Lecture Series Buenos Aires

18-3-2024 until 22-3-2024

Lecture M7 – Attosecond molecular physics

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Max-Born-Institut

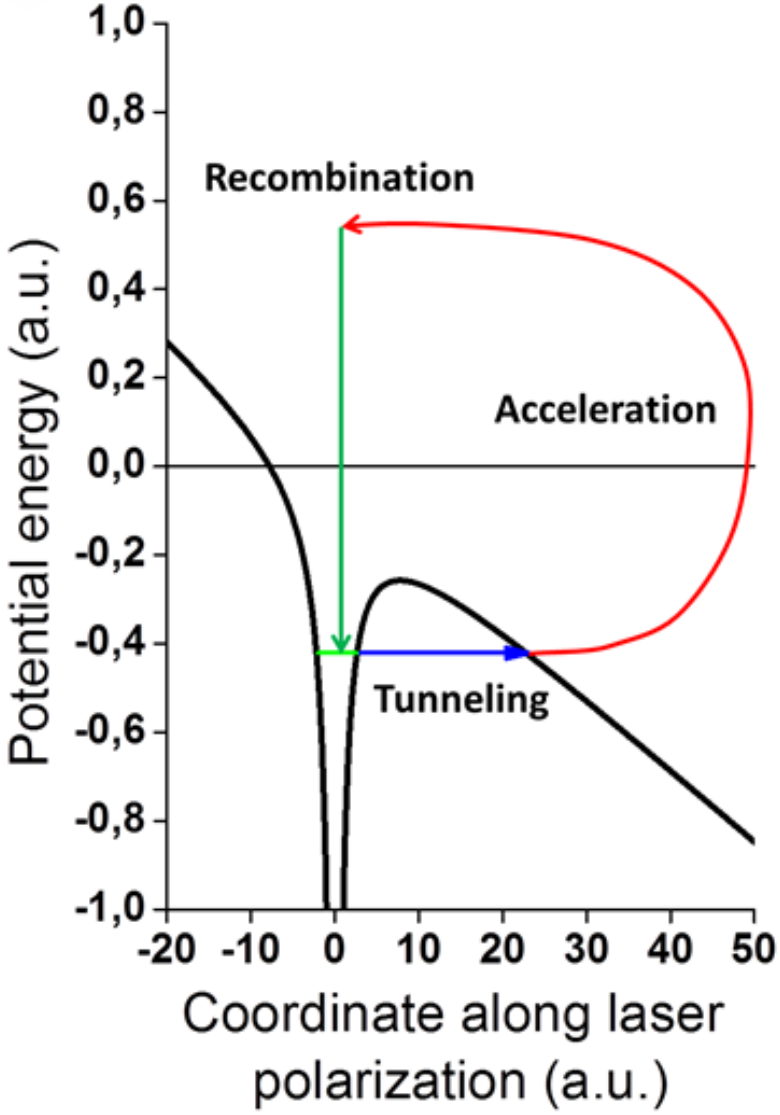
Contents

- High-harmonic generation in molecules

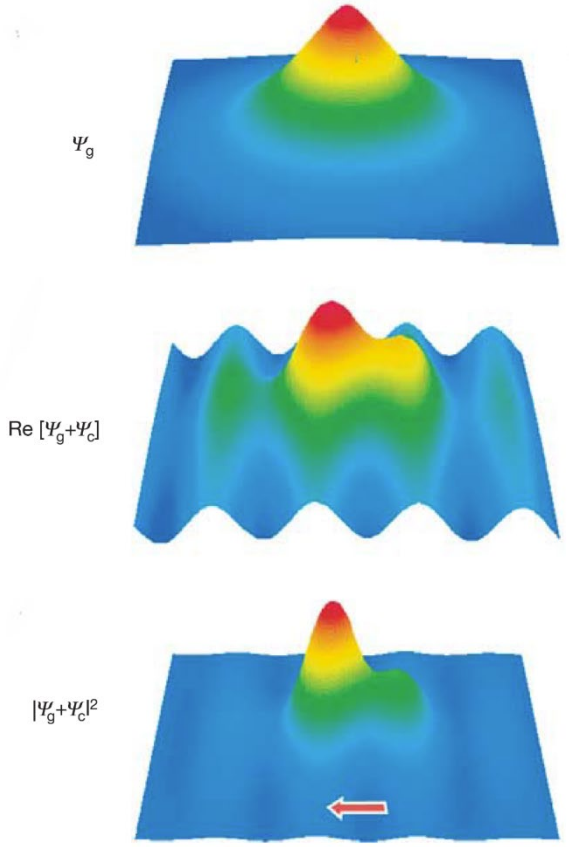
  „High –harmonic spectroscopy“

- Attosecond pump-probe spectroscopy in molecules

A quantum-mechanical view of the HHG process



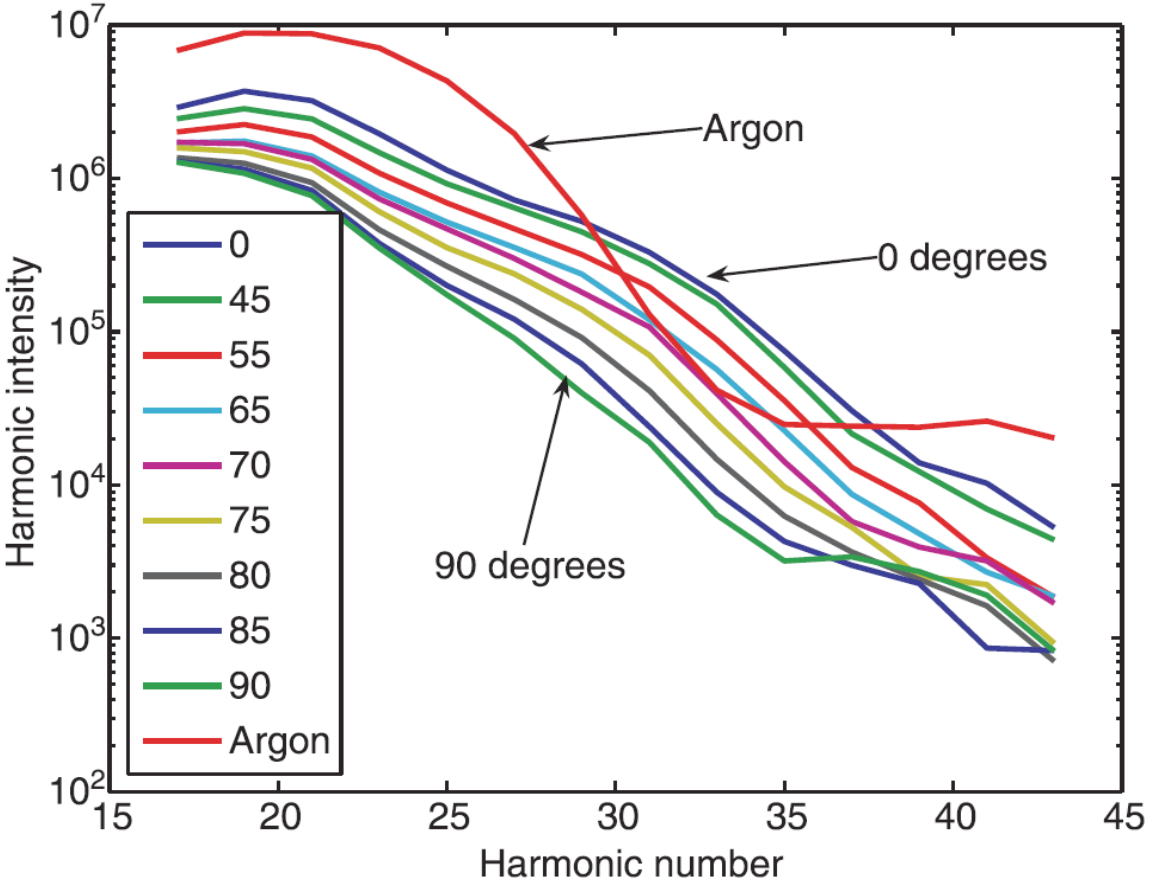
$$\mathbf{d}(\omega;\theta) = <\psi(\mathbf{r};\theta)|\mathbf{r}|\exp[ik(\omega)x]>$$



Itatani et al. 432, 867 (2003)

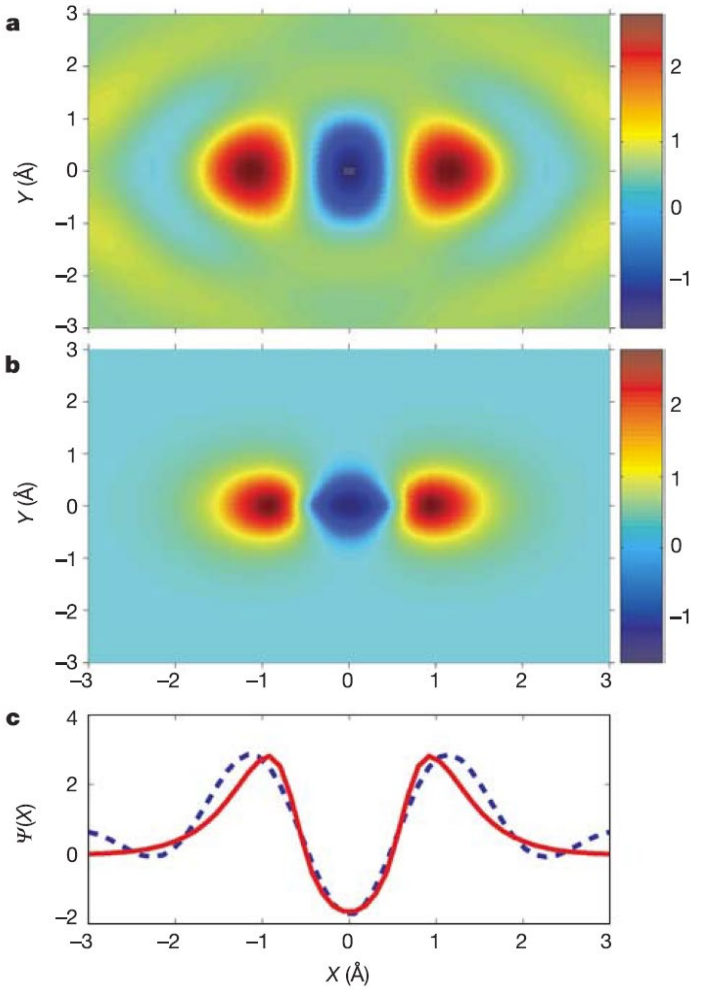
The dipole that leads to harmonic emission arises from interference between the ground state wavefunction and the recolliding electron

Recollision electrons can probe wave functions



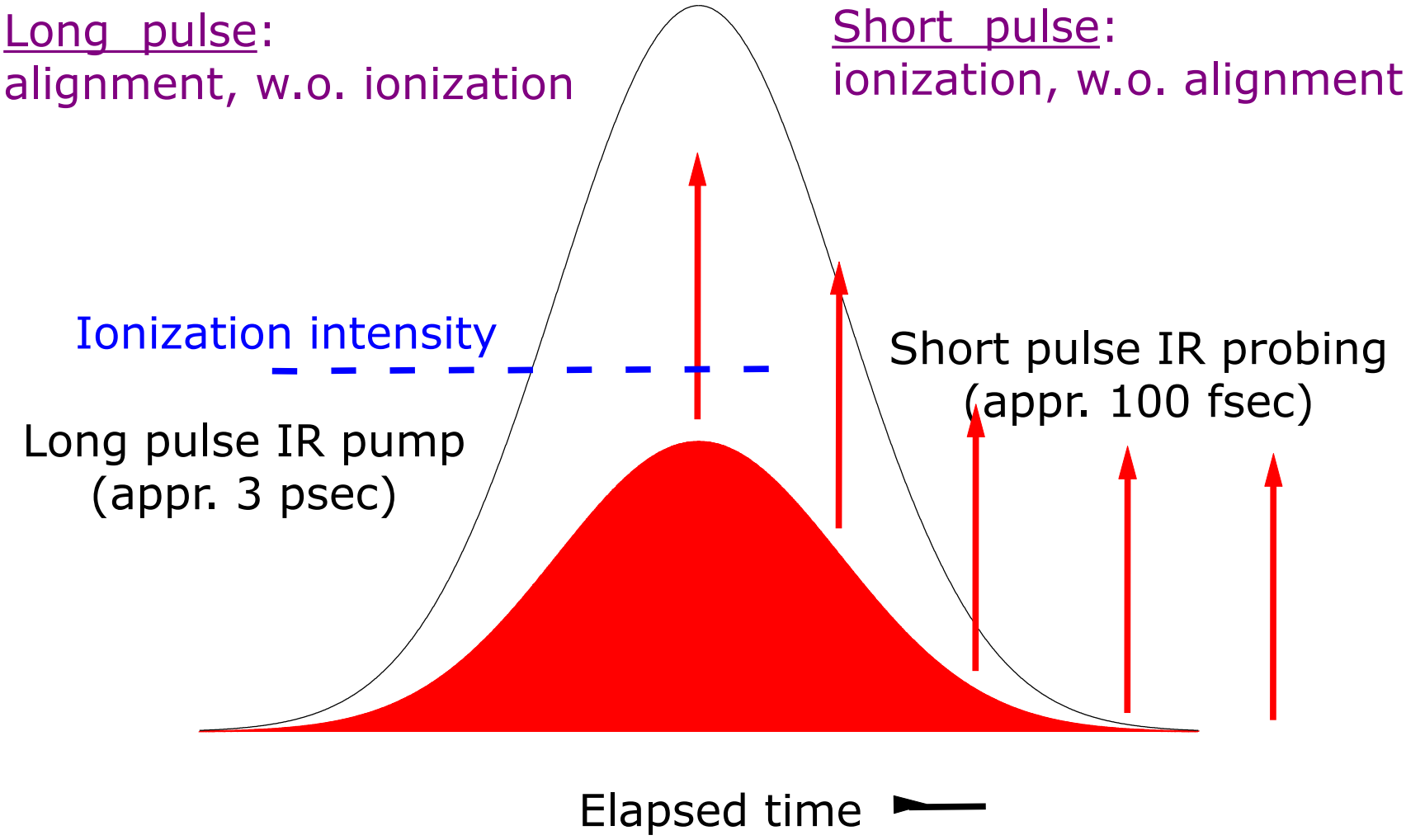
Experiment: HHG in N_2 molecules that are pre-aligned at different angles with respect to the HHG driver laser polarization axis

Experimentally determined N_2 ground state orbitals (amplitude & phase)



Itatani et al. 432, 867 (2003)

