Ultrafast charge migration following ionization

driven by electron correlation and relaxation

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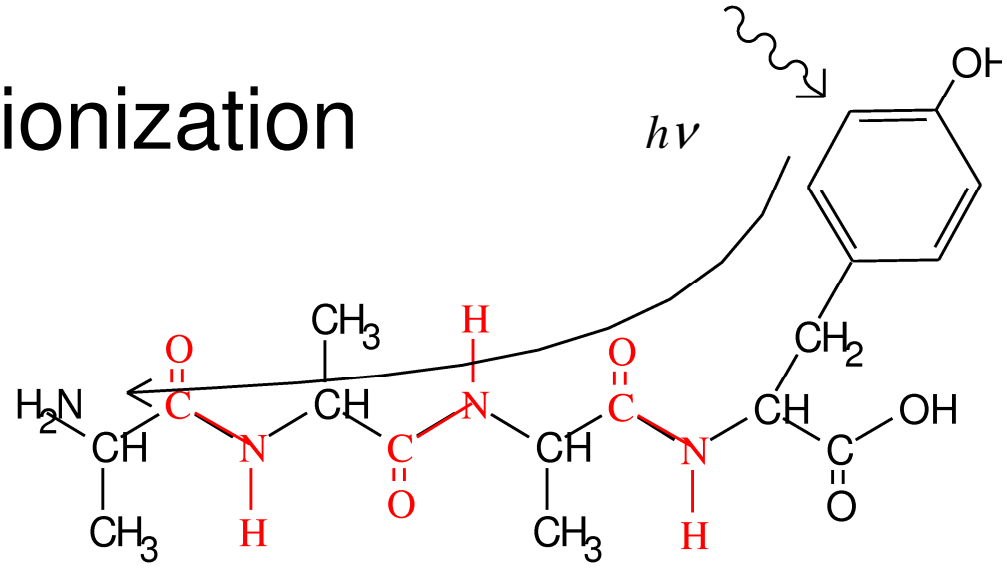
Motivation

- Understanding of charge transport in Nature, like in photosynthesis
- Role of electron correlation and relaxation

Charge transfer in Peptides

Fragmentation after ionization of the benzene ring



Alanin – alanin – alanin - tyrosin

R. Weinkauf et al., *J. Phys. Chem.* **1996**, *100*, 18567

Question:

What is the mechanism of the charge transport?

First *ab initio* calculations indicate that a purely electronic *ultrafast* charge transport caused by electron correlation and relaxation is possible

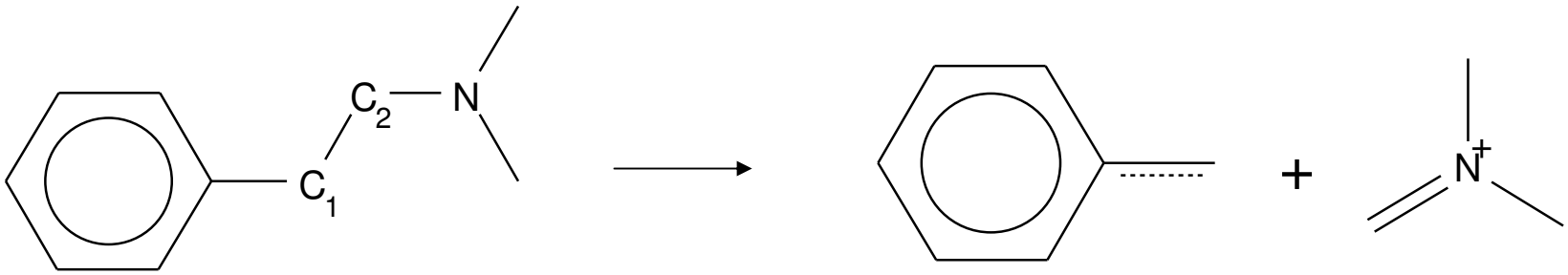
- charge transport on a femtosecond timescale
- no nuclear dynamics

L. S. Cederbaum et al *Chem. Phys. Lett.* **1999**, *307*, 205

	Charge transfer	**Charge migration**
caused by	nuclear dynamics	electron dynamics
timescale	~ ps	~ fs

Further experiments with femtosecondlasers

- PENNA (2-Phenylethyl-*N,N*-dimethylamine)
- Related to the amino acid phenylalanin
- Fragmentation after ionization of benzene ring
- Reported timescale of fragmentation: 80 ± 28 fs



L. Lehr et al *J. Phys. Chem. A* **2005**, *109*, 8074

Theoretical Methods for the calculation of the hole density

$$Q(\vec{r},t) := \langle\Psi_0|\hat{\rho}(\vec{r},t)|\Psi_0\rangle - \langle\Phi_i|\hat{\rho}(\vec{r},t)|\Phi_i\rangle = \rho_0(\vec{r}) - \rho_i(\vec{r},t)$$

electron density
of the ground state
(time independent)

electron density
of the produced cation
(time dependent)

$$Q(\vec{r},t) = \underbrace{\langle\Psi_0|\hat{\rho}(\vec{r},t)|\Psi_0\rangle}_{\rho_0(\vec{r})} - \underbrace{\langle\Phi_i|\hat{\rho}(\vec{r},t)|\Phi_i\rangle}_{\rho_i(\vec{r},t)},$$

$\hat{\rho}$ density operator

$|\Phi_i\rangle$ initial nonstationary cationic state

In an one-particle (orbial) basis $\{\varphi_p\}$

$$\boxed{Q(\vec{r},t) = \sum_{p,q} \varphi_p^*(\vec{r})\varphi_q(\vec{r})N_{pq}(t)}$$

$\mathbf{N}(t)$ hole density matrix with elements $N_{pq}(t)$

diagonlization of $\mathbf{N}(t)$ leads to

$$\boxed{Q(\vec{r},t) = \sum_{p} |\tilde{\varphi}_p(\vec{r},t)|^2 \tilde{n}_p(t)}$$

$\tilde{\varphi}_p(\vec{r},t)$ natural charge orbitals
$\tilde{n}_p(t)$ hole occupation numbers

How to calculate *Q*?

N is computed using *ab initio* many-body Green's functions (GF)

Two ways:

1. Diagonalization of GF – ADC – matrices
   as long as the matrices are small [1,2]

2. Propagation of the initial cationic state by
   multielectron wavepacket dynamics [3]

Visualization using graphical standard tools, i.e. gnuplot, Molden

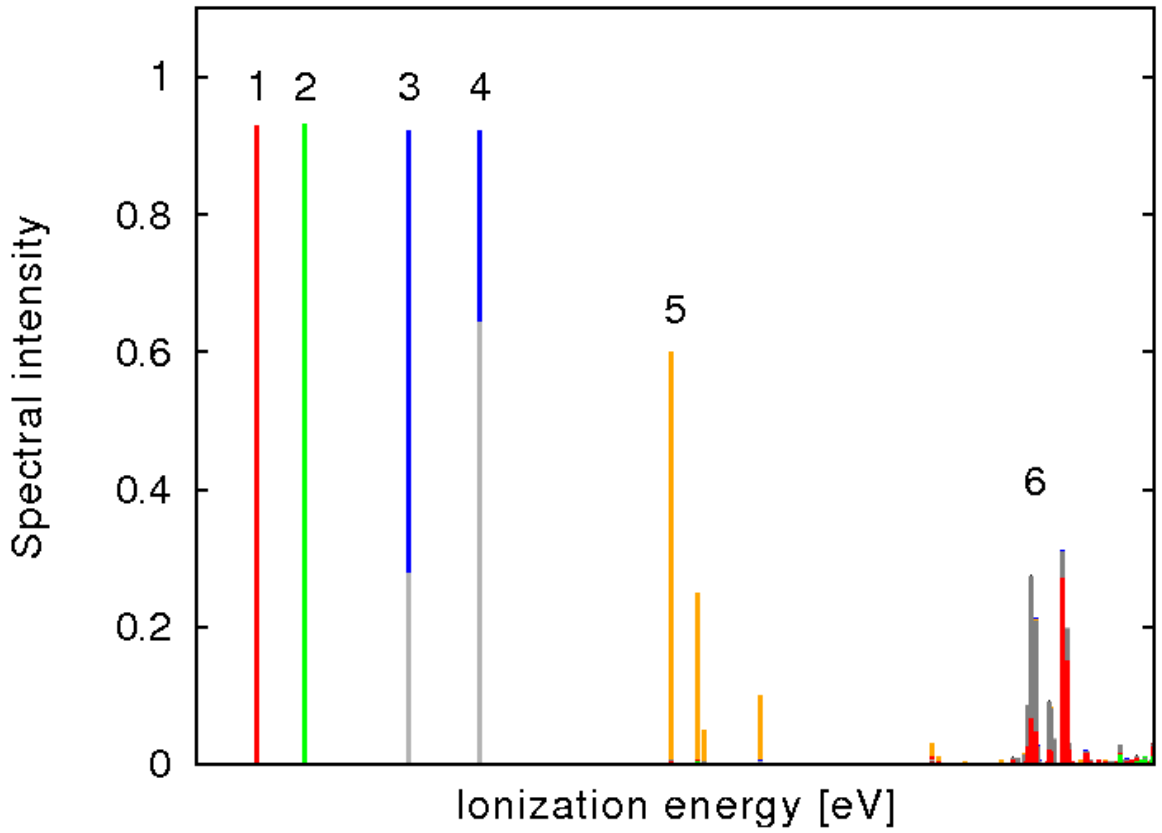
[1] J. Breidbach et al *J. Chem. Phys.* **2003**, *118*, 3983

[2] J. Breidbach et al *J. Chem. Phys.* **2007**, *126*, 34101

[3] A. I. Kuleff et al *J. Chem. Phys.* **2005**, *123*, 044111

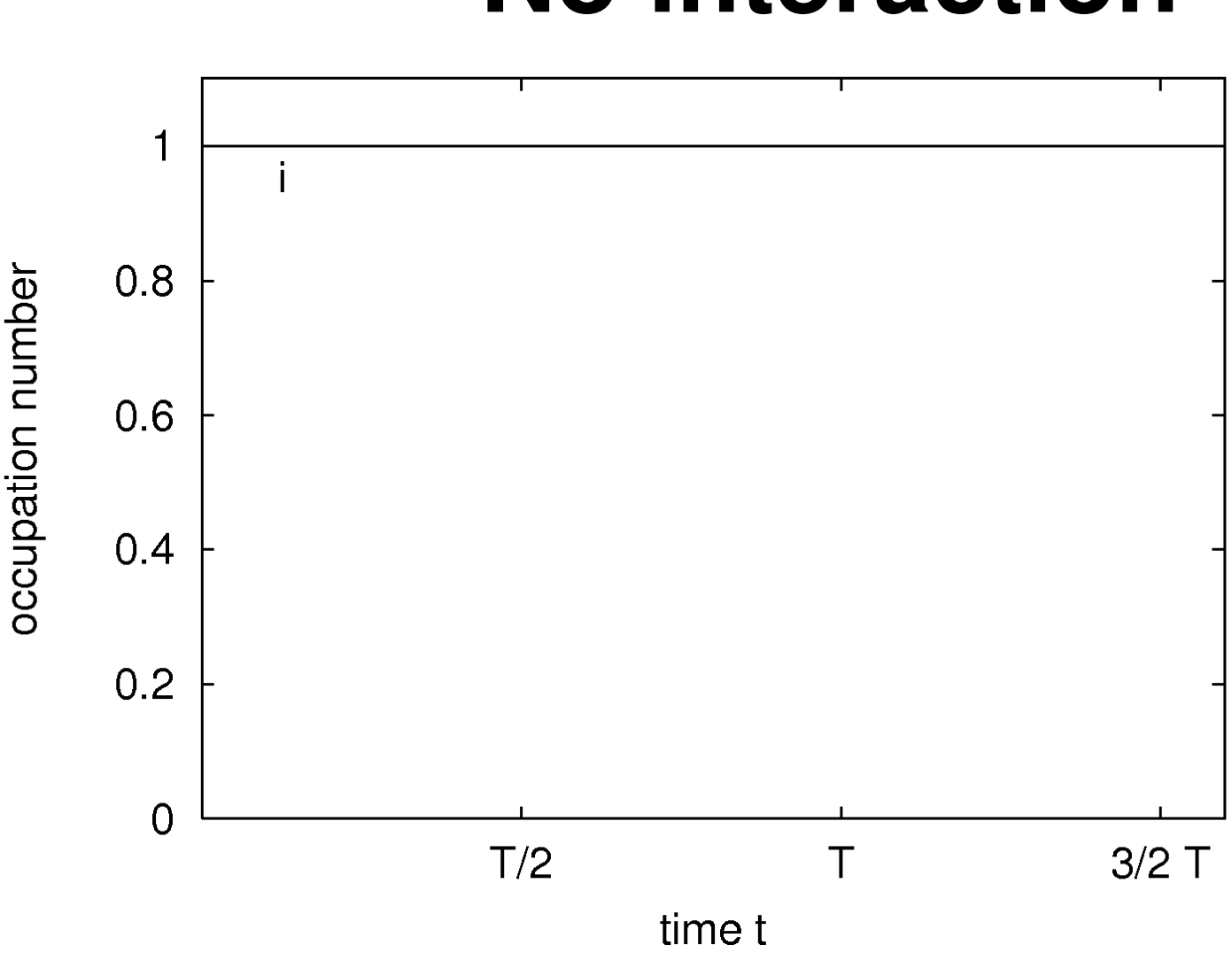
On the basic mechanisms of charge migration

