

Attosecond Spectroscopy of Small Organic Molecules: XUV pump-XUV probe Scheme in Glycine

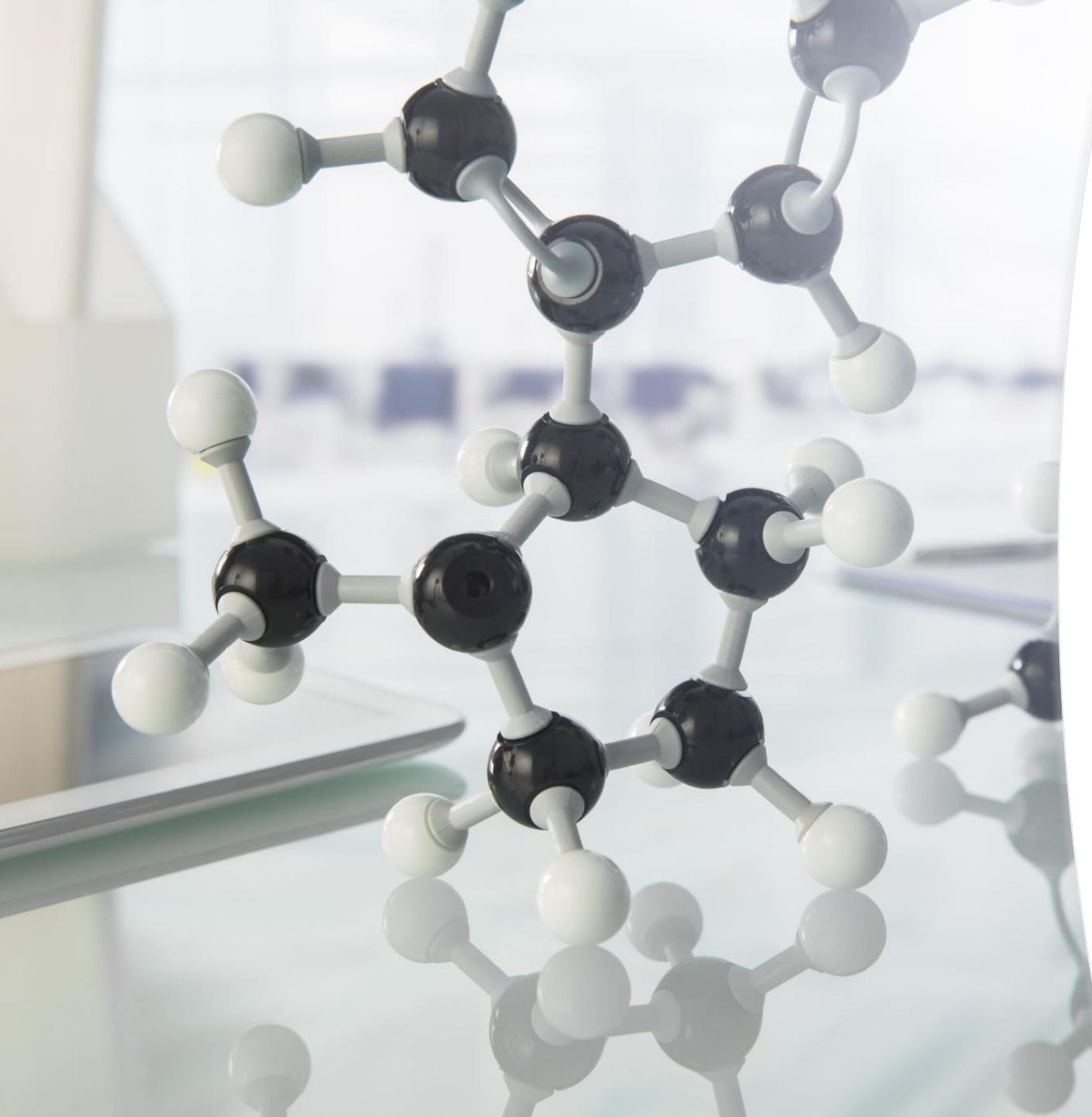
Jorge Delgado Guerrero

UAM/IMDEA Nanociencia

16 th USERS Conference

Cáceres 15th September 2022



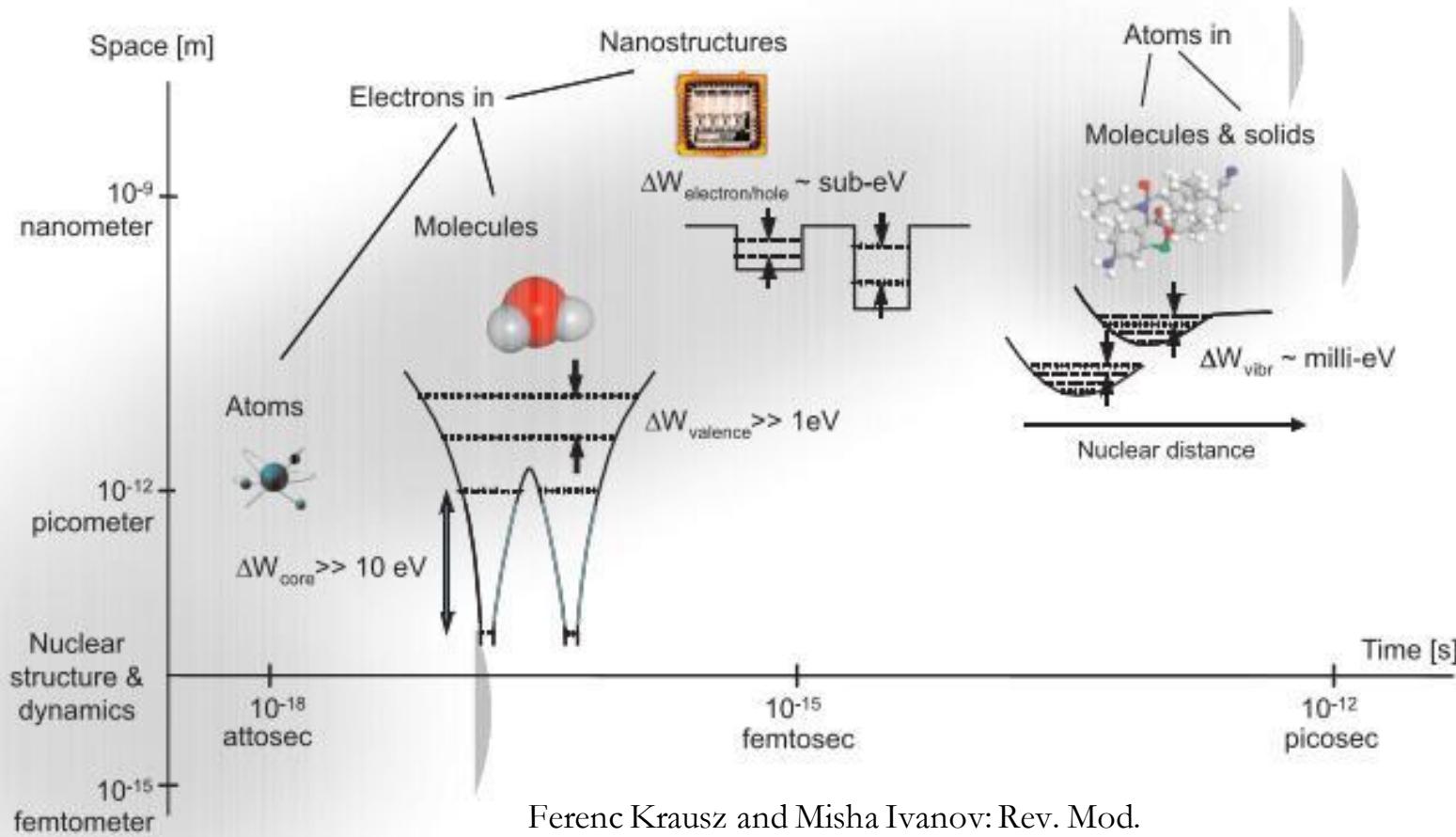


Outline

- Introduction
- Attosecond XUV Pump – XUV Probe in Glycine:
 - Computational techniques
 - Cation Results
 - Dication Results
 - Conclusions
 - What's next

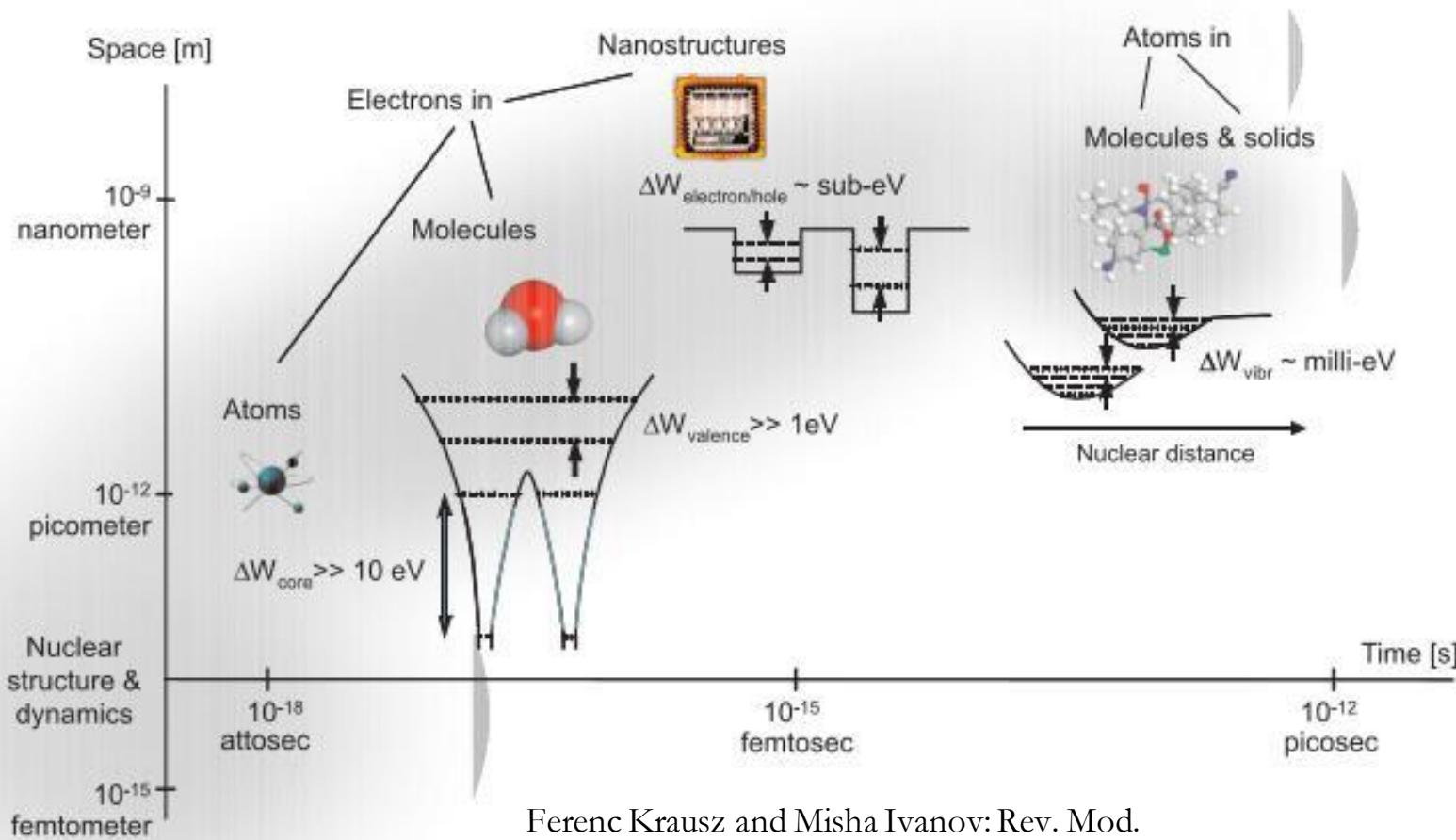
Introduction

Laser technology: time resolve evolution:



Ferenc Krausz and Misha Ivanov: Rev. Mod.
Phys., Vol. 81, No. 1, January–March 2009

Introduction

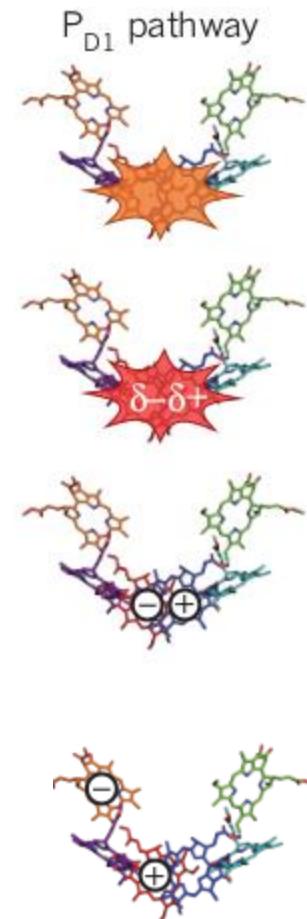


Laser technology: time resolve evolution:

- **1960** 1st Laser: ns (10^{-9} s) resolution
- **1970** ps (10^{-12} s) Picochemistry
- **1980** fs (10^{-15} s) Femtochemistry (Nobel Prize A. H. Zewail)
- **2000** as (10^{-18} s) Attochemistry
- **'Real time observation and control of electronic motion on atomic and subatomic length scales'** [Ferenc Krausz and Misha Ivanov Rev. Mod. Phys., Vol. 81, No. 1, January–March 2009]

Attosecond science:

- **charge transfer** (~ 100 fs) : Electron dynamics is accompanied by nuclear rearrangements

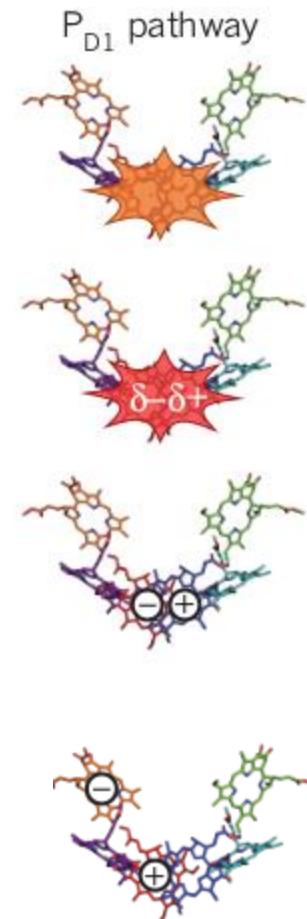


Romero E, et al. Nature 543, 355–365 (2017)

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Sub-fs dynamics that ignites this process ?