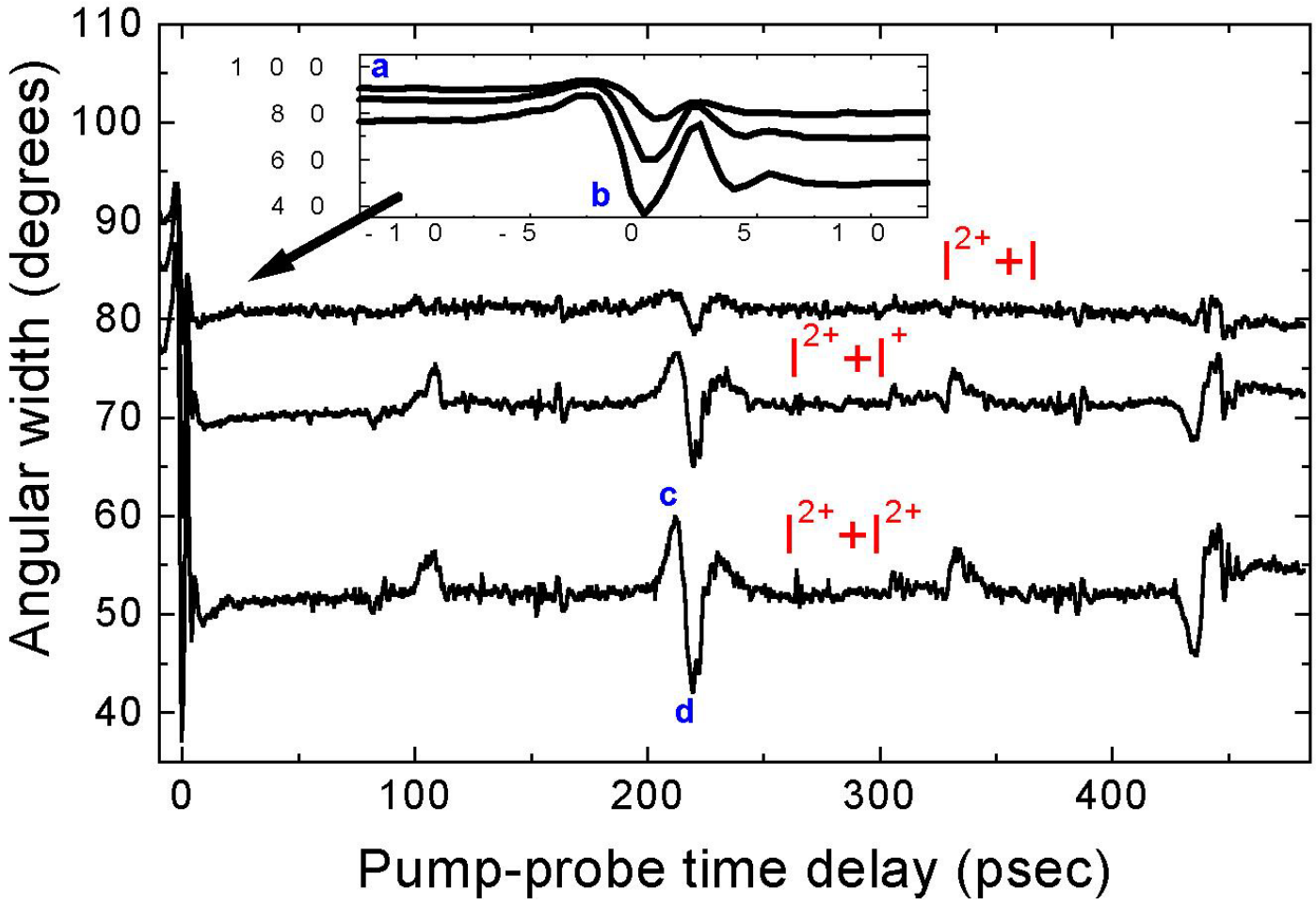
First impulsive alignment experiment

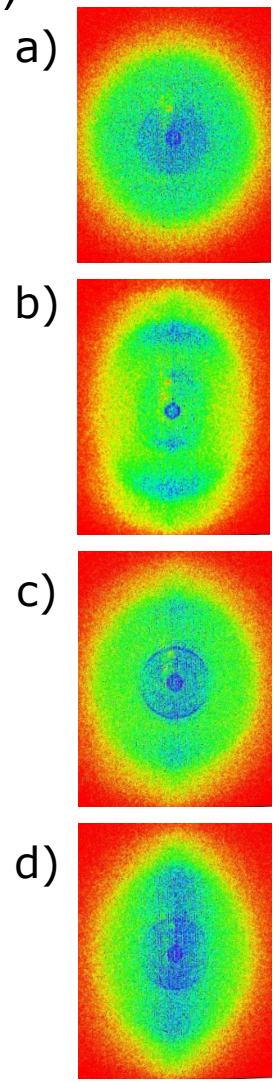


F. Rosca-Pruna and M.J.J. Vrakking, Phys. Rev. Lett. 87, 153902 (2001)

First impulsive alignment experiment

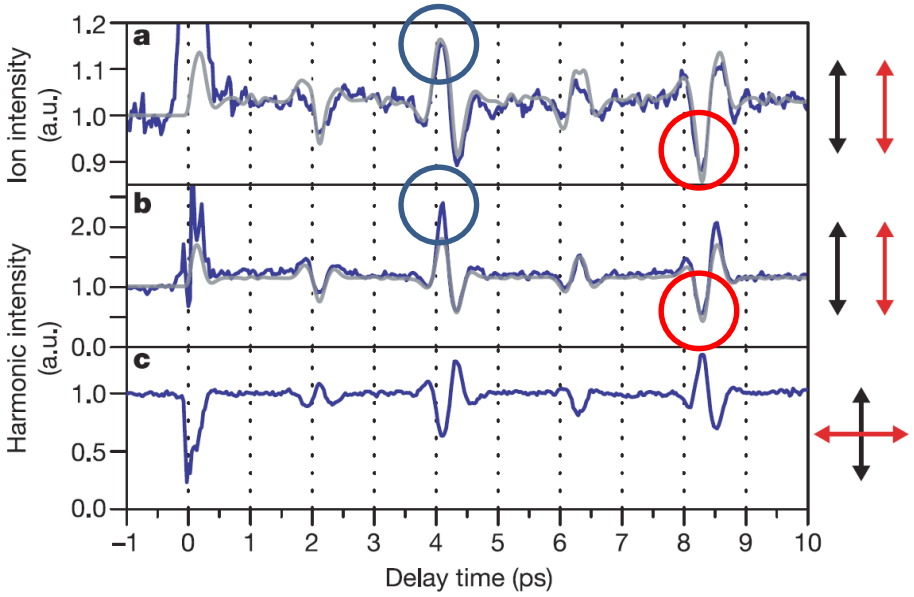
2001: Impulsive molecular alignment (Rosca-Pruna and Vrakking)



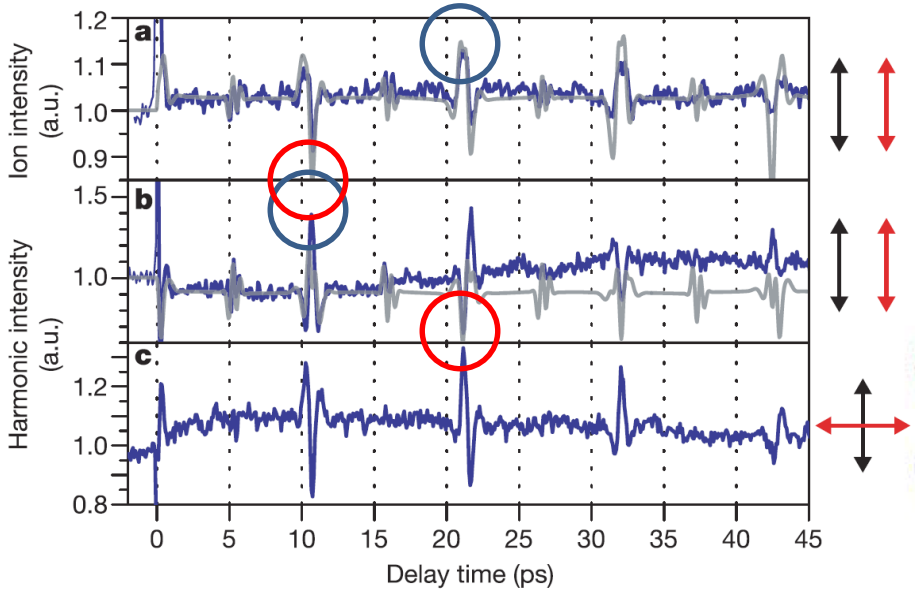


F. Rosca-Pruna and M.J.J. Vrakking, Phys. Rev. Lett. 87, 153902 (2001)

Recollision electrons can probe molecular structure



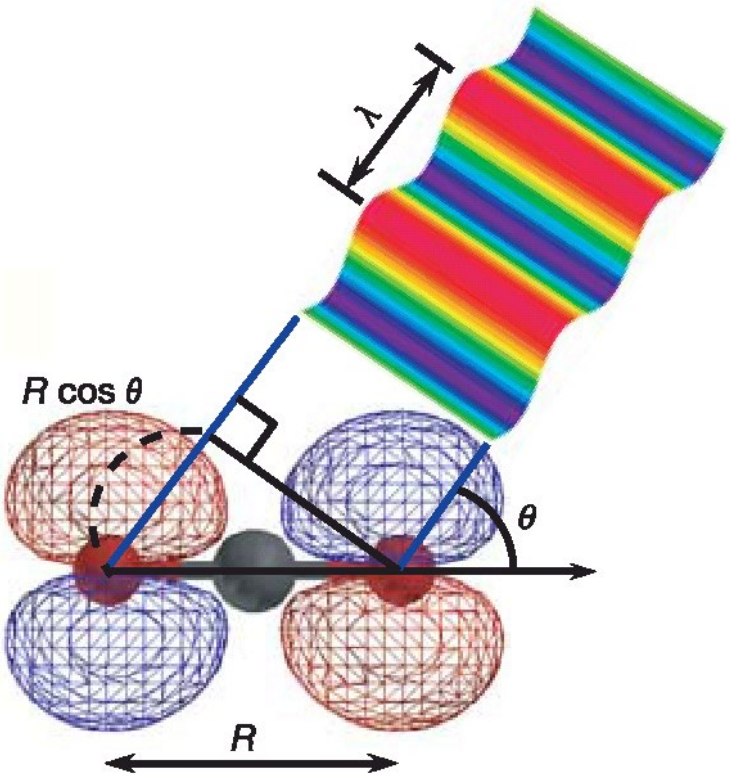
Ionization yield (a) and HHG yield (b,c) in N_2 when the HHG driver pulse is preceded by a pulse that aligns the N_2 internuclear axis: the HHG yield goes **up** when alignment of the molecule gives a **higher** ionization yield



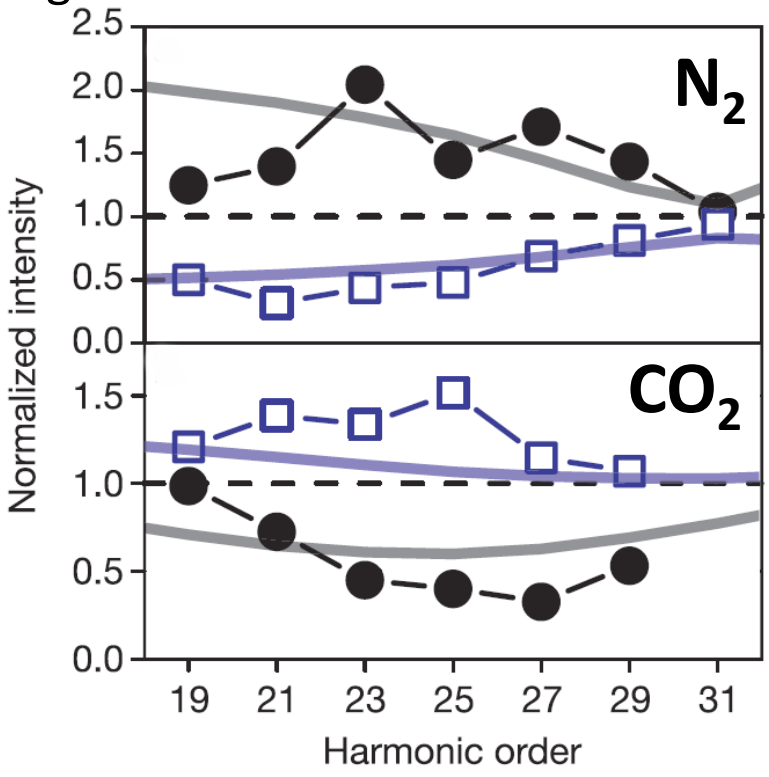
Ionization yield (a) and HHG yield (b,c) in CO_2 when the HHG driver pulse is preceded by a pulse that aligns the CO_2 internuclear axis: the HHG yield goes **up** when alignment of the molecule gives a **lower** ionization yield

H. Sakai etal., Nature 435, 470 (2005)

Recollision electrons can probe molecular structure



Diffraction of the recollision electron in the molecular frame shows up in the harmonic yield versus alignment angle.



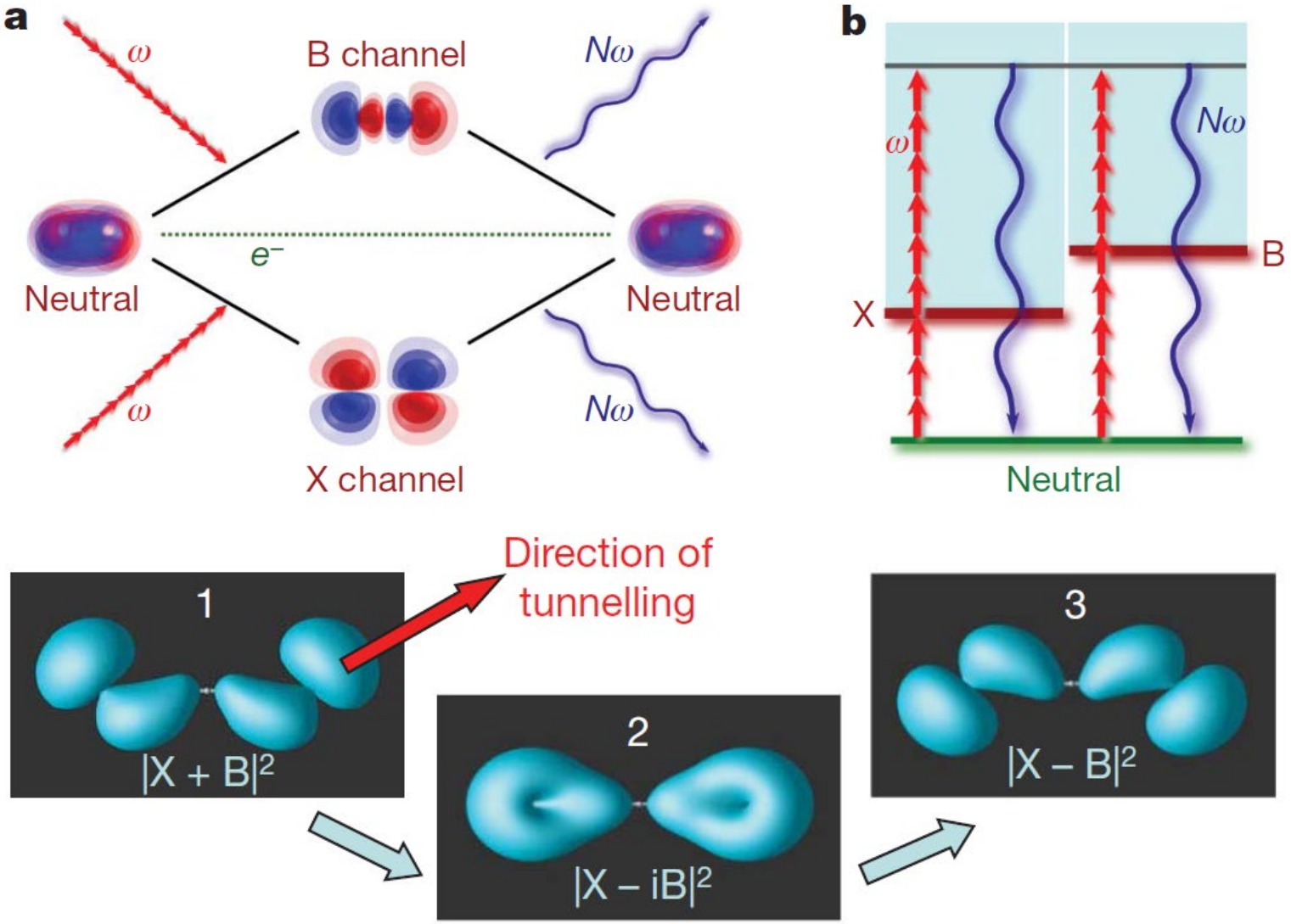
Ionization enhanced

Ionization suppressed

Attractive: the structural information shows up via diffraction, which relaxes the requirements on the availability of spectroscopic knowledge