A typical ionization spectrum



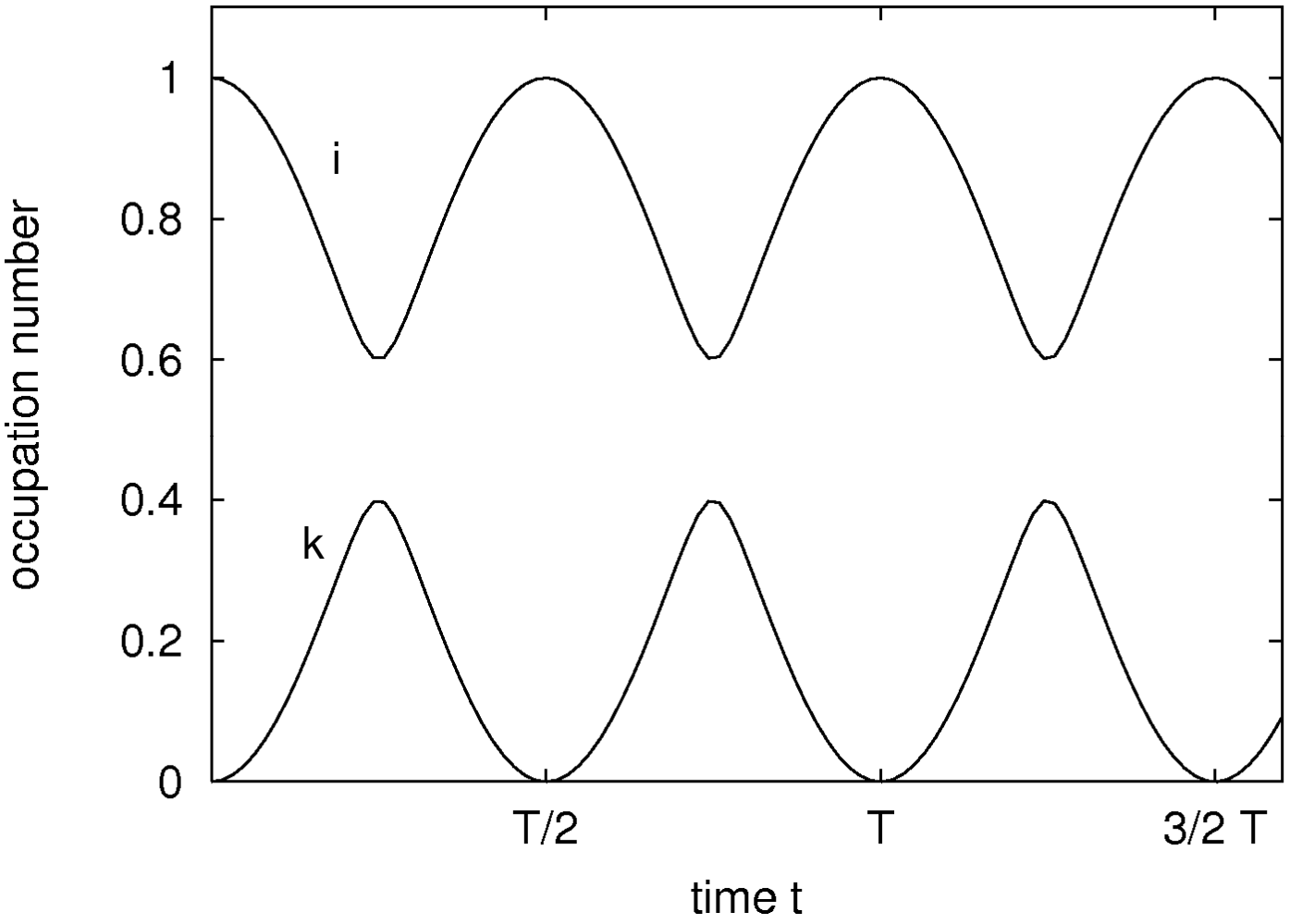
1,2: no interactions
3,4: hole mixing
5: satellites
6: breakdown of MO-picture

