Imaging ultrafast molecular wave-packets with a single chirped UV pulse

D. Jelovina[1], **J. Feist**[2,3], **F. Martín**[1,3,4], **A. Palacios**[*1]

1. Departamento de Química, Universidad Autónoma de Madrid, 28049 Madrid, Spain
2. Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain
3. Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain
4. Instituto Madrileño de Estudios Avanzados (IMDEA) en Nanociencia, 28049 Madrid, Spain

Free-electron-laser facitilites and high-harmonic generation techniques implemented in tabletop setups can nowadays provide intense ultrashort UV pulses with durations in the femtosecond and attosecond range [1][2]. These pulses allow for monitoring and manipulating electron dynamics in matter at its intrinsic time scale. One of the primary goals of attosecond science is to use UV-pump / UV-probe schemes [3][4][5], where one pumps an atom (molecule), creating a superposition of electronic (vibronic) states whose field free evolution is captured by a second UV pulse. Because of technical challenges, these schemes have proven elusive due to the still low intensities that can be reached nowadays in the laboratory and due to difficulties in producing two independent ultrashort pulses with well-controlled time delays. Therefore, most of the existing experiments have been performed combining a UV ultrashort pulse with an IR field. The latter distorts the potential created by the electrons and nuclei of the isolated system itself, and therefore leads to the observation of IR-induced dynamics more than probing the UV-pumped ultrafast dynamics. In the present work, we propose an alternative approach: the use of a single chirped UV pulse, which can be realized in a lab, to emulate a conventional UV-UV pump-probe scheme [6].

We demonstrate that by tuning a single parameter, the spectral chirp of an ultrashort UV pulse, we can achieve a significant amount of control over molecular multiphoton ionization, changing the total ionization yield by more than a factor of ten. In addition, we show how it is possible to emulate a standard pump-probe setup to obtain direct time-resolved imaging of ultrafast molecular dynamics. The vibronic (vibrational+electronic) wave packet pumped in the singly excited molecule can be simultaneously probed through the ionization fragments generated by the same pulse. The chirp is the parameter that encodes the time delay between the pump and probe frequencies. We choose a quadratic frequency chirp, which is experimentally achievable even in broadband pulses with Fourier-limited durations as short as a few hundreds of attoseconds [2][7][8], and perform ab initio simulations on the H_2^+ molecule.

The full-dimensional time-dependent Schrödinger equation is solved numerically, using a finite element discrete variable representation [9] for the molecular wave function, including both electronic and nuclear degrees of freedom. We also introduce a sequential model to demonstrate the direct mapping of the pumped wave packet into the energy distribution of the charged fragments after the Coulomb explossion of the molecule [6]. Although we employ the H_2^+ molecule as benchmark target, the method should also be suitable to probe wave packet dynamics in more complex molecules.

References

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[*]Corresponding author: alicia.palacios@uam.es