Research paper

Role of electron-nuclear coupled dynamics on charge migration induced by attosecond pulses in glycine

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ABSTRACT

We present a theoretical study of charge dynamics initiated by an attosecond XUV pulse in the glycine molecule, which consists in delocalized charge fluctuations all over the molecular skeleton. For this, we have explicitly used the actual electron wave packet created by such a broadband pulse. We show that, for the chosen pulse, charge dynamics in glycine is barely affected by nuclear motion or non adiabatic effects during the first 8 fs, and that the initial electronic coherences do not dissipate during the first 20 fs. In contrast, small variations in the initial nuclear positions, compatible with the geometries expected in the Franck-Condon region, lead to noticeable changes in this dynamics.

1. Introduction

Photoexcitation and photoionization of large molecules with ultraviolet (UV) or extreme ultraviolet (XUV) light initiate chemical reactions that are at the heart of many relevant biological processes [1,2]. Amongst them, processes that have a direct impact in human health, as e.g. vitamin D production [3] or DNA damage [4,5]. The electron dynamics triggered upon photoexcitation or photoionization of a molecule eventually drives the subsequent nuclear motion that leads to molecular restructuring or favors a particular chemical path. Pioneering work by Zewail and coworkers [6] in the eighties and the nineties demonstrated that one can visualize the induced nuclear dynamics by using pump-probe schemes in which an infrared (IR) femtosecond (fs) pulse excites the molecule and a second IR fs pulse, delayed in time, takes a "picture" of the system at that particular time. At the beginning of this century, they showed that the probe pulse can also be used to control nuclear displacements and therefore to drive a reaction into a desired pathway [7,8]. In both scenarios, the pulses are short enough to resolve or guide the nuclear dynamics generated in the excited molecule, which typically occur in tens or hundreds of femtoseconds.

During the last two decades, laser technology has rapidly evolved towards the generation of even shorter pulses, down to

tens of attoseconds [9–11], thus opening the way to investigate the much faster electron dynamics that ultimately drives the nuclear motion. Therefore, it is now possible to look into the very early stages of chemical rearrangements and, eventually, to achieve chemical control at the electronic level [12]. Consequently, a plethora of different phenomena arising from the ultrafast molecular response to attosecond UV or XUV pulses have been recently reported in the literature (see, e.g., [13–16] and references therein). One of these phenomena, which has drawn much attention of the scientific community because of its important role in biological processes, is the so-called ultrafast charge migration [17].

The concept of *ultrafast charge migration* was introduced by Cederbaum and Zobeley [17] in the late nineties to refer to charge fluctuations that were theoretically predicted to occur in the few-femtosecond time scale after sudden ionization of a biomolecule. This work followed experimental observations of Weinkauf and coworkers showing bond-selective cleavage of peptides chains [18], which was explained as the result of charge-directed reactivity induced by UV irradiation. The experimental demonstration of attosecond charge dynamics, however, was not achieved until 2014 [16], when a single attosecond XUV pulse resulting from high-harmonic generation was used in the pump step to photoionize phenylalanine and the subsequent sub-fs dynamics was analyzed by probing the system with a more standard femtosecond IR field. Theoretical calculations accompanying this experiment showed that electron dynamics triggered by the attosecond pulse is also responsible for charge fluctuations in the remaining cation occurring in the few-femtosecond time scale.

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Early theoretical work on charge migration assumed that ionization induced by the pump pulse is a sudden process in which an electron is removed from a well-localized molecular orbital of the neutral target [17,19–21]. This leads to a non-stationary electronic state of the cation, i.e., to a coherent superposition of cationic states, which can thus trigger charge dynamics over the molecular skeleton. The main theoretical prediction of this early work was that charge migration can occur in the sub-femtosecond time scale. This scenario changes significantly when attosecond pulses are used to induce the dynamics. Indeed, due to the broadband associated with the attosecond pulse, electrons can be removed from many different molecular orbitals, including delocalized ones, creating a coherent superposition of one-hole states in which the charge is delocalized from the very beginning. Consequently, at variance with previous works, an accurate evaluation of the ionization amplitudes associated with all open channels is required for a reliable representation of the initial electronic wave packet [16,22]. To do so, one has to describe the electronic continuum states of the molecule [16,22,23], which is not an easy task as these states cannot be generally obtained from standard quantum chemistry packages.

Thus, on the basis that electron dynamics is usually much faster than nuclear dynamics, most theoretical works on ultrafast charge migration processes have so far ignored the nuclear degrees of freedom. However, not all electronic processes are that fast, e.g., in the Auger decay or in the motion through conical intersections. Furthermore, the key aspect to understand the consequences of the induced electron dynamics on the subsequent chemical reactivity, through bond breaking and bond forming, is entirely dictated by the coupling between electron and nuclear dynamics at a given stage. Whether this coupling is important at the early or the late stages of the system's evolution or can even erase the coherences induced by the attosecond pulse is not known with precision yet, mainly because a large number of electronic and nuclear degrees of freedom may be involved in the process [24]. Preliminary theoretical attempts to investigate this problem, based on an Ehrenfest semiclassical description of the nuclear dynamics that includes the effect of non adiabatic couplings [25–27] or on an approximate quantum description of nuclear motion [28,29], have shown that nuclear rearrangements may indeed introduce decoherence preventing the observation of ultrafast charge oscillations after only a few femtoseconds. The starting point for these simulations was either a well-defined localized one-hole state [25,27], as in early theoretical work on charge migration, or an artificially created superposition of two of such states (see e.g. [26,28,29] and references therein).