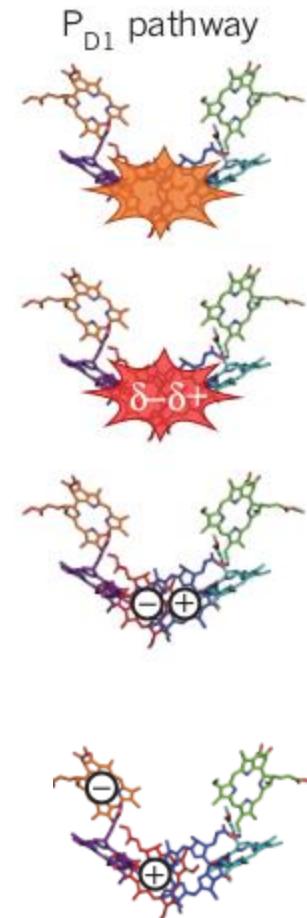
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Charge migration



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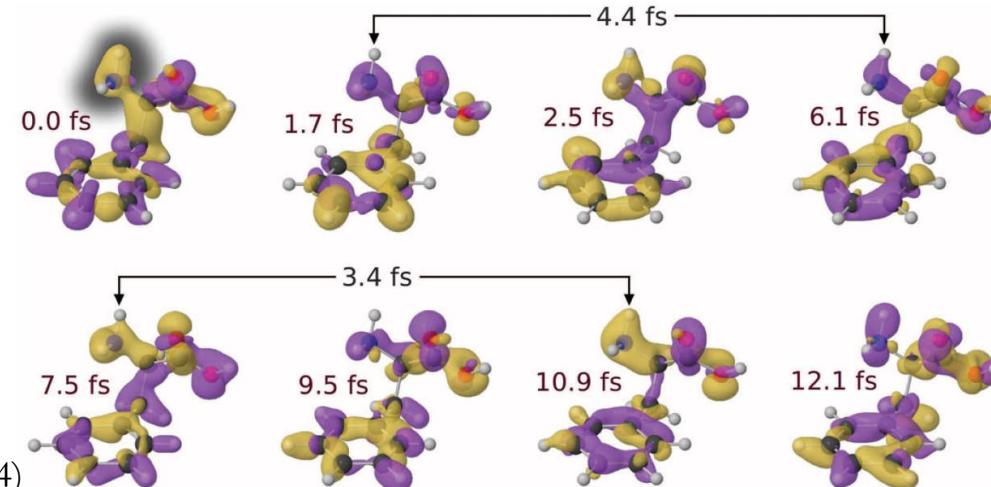
- Sub-fs electron dynamics: ***charge migration*** (\sim 1-10 fs)
- First simulations: **fixed-nuclei** approximation:
 - **Holes** resulting from valence ionization of a molecule, **redistribute over the molecular skeleton in just a few femtoseconds**
[F. Remacle and R. D. Levine, Proc. Natl. Acad. Sci. U. S. A., 2006, 103, 6793–6798]
 - Charge migration: it results from the **superposition of electronic states which arises after molecular excitation or ionization.**
[A.I. Kuleff and L. S. Cederbaum, J. Phys. B: At., Mol. Opt. Phys., 2014, 47, 124002]

Attosecond science:

- Sub-fs electron dynamics: **charge migration** (\sim 1-10 fs)
 - First simulations: **fixed-nuclei** approximation:
 - Ultrafast electronic response to and UV pulse: initial electronic wave packet results in a charge dynamics which is significantly different from the charge dynamics generated by removing an electron from a particular orbital
- [D. Ayuso, A. Palacios, P. Decleva and F. Martín, Phys. Chem. Chem. Phys., 2017, 19, 19767–19776]

- Observation of sub-fs electron dynamics after valence ionization of phenylalanine with an attosecond pulse
Sub-fs electron dynamics: associated to specific fragmentation channels.

[F. Calegari et al. Science 346, 336 (2014)]



Attosecond science:

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[D. Ayuso, A. Palacios, P. Decleva, I. Tavernelli, M. Lara-Astiaso, Chem. Phys., 2017, 469, 19767–19776]

Nuclear Movement

- **Observation of nuclear movement with an attosecond pulse**

Sub-fs electron Ehrenfest Dynamics: charge dynamics created by an attosecond XUV pulse is

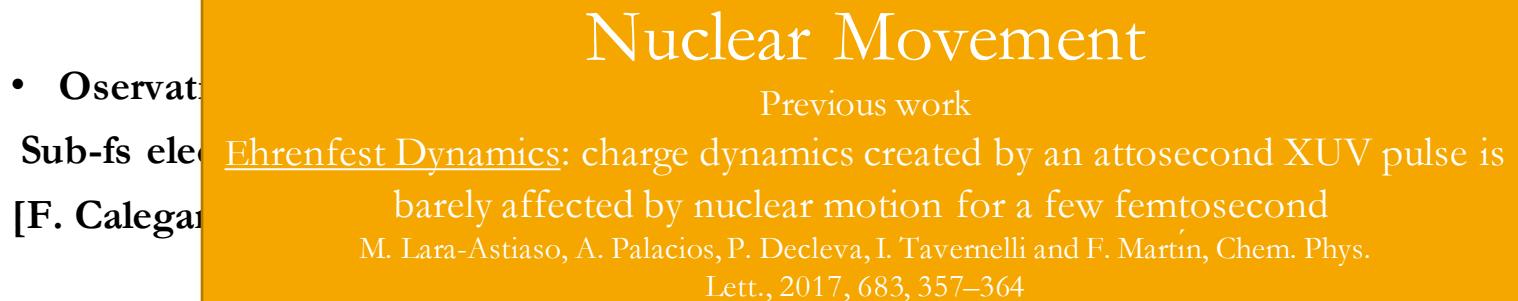
[F. Calegaro] barely affected by nuclear motion for a few femtosecond

M. Lara-Astiaso, A. Palacios, P. Decleva, I. Tavernelli and F. Martin, *Chem. Phys. Lett.*, 2017, 683, 357–364

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[D. Ayuso, A. Palacios, P. Decleva, I. Tavernelli, F. Martin, Chem. Phys., 2017, 469, 2017–2024] 19767–19776]



Attosecond science:

Unsolved questions:

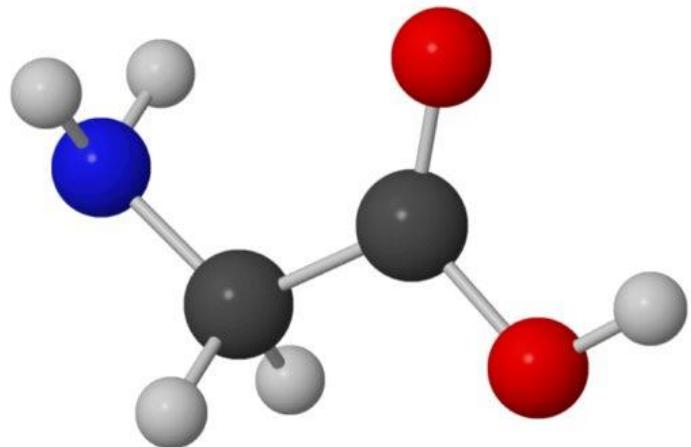
- Link between **charge migration** and **charge transfer**?
- Sub-fs electron dynamics, Can they be **identified unambiguously in an experiment**?
- Will **electronic coherences** resulting from attosecond ionization **survive** when nuclear motion comes into play?

Attosecond XUV-pump/XUV-probe scheme in glycine

- J. Delgado, M. Lara-Astiaso, J. Gozález-Vázquez, P. Decleva, A. Palacios, F. Martín Faraday Discuss., 228, 349-377, (2021)

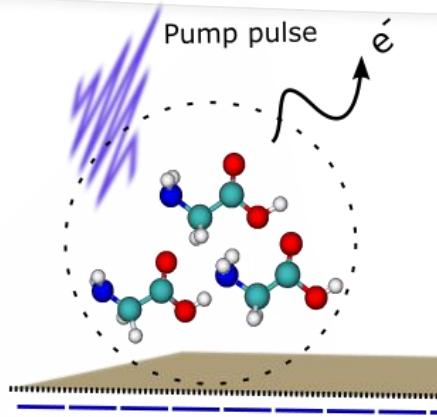
Attosecond XUV-pump/XUV-probe scheme in glycine

MOLECULE

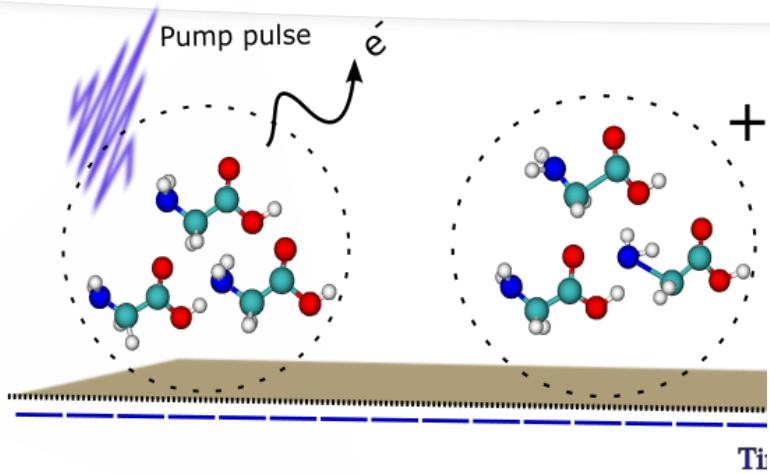


- Simplest aminoacid
- 40 electrons
- Main function: precursor of proteins
- Gly-I: most abundant conformer in standard conditions

