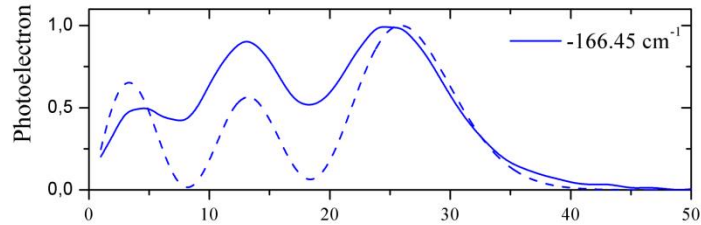
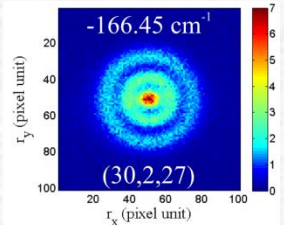
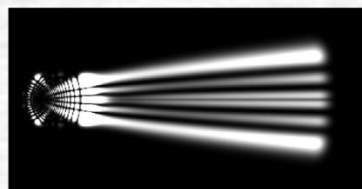
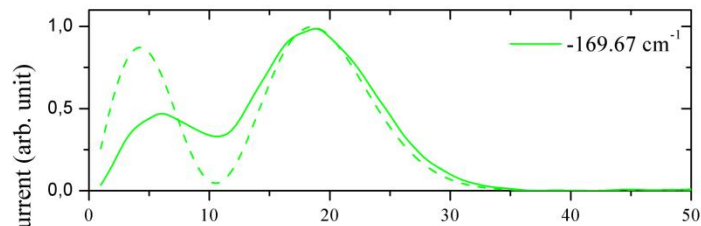
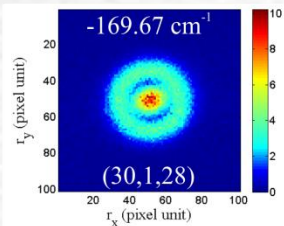
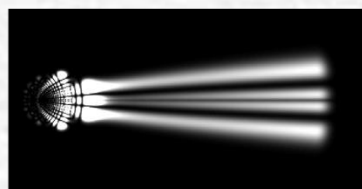
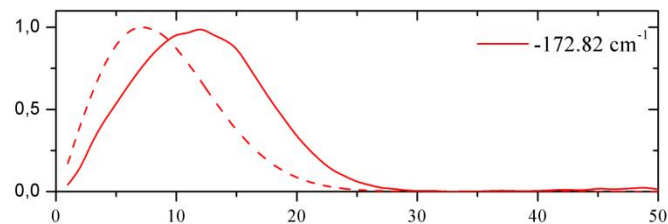
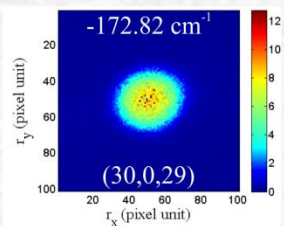
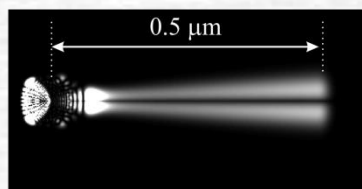