In this work, we go a step farther and perform a similar study on the glycine molecule by starting from the *actual* coherent superposition of states that is created by an attosecond XUV pulse currently produced in the laboratory [10]. To evaluate the ionization amplitudes that define such a wave packet, we have used the static-exchange density functional theory (DFT) method [30,31], successfully applied to describe ionization of complex molecules [32], among them phenylalanine [16,22]. The subsequent field-free charge dynamics is described by means of a time dependent DFT-Ehrenfest dynamics (TDDFT-ED) method, in which, at variance with earlier work on phenylalanine [16,22], electron-electron correlations, nuclear motion and non adiabatic effects are included. Our results show that, for the chosen attosecond pulse, charge dynamics in glycine is barely affected by nuclear motion and non adiabatic effects within the first 8 fs and that the emergence of such effects at a later stage do not lead to a significant distortion of the original electronic coherences up to 20 fs. In contrast, the observed dynamics noticeably depends on the initial nuclear positions compatible with the geometries expected in the Franck-Condon (FC) region, thus suggesting that a set of initial conditions mimicking the distribution of

nuclear positions in the FC region should ideally be used for a more realistic description of the dynamics after ionization [26]. We also show that the observed dynamics mainly results from the coherent superposition of the one-hole (1h) states accessible by the XUV pulse and that electron correlation effects due to nh$(n-1)$p states (where p stands for "particle") do not change this picture significantly within the first 20 fs.

2. Methodology

According to the Runge-Gross theorem, all the properties of the system are functionals of the density and hence, this density can be used to monitor the electronic dynamics generated in the ion by the attosecond pulse. In a real experiment, this information is usually retrieved by interrogating the singly ionized target at different times by using another pulse that brings the system into a different [16,33] or the same final state [34]. In this work, we will limit ourselves to describe the dynamics generated by the attosecond pulse and will ignore the probing step.

The starting point is to describe the ionization step. For this, we have used the static-exchange DFT method [30,31] in combination with time-dependent perturbation theory [35]. The time-dependent wave packet, $\Psi(\vec{r}_1, \ldots, \vec{r}_N, t)$, that describes the system immediately after the interaction with the attosecond pulse is written as a linear combination of electronic continuum states of glycine:

$$\Psi(\vec{r}_1, \ldots, \vec{r}_N, t) = \sum_{\alpha,l} \int c_\alpha^{l,m}(\varepsilon_\alpha, T) e^{-i(E_\alpha + \epsilon_\alpha)t} \ \Psi_\alpha^{l,m}(\vec{r}_1, \ldots, \vec{r}_N, \varepsilon_\alpha) \ d\varepsilon_\alpha$$

(1)

where $\Psi_\alpha^{l,m}(\vec{r}_1, \ldots, \vec{r}_N, \varepsilon_\alpha)$ is a properly anti-symmetrized continuum state representing a molecular cation with a hole in the α spin-orbital and a photoelectron with angular quantum numbers l, m and energy $\varepsilon_\alpha, c_\alpha^{l,m}(\varepsilon_\alpha, T)$ is the corresponding ionization amplitude, evaluated at the end of the pulse, $t = T$, $\vec{r}_i$ denotes the electronic coordinates of electron i and t is the time. We notice that, in the above expansion, 2h1p and higher order states associated to excitation-ionization processes energetically accessible by the attosecond pulse are not taken into account and, therefore, that potential satellite lines arising in the photoelectron spectra cannot be described. Attosecond XUV pulses, as currently produced in high-harmonic generation, have a relatively low intensity. Therefore, the ionization amplitude can be obtained from first-order perturbation theory,

$$c_\alpha^{l,m}(\varepsilon_\alpha, T) = -i \ \langle \Psi_\alpha^{\varepsilon_\alpha,l,m}|\hat{\mu}| \ \Psi_0 \rangle \ \mathcal{E}(\omega),$$

(2)

where $\hat{\mu}$ is the dipole operator in the length representation, $\langle \Psi_\alpha^{\varepsilon_\alpha,l,m}|\hat{\mu}| \Psi_0 \rangle$ is the transition dipole matrix element connecting the ground state of the molecule, Ψ_0, and any of the accessible continuum states $\Psi_\alpha^{\varepsilon_\alpha,l,m}$, $\mathcal{E}(\omega)$ is the Fourier transform (FT) of the XUV electric field, $\mathcal{E}(t)$, with $\omega = (E_\alpha - E_0 + \varepsilon_\alpha)$, E_α is the energy of the α one-hole state and E_0 is the ground state energy. The energy E_α has been evaluated by subtracting the energy of the α Kohn-Sham spin-orbital from the ground state energy [36]. In this work we have used the $\mathcal{E}(\omega)$ distribution that actually corresponds to the attosecond pulse used in the phenylalanine experiments reported in [16]. Such pulse has a bandwidth of roughly 19 eV, ranging from 16 to 35 eV photon energies, so that it can ionize the molecule from the highest occupied molecular orbital (HOMO) down to the HOMO-14 (i.e., a total of fifteen molecular orbitals comprising valence and inner-valence ones).

The ground state of the neutral species, Ψ_0, has been computed by using density functional theory (DFT) with an LB94/DZP func-