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Attosecond XUV-pump/XUV-probe spectroscopy of glycine

**M Lara-Astiaso[1], A Palacios[1,2] *, J Delgado[5], J González-Vázquez[1],
P Decleva[3] and F Martín[1,4,5]**

[1] Departamento de Química, Universidad Autónoma de Madrid (UAM), 28049 Madrid, Spain
[2] Institute of Advanced Research in Chemical Sciences (IAdChem), UAM, 28049 Madrid, Spain
[3] Dipartimento di Scienze Chimiche e Farmaceutiche, Università di Trieste, 34127 Trieste, Italy
[4] Condensed Matter Physics Center (IFIMAC), UAM, 28049 Madrid, Spain
[5] Instituto Madrileño de Estudios Avanzados (IMDEA) en Nanociencia, 28049 Madrid, Spain

Synopsis   We theoretically describe the outcome of an attosecond XUV pump-probe experiment in the smallest amino acid, glycine. We accurately evaluate the ionization amplitudes for the pump and the probe pulses. The molecular wave packet is then time-propagated using a trajectory-based Surface Hopping approach, accouting for the momentum distributions of the nuclei. Experimentally measurable photoelectron spectra are retrieved.

We investigate the ultrafast electron dynamics in ionized glycine using an attosecond XUV-pump/XUV-probe scheme. The existence of ultrafast charge migration was originally discussed by Weinkauf and collaborators after their pioneering studies on peptide chains [1]. Subsequent theoretical investigations by Cederbaum and collaborators demonstrated that sub-femtosecond charge fluctuations where observed in several biomolecules after sudden ionization, as a result of a superposition of cationic states [2]. The first experimental evidence was obtained in 2014 in the aminoacid phenylalanine, using an attosecond UV-pump/IR-probe scheme [3]. In this experiment, the large bandwidth of the attosecond pulse generates a superposition of one-hole states leading to a highly delocalized hole density that also fluctuates in the attosecond time scale.

A theoretical description of ultrafast charge migration in molecules first requires an accurate evaluation of the ionization amplitudes, which has only be achieved by a few theoretical approaches [3, 4]. Despite the theoretical efforts devoted to understand this phenomenon in large molecules, most prevoius studies assume the nuclei to be frozen, which is a valid approach for the first few femtoseconds [5], but unable to predict the subsequent molecular fragmentation. More importantly, existing methods to date have focused on describing the electron dynamics following the ionization induced by the pump pulse, but ignored the role of the probe pulse, except in a recent theoretical study in CO_2 [6]. The present work presents our progress to describe a complete XUV-pump/XUV-probe experiment in glycine.

Ionization amplitudes are accurately evaluated using the static-exchange DFT approach within the time-dependent perturbation theory formalism [5], while the coupled electron-nuclear motion is then described using a Surface Hopping approach [7]. The final photoelectrum spectrum is retrieved for different probe pulses. Ongoing progress to retrieve different fragmentation paths will be presented.
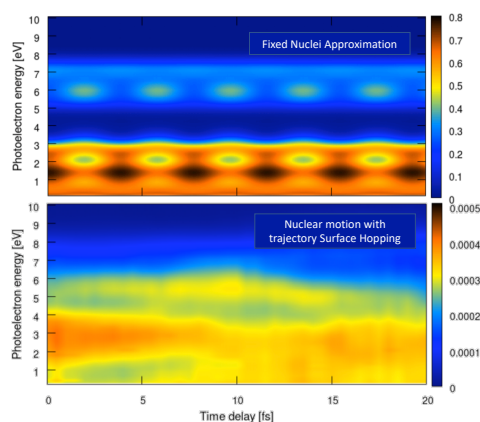

Figure 1. XUV-pump/XUV-probe time-resolved photoelectron spectra for glycine.

References

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*E-mail: alicia.palacios@uam.es