No interaction



i: initially ionized orbital

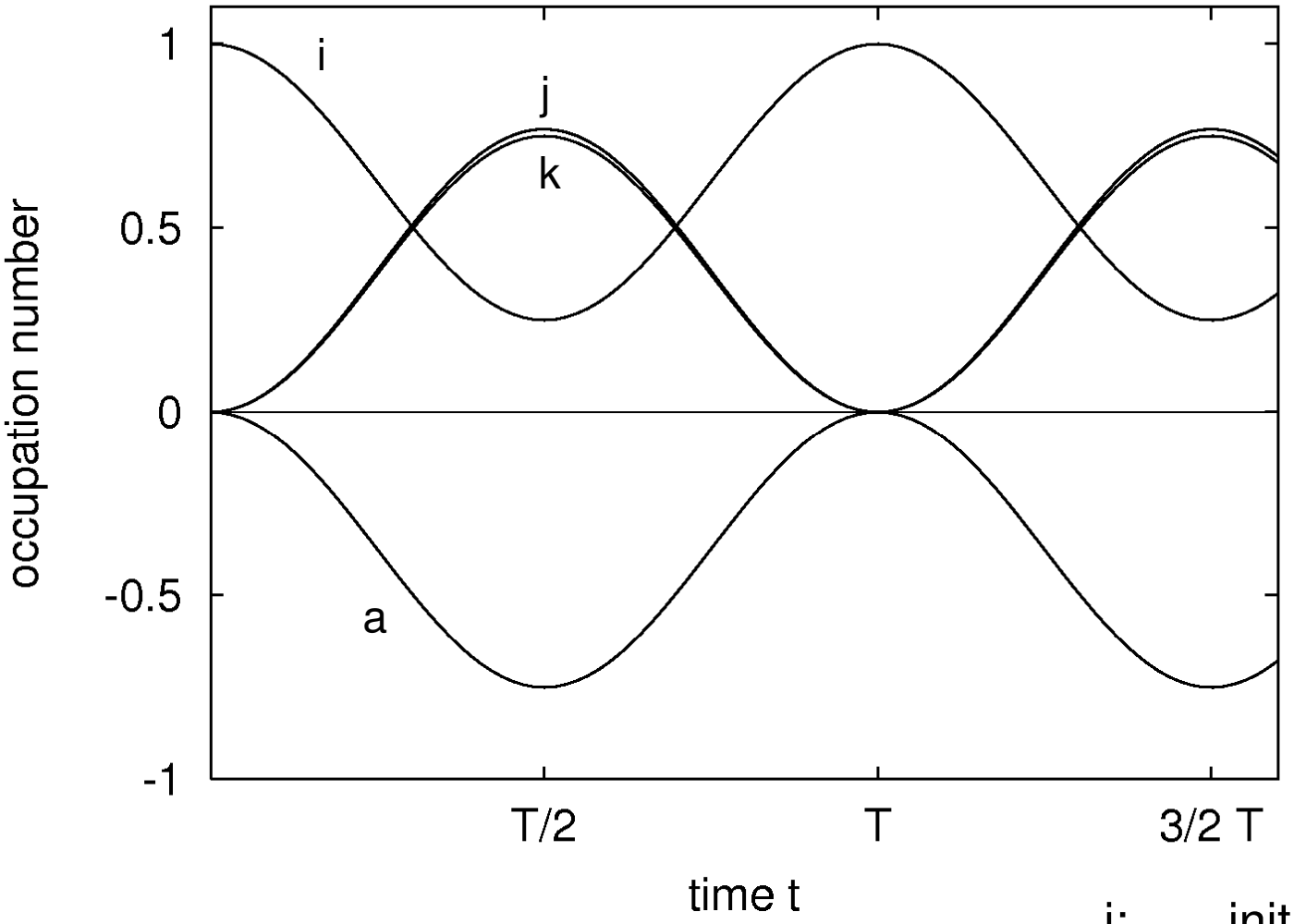
Case of hole mixing



i: initially ionized orbital

k: partner orbital

Case of correlation satellite

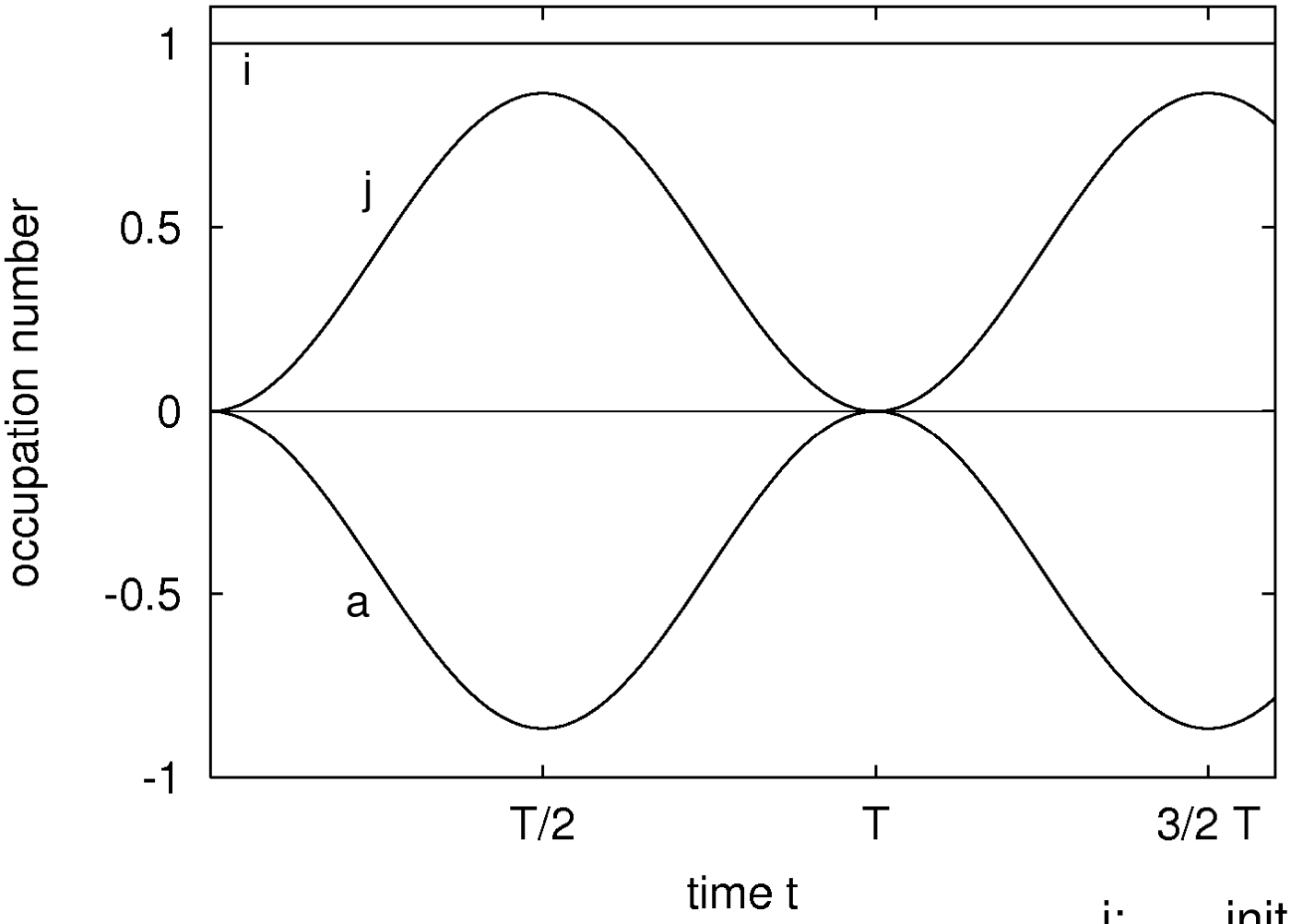


i: initially ionized orbital

j,k: partner orbital

a: virtual orbital

Case of relaxation satellite

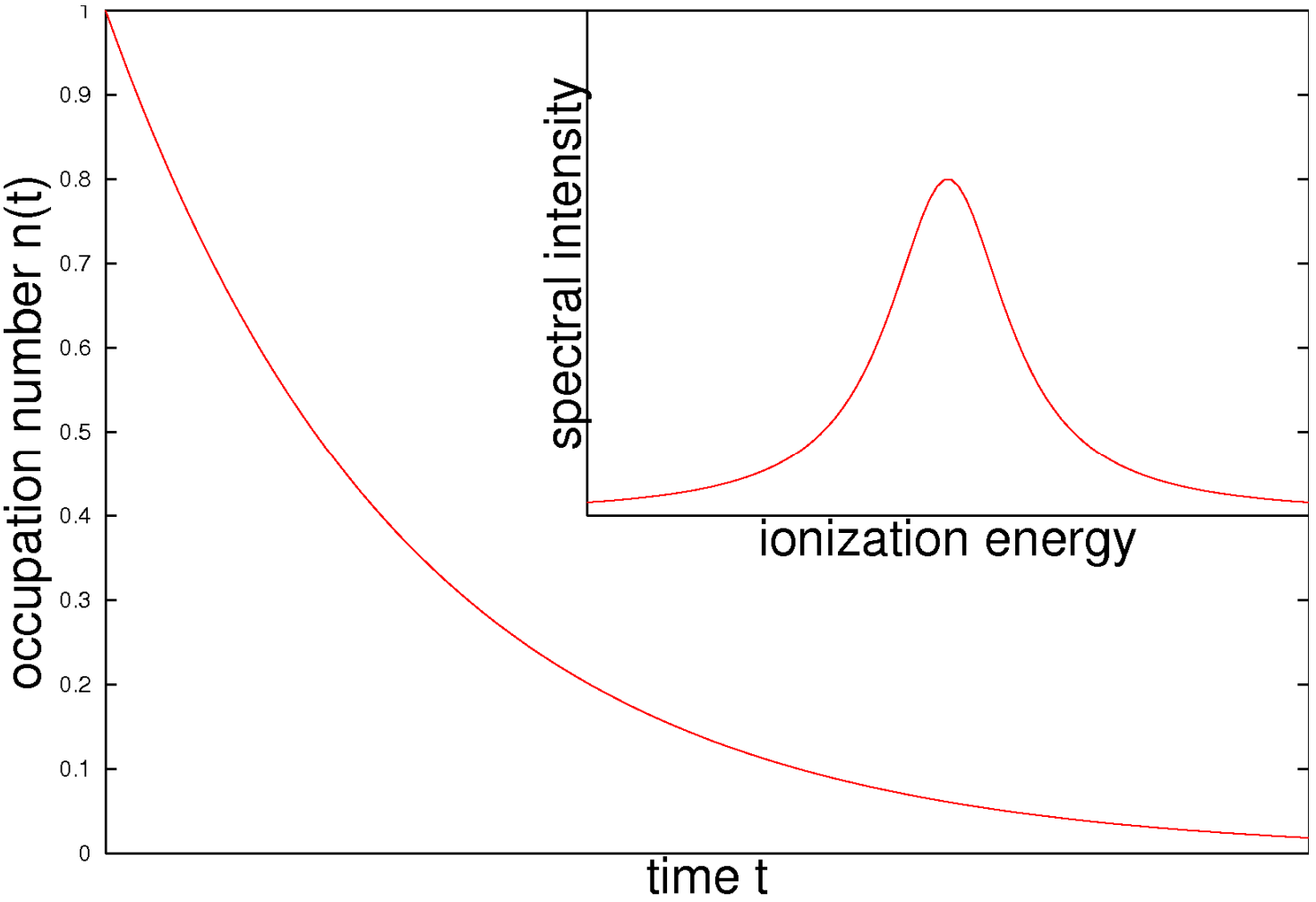


i: initially ionized orbital

j: partner orbital

a: virtual orbital

Case of breakdown of MO-picture



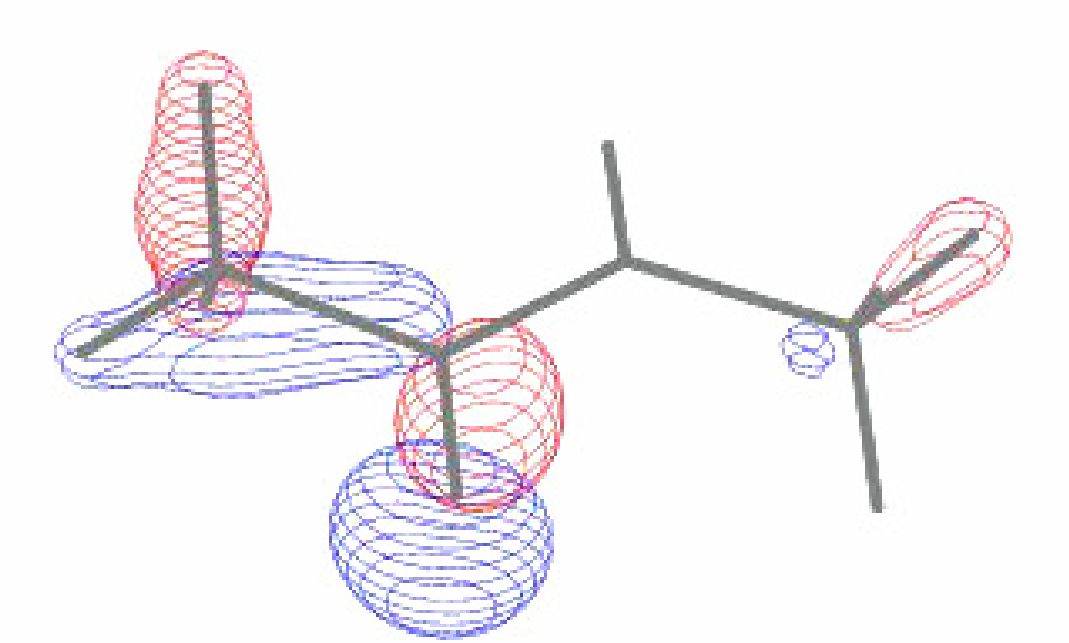
Typically, the initially created hole is distributed in time over the whole system

Examples

Ionization in the inner-valence regime

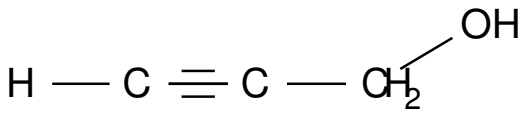
The example of a peptide bond

(N-methyl Acetamide)



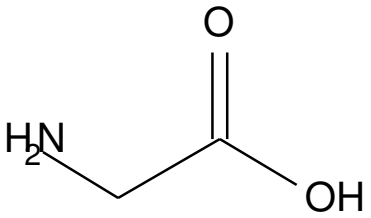
H. Hennig et al *J. Phys. Chem. A* **2005**, *109*, 409

Other interesting cases



2-propyn-1-ol: Hole mixing [1]

3-fluoro-2-propynenitrile: Dominant satellite [1]



Glycine: Dom. satellite and hole mixing [2]

5-fluoro-2,4-pentadiynenitril: Breakdown of MO [1]

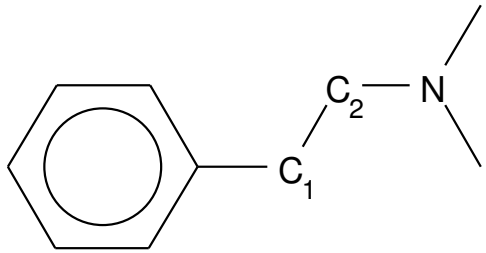
[1] J. Breidbach et al *J. Chem. Phys.* **2003**, *118*, 3983

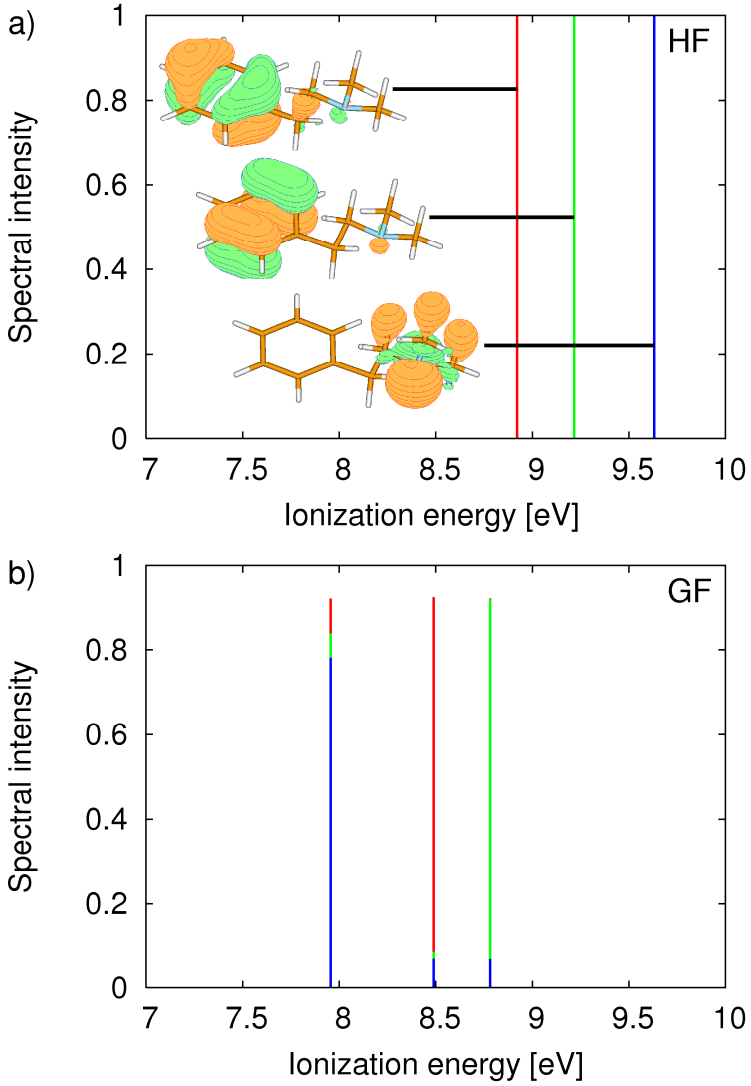
[2] A. I. Kuleff et al *J. Chem. Phys.* **2005**, *123*, 044111

Ionization of outer-valence electrons

The ionization spectrum of PENNA

- 2-Phenylethyl-*N,N*-dimethylamine
- 2.6 eV gap to the inner valence
- failure of Koopmans‘ Theorem
- Mixing of one hole (1h) states