→ can recognize n_1 , related to quantization in ξ coordinate



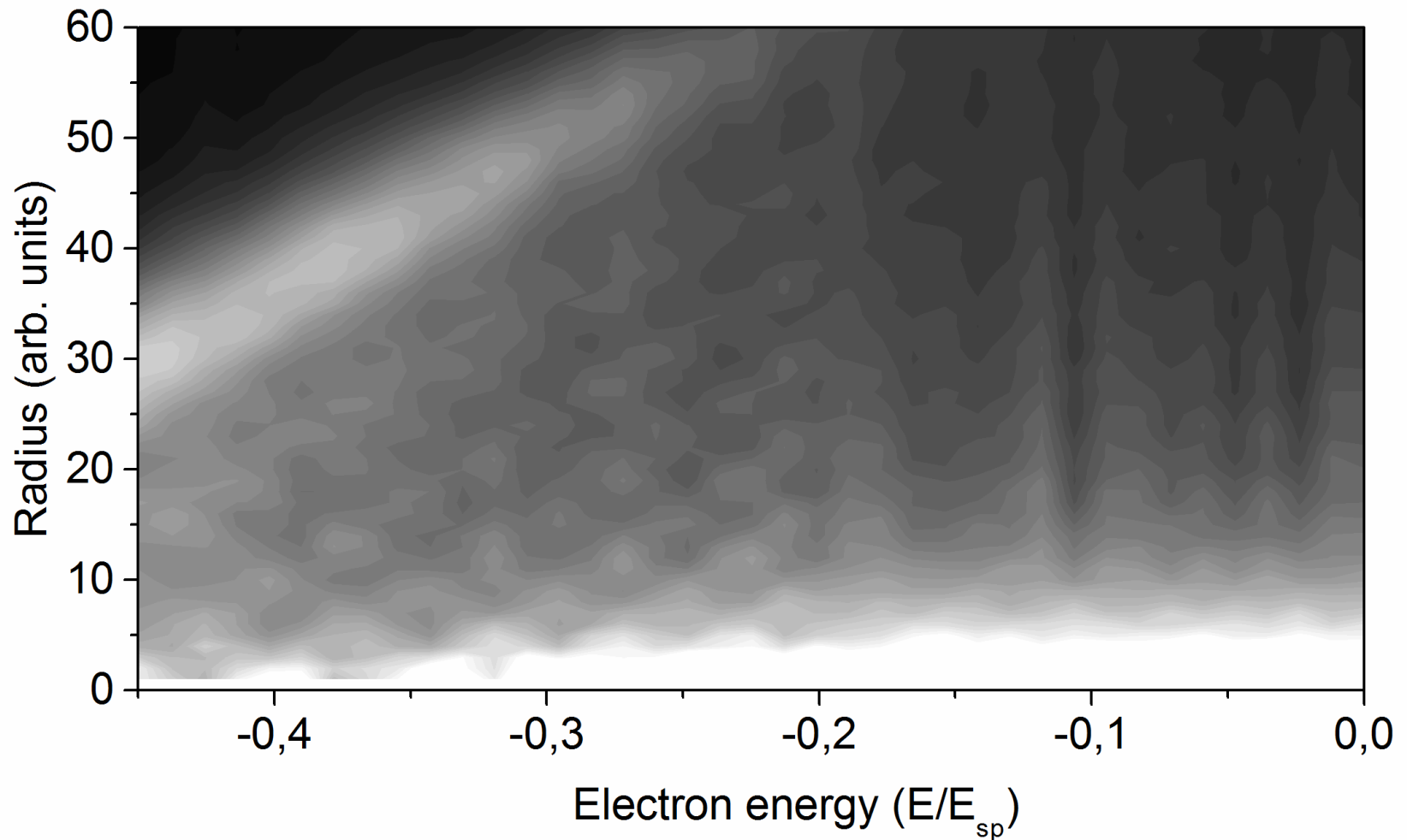
Hydrogen Atoms under Magnification: Direct Observation of the Nodal Structure of Stark States

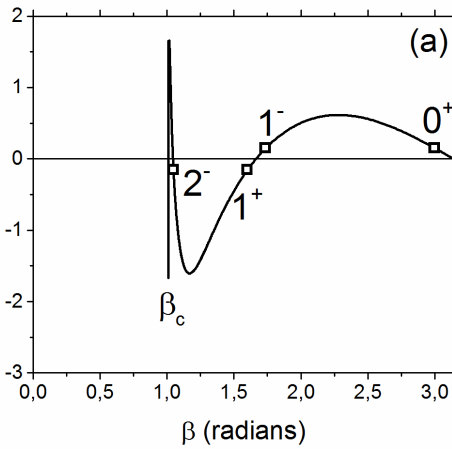
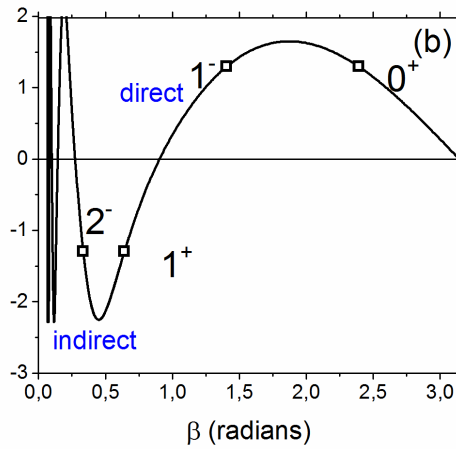
A. S. Stodolna,^{1,*} A. Rouzée,^{1,2} F. Lépine,³ S. Cohen,⁴ F. Robicheaux,⁵
 A. Gijsbertsen,¹ J. H. Jungmann,¹ C. Bordas,³ and M. J. J. Vrakking^{1,2,*}