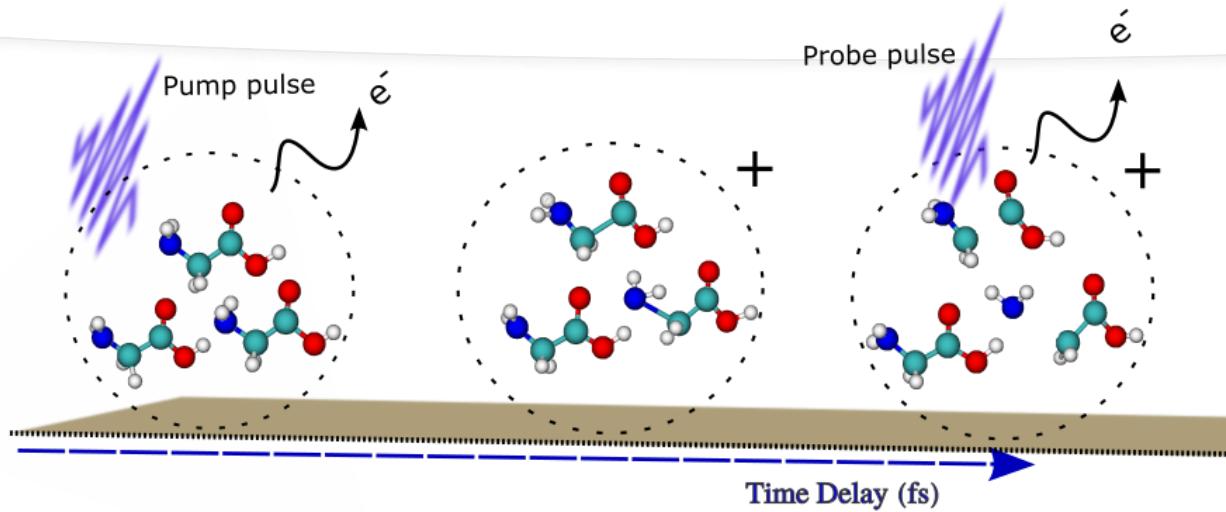
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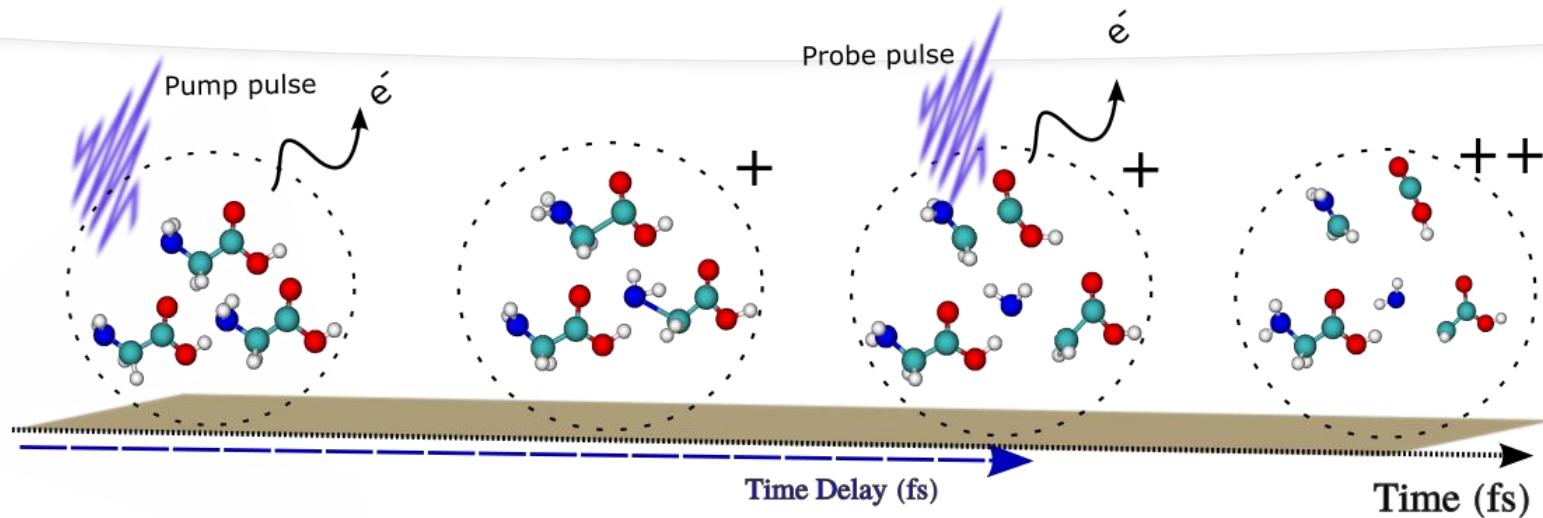
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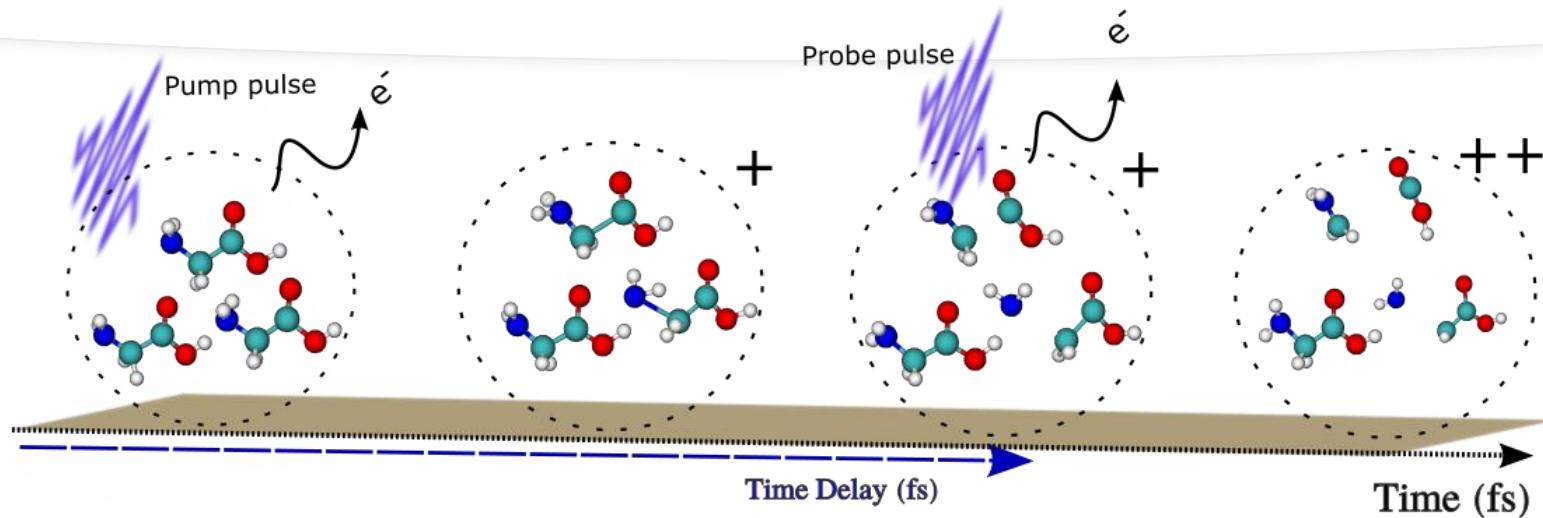
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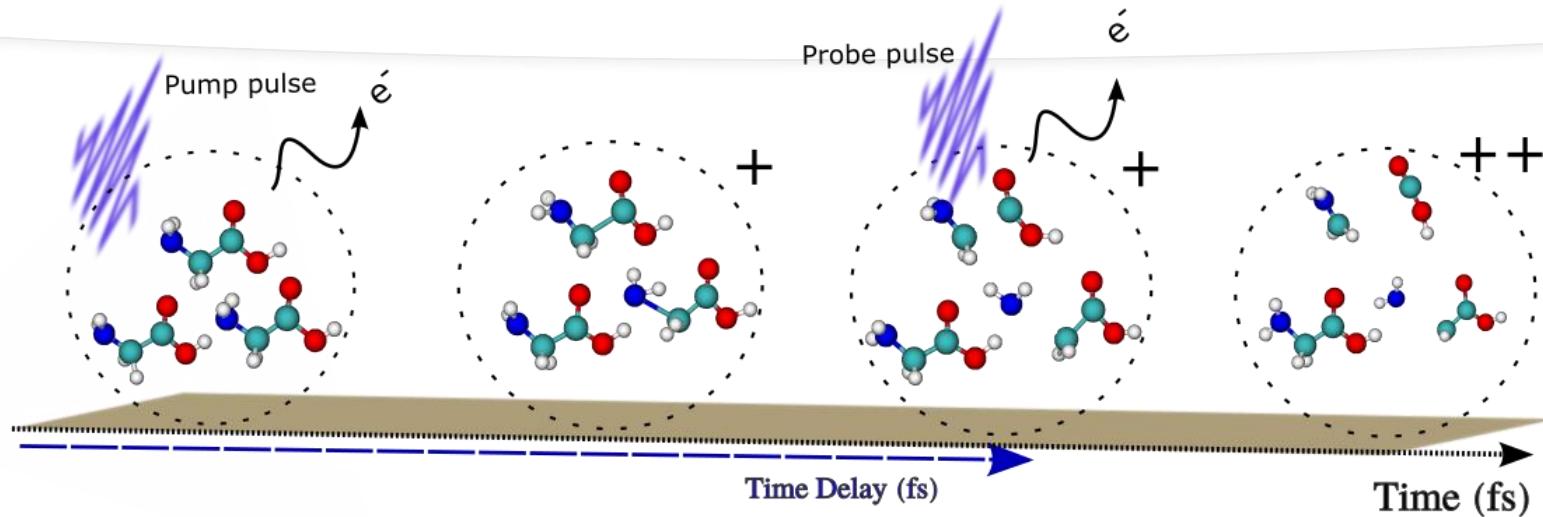


Attosecond XUV-pump/XUV-probe scheme in glycine



Full quantum-mechanical description
of the experiment: computationally
unaffordable (N-power scaling with the
N-nuclear degrees of freedom)

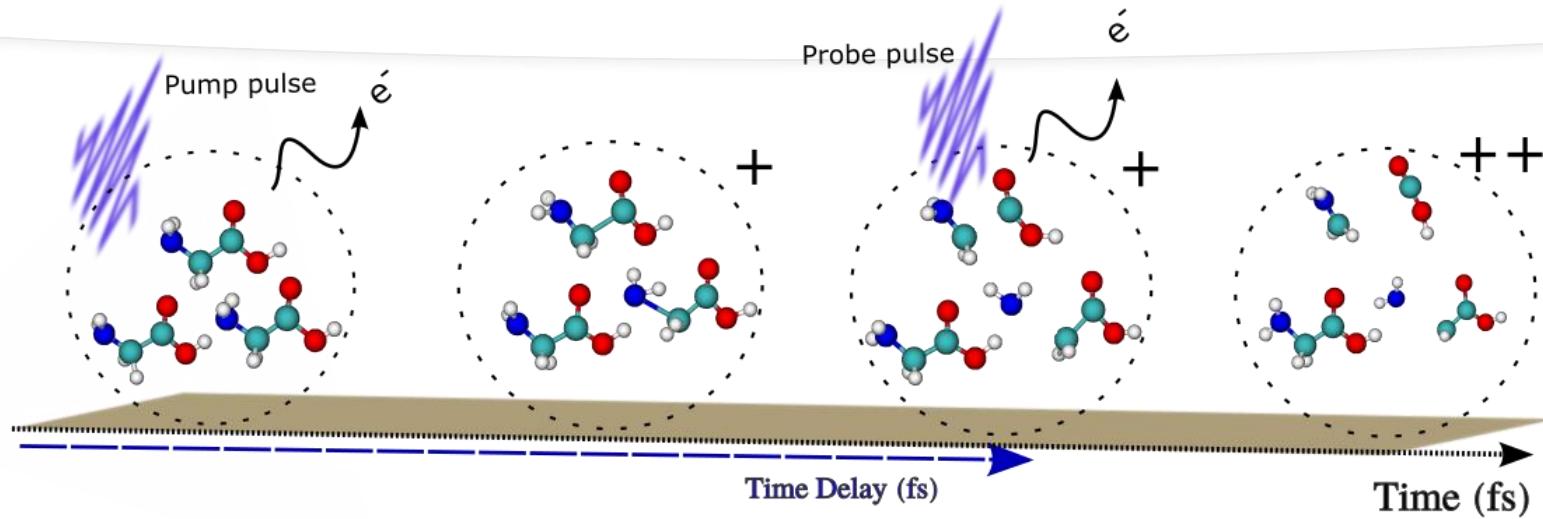
Attosecond XUV-pump/XUV-probe scheme in glycine



Full quantum-mechanical description
of the excited states is computationally
unaffordable (exponential scaling with the
N-nucleon times of $N^{3/2}$)

- **Affordable: semiclassical approach:**
 - Electrons: quantum-mechanical treatment
 - Nuclei: classical treatment (some quantum effects cannot be described)

Attosecond XUV-pump/XUV-probe scheme in glycine



Full quantum-mechanical description
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- **Affordable: semiclassical approach:**
 - Electrons: quantum-mechanical treatment
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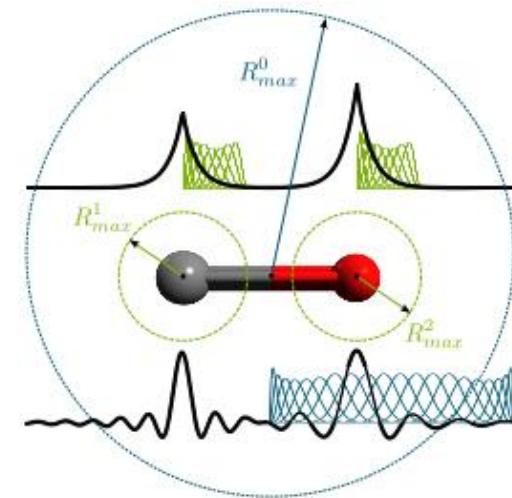
- How can we tackle the semiclassical problem? We divide it into:
 1. **Ionization process:** action of the pulse, **1st order TDPT**
 2. **Propagation:** Tully Surface Hopping Algorithm

Attosecond XUV-pump/XUV-probe scheme in glycine: Ionization process

- Broadband of the XUV pulse: ionize **multiple ionization channels**
- We need a **multi-configurational approach: CAS-DFT approach**

Attosecond XUV-pump/XUV-probe scheme in glycine: Ionization process

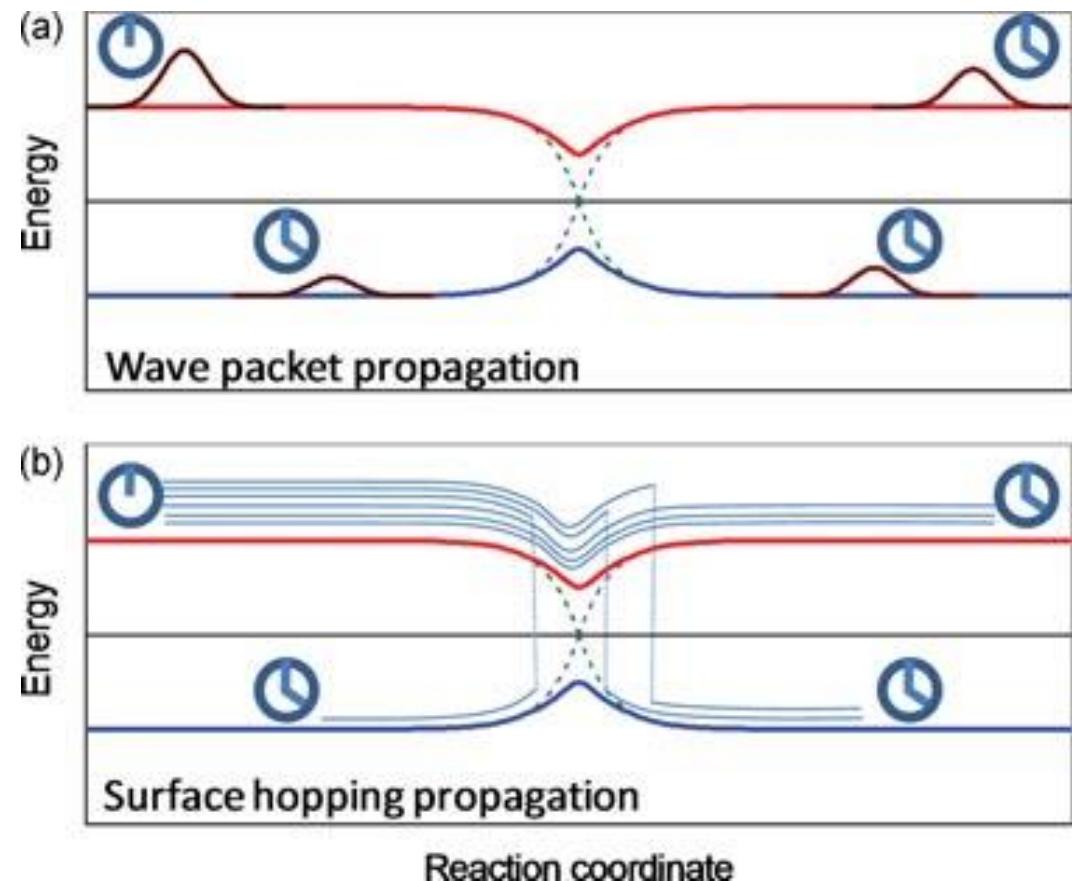
- Broadband of the XUV pulse: ionize **multiple ionization channels**
- We need a **multi-configurational approach: CAS-DFT approach**
 - **CAS-DFT approach:**
 - Description N-1 electron **cation: Dyson orbitals** (MCSCF approach)
 - [A. Ponzi, et al. J.Chem. Phys., 2016, 144, 084307]
 - **Continuum orbitals:** Static-Exchange DFT method (**DFT approach**)
[M. Nisoli, P. Decleva, F. Calegari, A. Palacios and F. Martín, Chem. Rev., 2017, 117, 10760–10825]
 - Galerkin approach
 - Sudden ionization
 - Koopman's picture of KS-DFT
 - **Multicenter B-Spline Basis**