S. Lünnemann et al *Chem. Phys. Lett.* **2008**, *450*, 232

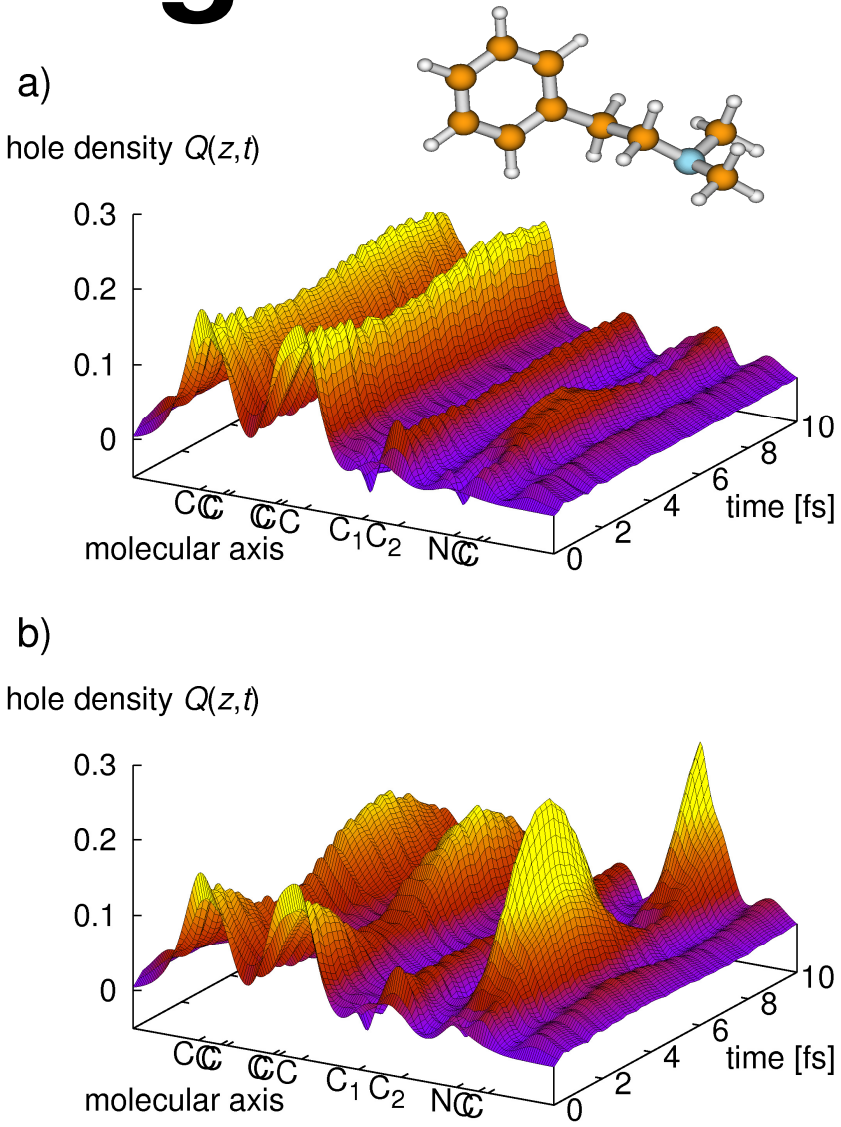
The charge migration

a) ground state geometry

- some charge from ring to N

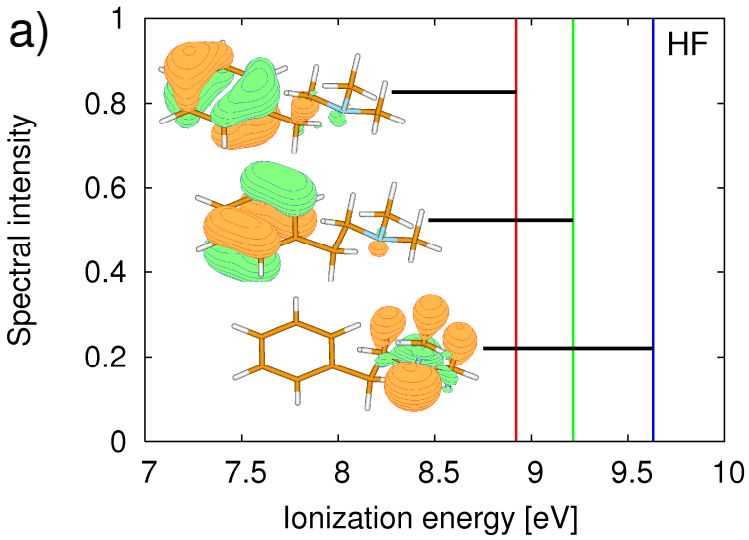
b) elongated C_1-C_2-bond: 20 pm

- substantial charge from ring to N

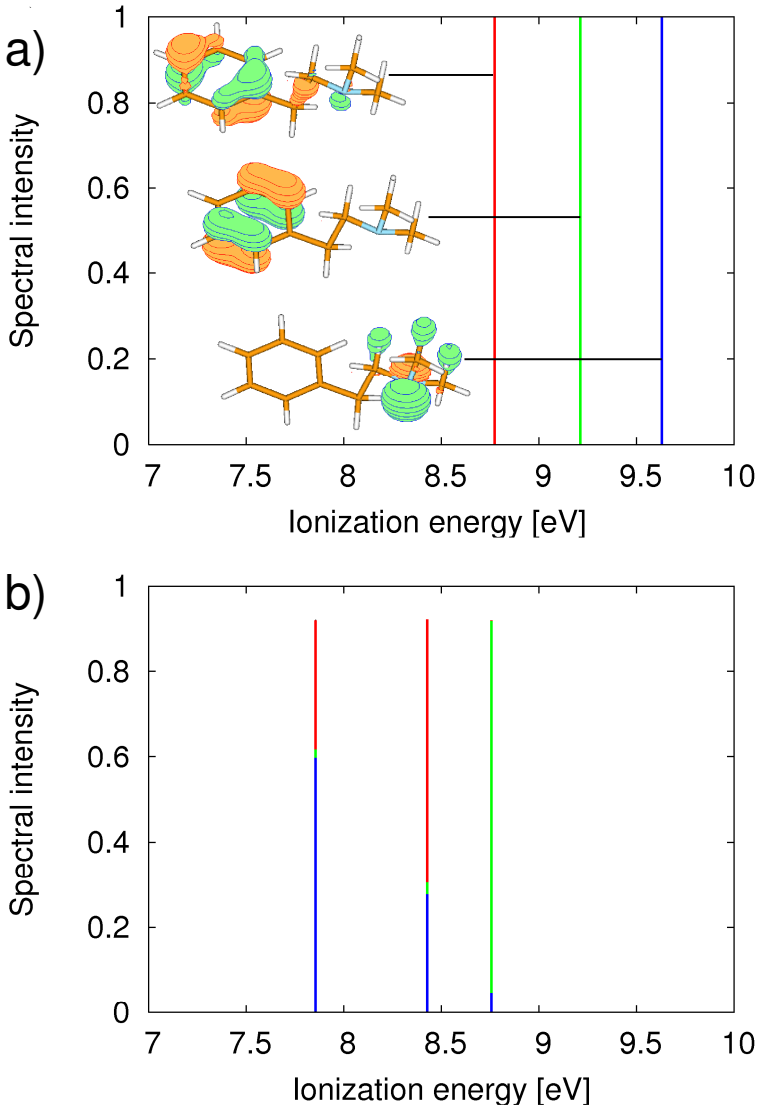


Ionization spectra of PENNA

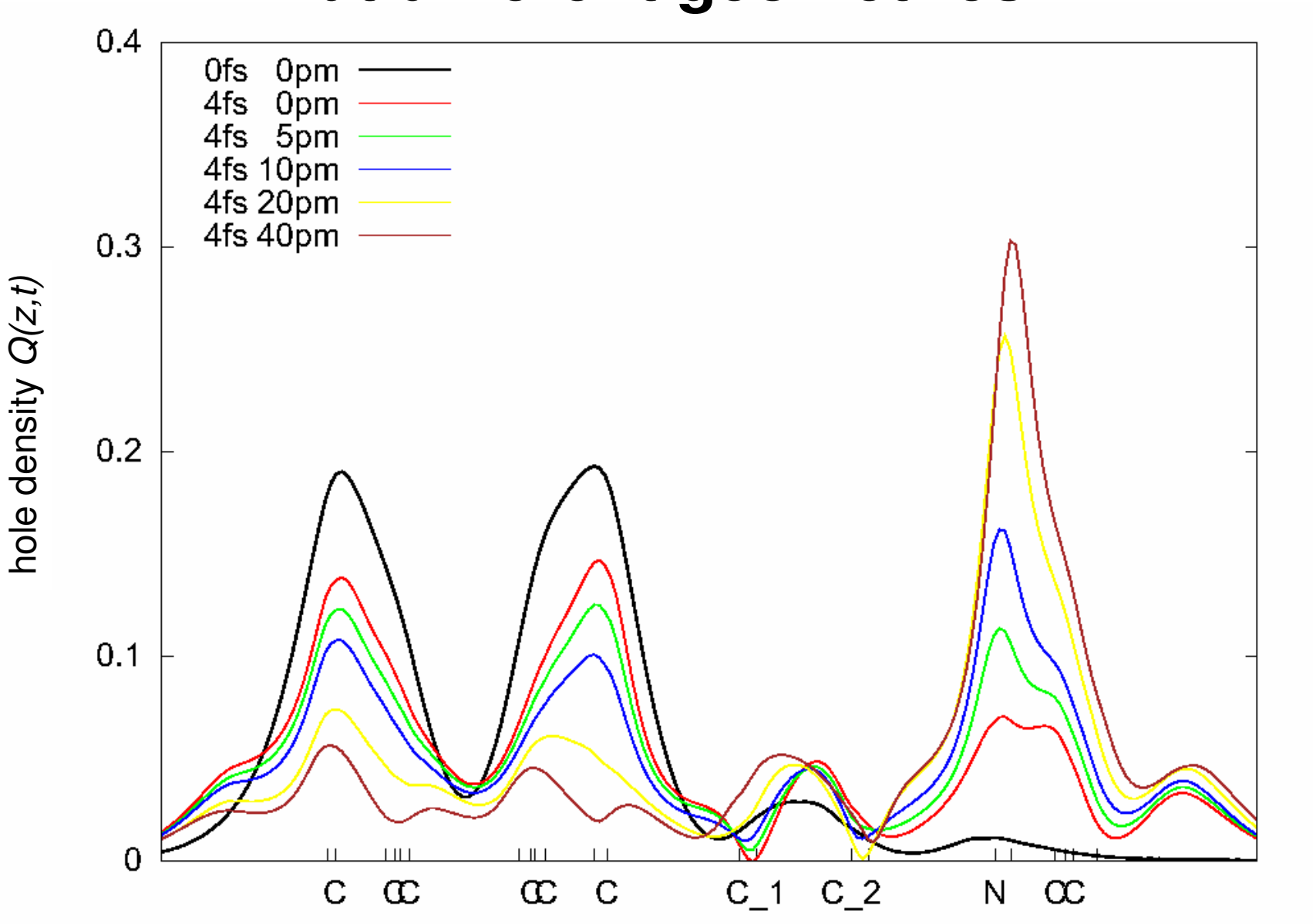
Ground state geometry



Elongated C_1-C_2 bond

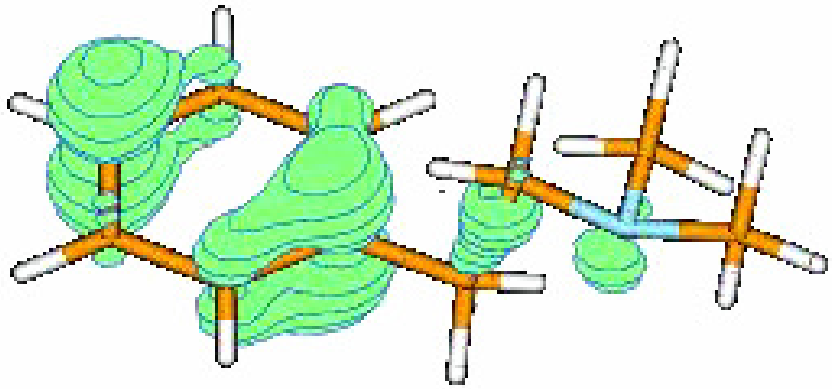


Charge distribution at 4 fs after ionization at different geometries



The charge migration with the C_1-C_2-bond elongated by 20 pm

- time = 00.00 fs



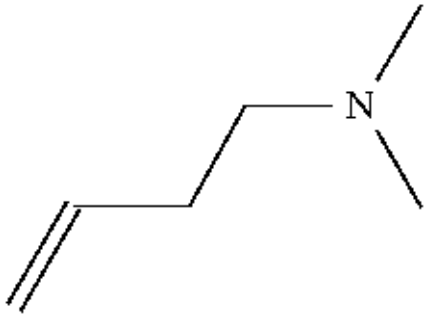
Suggestion for a mechanism of charge migration and bond breaking

1. Step: Ionization of the benzene ring
2. Step: Some charge oscillates from the ring to N
3. Step: Elongation of the C_1-C_2-bond
4. Step: Migration of hole charge intensifies
5. Step: The bond breaks and the hole charge is trapped at the energetically favourable N-site

Is the molecule PENNA special or is the scheme chromophore – C_2-Bridge – Nitrogen general for charge migration?

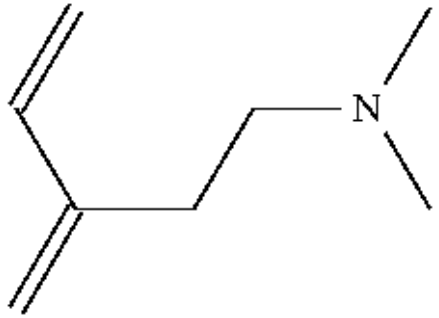
Many related systems computed (also different conformers).

Two examples:



BUNNA

3-Buten-*N,N*-dimethylamine

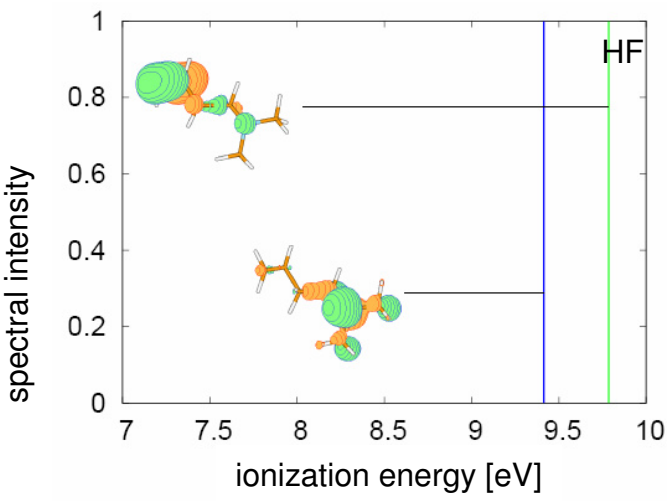


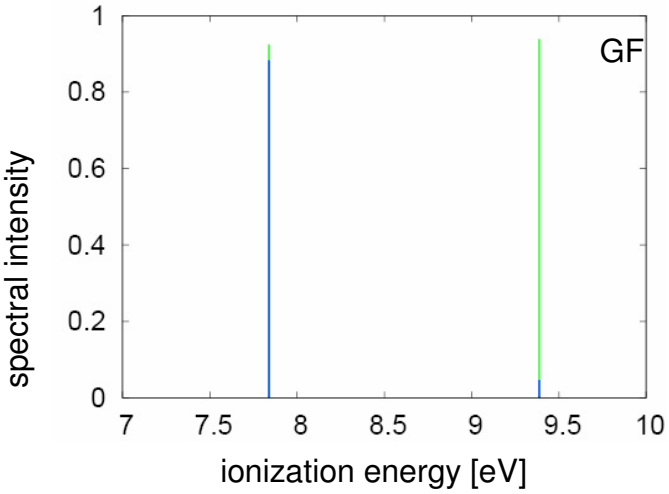
MePeNNA

3-Methylen-4-penten-*N,N*-dimethylamine

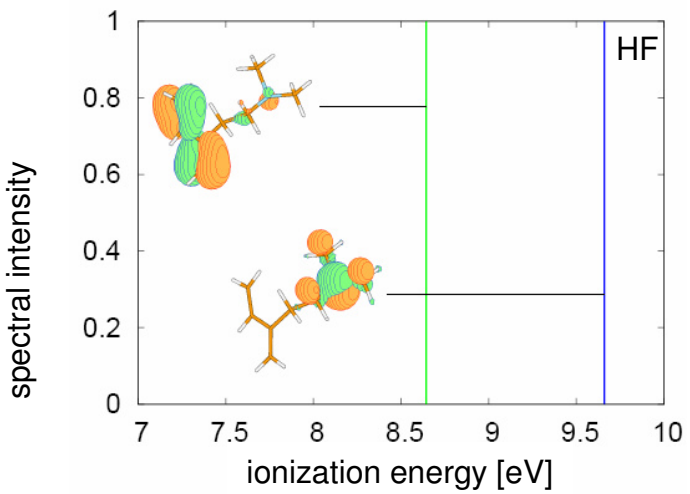
The ionization spectra

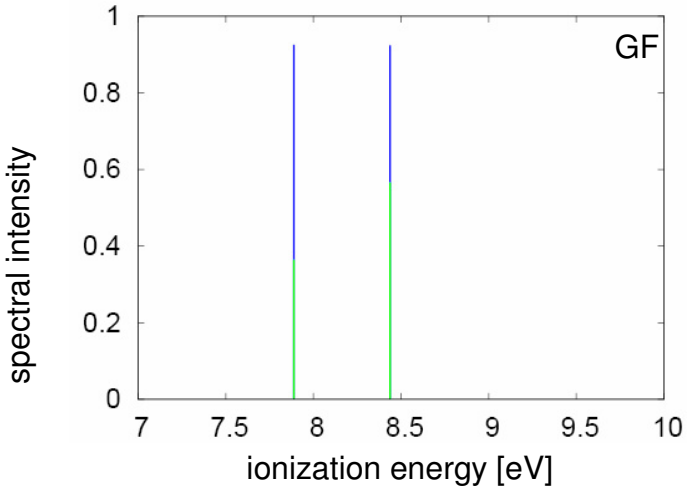
BUNNA



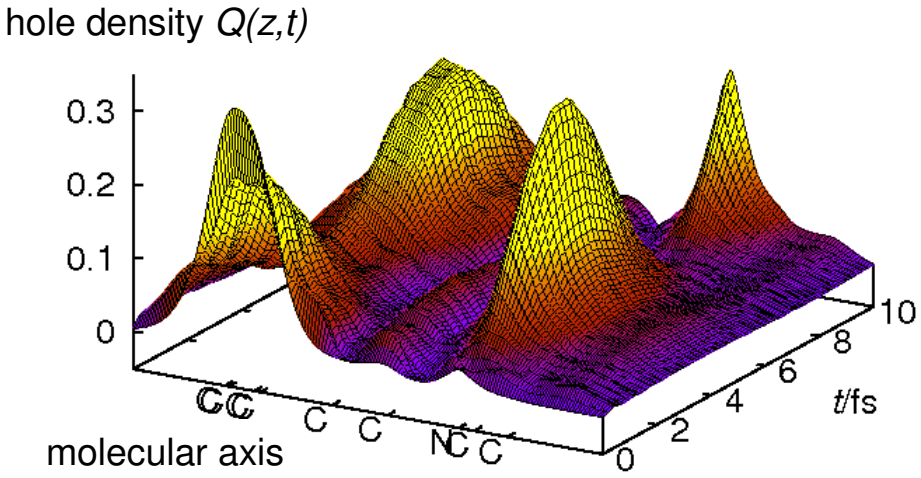


MePeNNA



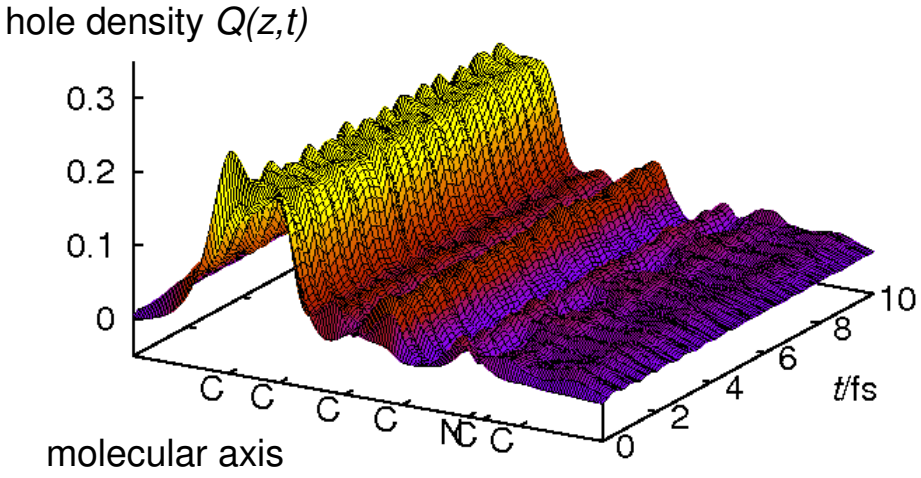


The charge migration



MePeNNA:

nearly the complete hole charge migrates from the chromophore to the Nitrogen



BUNNA:

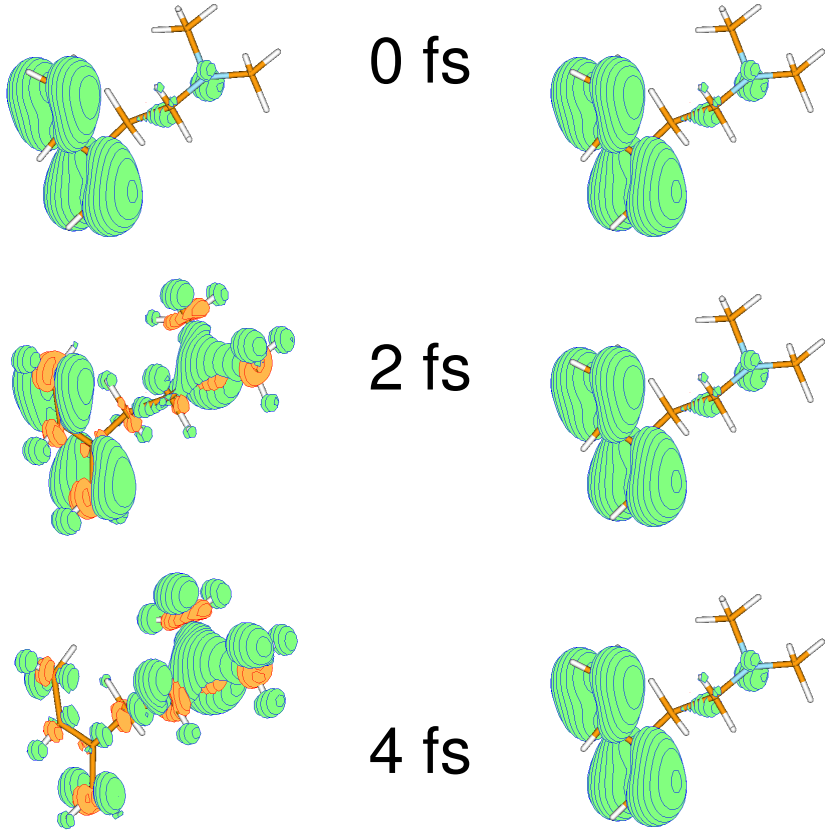
no charge migration at all

S. Lünnemann et al *J. Chem. Phys.* **2008**, *129*, 104305

The role of 2h1p-configurations

The hole density in real space

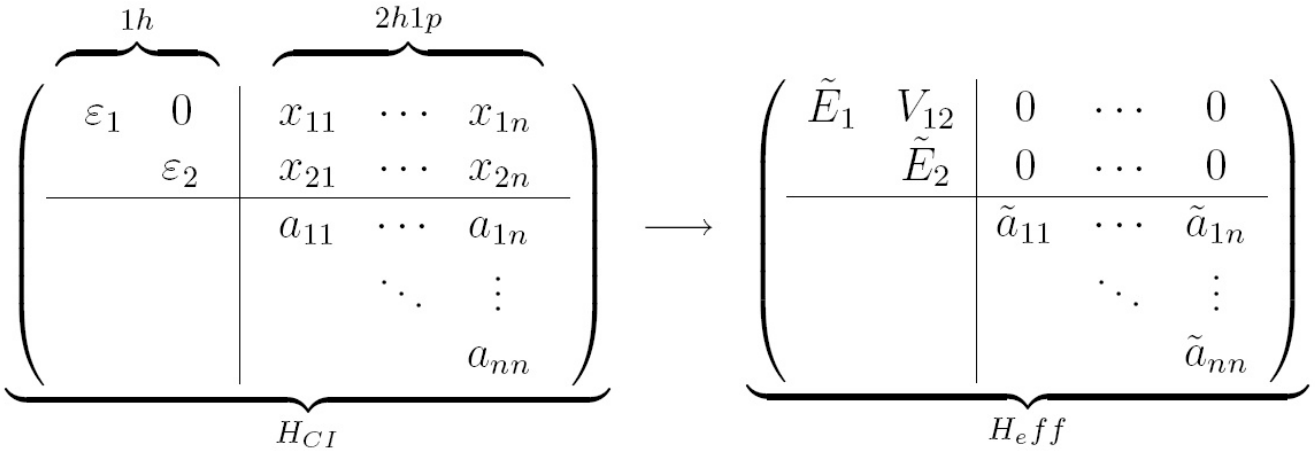
with and without 2h1p-interactions



no charge migration

without the 2h1p-interactions

Analysis of the charge migration mechanism: The exact effective Hamiltonian (EEH)-Method



large V_{12} + small $\Delta\tilde{E}$
→ large coupling

small V_{12} + large $\Delta\tilde{E}$
→ small coupling

PENNA

$$\begin{pmatrix} 8.00 & 0.15 \\ \cdots & 8.44 \end{pmatrix}$$

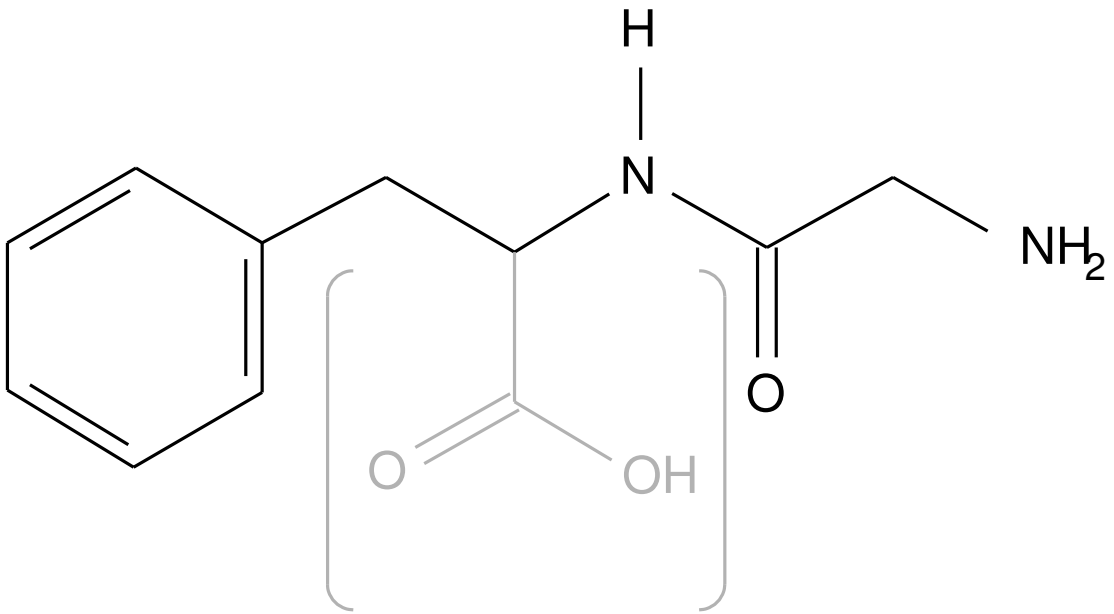
BUNNA

$$\begin{pmatrix} 7.91 & 0.32 \\ \cdots & 9.32 \end{pmatrix}$$

MePeNNA

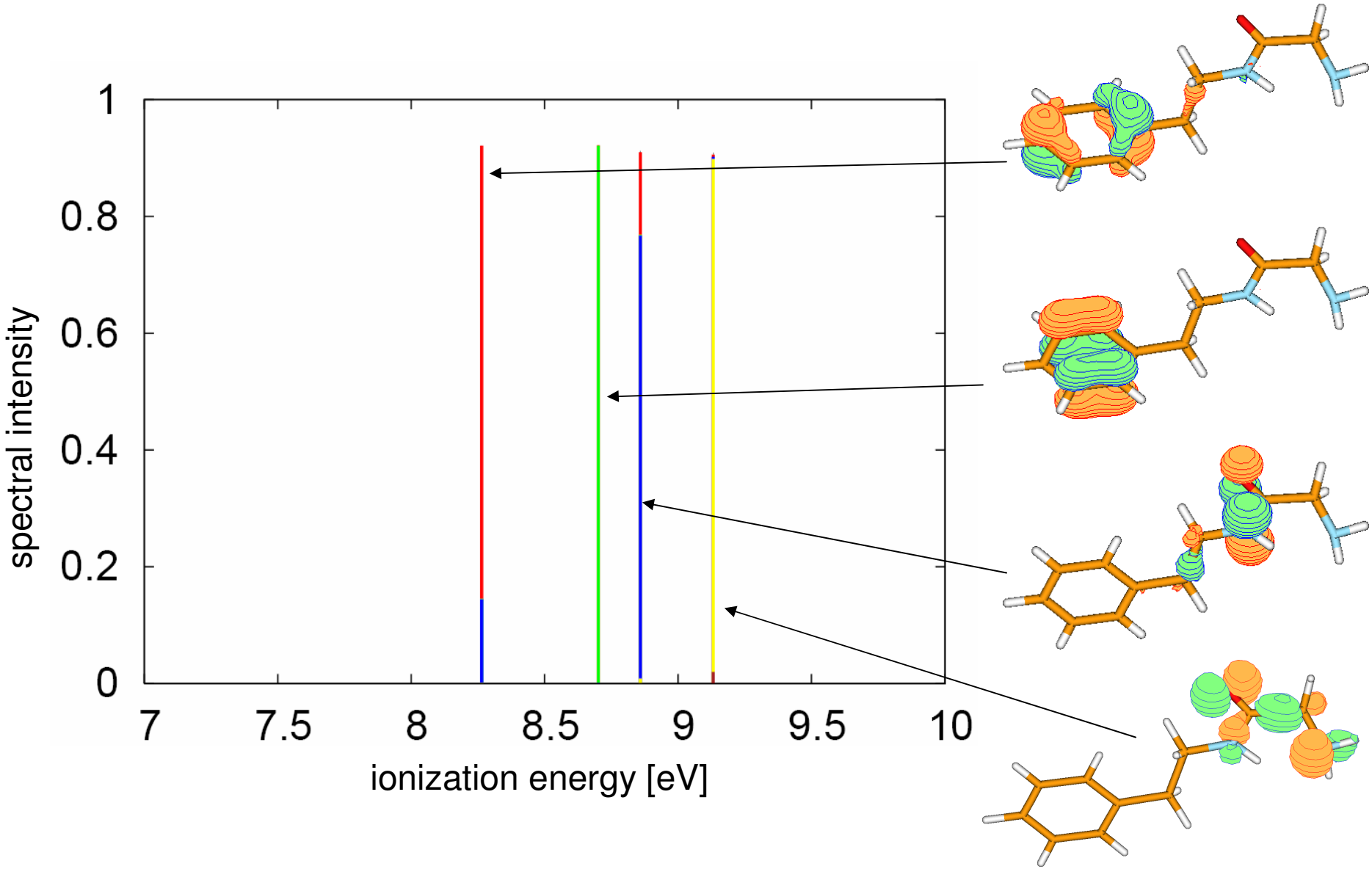
$$\begin{pmatrix} 8.13 & 0.30 \\ \cdots & 8.20 \end{pmatrix}$$

A first step on the way to polypeptides:
reduced dipeptide Glycin-Phenylalanin
(Gly-Phe; carboxylgroup of Phe removed)

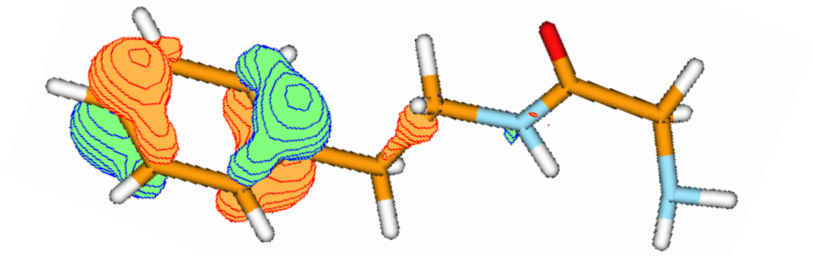


Does this molecule show charge migration
after ionization of the chromophore?