R (pixel unit)

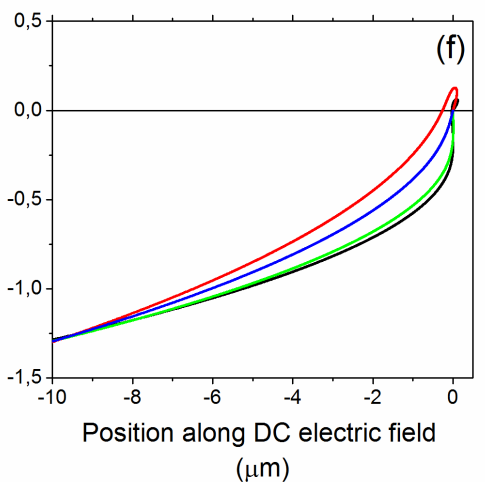
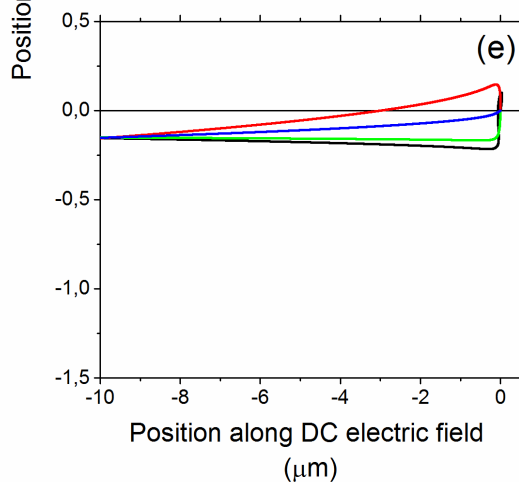
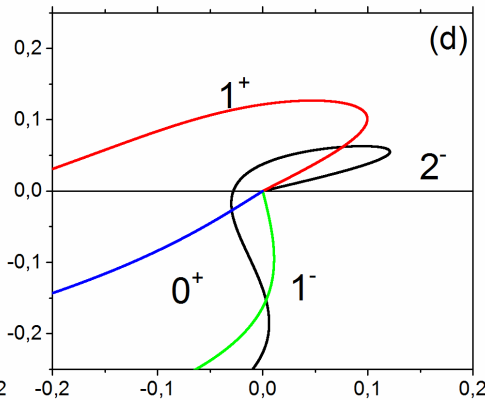
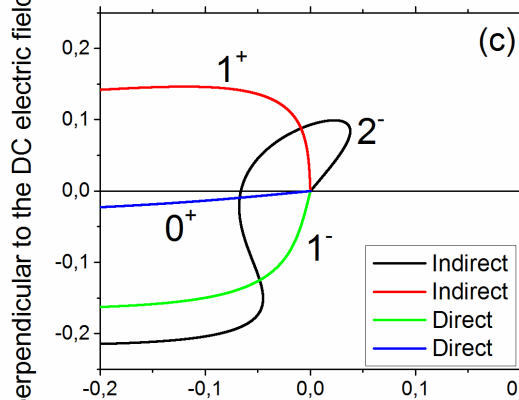
Interference between direct and indirect trajectories encode photoionization time delays