H. Sakai etal., Nature 435, 470 (2005)

Recollision electrons can probe electron dynamics

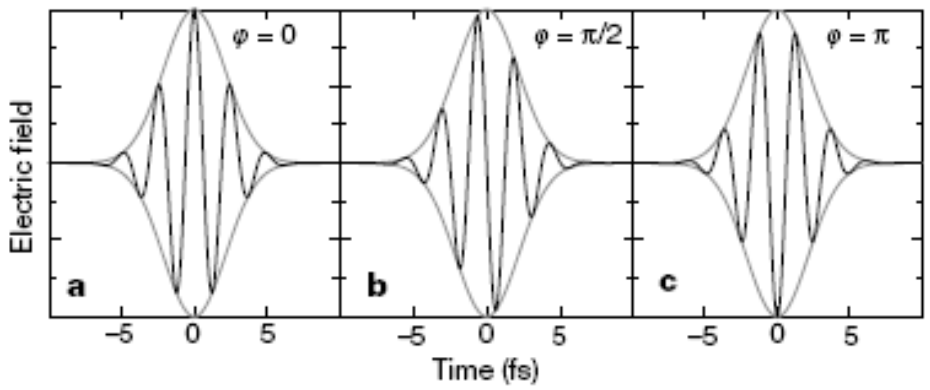


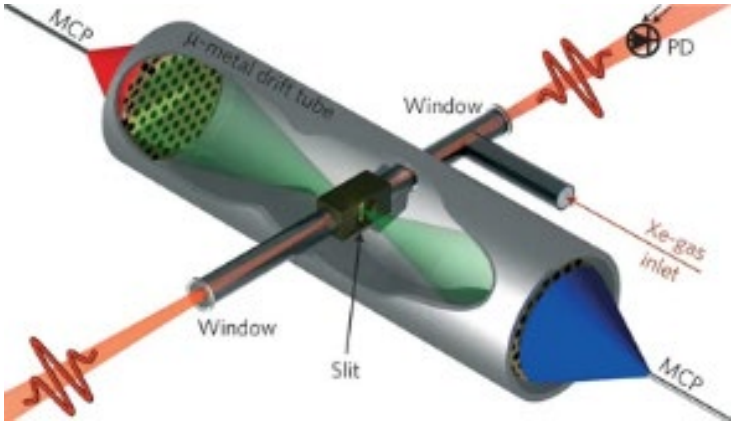
O. Smirnova et al., Nature 460, 972 (2009)

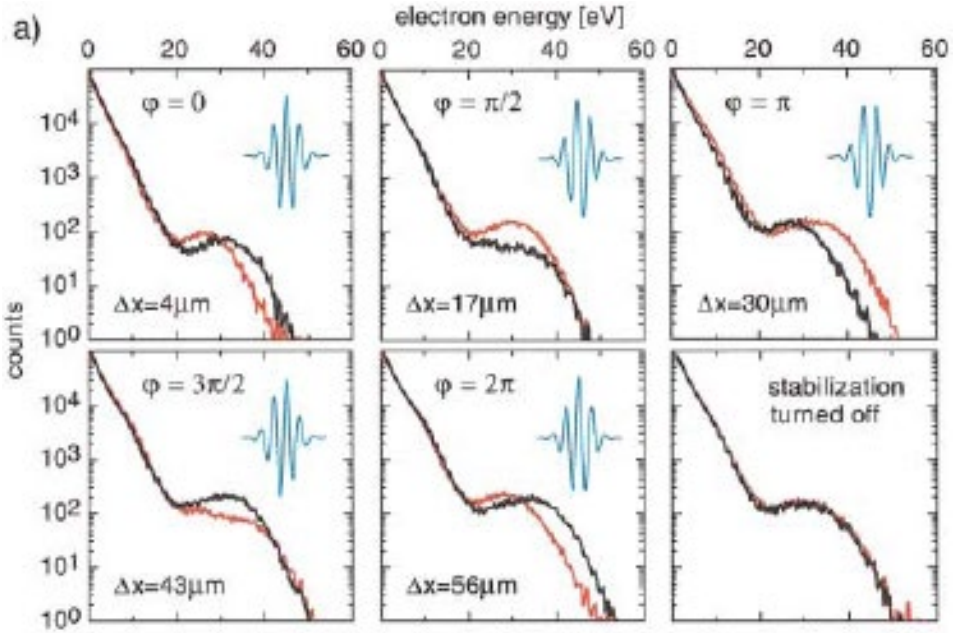
Contents

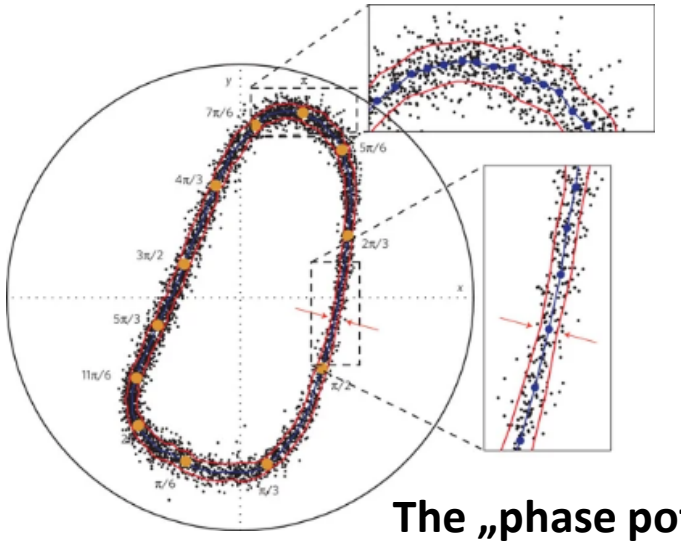
- Attosecond pump-probe spectroscopy in molecules

Lecture M2: CEP Effects in Atomic Ionization







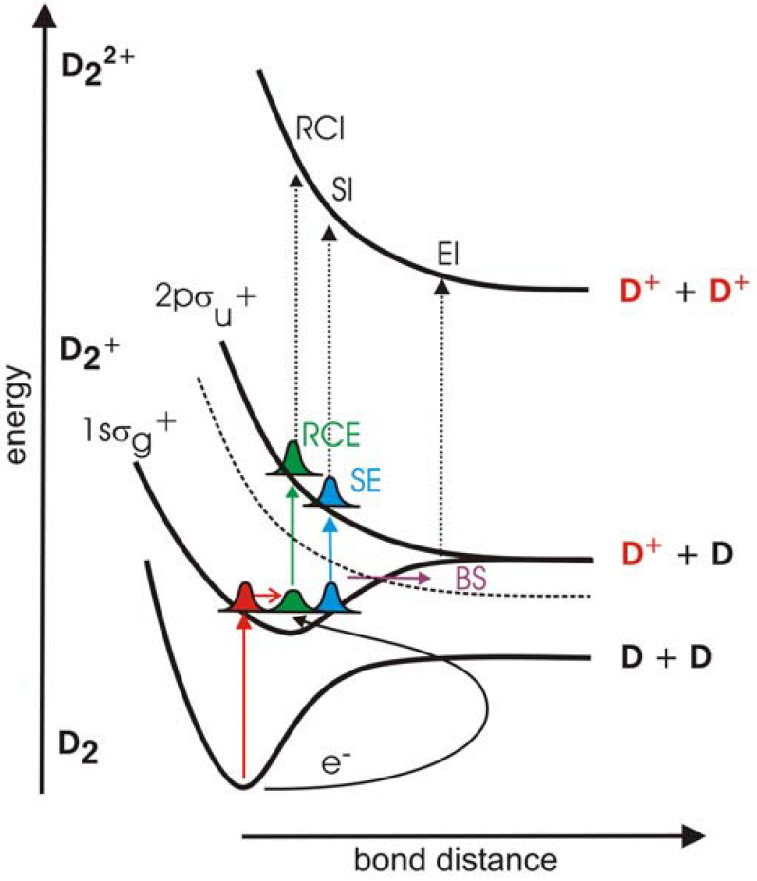


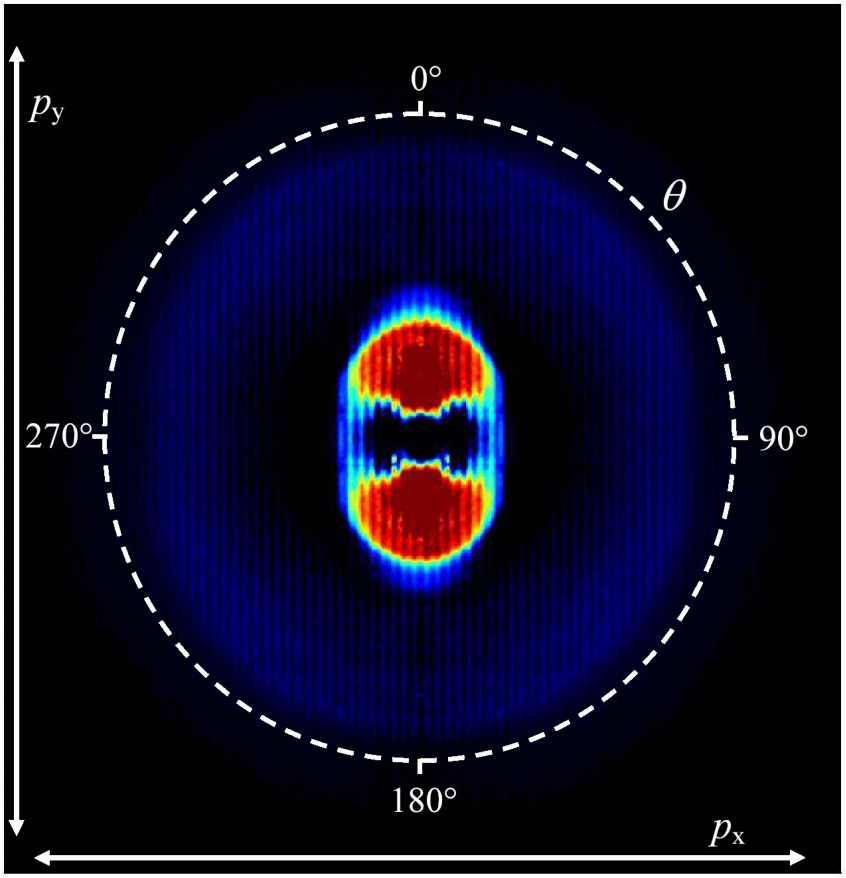
The „phase potato“

Can carrier envelope phase control electron motion *inside* molecules?

Paulus et al, Nature 414, 182 (2001)
Wittmann et al., Nat. Phys. 5, 357 (2009)

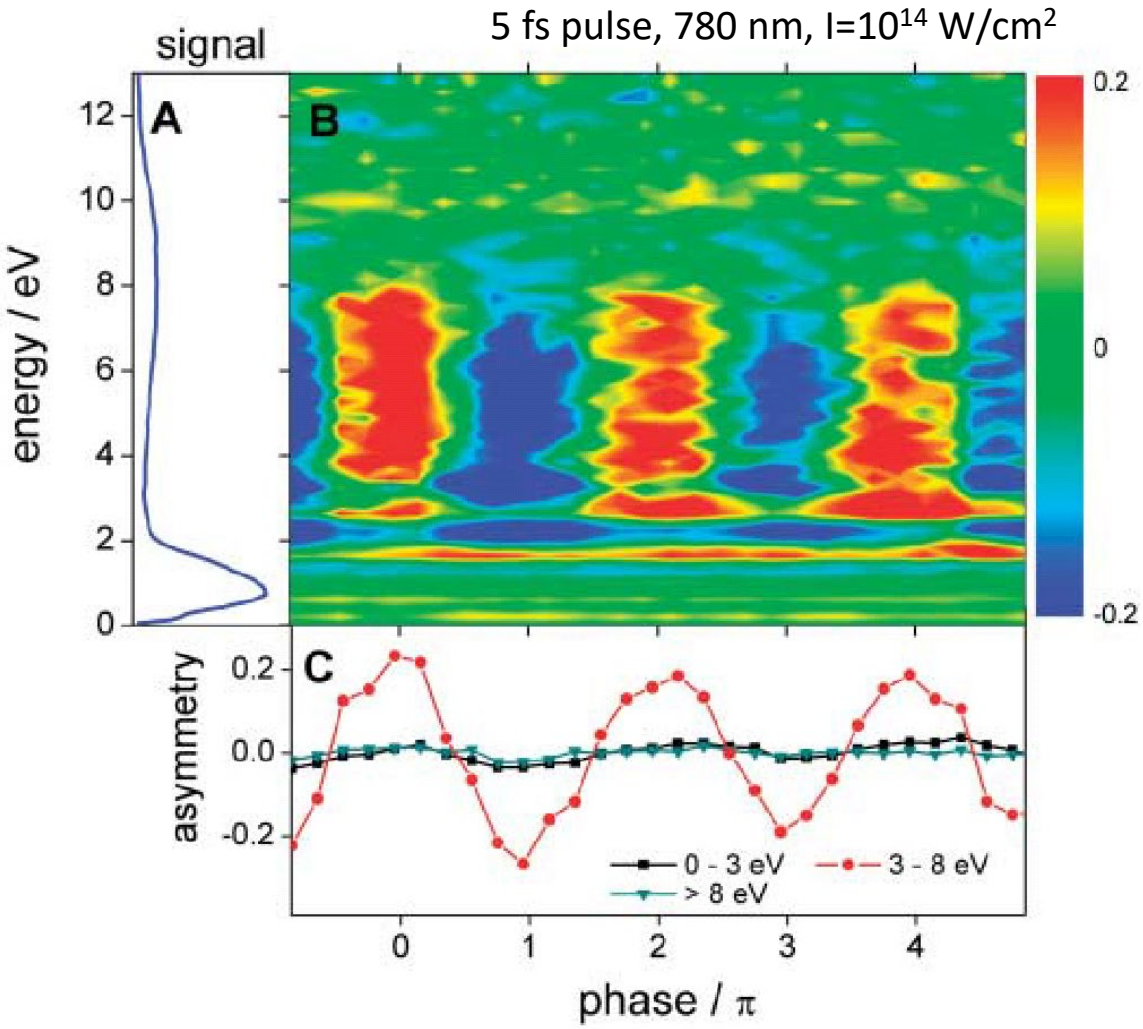
Attosecond electron dynamics in molecules CEP control of electron localization





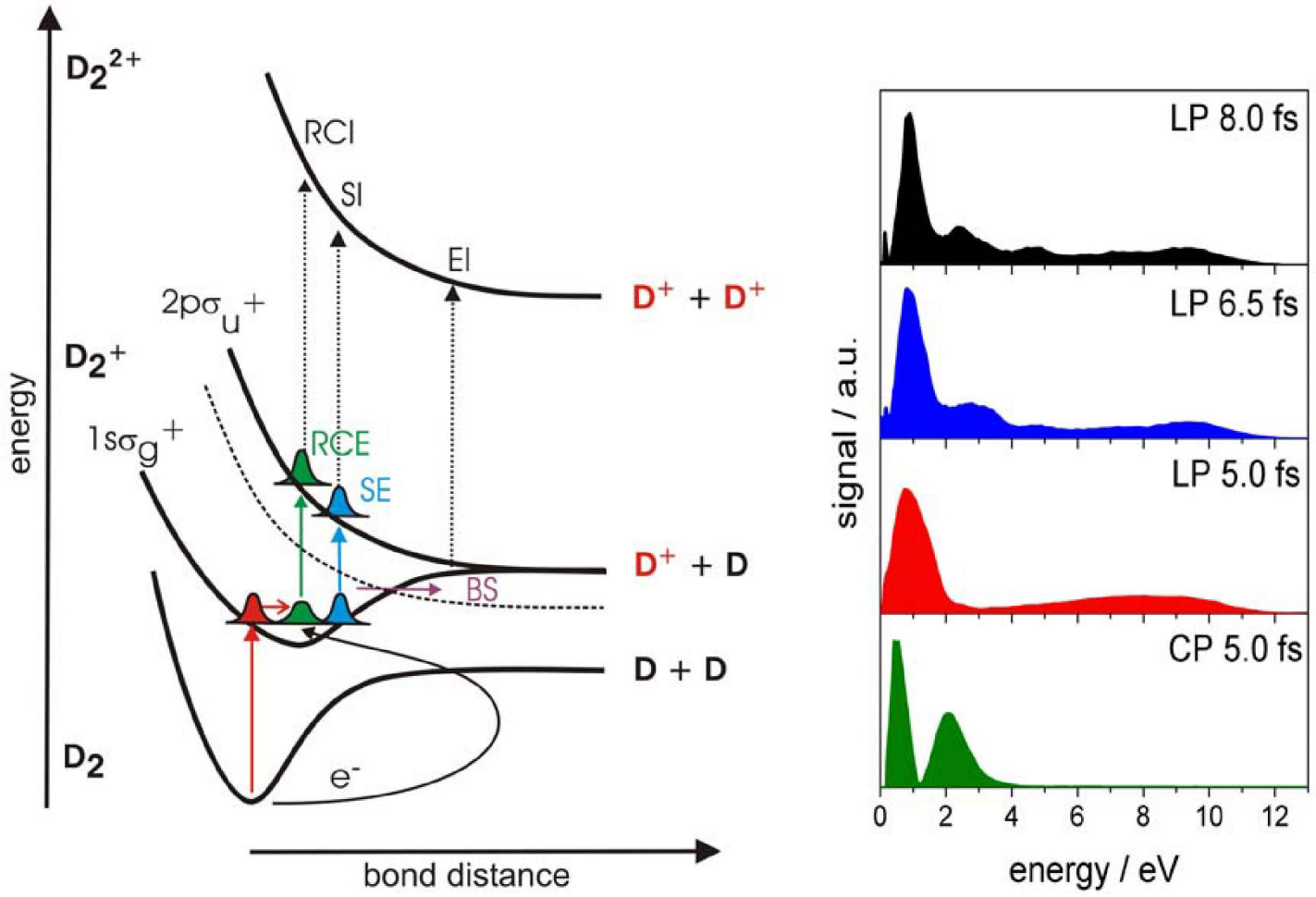
Angle-resolved D^+ ion imaging using CEP-locked few-cycle laser pulses (w. Ferenc Krausz)