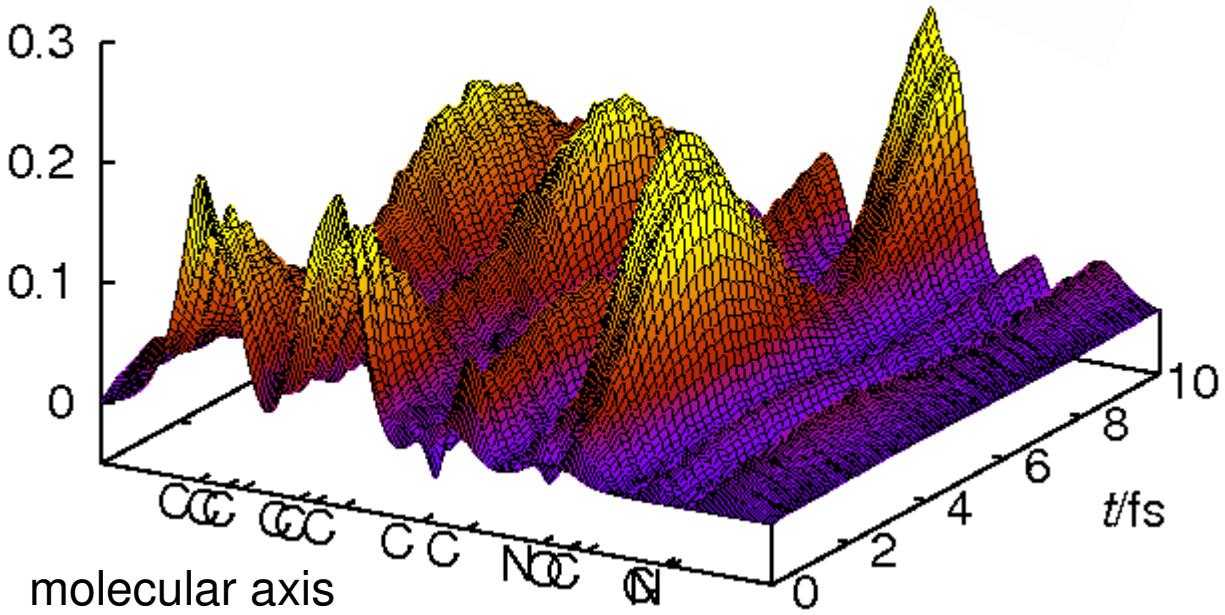
The ionization spectrum and HF-Orbitals



The charge migration following ionization



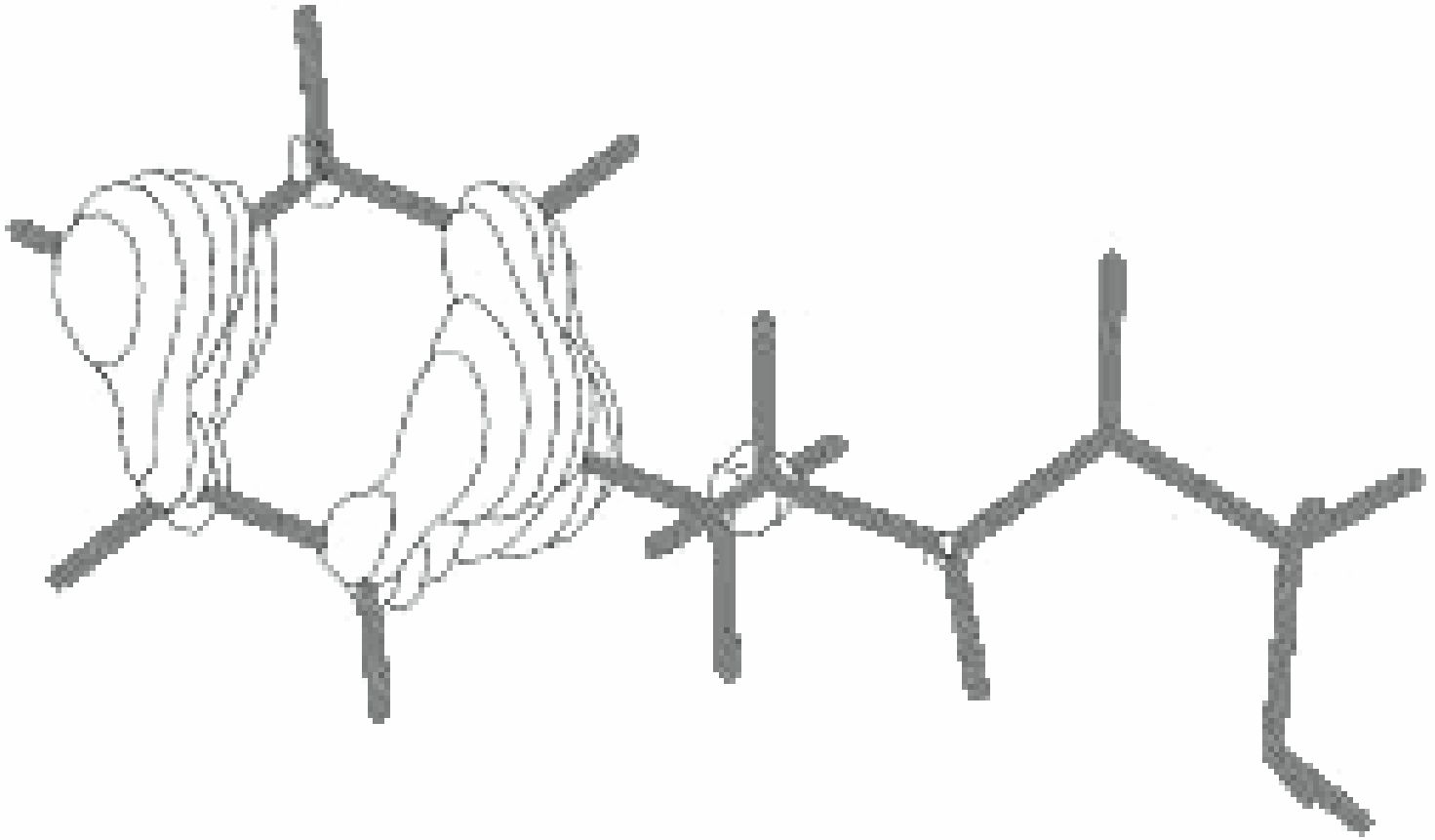
hole density $Q(z,t)$



0 fs:
charge on chromophore

4 fs:
charge on amid (peptidebond)

- time = 00 fs

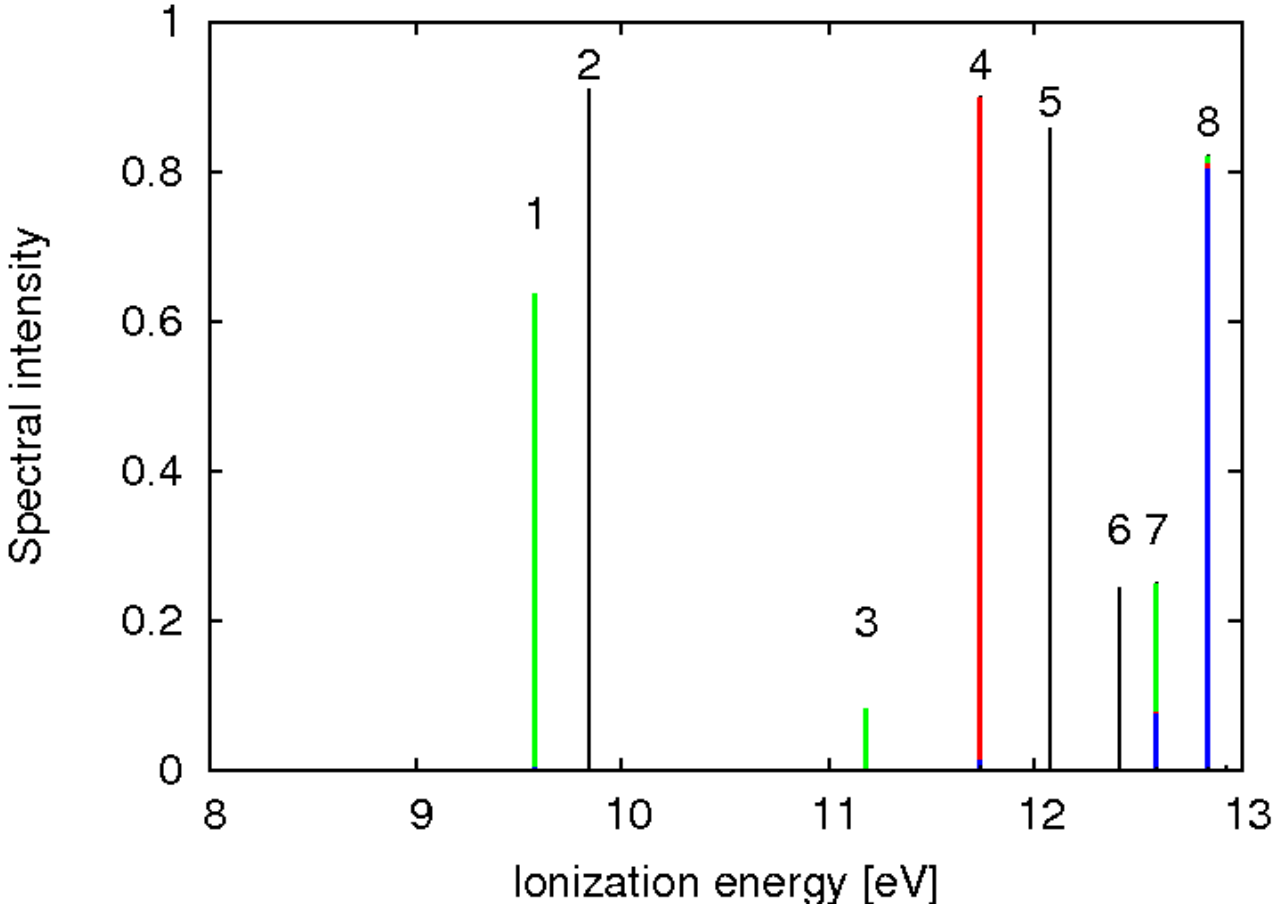


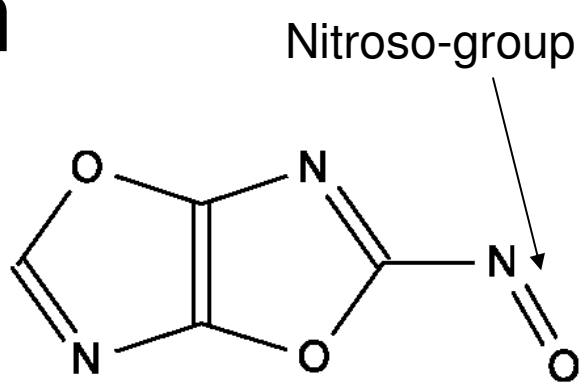
The role of satellite states

Relaxation satellite:

The nitroso molecule

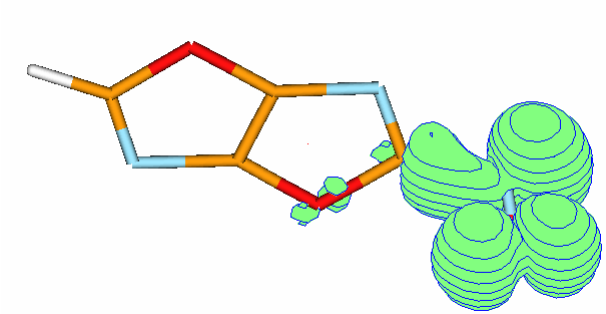
The ionization spectrum



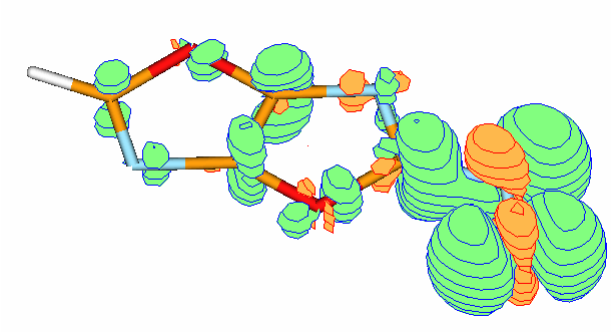


1: 29a‘ + (29a‘6a‘‘ 7a‘‘)
2: 6a‘‘
3: (29a‘) + 29a‘6a‘‘ 7a‘‘
4: 28a‘
5: 5a‘‘
6: (4a‘‘) + 6a‘‘6a‘‘ 7a‘‘
7: (29a‘ + 27a‘)
+ 29a‘6a‘‘ 7a‘‘

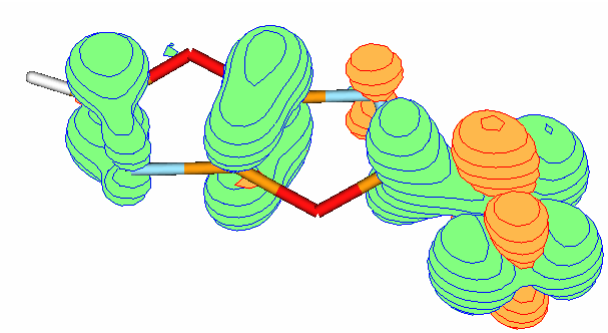
The charge migration following ionization of the HOMO (29a‘ orbital)



0 fs



0.7 fs



1.4 fs

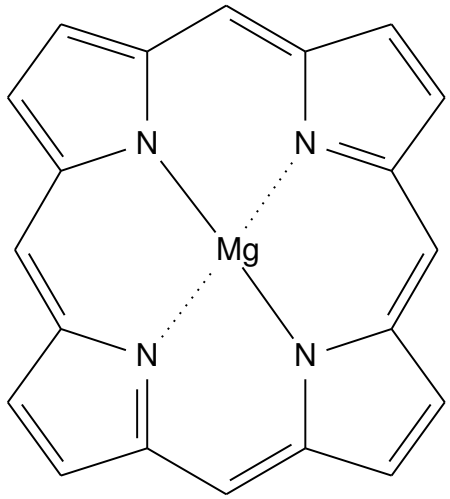
Correlation satellite:

A molecule related to Chlorophyll:

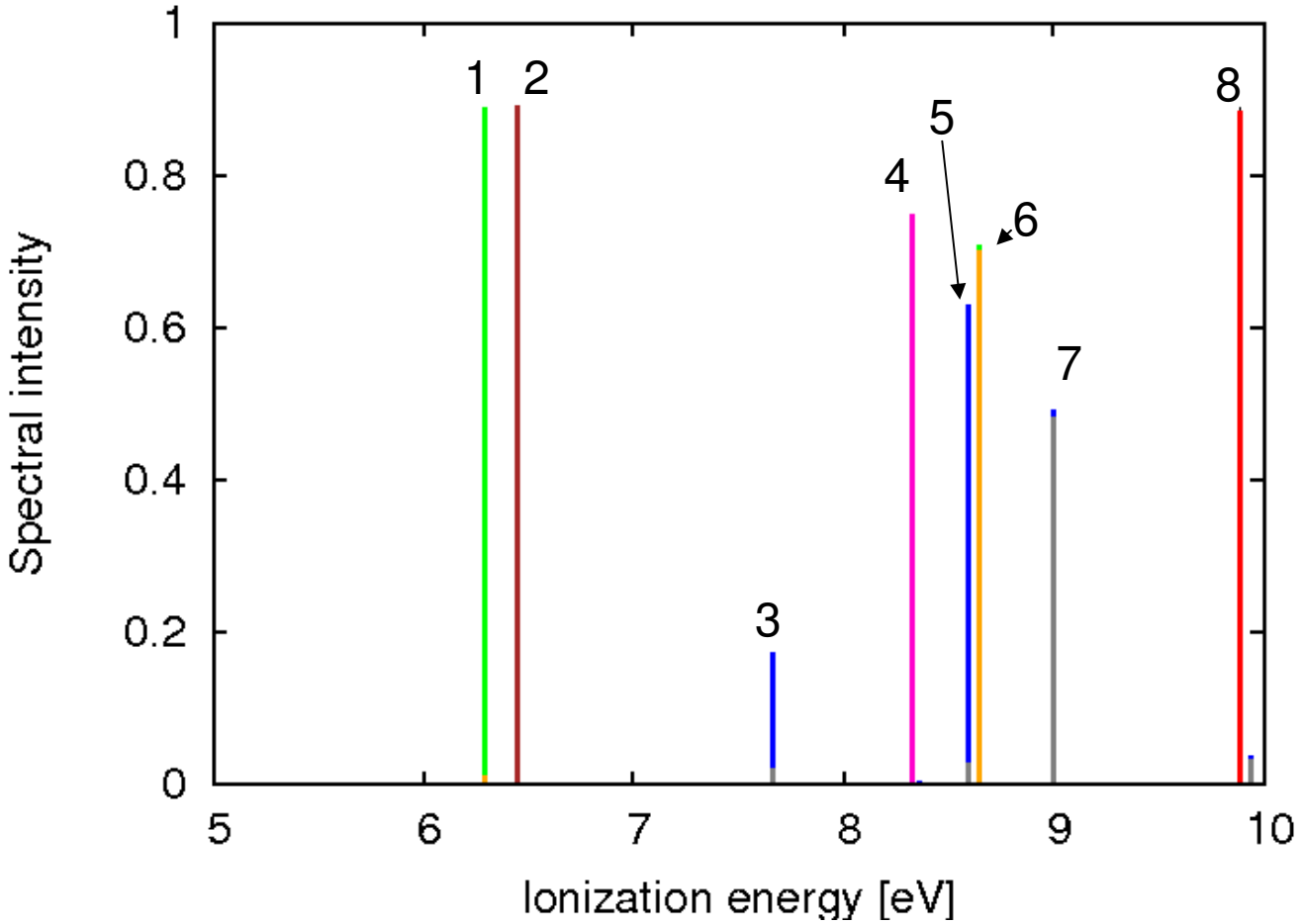
Mg-Porphyrin

(Active site in Photosythesis)