Etienne Plèsiat, PhD thesis (2012)

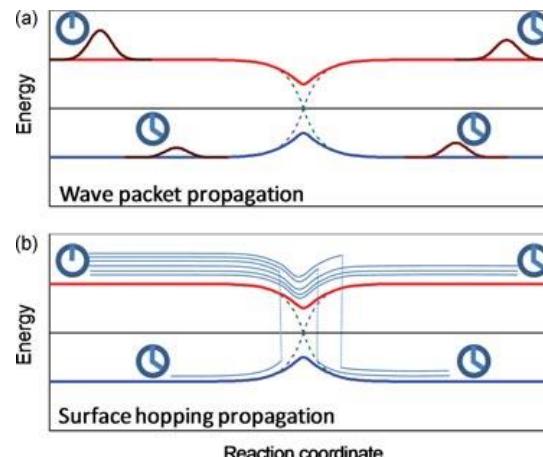
Attosecond XUV-pump/XUV-probe scheme in glycine: Propagation process

- Tully Surface Hopping Algorithm: mimic the quantum-mechanical behaviour by means of a semiclassical approach [M. Richter, P. Marquetand, J. González-Vázquez, I. Sola and L. González, *J. Chem. Theory Comput.*, 2011, 7, 1253–1258]



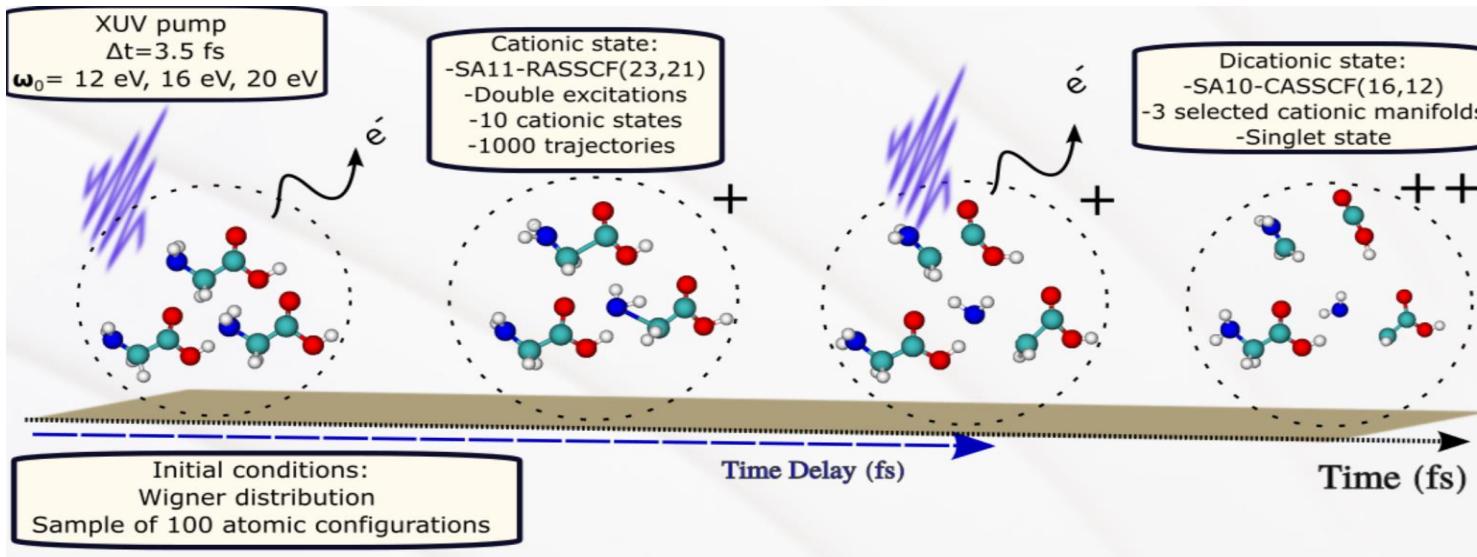
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- Initial wavepacket: Wigner distribution (~ 100 geometries)
- For each geometry
 - Single point calculation of the electronic structure using RASSCF
 - Propagate nuclei using Newton's Equation
 - Every electronic wavefunction is solved using TDSE
- Decoherence factor, PE curves on the fly, non-adiabatic effects

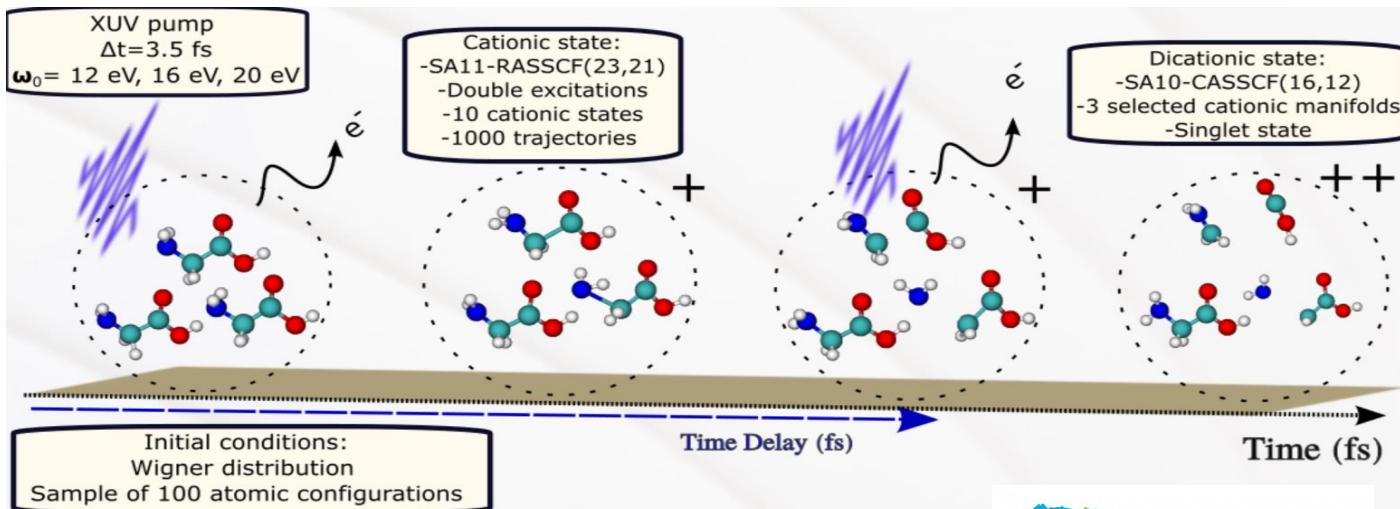
Attosecond XUV-pump/XUV-probe experiment in glycine: Full Picture



- Cation: 1000 trajectories, Firefly QC
- Dication: Molcas QC
- From Cation to Dication:
 - $1000 * (\text{singlet} + \text{triplet}) * 10$ dicationic states at every time step. Assuming 200 propagation points...
- Multicenter B-Spline basis:
 - One-center expansion: $R_{\max} = 30 \text{ a.u.}$, $L_{\max} = 14$, 188 B-Splines
 - Off-center expansion: spheres from 0.8 to 1.0 a.u.; $l_{\max} = 2$



Attosecond XUV-pump/XUV-probe experiment in glycine: Full Picture



HPC: mandatory

Each calculation: Requires HPC machinery
We need to perform multiple calculations

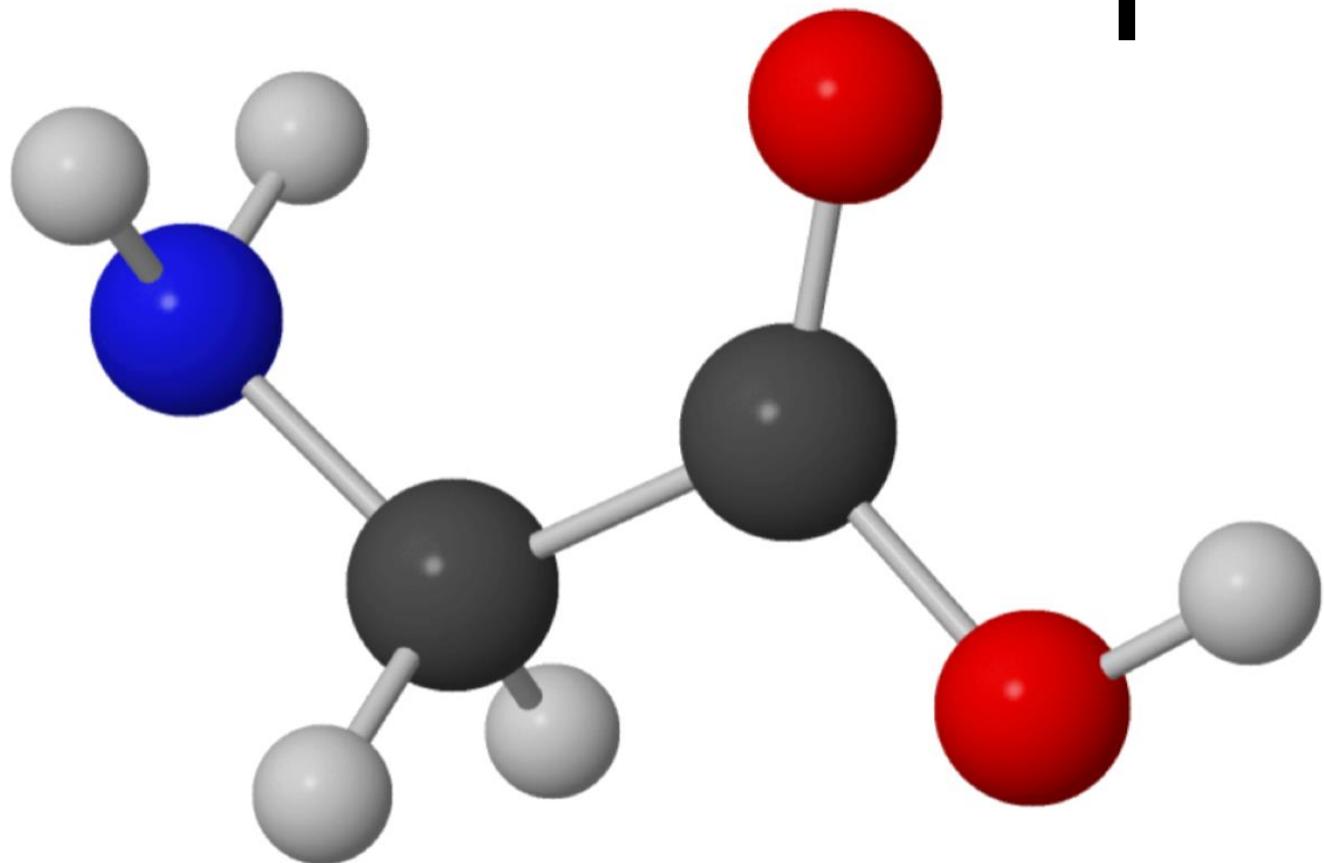


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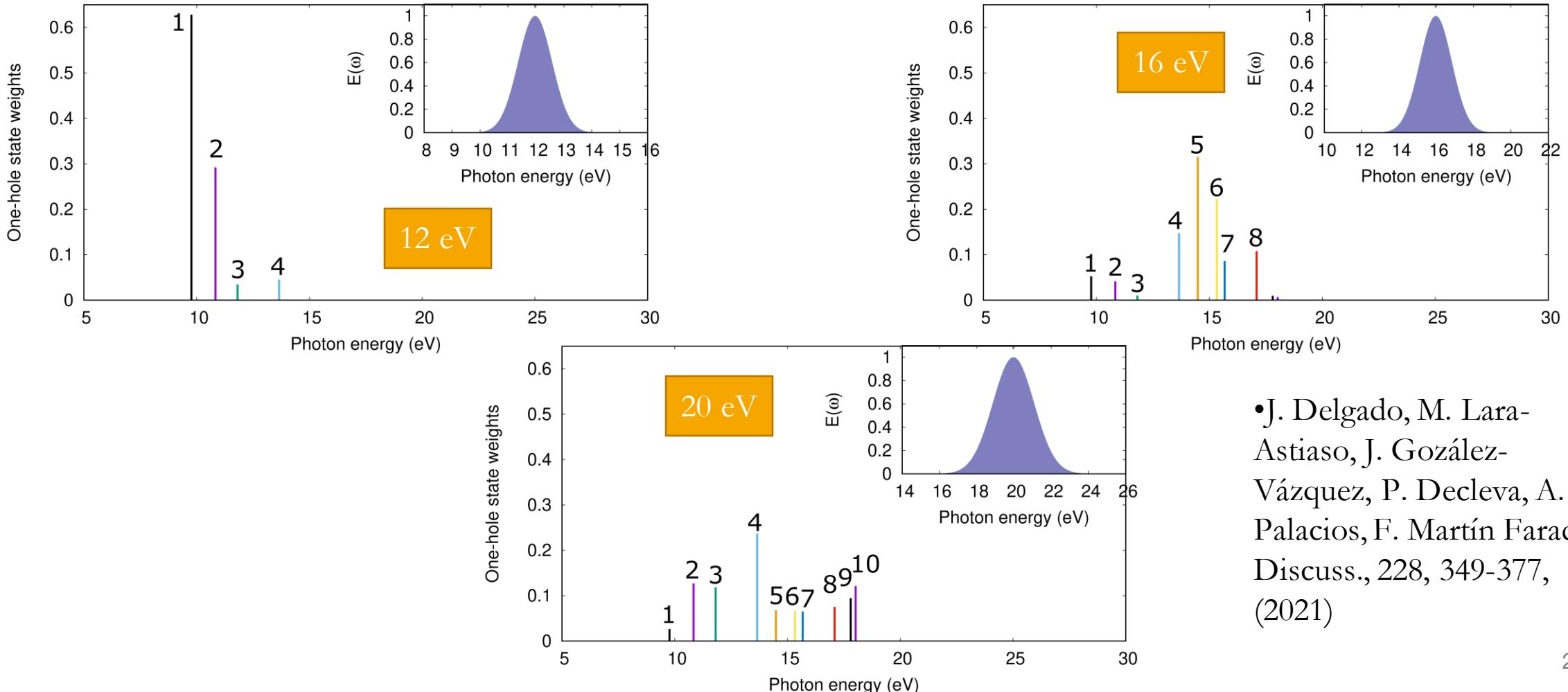
Attosecond XUV-
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Cation results