Asymmetry $(D^+_{up}-D^+_{down})/(D^+_{up}+D^+_{down})$



M. Kling et al., *Science* 312, 246 (2006)

Phase Control Mechanism



Recollision-induced population of the $2p\sigma_u^+$ state

First example of importance of attosecond time-scale electron dynamics in a molecule

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

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

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

$$|l\rangle = \frac{1}{\sqrt{2}}\left(|g\rangle + |u\rangle\right)$$
$$|r\rangle = \frac{1}{\sqrt{2}}\left(|g\rangle - |u\rangle\right)$$

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

Phase-adiabatic/Quasi-static states

In phase-adiabatic/quasi static states the interaction of the laser field with the molecule is ***instantaneously*** taken into account.
The phase-adiabatic states are obtained by diagonalization of the potential energy operator V

$$\hat{V}(R,t) = \begin{pmatrix} -\omega_0/2 & V_{g,u} \\ V_{g,u} & \omega_0/2 \end{pmatrix}$$

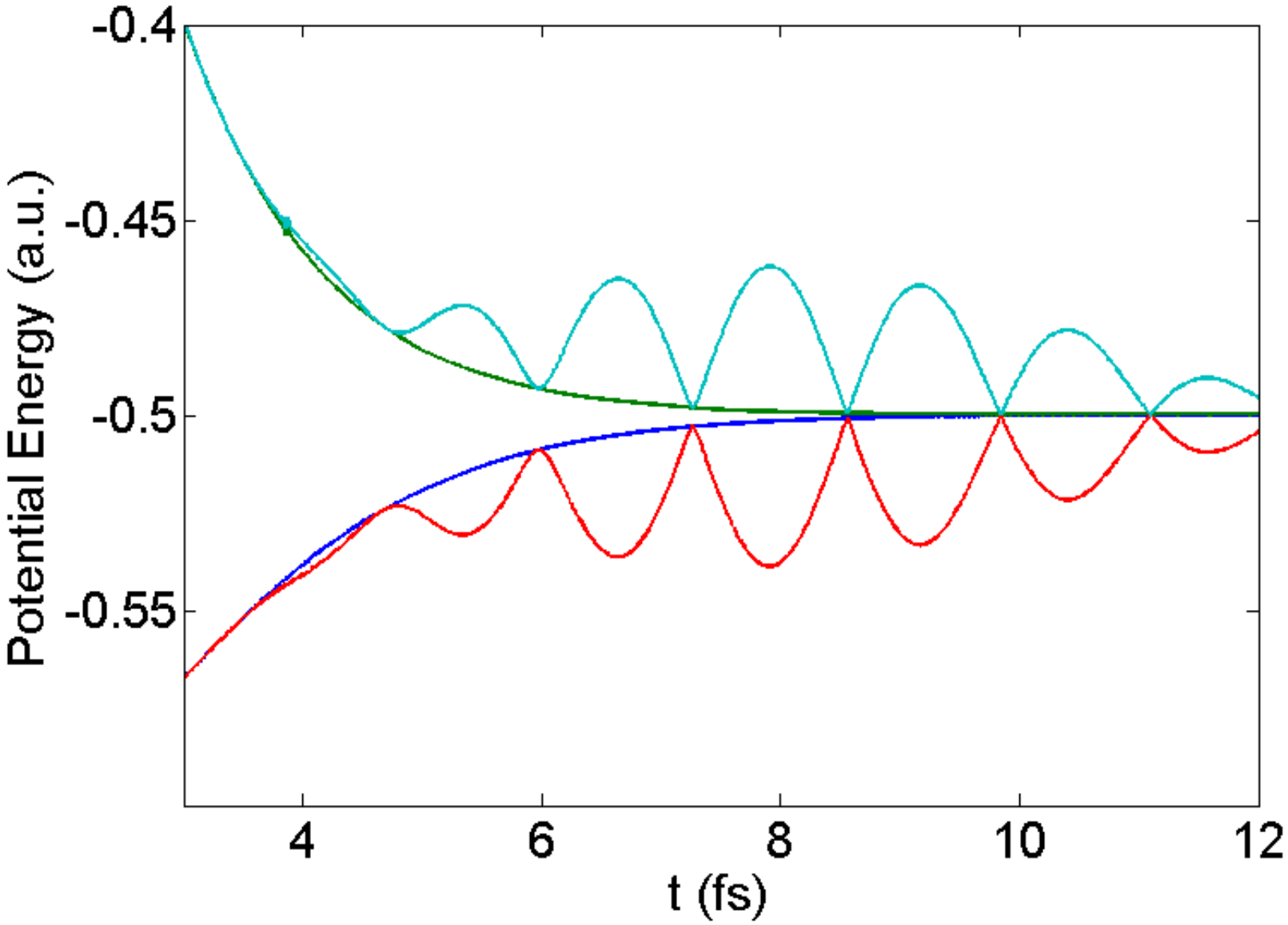
$$V_{g,u} = -\mu(R)E(t)$$

$$\omega_0 = V_u(R) - V_g(R)$$

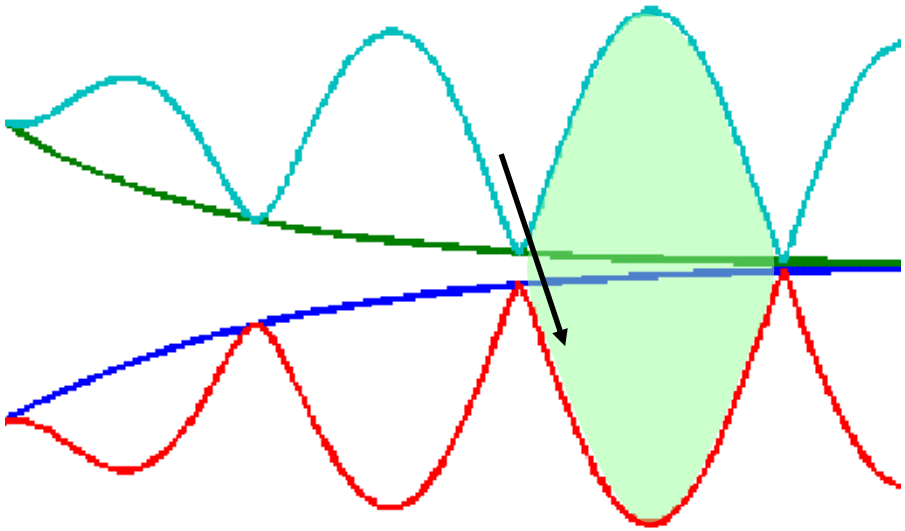
leading to the following expressions for the phase-adiabatic states

$$V_{1,2}(R,t) = \frac{V_g(R) + V_u(R)}{2} \mp \sqrt{\frac{\omega_0^2}{4} + V_{g,u}^2}$$

Phase-adiabatic/Quasi-static states



Modelling in terms of a sequence of laser-induced Landau-Zener transitions

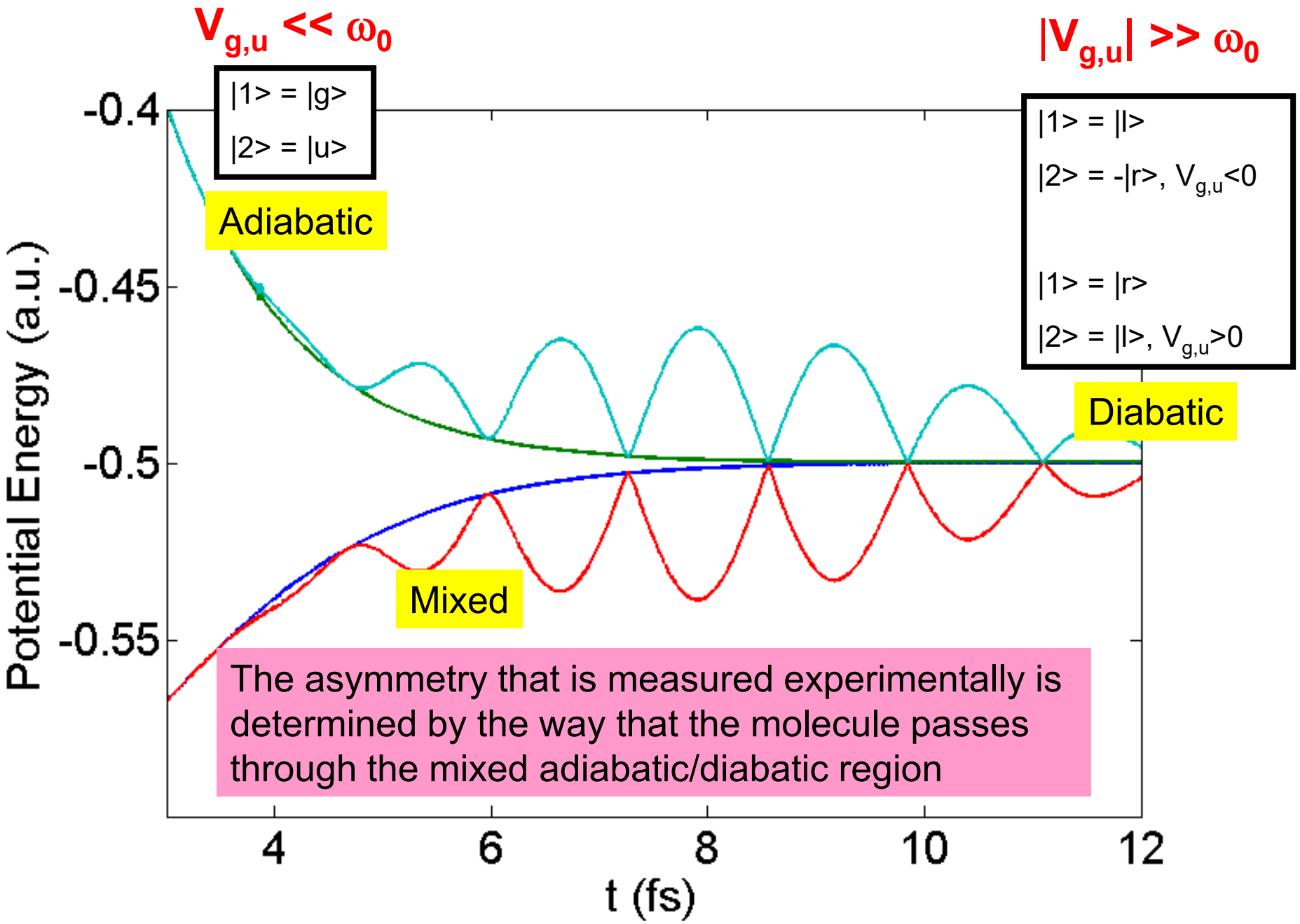


$$W_{1,2} \propto e^{-\frac{\pi \omega_0^2}{4\omega_l \mu E_0}}$$

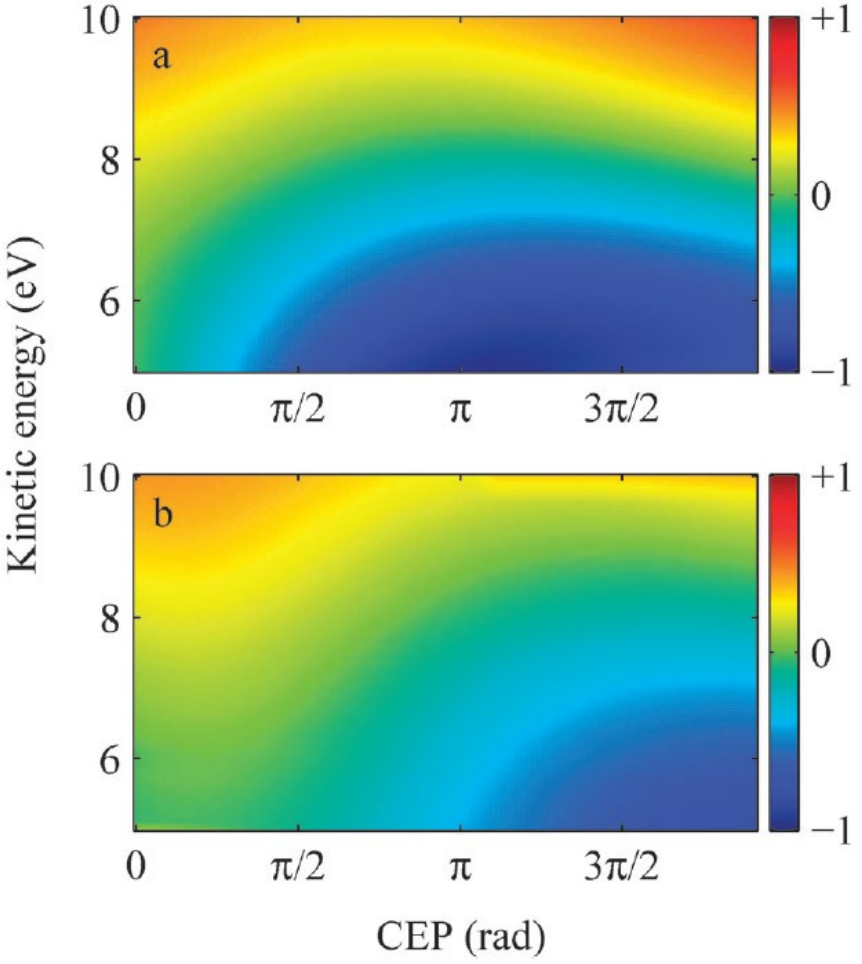
$$\omega_0 = V_u(R) - V_g(R)$$

$$E(t) = E_0 \sin \omega_l t$$

Sequence of Landau-Zener crossings and propagation in the laser field


$V_{g,u} << \omega_0$
$|V_{g,u}| >> \omega_0$
|1> = |g>
|2> = |u>
Adiabatic
|1> = |l>
|2> = -|r>, $V_{g,u}$<0
|1> = |r>
|2> = |l>, $V_{g,u}$>0
Diabatic
Mixed
The asymmetry that is measured experimentally is determined by the way that the molecule passes through the mixed adiabatic/diabatic region
Potential Energy (a.u.)
-0.4
-0.45
-0.5
-0.55
4
6
8
10
12
t (fs)