The ionization spectrum



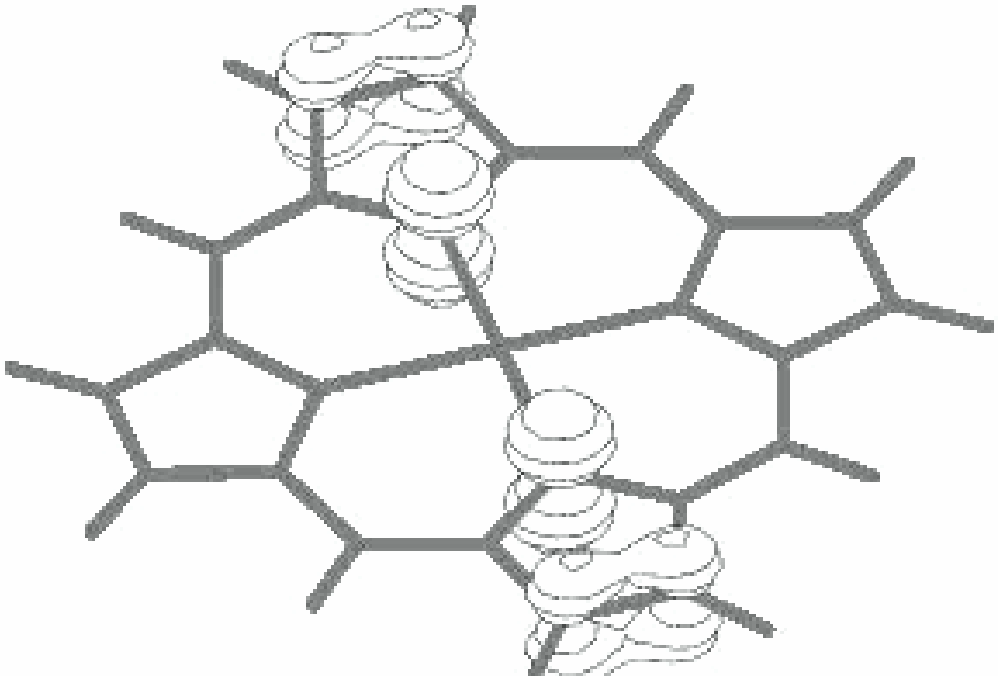
point group: D_{2h}



1: $6b_{1u}$ + ...
2: $2a_{1u}$ + ...
3: $6b_{1u}2a_{1u}\ 4b_{3g}$
+ $2a_{1u}2a_{1u}\ 4b_{2g}$
+ $3b_{2g}$
+ $6b_{1u}6b_{1u}\ 4b_{2g}$ + ...
4: $5b_{1u}$ + ...
5: $3b_{2g}$
+ $2a_{1u}2a_{1u}\ 4b_{2g}$ + ...
6: ...
7: ...

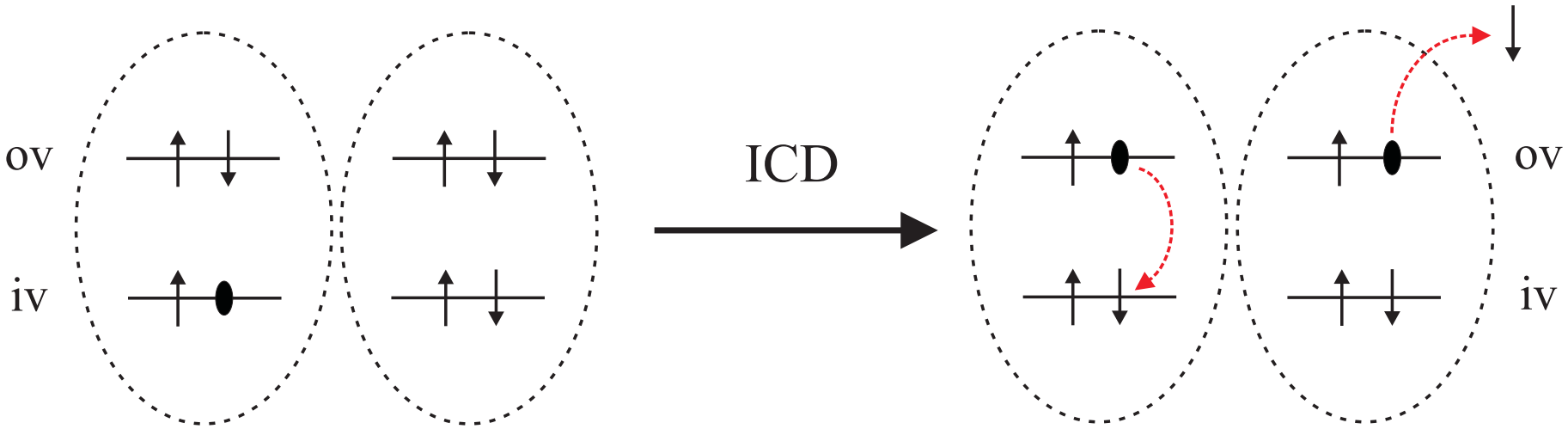
The charge migration following ionization of the $3b_{2g}$ orbital

- time = 0 fs



ICD

Interatomic
Coulombic
Decay



- ICD is a general phenomenon
  - van der Waals clusters – Ne_n, Ne_nAr_m, MgNe, CaNe, ...
  - hydrogen bonded clusters – $(H2O)_n$, $(HF)_n$, ...
  - endohedral fullerens – $Ne@C_{60}$, $Ar@C_{60}$
- Ultrafast process – fs time domain
- Source of LEE → biological relevance

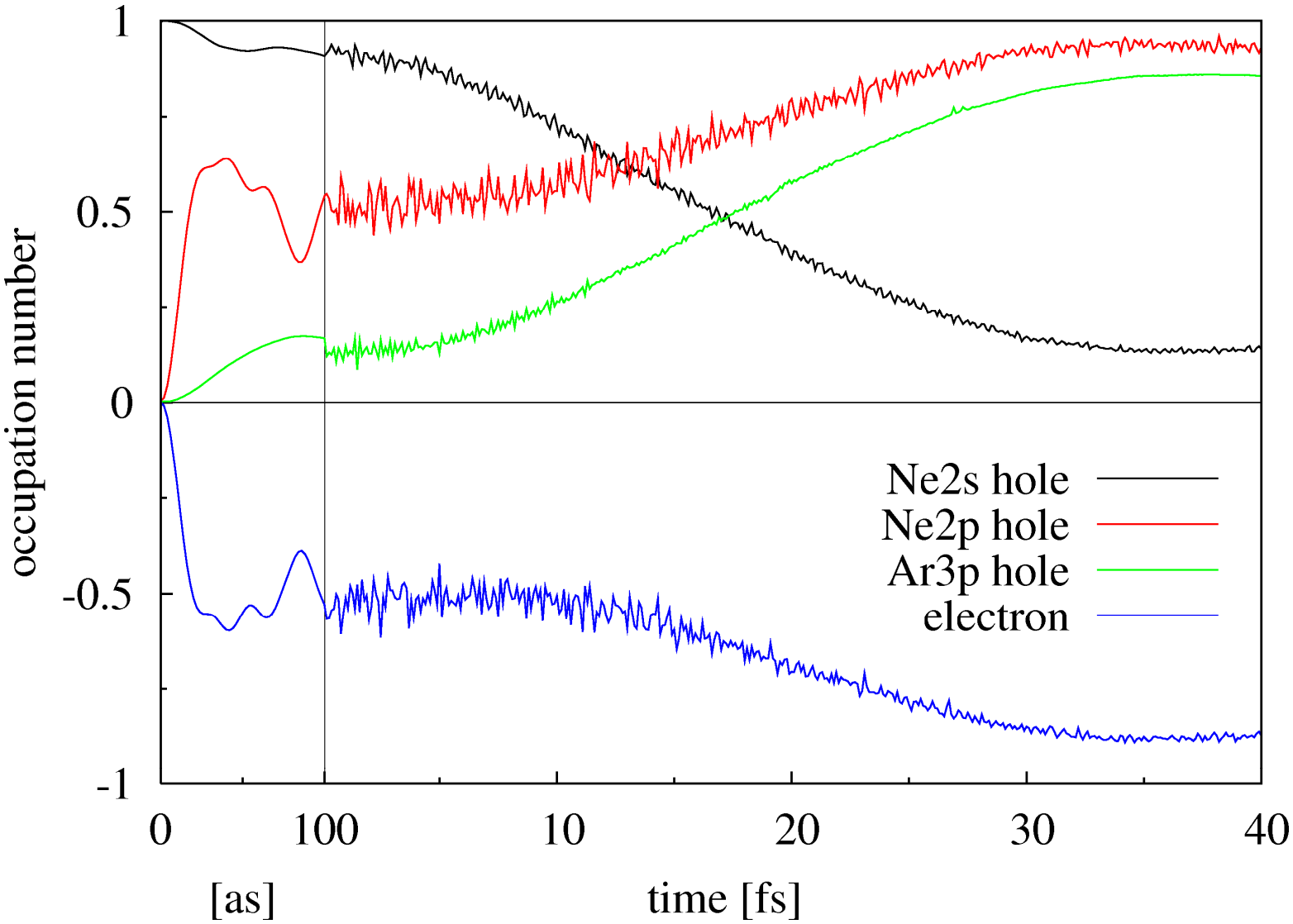
L. S. Cederbaum et al *Phys. Rev. Lett* **1997**, *79*, 4778

Tracing ultrafast interatomic electronic decay processes in real time and space

- Femto-second spectroscopy. Using lasers with femto-second pulses to „see“ the nuclear motion. Standard techniques nowadays.
- Atto-second spectroscopy. 1 as = 10^{-18} seconds. Using lasers with atto-second (sub-femto-second) pulses to „see“ the electronic motion. Future techniques. First important steps already done.
- The observation of the ICD process is an appealing project for atto-second spectroscopy.

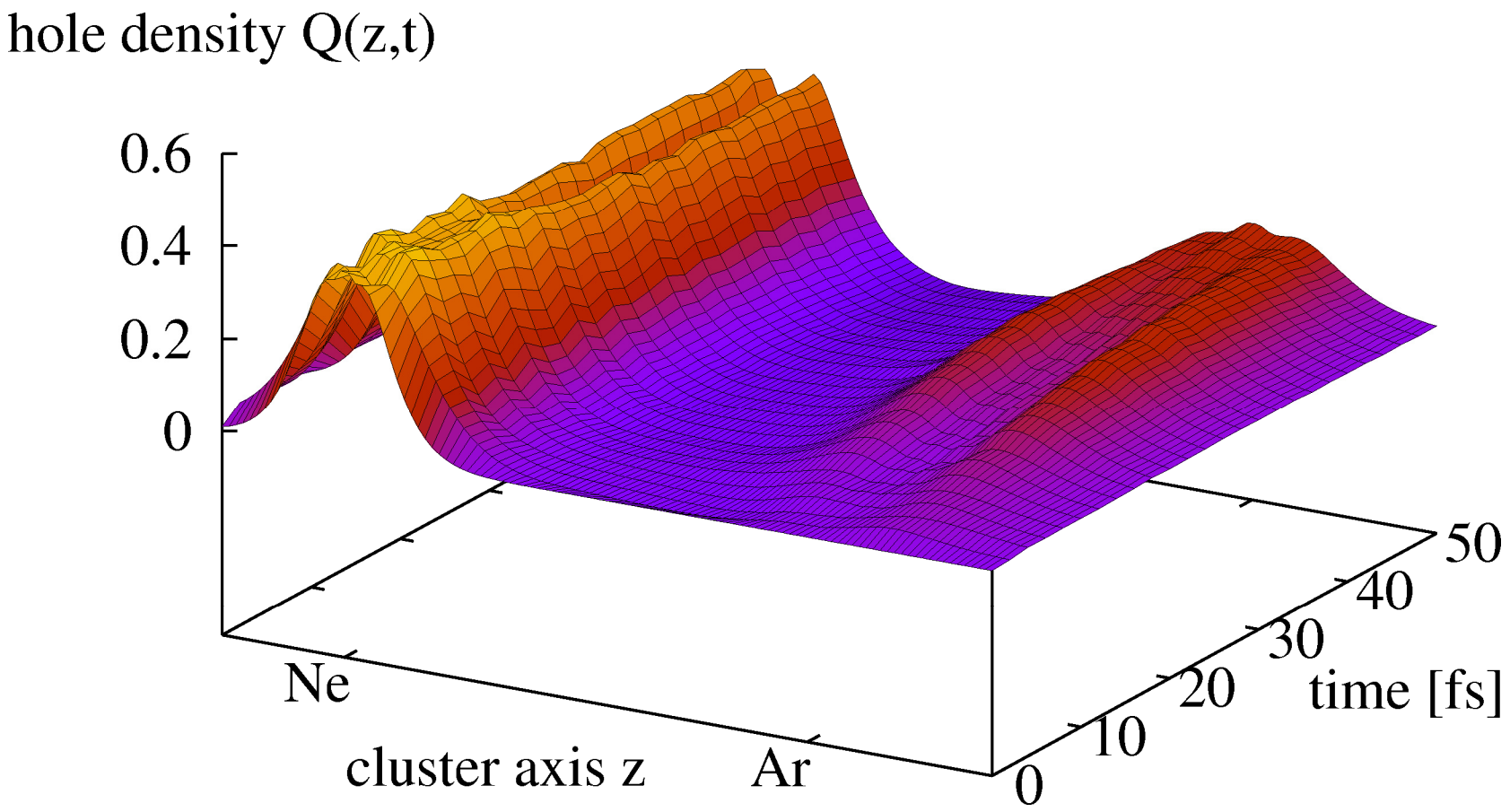
A. I. Kuleff et al *Phys. Rev. Lett* **2007**, *98*, 083201