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Attosecond XUV-pump/XUV-probe experiment in glycine: Cation Results

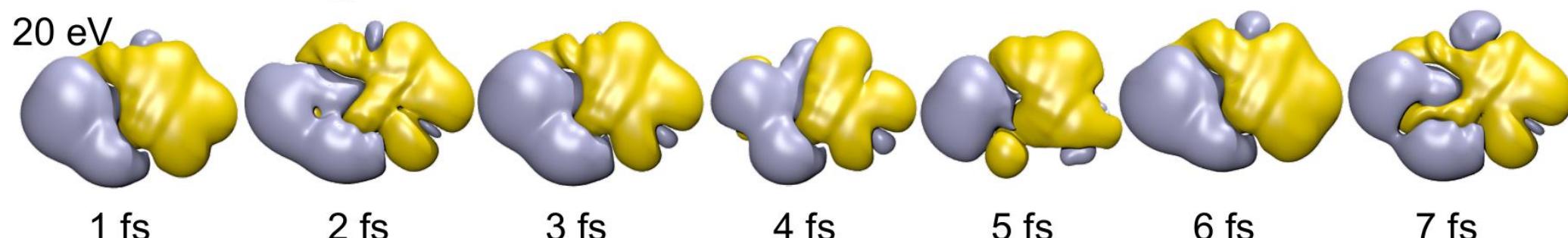
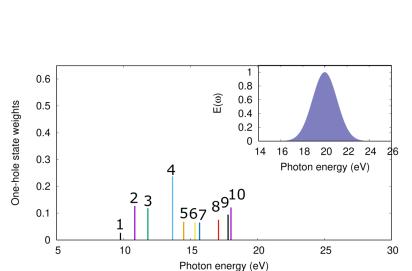
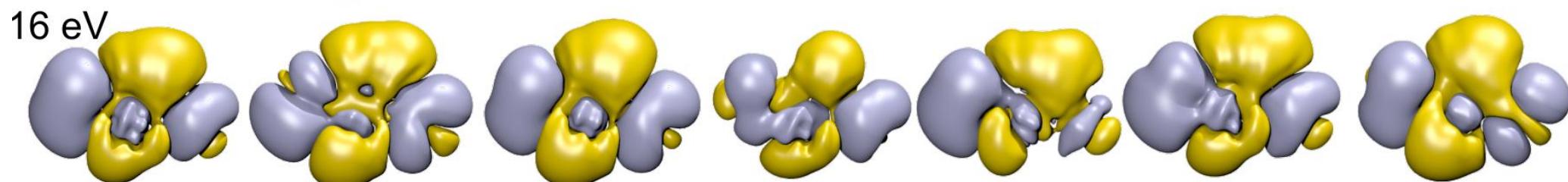
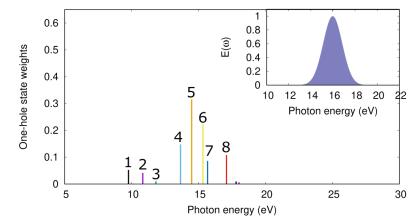
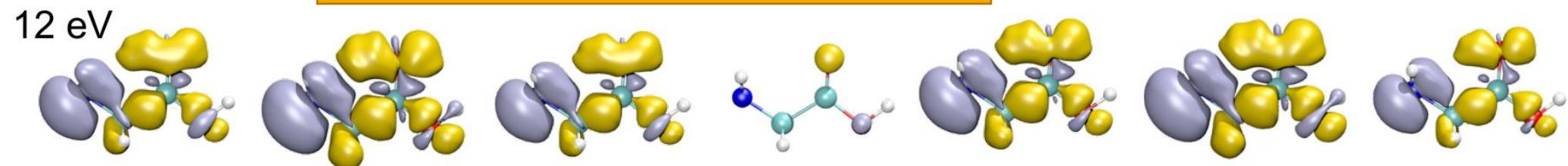
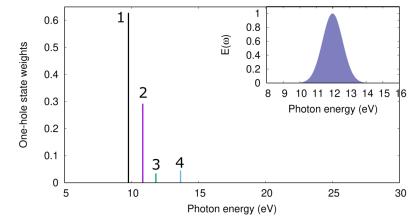
Ionization Probabilities



• J. Delgado, M. Lara-Astiaso, J. Gozález-Vázquez, P. Decleva, A. Palacios, F. Martín Faraday Discuss., 228, 349-377, (2021)

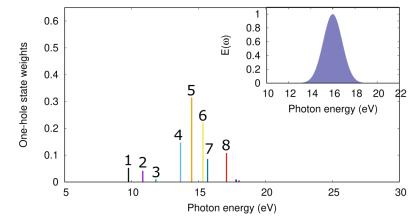
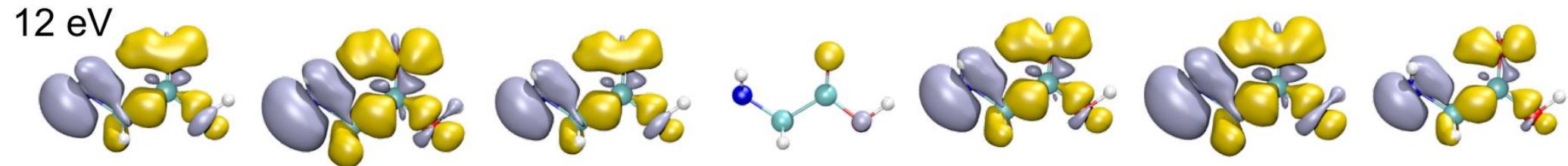
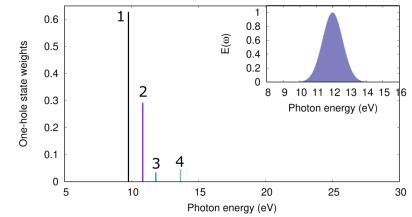
Attosecond XUV-pump/XUV-probe experiment in glycine: Cation Results

Electronic-coherences (Fixed nuclei)

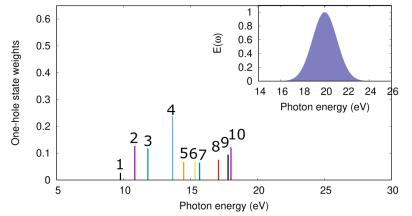
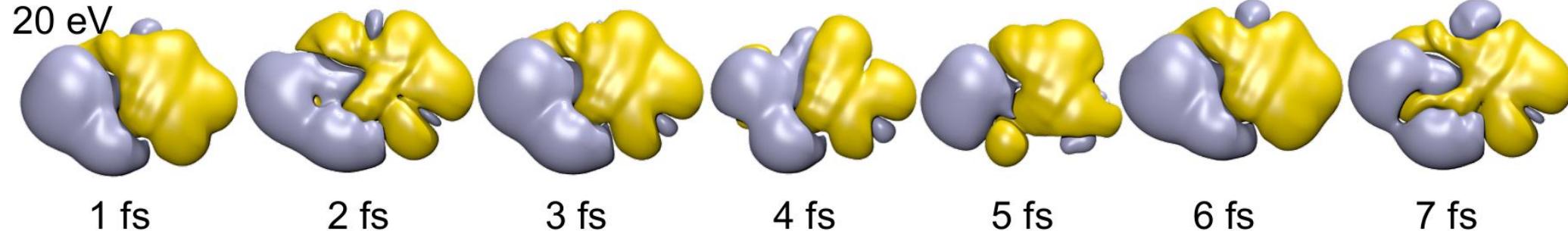


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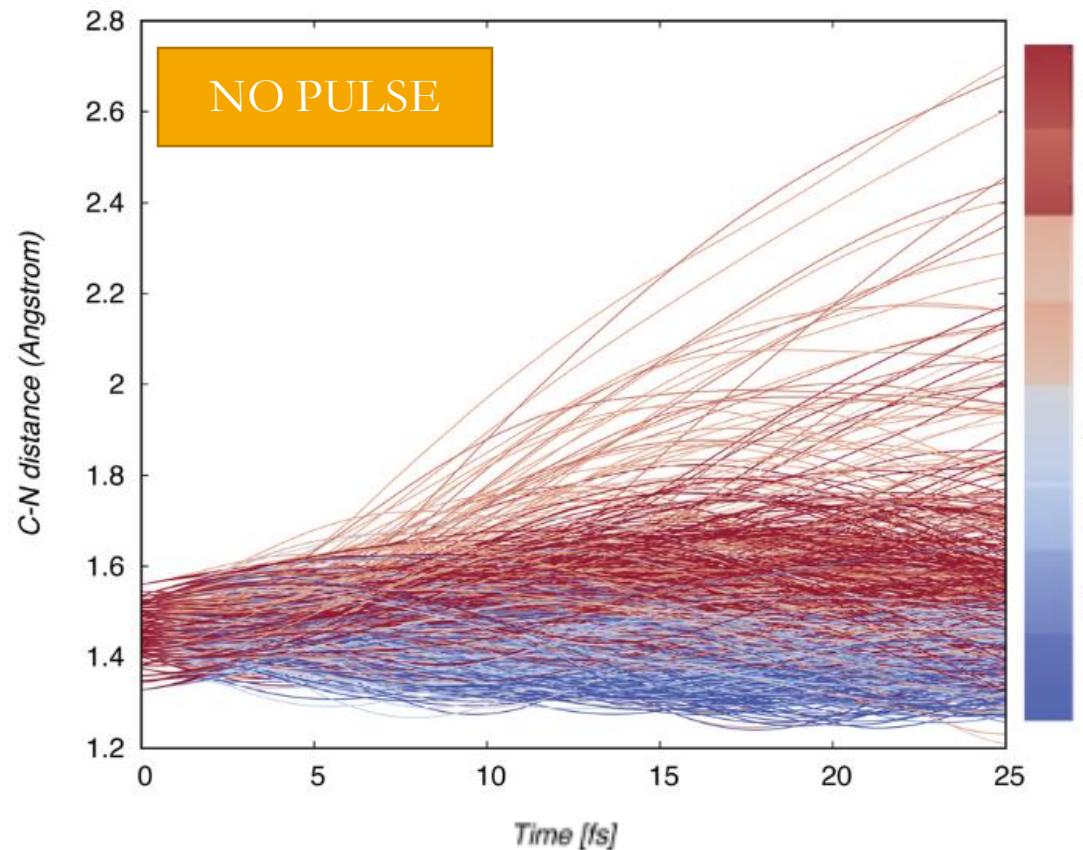
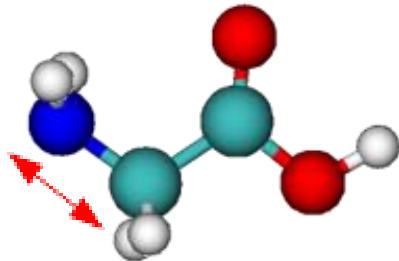
- Will **electronic coherences** resulting from attosecond ionization **survive** when nuclear motion comes into play?



1 fs 2 fs 3 fs 4 fs 5 fs 6 fs 7 fs

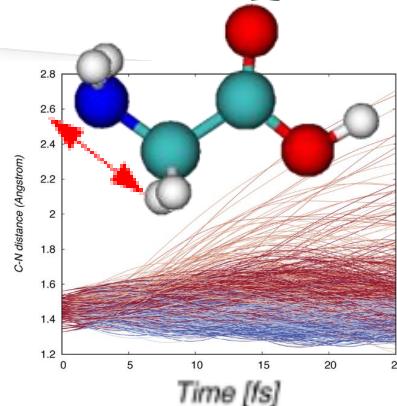
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Nuclear Dynamics

