

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

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Synopsis We present a theoretical study on the manipulation of two-photon molecular ionization by using a single frequency-chirp ultrashort UV pulse. We emulate a conventional pump-probe scheme using a single pulse to obtain a direct time-resolved image of the ultrafast dynamics. The chirp parameter introduces a spectral phase in time that encodes the delay between the pump and the probe frequencies. We perform full dimensional ab initio calculations in H_2^+ to show the reconstruction of the vibronic wave packet in a molecule that is simultaneously pumped and probed by a single chirped UV pulse. As a result, the total ionization yield can also be modulated in more than an order of magnitude [1].

Free-electron-laser facilities and high-harmonic generation techniques implemented in tabletop setups can nowadays provide intense ultrashort UV pulses with durations in the femtosecond and attosecond range [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], 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 and to the difficulties in producing two independent ultrashort pulses with well-controlled time delays. Thus, 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 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 realistic single chirped UV pulse to emulate a conventional UV-UV pump-probe scheme.

We demonstrate that by tuning the spectral chirp of an ultrashort UV pulse, we can achieve a significant amount of control over molecular multiphoton ionization, changing the total yield by more than a factor of ten (see Fig. 1). 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 broad-

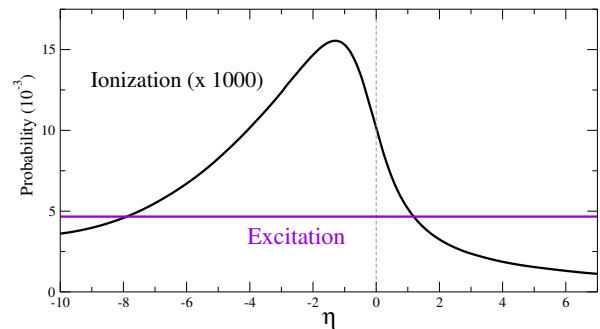


Figure 1. Total excitation and ionization probabilities as a function of the chirp parameter.

band pulses with Fourier-limited durations as short as a few hundreds of attoseconds [2, 5, 6], 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 [7] 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 explosion of the molecule. 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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