Energy dependence of the asymmetry using Landau-Zener formulation

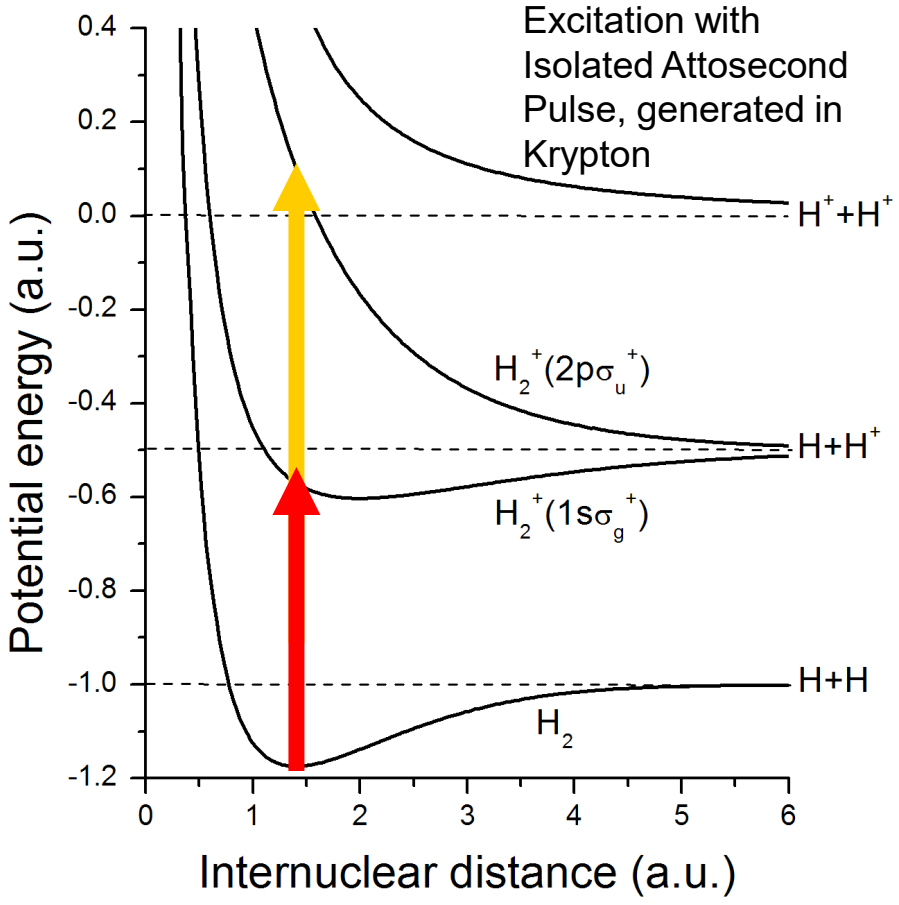


TDSE

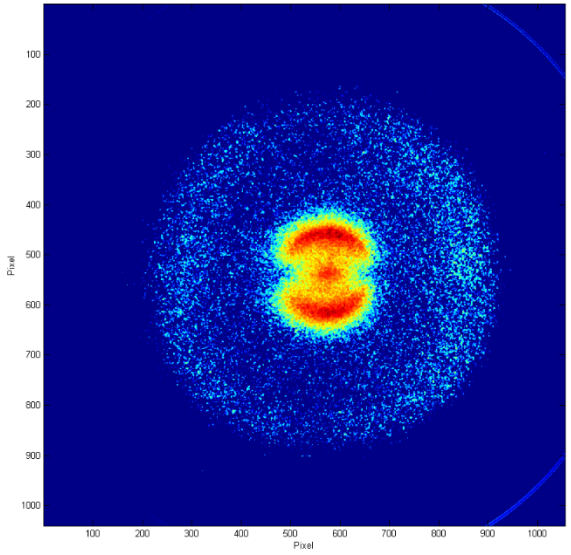
LZ

F. Kelkensberg et al, PCCP 13, 8647 (2011)

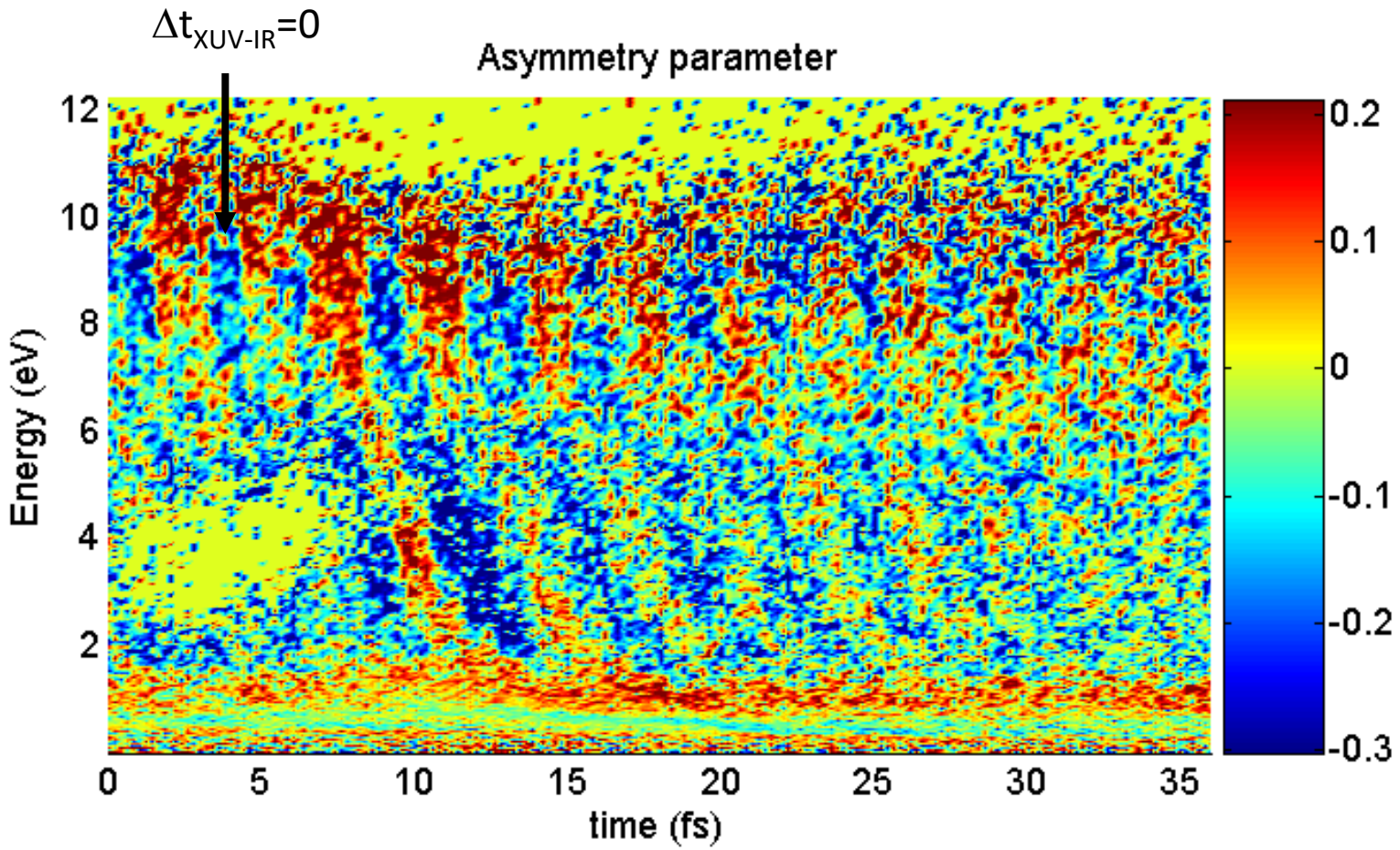
XUV-IR Pump-probe experiments on H_2 and D_2



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 H_2 and D_2



Sansone et al., Nature 465, 763 (2010)

Electron localization in H_2^+

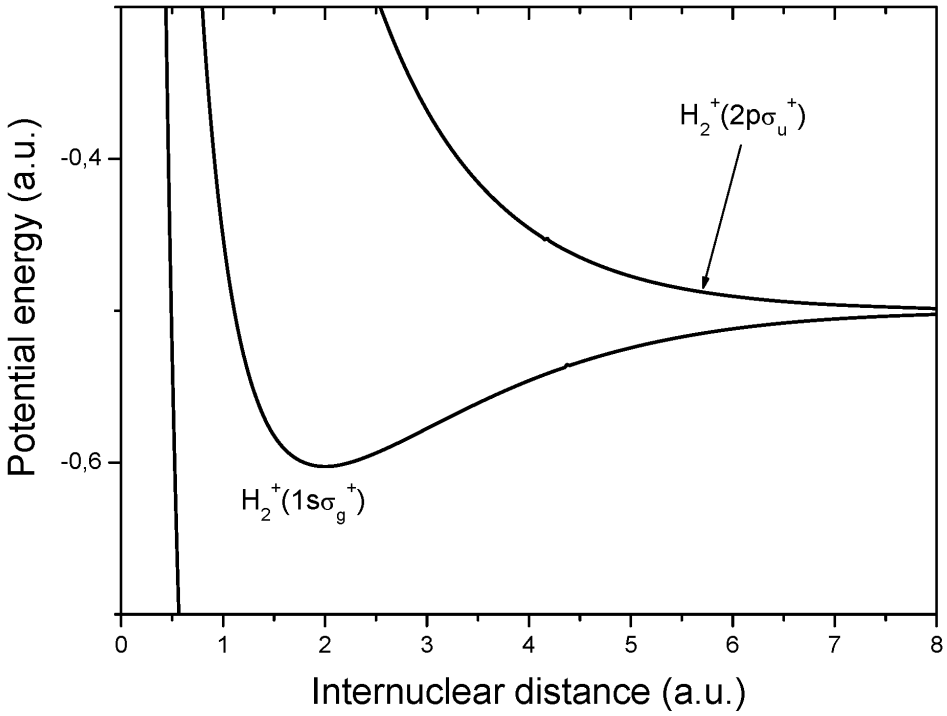
$$\psi_g = (1/\sqrt{2})\{\psi_{left} + \psi_{right}\}$$

$$\psi_u = (1/\sqrt{2})\{\psi_{left} - \psi_{right}\}$$

Rewrite

$$\psi_{left} = (1/\sqrt{2})\{\psi_g + \psi_u\}$$

$$\psi_{right} = (1/\sqrt{2})\{\psi_g - \psi_u\}$$



The observation of electron localization requires that the parity of the ionic wavefunction is broken

Consider the wavefunction of the ion+electron

$$\Psi = c_1[\psi_g \varepsilon l_g]_g + c_2[\psi_g \varepsilon l_u]_u + c_3[\psi_u \varepsilon l_u]_g + c_4[\psi_u \varepsilon l_g]_u$$

Rewrite

$$\Psi = \frac{1}{2}\sqrt{2}(c_1 + c_4)\psi_l \; \varepsilon l_{gf} + \frac{1}{2}\sqrt{2}(c_2 + c_3)\psi_l \; \varepsilon l_{uf}$$
$$+ \frac{1}{2}\sqrt{2}(c_1 - c_4)\psi_r \; \varepsilon l_{gg} + \frac{1}{2}\sqrt{2}(c_2 - c_3)\psi_r \; \varepsilon l_{gu}$$

Determine the probability the bound electron / fragment ion is found on the right or on the left.

Consider the wavefunction of the ion+electron

$$\Psi = \frac{1}{2}\sqrt{2}(c_1 + c_4)\psi_{left}\,\varepsilon_{left} + \frac{1}{2}\sqrt{2}(c_2 + c_3)\psi_{left}\,\varepsilon_{left}$$

$$+ \frac{1}{2}\sqrt{2}(c_1 - c_4)\psi_{right}\,\varepsilon_{right} + \frac{1}{2}\sqrt{2}(c_2 - c_3)\psi_{right}\,\varepsilon_{right}$$

$$I_{left} = \frac{1}{2}\left|c_1 + c_4\right|^2 + \frac{1}{2}\left|c_2 + c_3\right|^2 \qquad I_{right} = \frac{1}{2}\left|c_1 - c_4\right|^2 + \frac{1}{2}\left|c_2 - c_3\right|^2$$

Dipole selection rules **forbid** that a difference occurs between I_{left} and I_{right} in single-photon ionization, since c_1 and c_3 are zero

Consider the wavefunction of the ion+electron

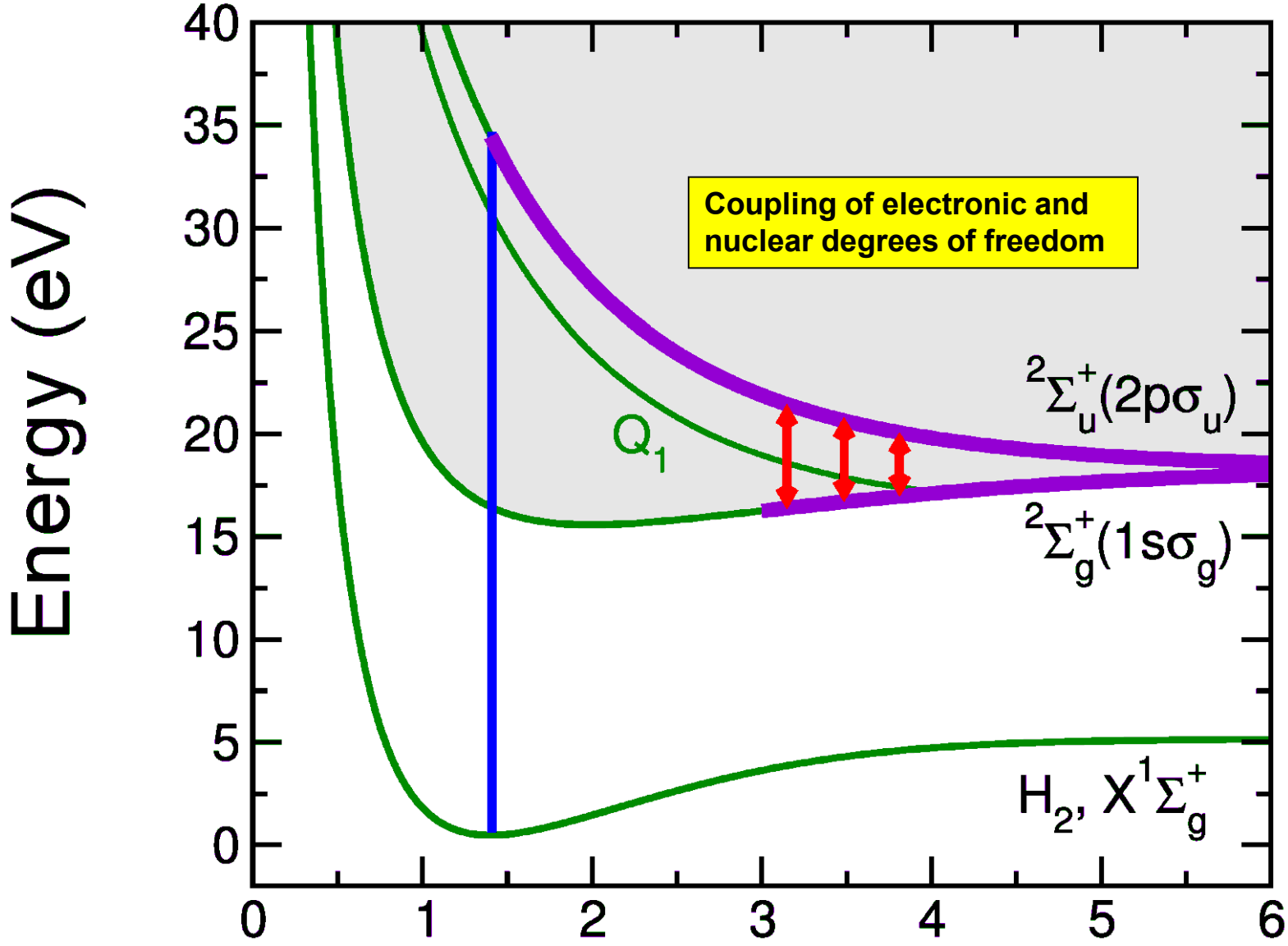
$$\Psi = c_1[\psi_g \mathcal{E}l_g]_g + c_2[\psi_g \mathcal{E}l_u]_u + c_3[\psi_u \mathcal{E}l_u]_g + c_4[\psi_u \mathcal{E}l_g]_u$$