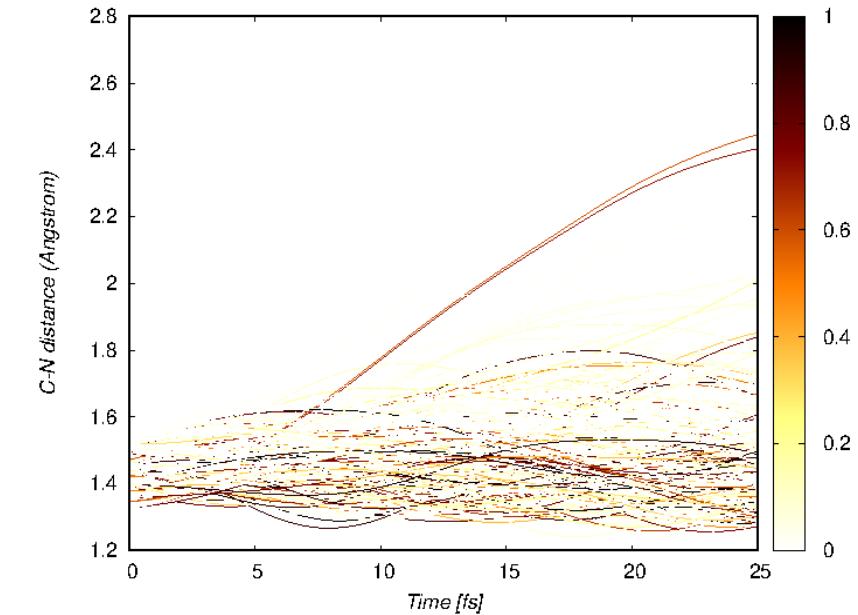
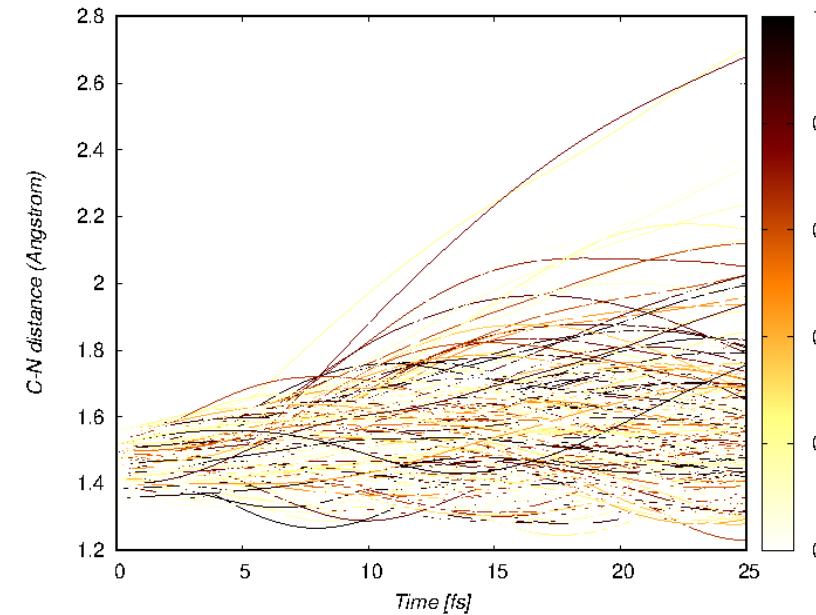
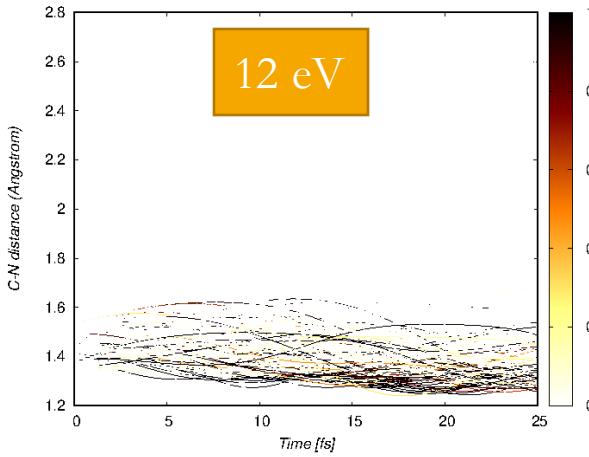


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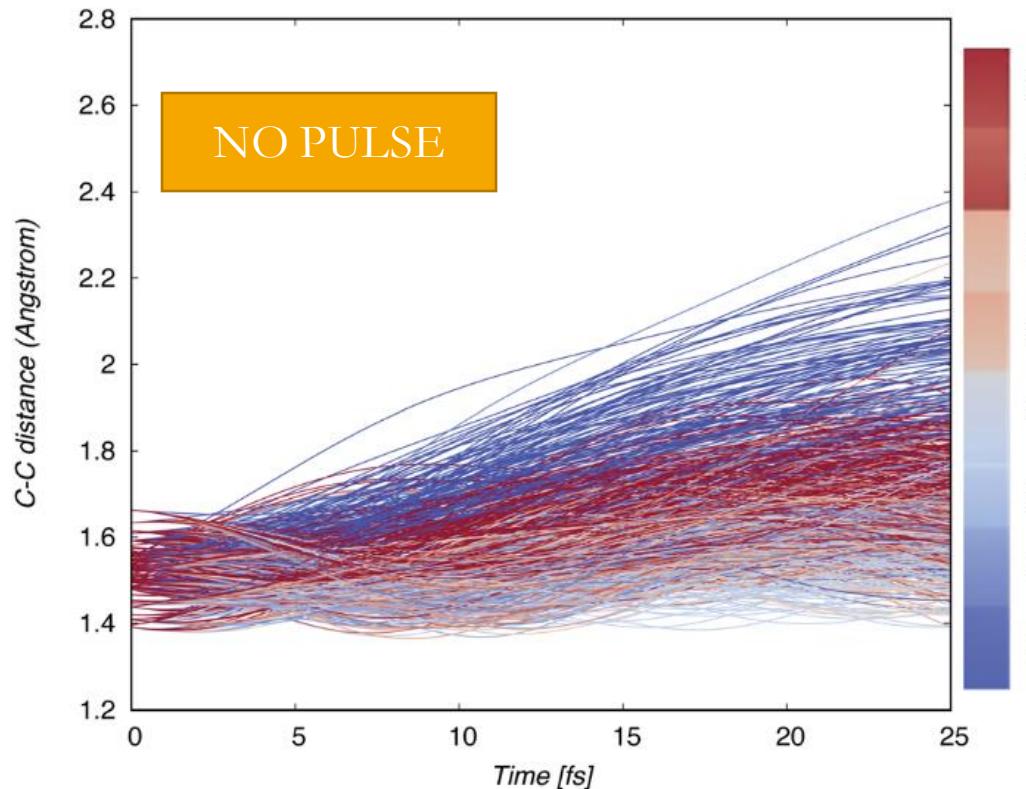
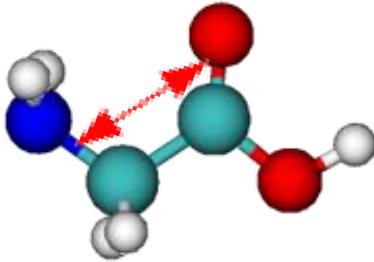


Nuclear Dynamics



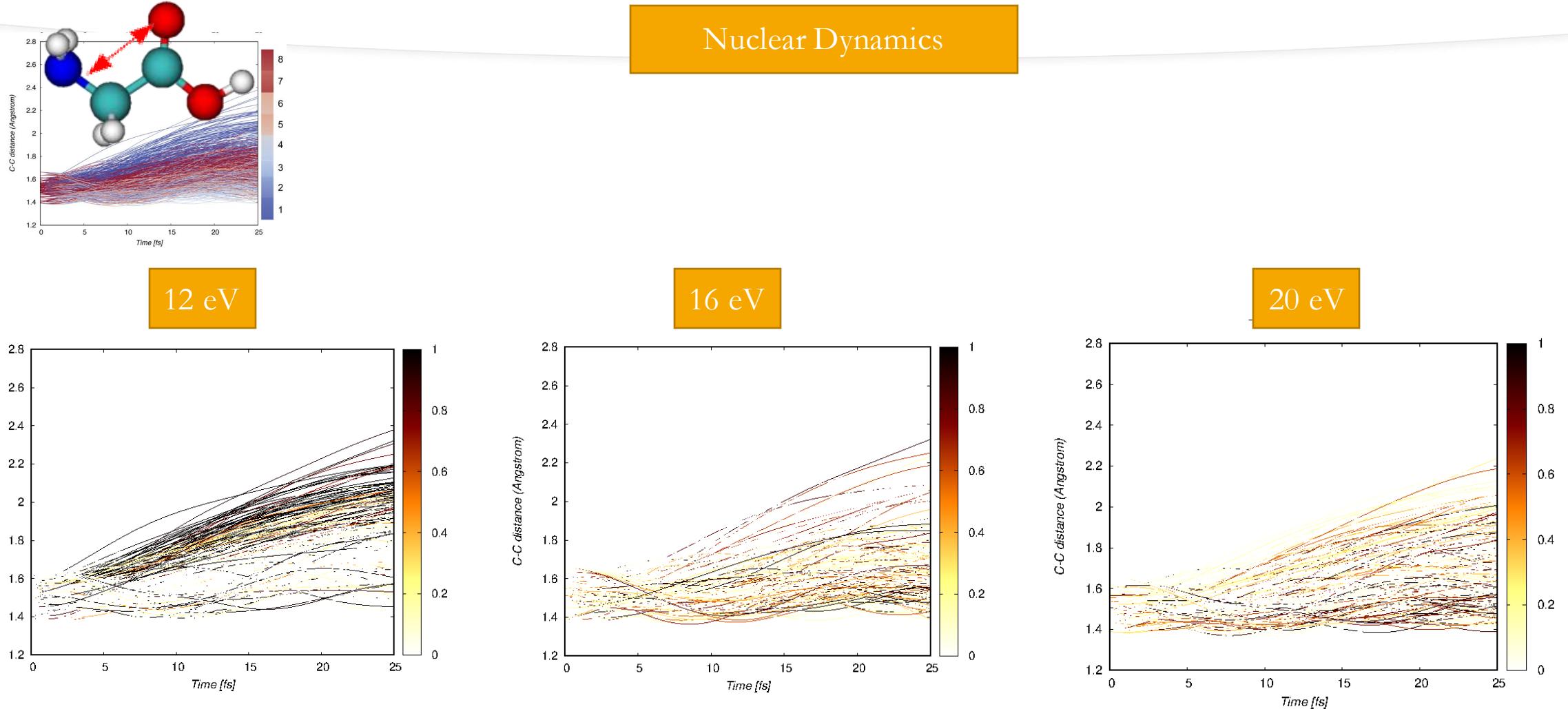
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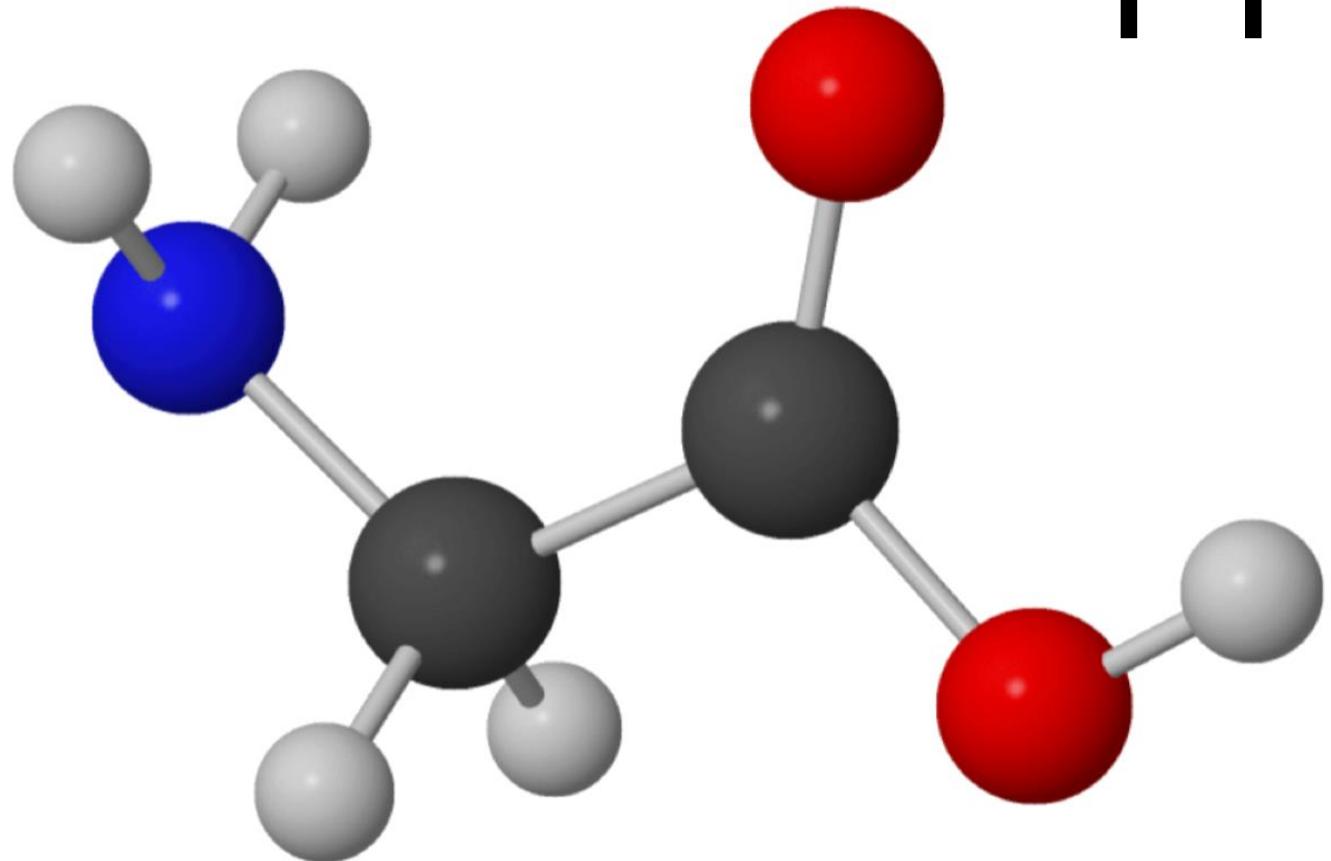


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Attosecond XUV-pump/XUV-probe experiment in glycine: Cation Results



Attosecond XUV-
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Dication results