ICD in NeAr



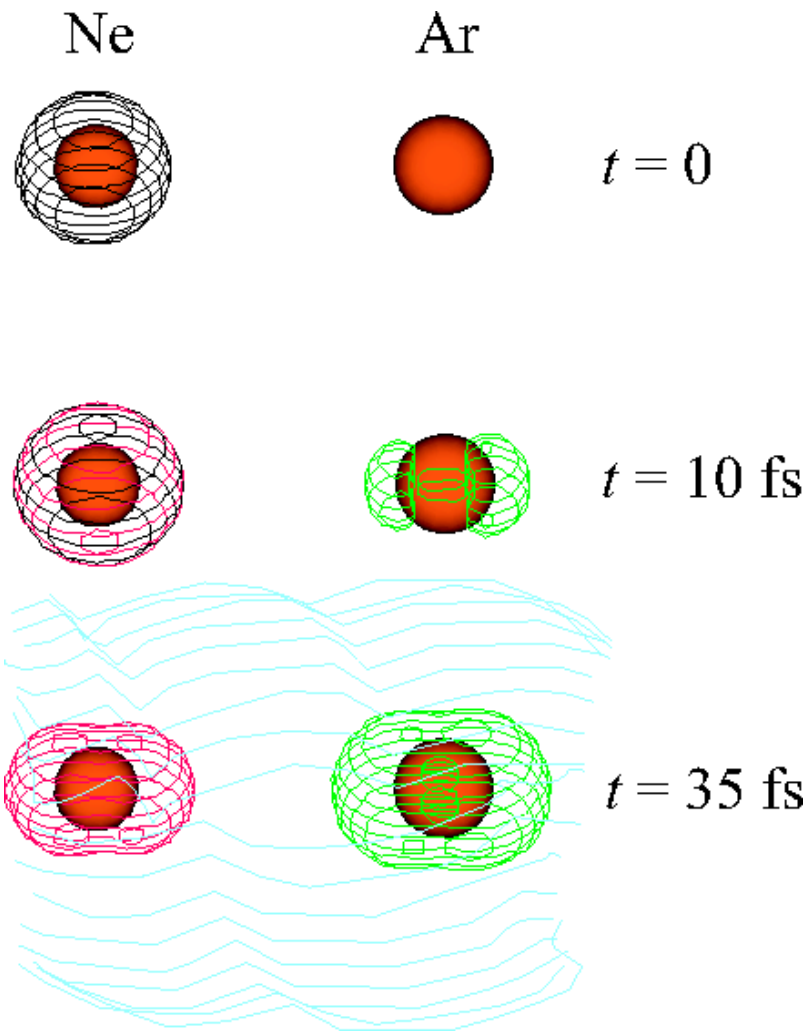
A. I. Kuleff et al *Phys. Rev. Lett* **2007**, *98*, 083201

ICD in NeAr



A. I. Kuleff et al *Phys. Rev. Lett* **2007**, *98*, 083201

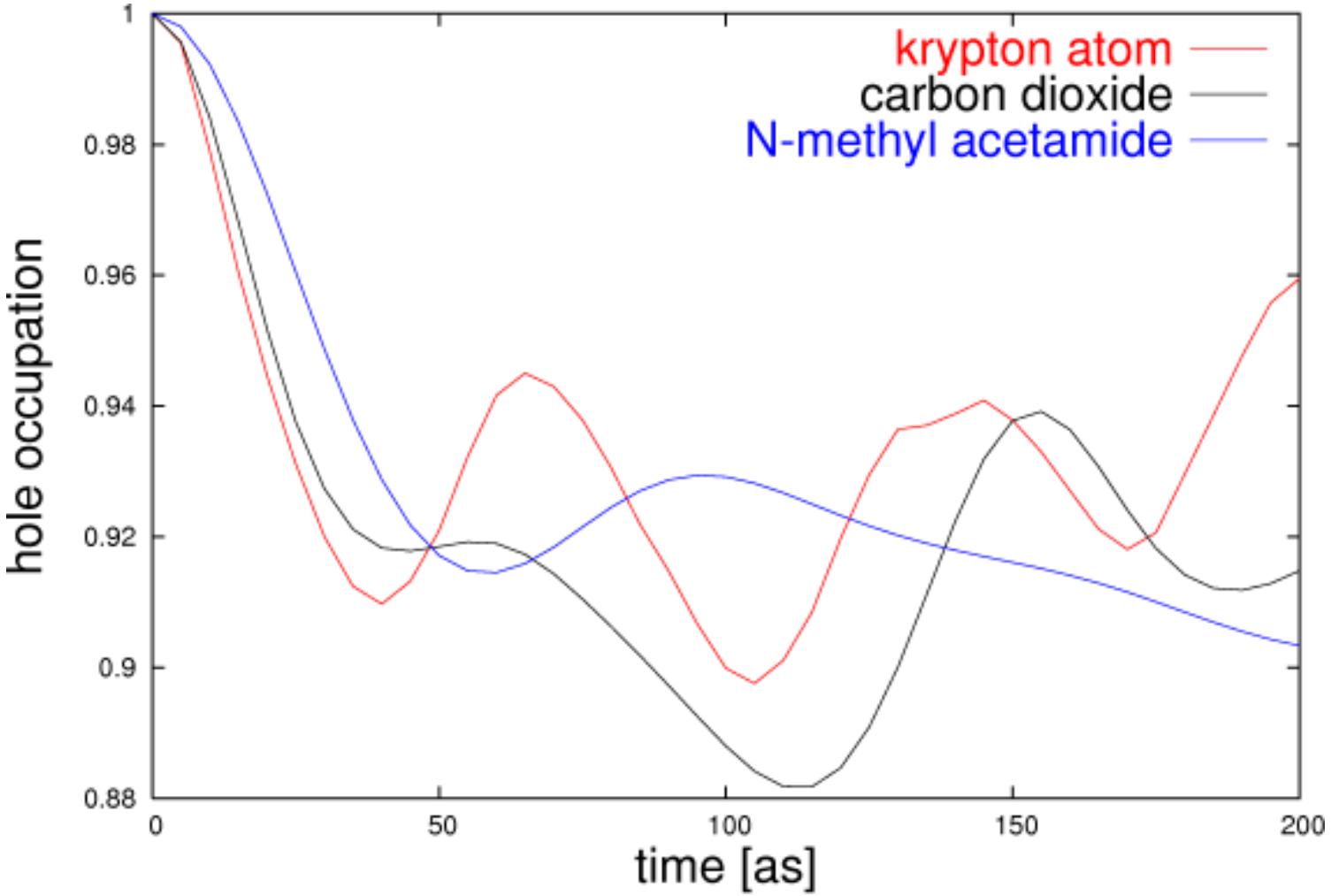
ICD in NeAr



A. I. Kuleff et al *Phys. Rev. Lett* **2007**, *98*, 083201

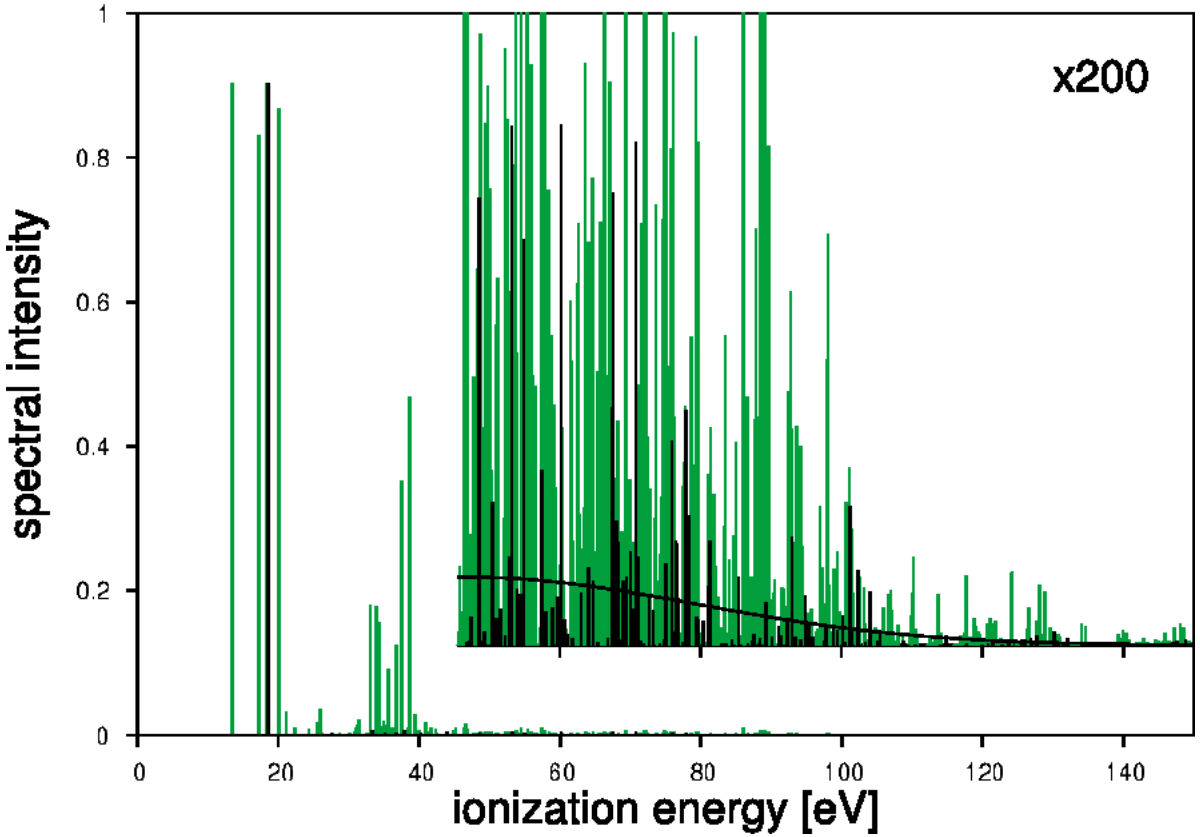
Universal Attosecond response to the removal of an electron

The hole occupation on a 200 as time scale for different systems



[1] J. Breidbach et al *Phys. Rev. Lett* **2005**, *94*, 033

The ionization spectrum of CO_2

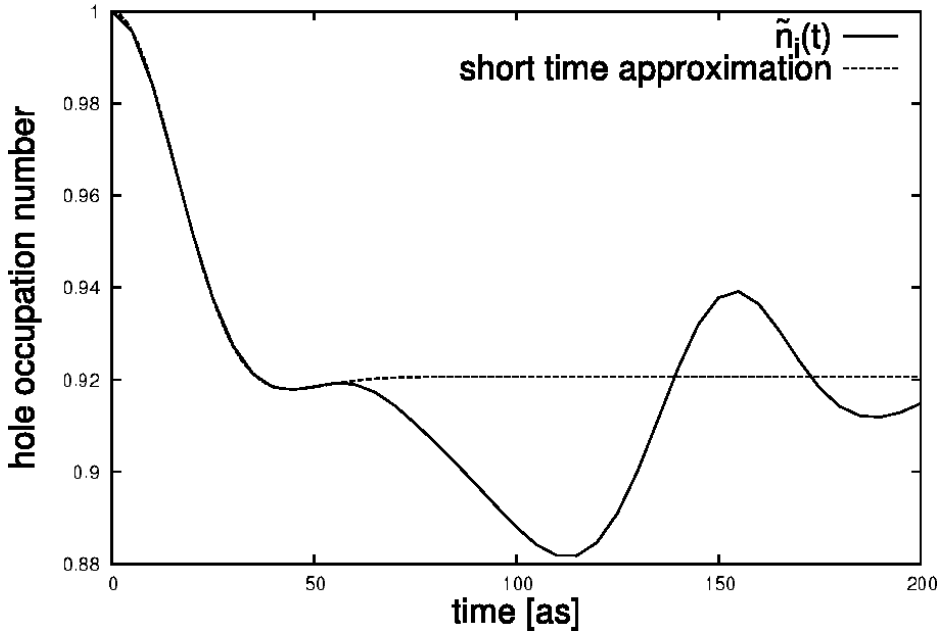


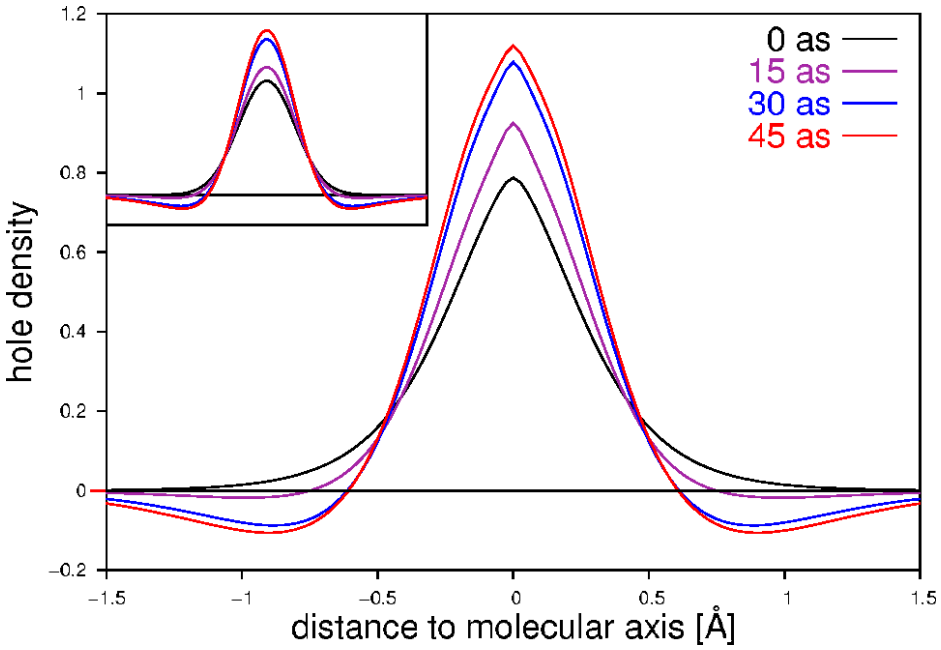
lines in black correspond to the eigenstates

contributing to the nonstationary state prepared

[1] J. Breidbach et al *Phys. Rev. Lett* **2005**, *94*, 033

Attosecond response





$$\tilde{n}_i(t) = 1 - A\left[1 - cos(\Omega t)exp(-\Delta^2 t^2)\right], \Omega = \bar{E} - E_{I_0}$$

$$Q(\vec{r}, t) = c(t)\left\{|\tilde{\varphi}_i(\vec{r})|^2 - \alpha h(\vec{r})\left[1 - cos(\Omega t)exp(-\Delta^2 t^2)\right]\right\}$$

$h(\vec{r})$ exchange-correlation hole function

[1] J. Breidbach et al *Phys. Rev. Lett* **2005**, *94*, 033

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