We can imaging two ways to construct a coherent superpositon of the „g“ and „u“ state starting from this wavefunction

(1) Use the laser to convert „g“ into „u“ or „u“ into „g“ (remember electron localization with CEP-stable few-cycle pulses)

(2) Take one of the allowed terms in the expression shown above and change the angular momentum of the photoelectron from „u“ to „g“ or from „g“ to „u“

Mechanism I


Energy (eV)
40
35
30
25
20
15
10
5
0
0
1
2
3
4
5
6
Coupling of electronic and nuclear degrees of freedom
$^2\Sigma_u^+(2p\sigma_u)$
Q_1
$^2\Sigma_g^+(1s\sigma_g)$
H_2, $X\,^1\Sigma_g^+$

Once more: Phase-adiabatic/Quasi-static states

In phase-adiabatic/quasi static states the interaction of the laser field with the molecule is ***instantaneously*** taken into account.
The phase-adiabatic states are obtained by diagonalization of the potential energy operator V

$$\hat{V}(R,t) = \begin{pmatrix} -\omega_0/2 & V_{g,u} \\ V_{g,u} & \omega_0/2 \end{pmatrix}$$

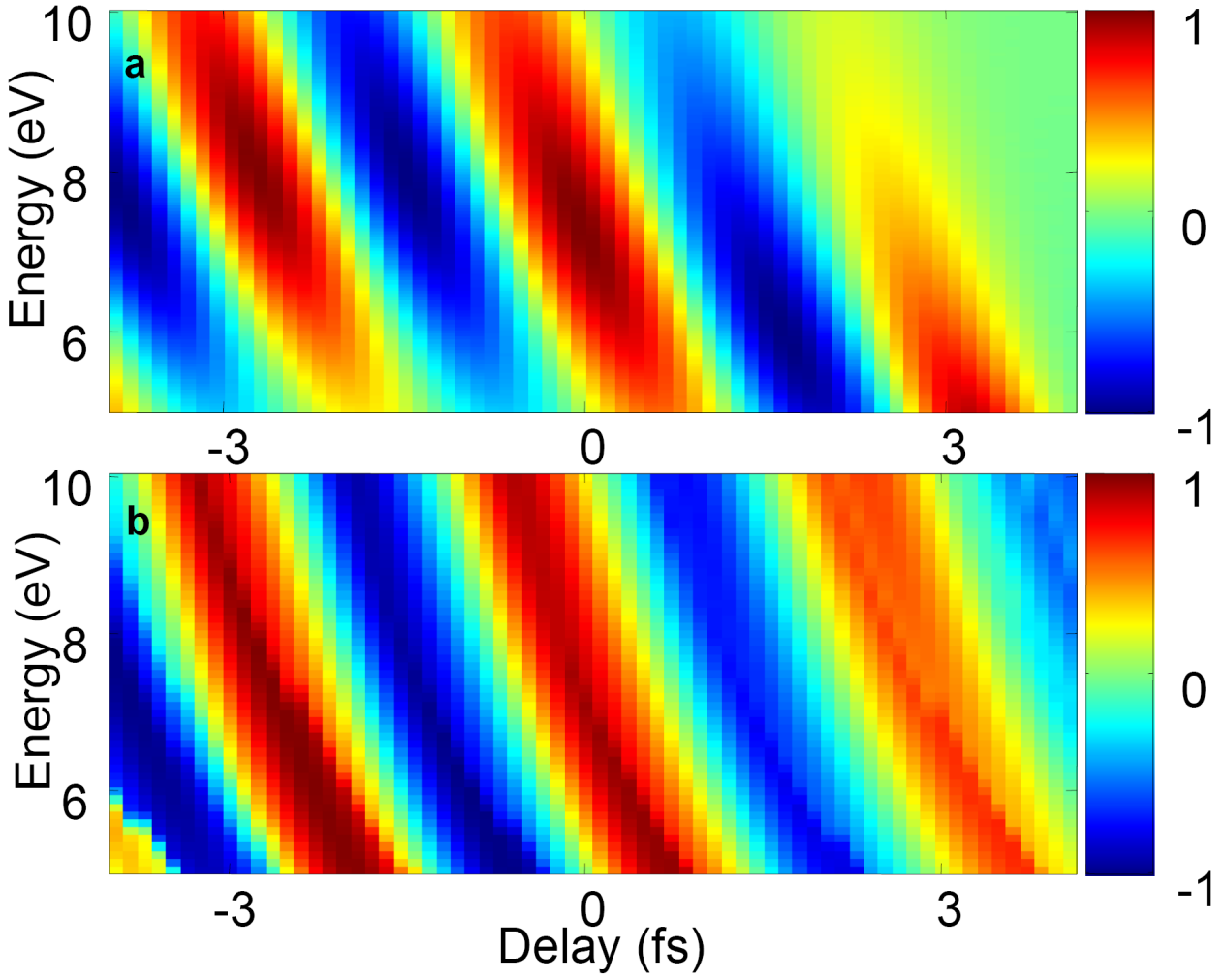
$$V_{g,u} = -\mu(R)E(t)$$

$$\omega_0 = V_u(R) - V_g(R)$$

leading to the following expressions for the phase-adiabatic states

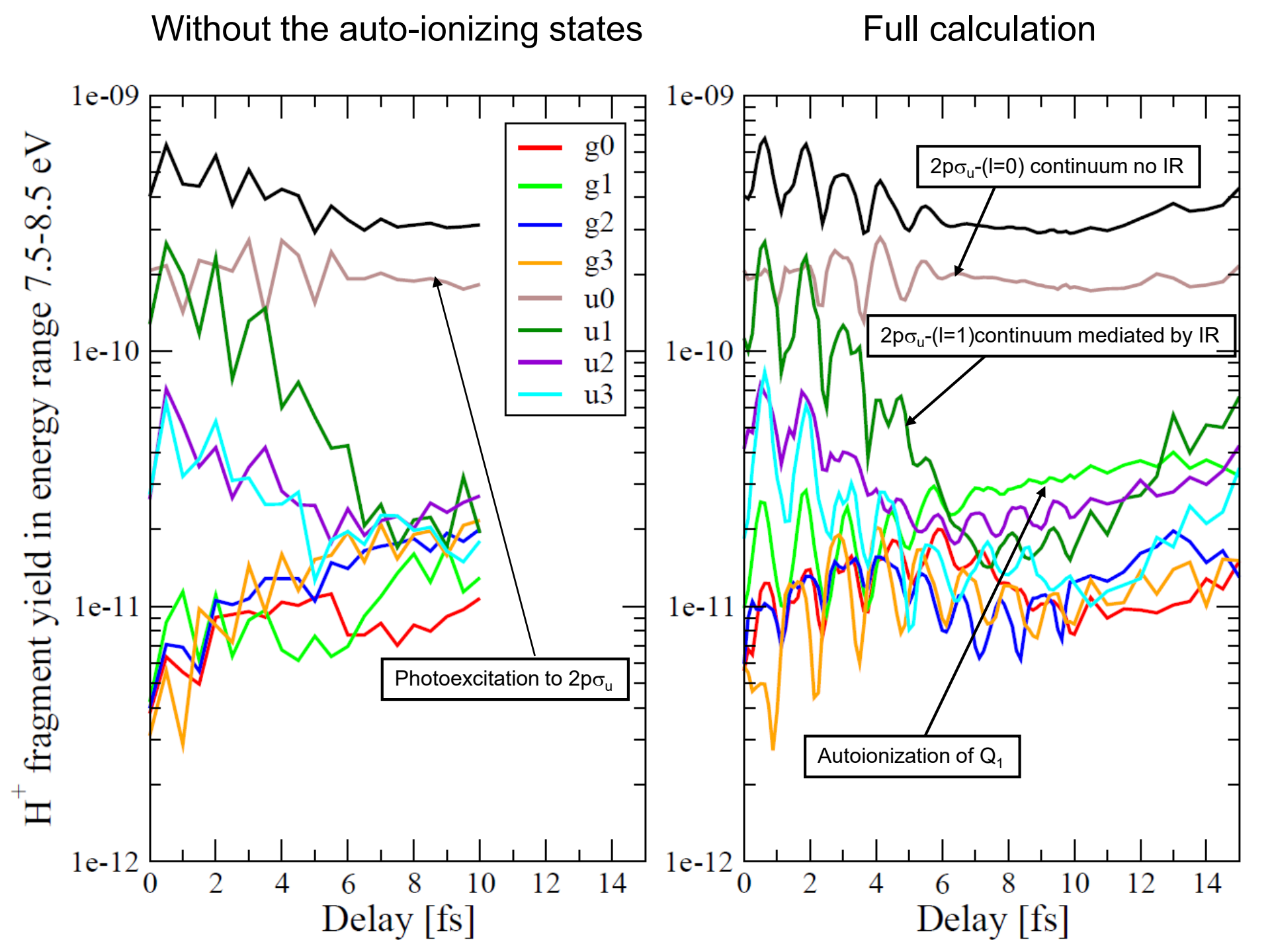
$$V_{1,2}(R,t) = \frac{V_g(R) + V_u(R)}{2} \mp \sqrt{\frac{\omega_0^2}{4} + V_{g,u}^2}$$

Energy dependence of the asymmetry using Landau-Zener formulation

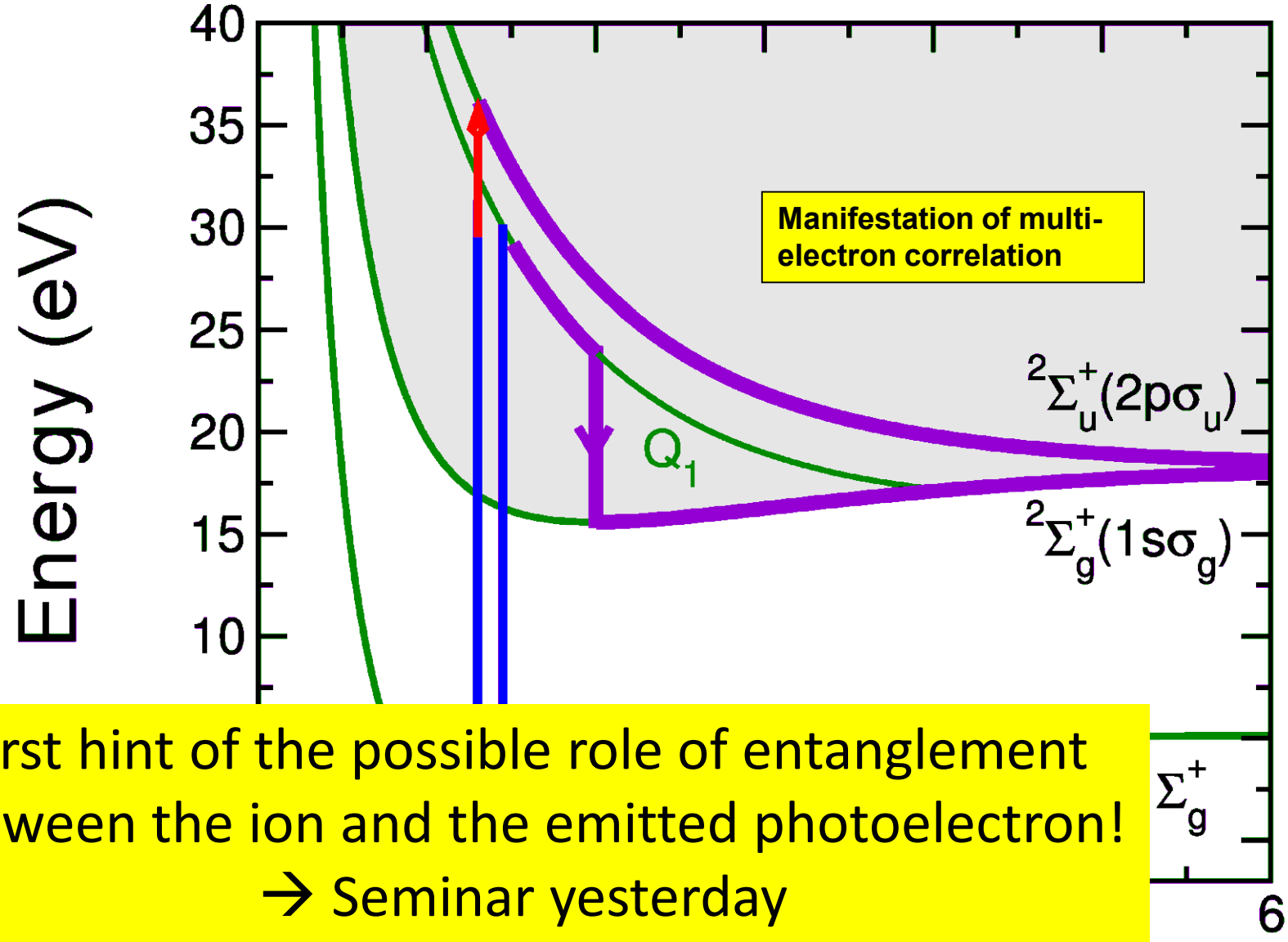


F. Kelkensberg et al., Phys. Chem. Chem. Phys. 13, 8647 (2011)

Collaboration with F. Martin and co-workers
Copyright 2005. Barcelona Supercomputing Center - BSC


Without the auto-ionizing states
Full calculation
H+ fragment yield in energy range 7.5-8.5 eV
1e-09
1e-10
1e-11
1e-12
0
2
4
6
8
10
12
14
Delay [fs]
g0
g1
g2
g3
u0
u1
u2
u3
Photoexcitation to 2pσu
2pσu-(l=0) continuum no IR
2pσu-(l=1)continuum mediated by IR
Autoionization of Q1

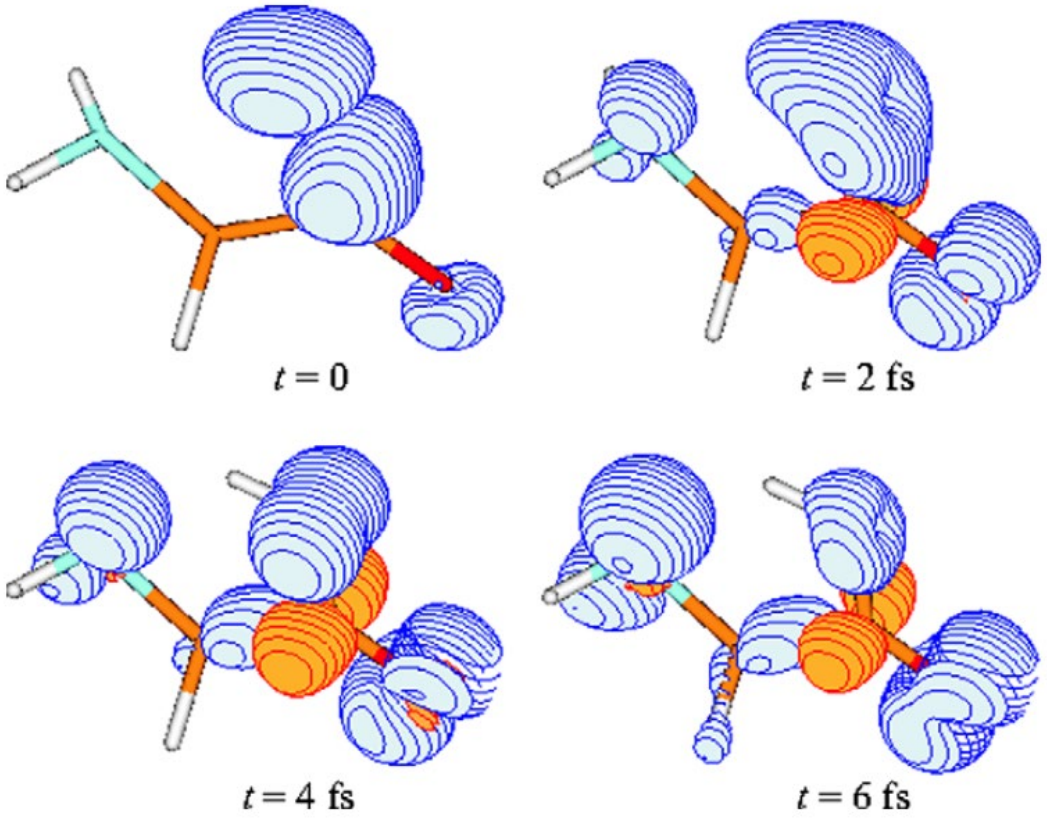
Mechanism II



First hint of the possible role of entanglement between the ion and the emitted photoelectron!
→ Seminar yesterday