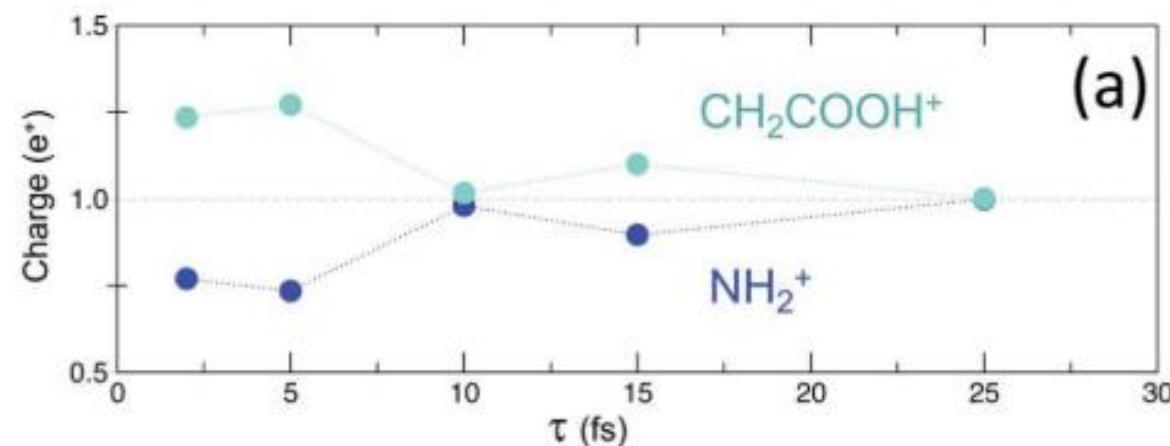
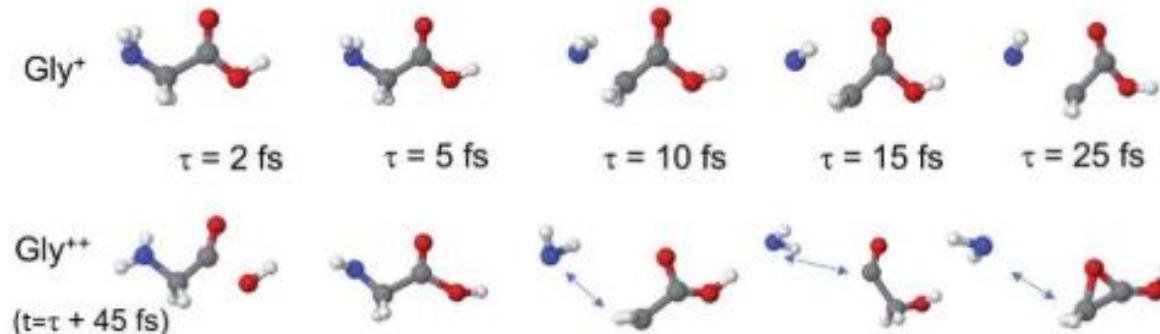
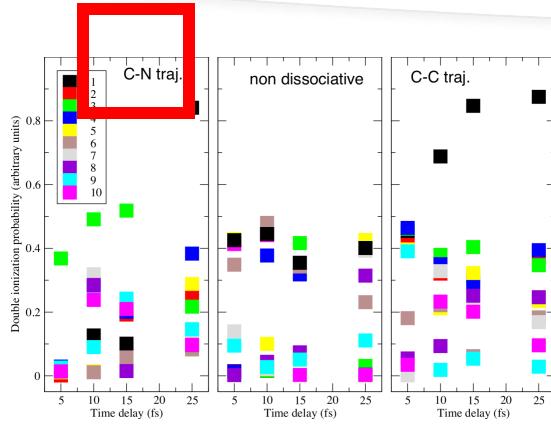


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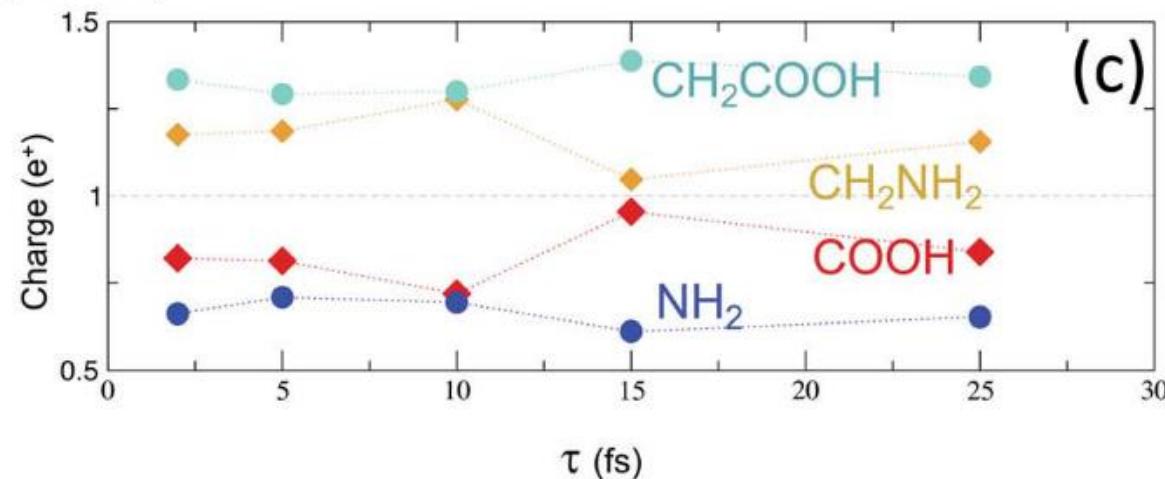
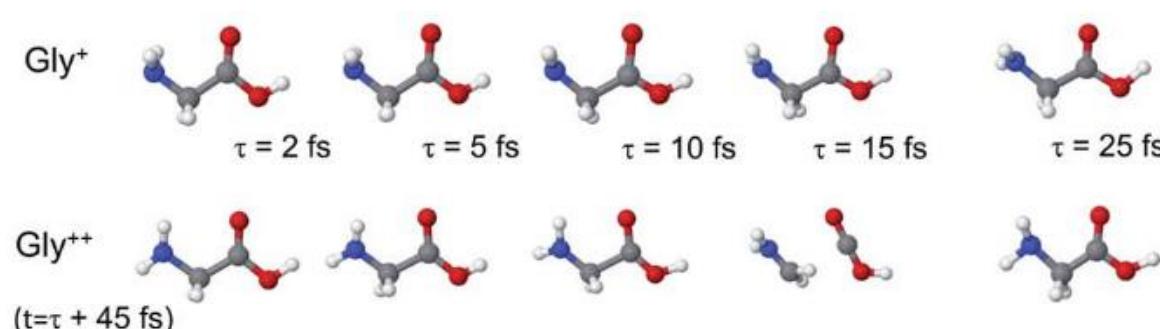
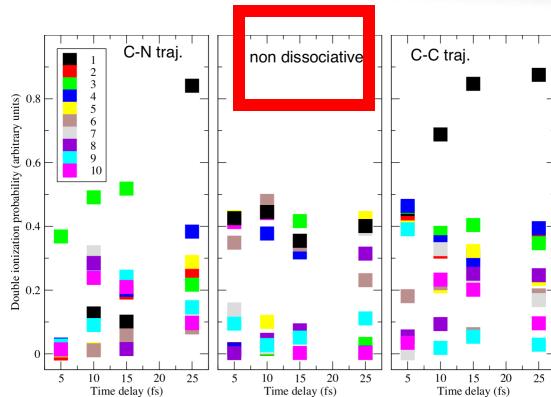
Attosecond XUV-pump/XUV-probe experiment in glycine: Dication Results

- Qualitatively analysis: Just present 3 trajectories
 - C-C bond breaking
 - No bond-breaking
 - C-N bond-breaking
- Question: Can we retrieve some information of the dynamics triggered by the pump pulse from the dicationic dynamics?
- Ionization with the pump pulse has not been considered. Considering the dyson norm, we just promote the cationic geometry to a dicationic state at a particular time delay, and then propagates it
 - From RASCCF(23,21)⁺ to CASSCF(16,12)⁺⁺
- Observable: charge of the fragments

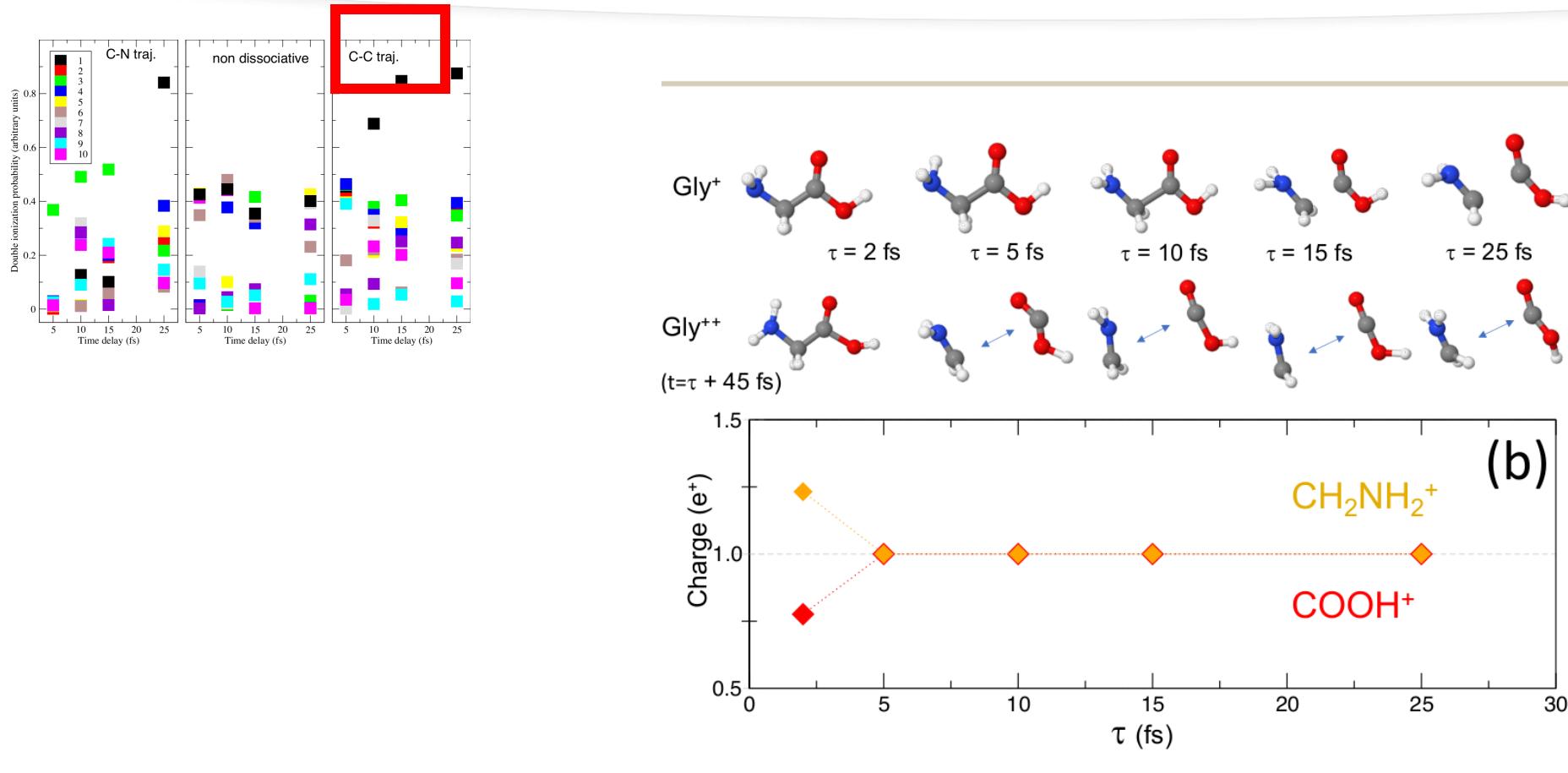
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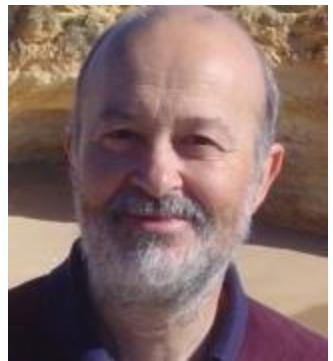
Attosecond XUV-pump/XUV-probe experiment in glycine: Dication Results



Conclusions

- We have proposed a model for a complete theoretical representation of a XUV pump-XUV probe scheme in the glycine molecule
- We have explored the most probable fragmentation pathways on Glycine and the possibility of selecting different fragmentation channels by engineering the central frequency of pump pulse
- Considering a qualitative approach, we have studied the role of the probe pulse in the dynamics, and the possibility to retrieve a signature of the electronic dynamics triggered by the pump pulse