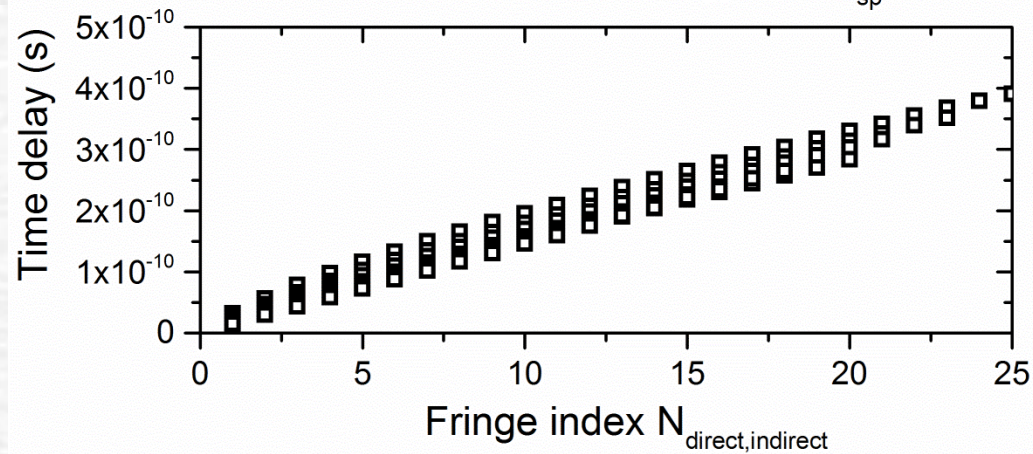
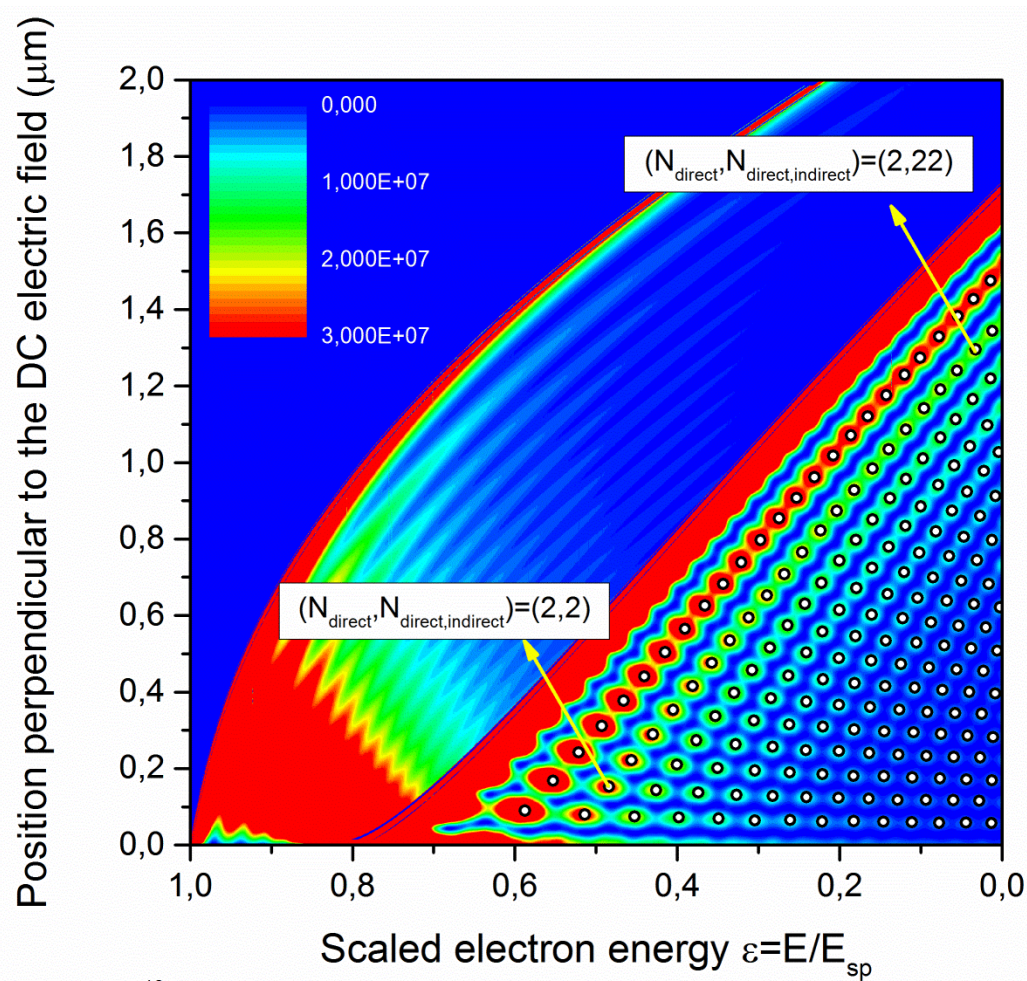
$\varepsilon=0.485$  $\varepsilon=0.033$ 

At each energy there are two dominant direct and two dominant indirect trajectories

Beating between the interference patterns „measures“ the time delay between the 1^+ and the 1^- trajectory



Assignment of fringes



Linear relation between fringe index and time delay