The Holy Grail: Attosecond electron dynamics in complex molecules

Charge migration upon sudden ionization (Glycine II):



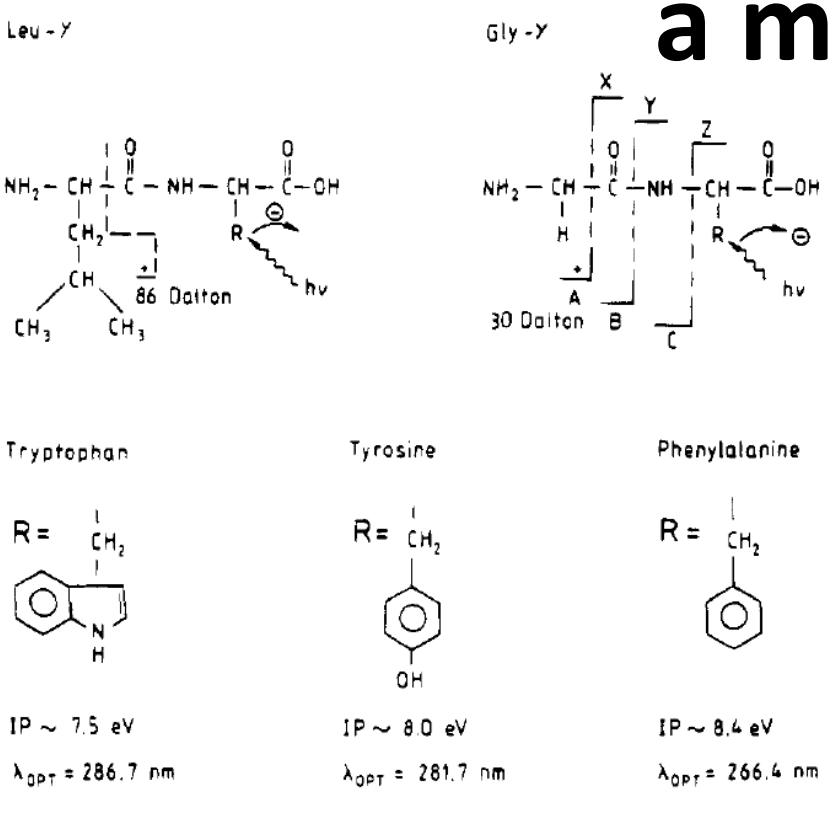
electron density

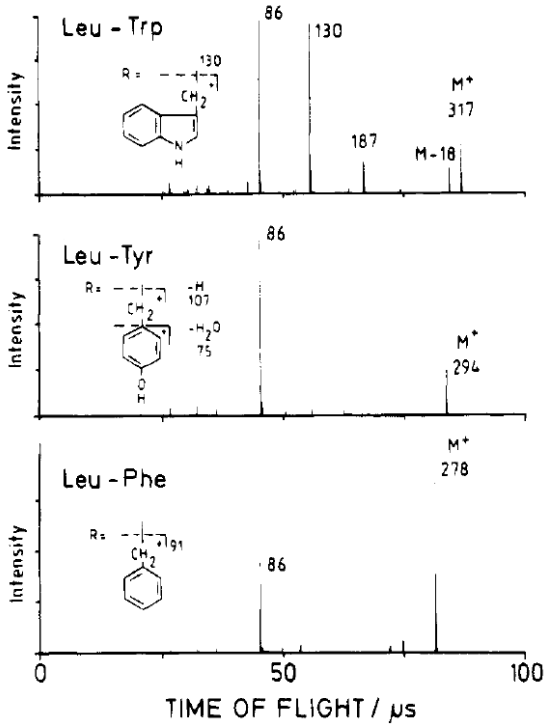
hole density

Coherent preparation of ionic states

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

Attosecond electron dynamics in a molecule





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

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

Electron correlation-induced charge migration

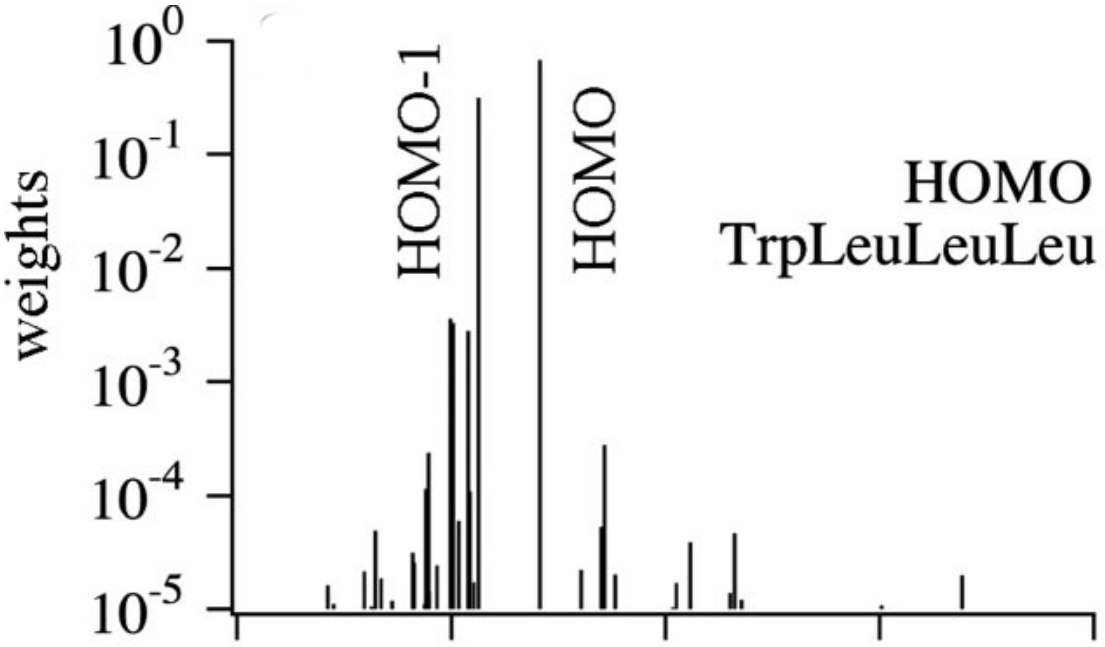
Koopmans´theorem: the first ionization energy of a molecular system is equal to the negative of the orbital energy of the highest occupied molecular orbital (HOMO)

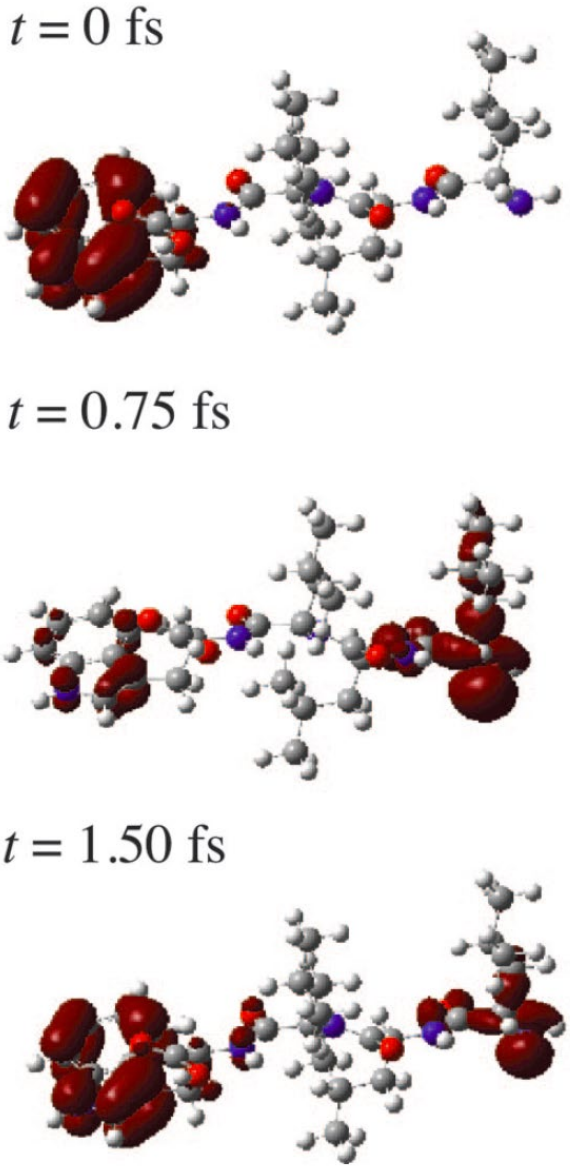
→ Removal of single electrons requires a certain amount of energy and leaves the orbitals of all other electrons *unchanged*.

Attosecond dynamics in molecules can result from a breakdown of Koopmans theorem

→ Removal of single electrons leads to the excitation of multiple ionic states, which have different energies → coherent evolution of the hole in the charge density without participation of nuclear degrees of freedom („charge migration“)

Example: $TrpLeu_3$ complex



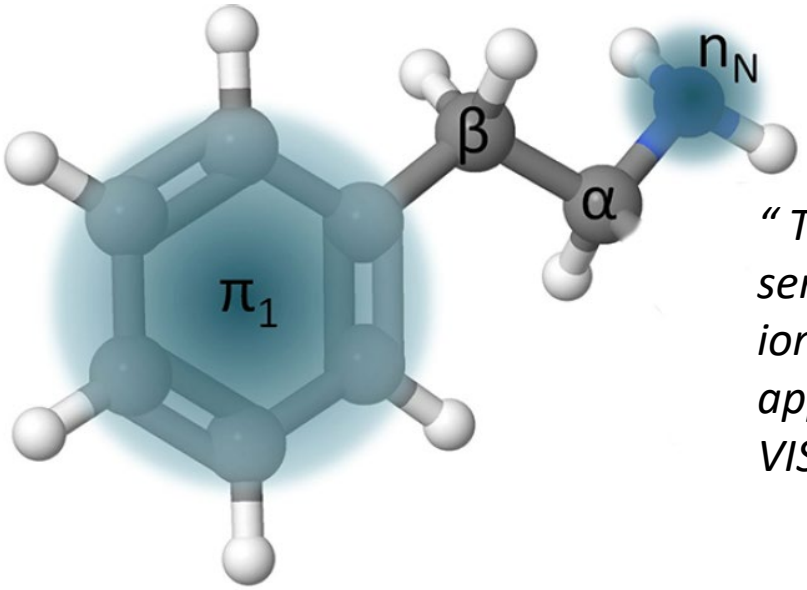


The highest-occupied-molecular orbital (HOMO) of TrpLeu3 ionizes predominantly into the ground (HOMO) and first excited (HOMO-1) state of the cation, which are separated by 2.84 eV (0.105 a.u.)

Anticipate beat period of $2\pi/\Delta E$ = 60 a.u. = 1.45 fs

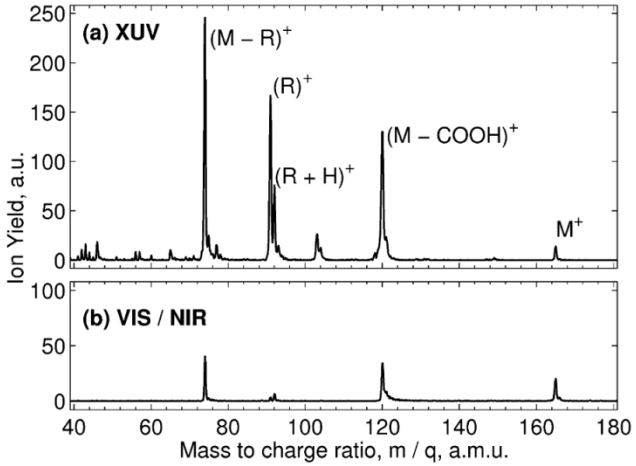
Remacle & Levine, PNAS 103 6793 (2006)

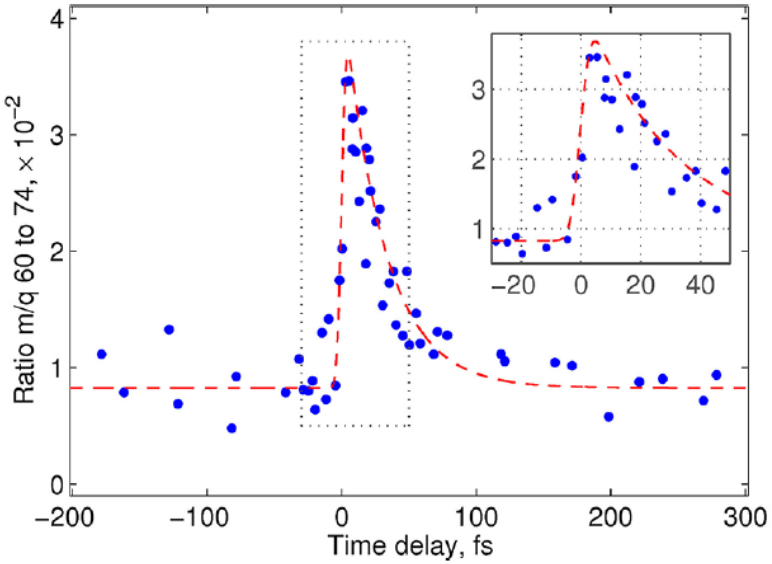
First experimental demonstration?



Phenylalanine → Doubly-charge immonium

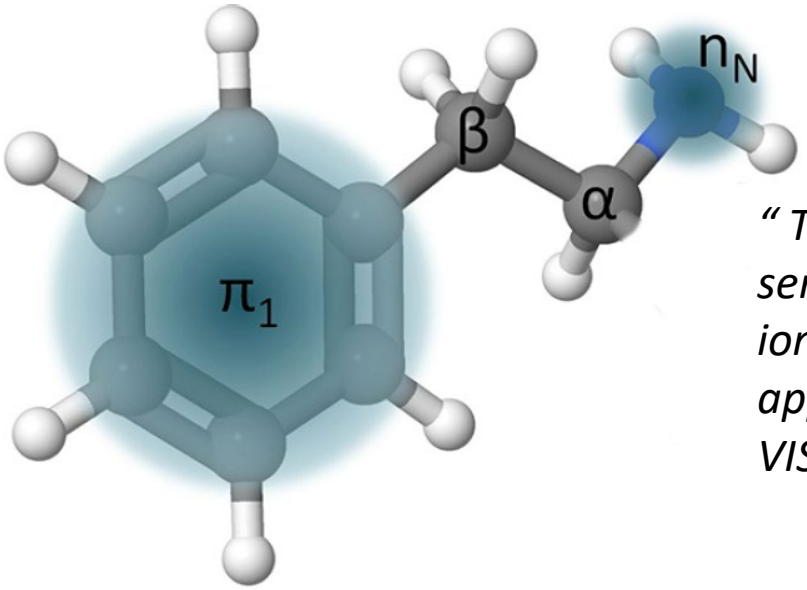
" The yield of immonium dications is a particularly sensitive probe of charge location because the local ionization potential will increase as the hole approaches the amine group causing ionization by the VIS/NIR pulse to be suppressed."