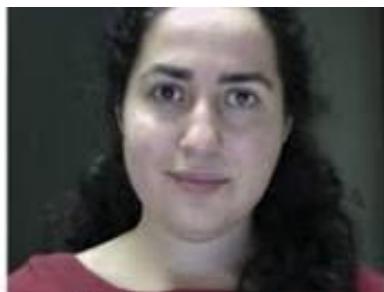
Acknowledgements



Fernando Martín



Alicia Palacios



Piero Decleva



Jesús
González-
Vázquez



Manuel Lara-Astiaso

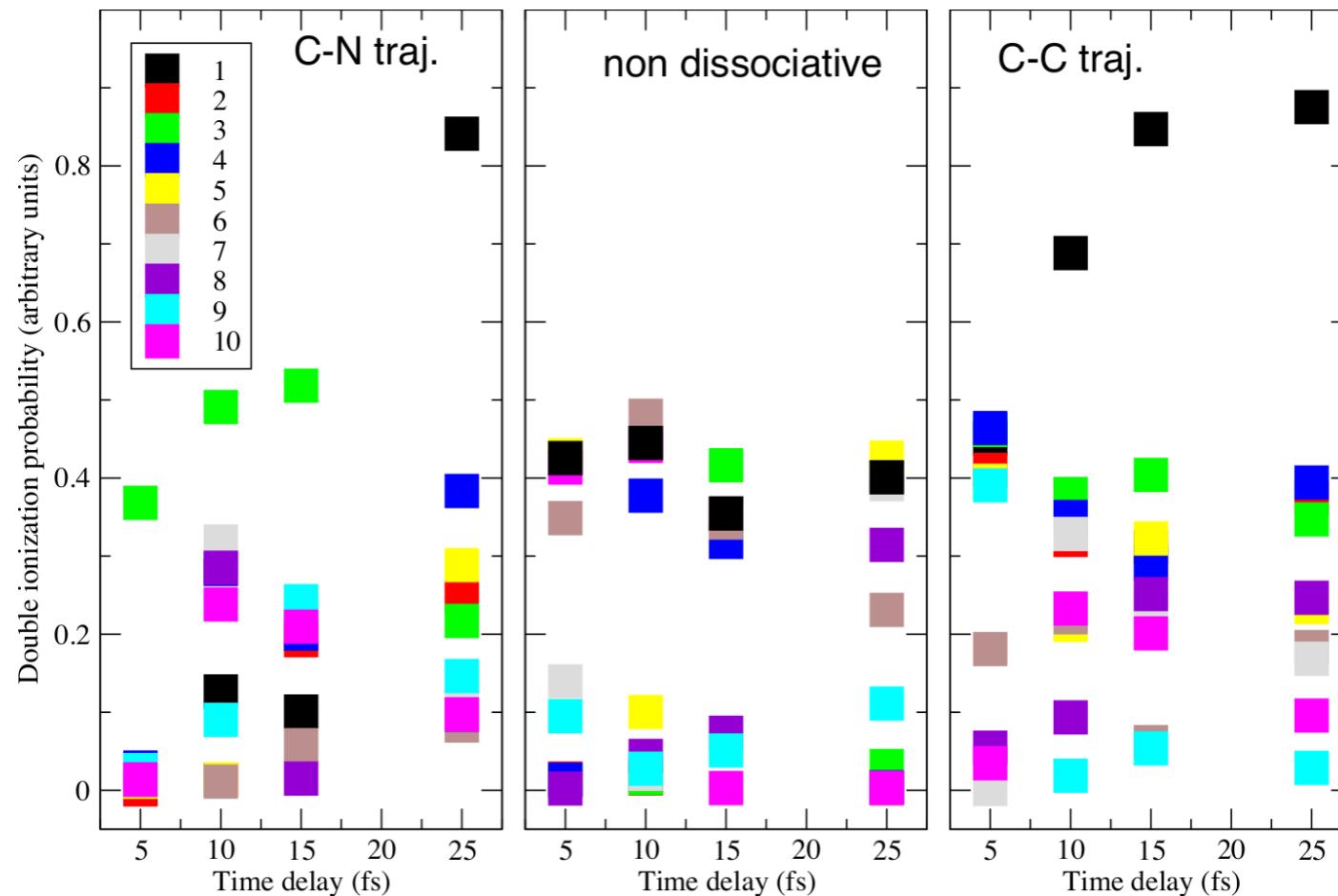


Appendix: Ionization equations

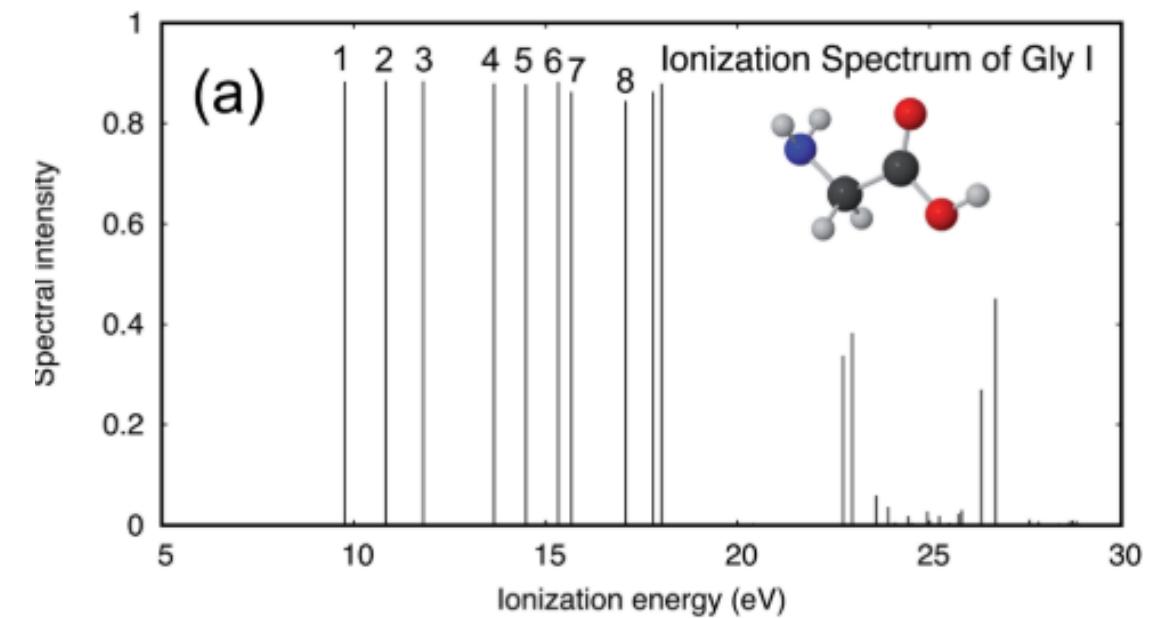
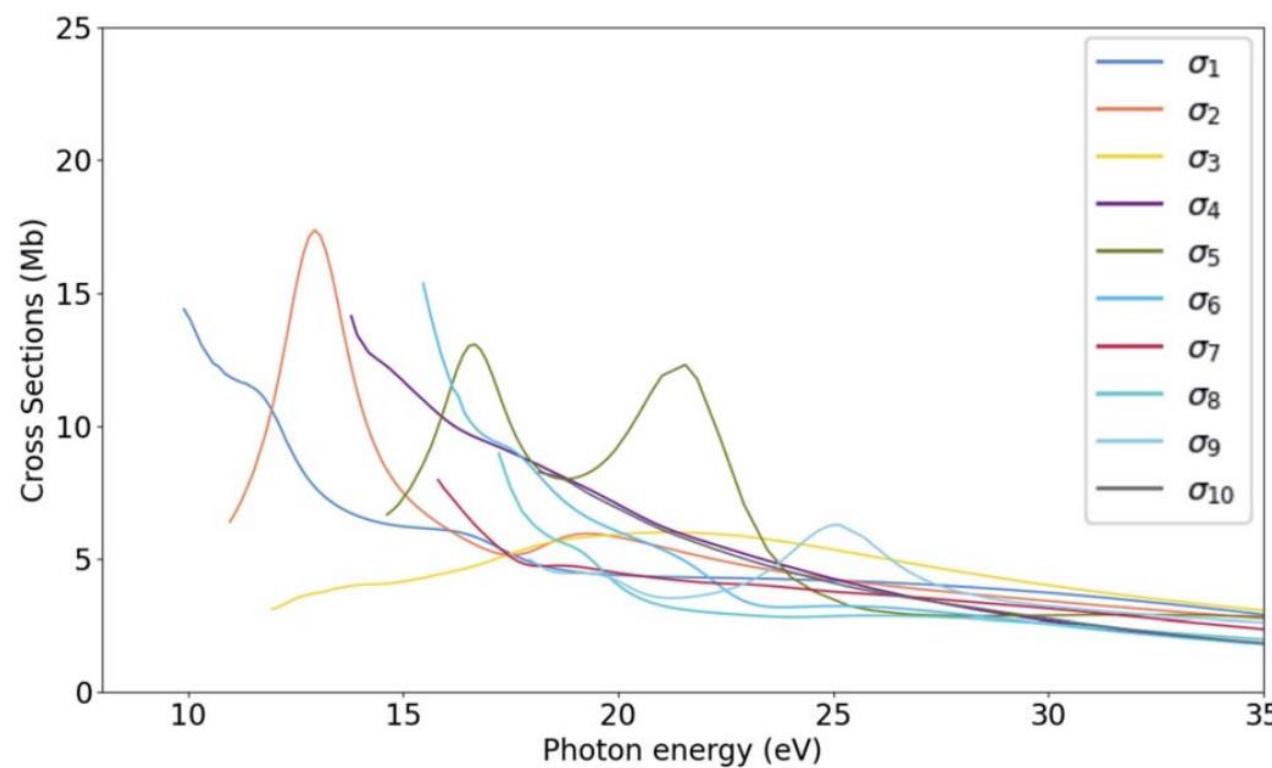
- **Dyson Orbitals:** overlap integral between the N-electron **ground-state** of the neutral molecule, and the N-1 electron function of the **cationic state** $\Psi_D^\alpha(r_n) = \langle \Phi_\alpha^{N-1} | \Phi_0^N \rangle$
- **Continuum orbitals** $\Phi_{\alpha,\varepsilon,\xi}^N(\vec{r}) = \mathcal{A} \left[\Phi_\alpha^{N-1}(r_1, \dots, r_{N-1}) \psi_{\varepsilon,\xi} \right]$
- **Dipole elements** $D_{\alpha,\varepsilon,\xi} = \langle \Phi_{\alpha,\varepsilon,\xi}^N | \sum_i d_i | \Phi_0^N \rangle = \langle \Psi_{\varepsilon,\xi} | d | \Psi_\alpha^D \rangle$
- **Ionization amplitudes** $c_{\alpha,\varepsilon,\xi}^k = -\frac{i}{\hbar} D_{\alpha,\varepsilon,\xi} \int_{-\infty}^{\infty} E(t) \exp(-i(E_\alpha + \varepsilon - E_0)t) dt$
- **Cross-sections** $\sigma_\alpha(\omega) = \frac{4\pi\omega^2}{3\hbar c} \int_\varepsilon \sum_\xi | D_{\alpha,\varepsilon,\xi} |^2$

Appendix: Dication Results

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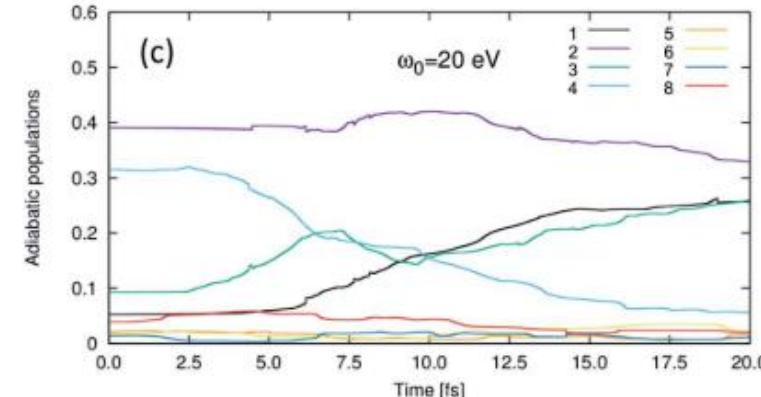
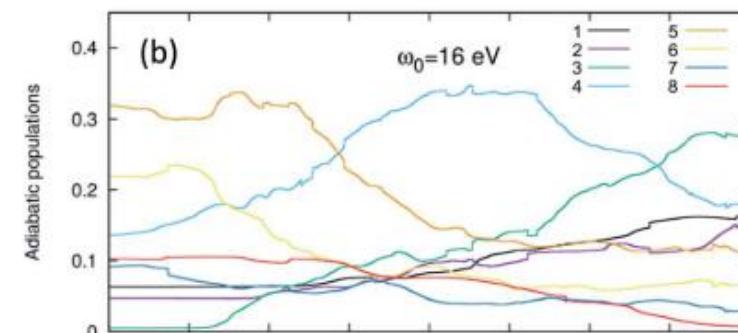
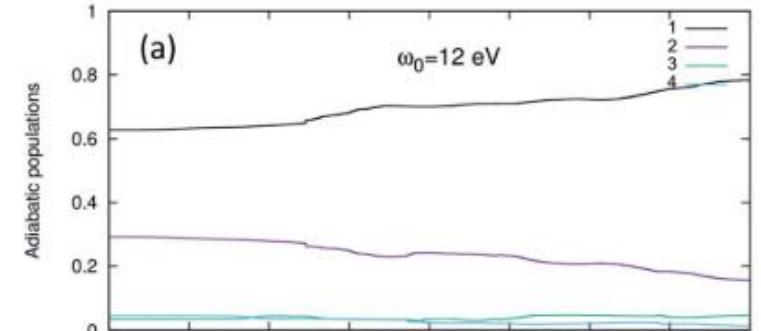
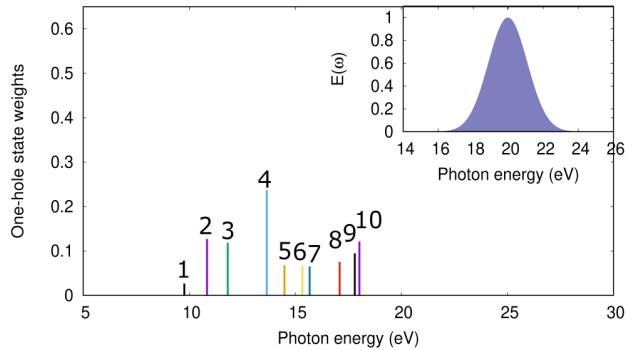
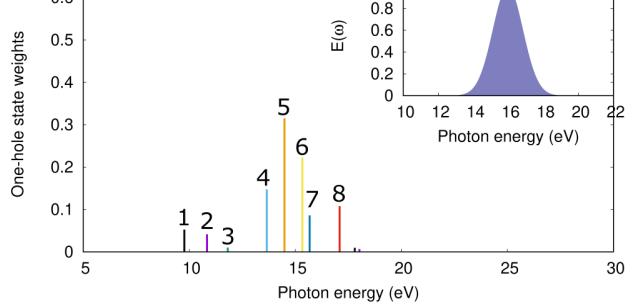
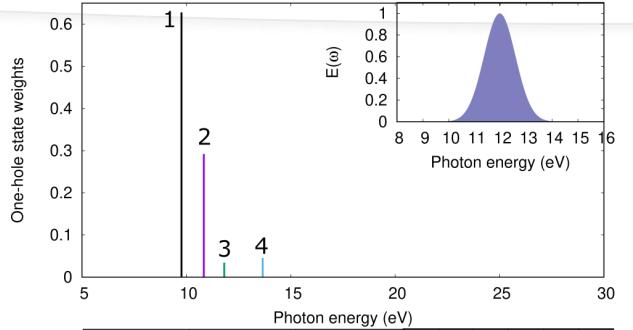


Appendix: Cross-sections and Dyson Norms



Appendix: Adiabatic Populations

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Appendix

- This electron transit is the basis of many biological processes
- It is essential to understand the early electron dynamics which is responsible of these processes.