Belshaw et al., J. Phys. Chem. Lett. 3, 3751 (2012)

Yes: First experimental demonstration



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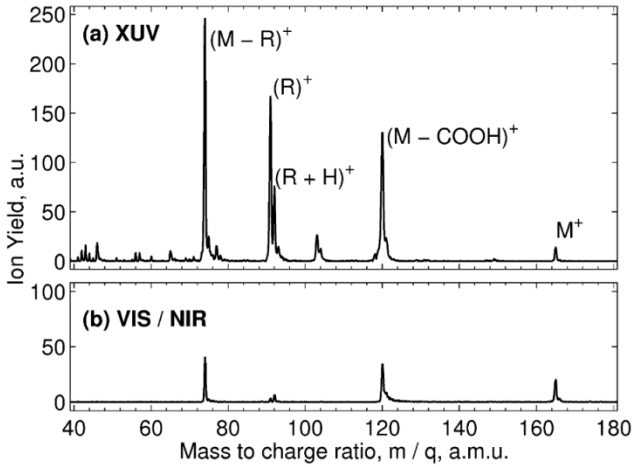
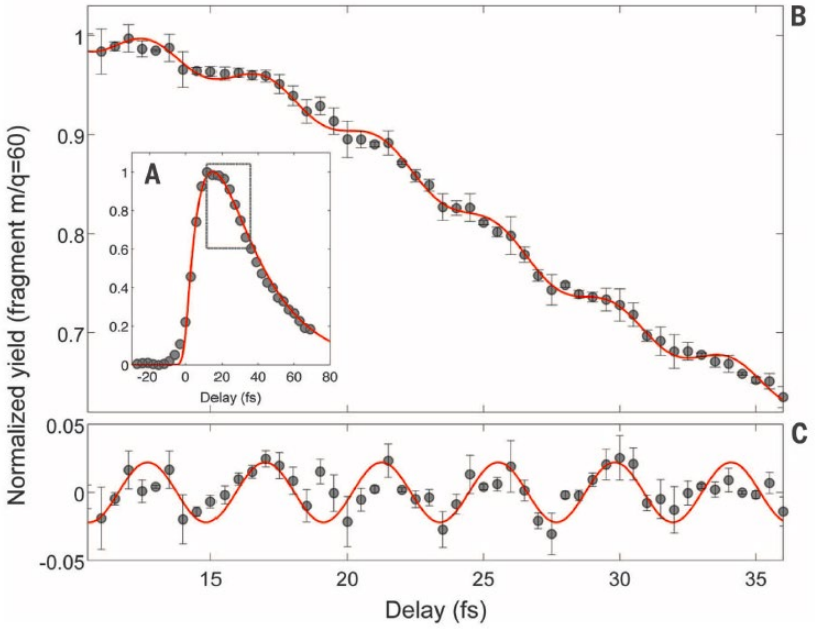
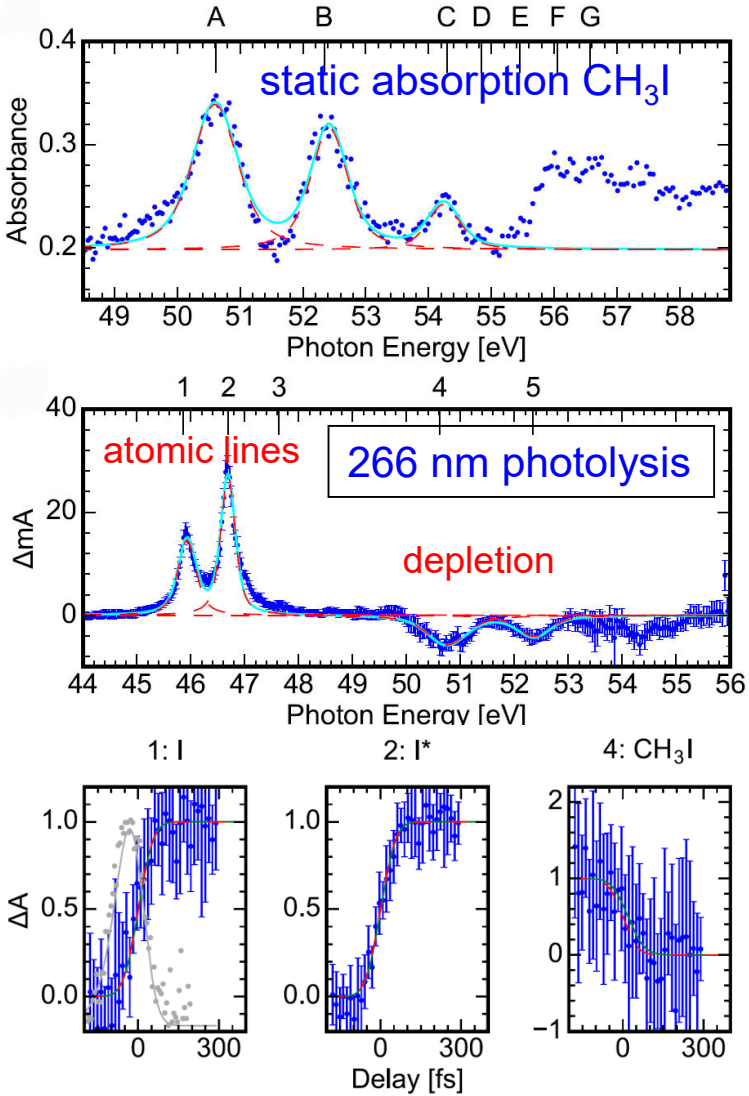


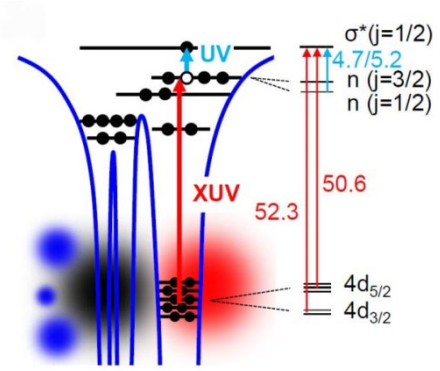


F. Calegari et al., Science 346, 6207 (2014)

Transient absorption with femtosecond time-resolution and atomic specificity

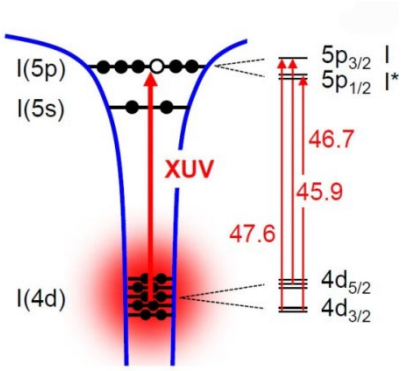


Before dissociation

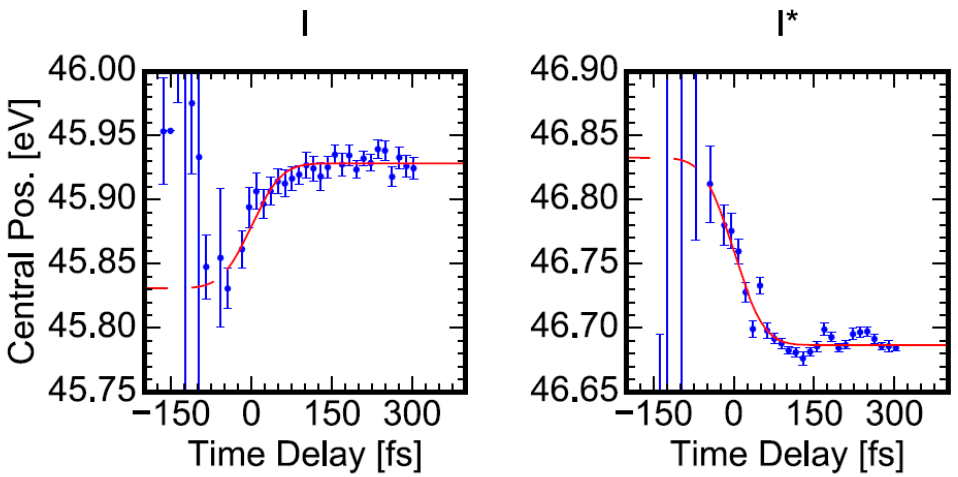


„molecular“

After dissociation

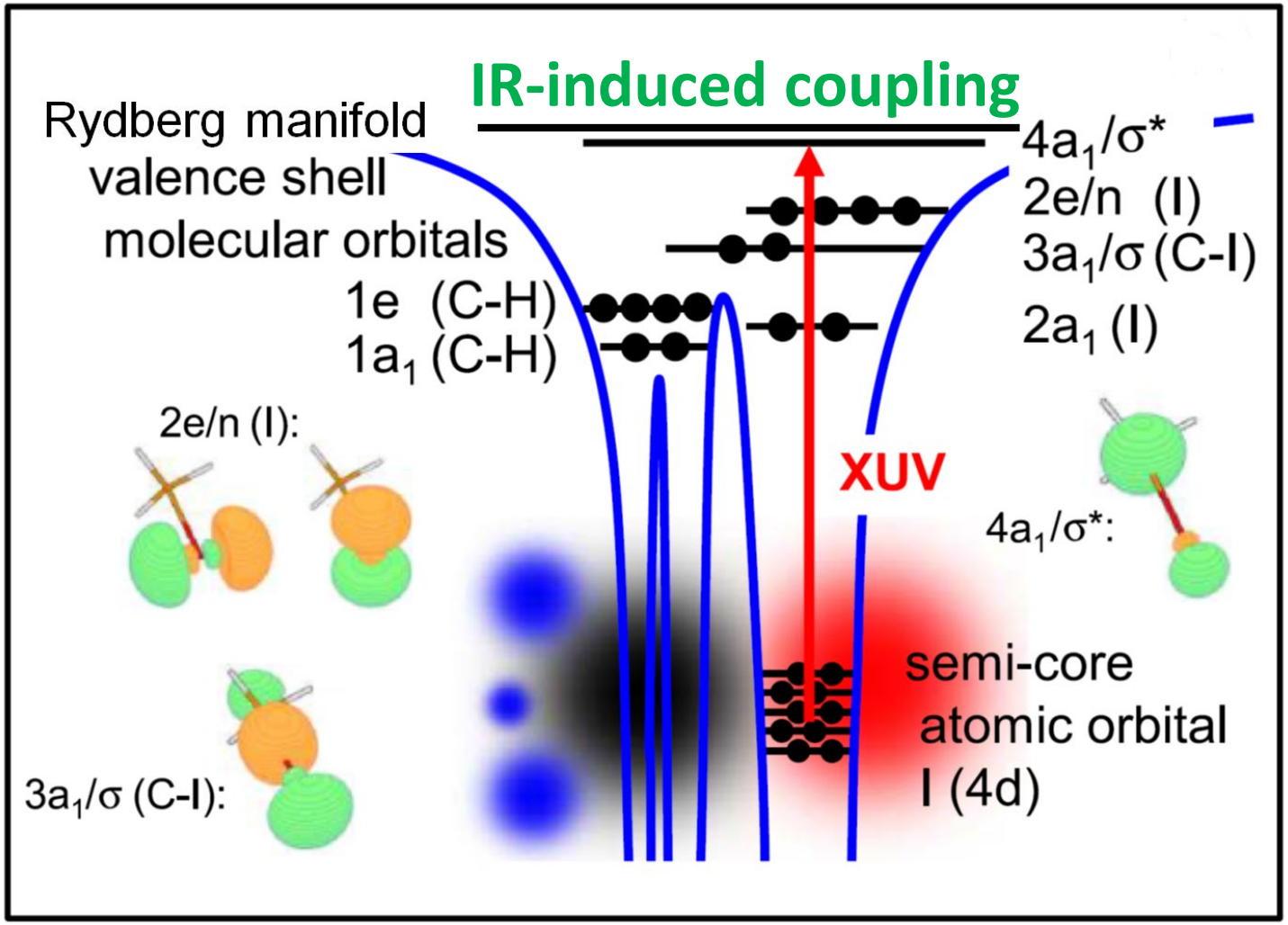


„atomic“



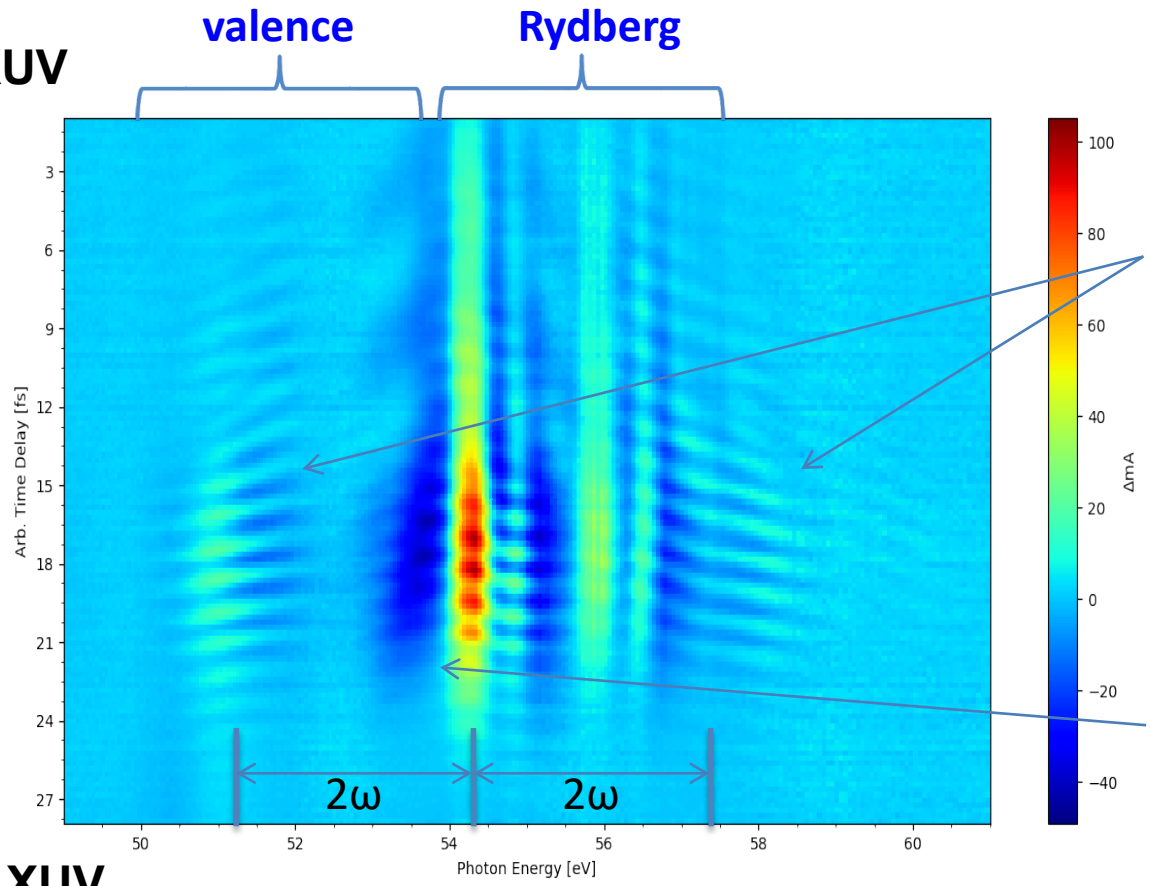
Drescher et al., J. Chem. Phys. 145, 011101 (2016)

Transient absorption with attosecond time-resolution and atomic specificity



L. Drescher, J. Phys. Chem. Lett. 10, 265 (2019)

Transient absorption with as time-resolution and atomic specificity



Light-induced states: New absorption features shifted by 2x IR photon energy during overlap.

Light-induced phase: Lineshape modulated due to AC Stark shift.

Dominant response now on Rydberg states, rather than valence states!

L. Drescher, J. Phys. Chem. Lett. 10, 265 (2019)

Useful materials for further reading:

J. Posthumus, *Molecules in Intense Laser Fields,* Rep. Progr. Phys. 67, 623-655 (2004)

P. Agostini and L. Dimauro, „The physics of attosecond light pulses”, Rep. Prog. Phys. 67, 813 (2004).

F. Krausz and M. Ivanov, “Attosecond physics”, Rev. Mod. Phys. 81, 163 (2009)

+ several chapters in „Attosecond and XUV Physics“ (ed. by M.J.J. Vrakking and Th. Schultz, Wiley, december 2013)