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Ultrafast Charge Dynamics in an Amino Acid Induced by Attosecond Pulses

Francesca Calegari, David Ayuso, Andrea Trabattoni, Louise Belshaw, Simone De Camillis, Fabio Frassetto, Luca Poletto, Alicia Palacios, Piero Decleva, Jason B. Greenwood, Fernando Martín, and Mauro Nisoli

Abstract—In the past few years attosecond techniques have been implemented for the investigation of ultrafast dynamics in molecules. The generation of isolated attosecond pulses characterized by a relatively high photon flux has opened up new possibilities in the study of molecular dynamics. In this paper, we report on experimental and theoretical results of ultrafast charge dynamics in a biochemically relevant molecule, namely, the amino acid phenylalanine. The data represent the first experimental demonstration of the generation and observation of a charge migration process in a complex molecule, where electron dynamics precede nuclear motion. The application of attosecond technology to the investigation of electronic dynamics in biologically relevant molecules represents a multidisciplinary work, which can open new research frontiers: those in which few-femtosecond and even sub-femtosecond electron processes determine the fate of biomolecules. It can also open new perspectives for the development of new technologies, for example in molecular electronics, where electron processes on an ultrafast temporal scale are essential to trigger and control the electron current on the scale of the molecule.

Index Terms—Molecular physics, attosecond, femtosecond, extreme-ultraviolet (XUV) spectroscopy, high harmonics, ultrafast optics.

I. INTRODUCTION

UltrafaST DYNAmics in molecules is at the root of a number of physical, chemical and biological processes [1]-[3]. Indeed, chemical reactions are the result of bond breaking and formation, a dynamical process that is initiated by changes in the electronic structure. The study of the dynamics associated to the nuclear motion belongs to the realm of femtochemistry, a well-established field that for more than twenty years has been able to capture and even control the nuclear motion in chemical reactions and intramolecular processes [4]. The initial step, i.e., electron rearrangement, remains to be fully understood.

Time-resolved studies on electron dynamics can shed light on the underlying mechanisms in a variety of processes such as photosynthesis, cellular respiration or electron transport along large peptides and proteins [5], [6]. Electron dynamics of those processes are induced by absorption of photons in the ultraviolet (UV) and extreme UV (XUV) range and occur in the attosecond time scale. Experimental tools and techniques able to provide such time resolution in complex molecular targets are still in their infancy [7]. The first pump-probe experiment on molecules using an isolated attosecond pulse to launch electron dynamics was reported in 2010, where electron localization was then measured in $H_2$ and $D_2$ using an infrared (IR) probe pulse and recorded with attosecond time resolution [8]. One year later, trains of attosecond pulses were also used to investigate how a moderately intense IR field affects the electronic dynamics induced by the XUV photoionization of hydrogen molecules [9], or to demonstrate the possibility of controlling dissociative ionization of oxygen molecules [10]. Attosecond pulse trains have been also combined with two near-IR pulses to coherently excite and control the outcome of a simple chemical reaction in $D_2$ molecules [11].
Further applications of attosecond technology nowadays focus on larger and complex targets. Already in 2012, successful results have been reported on the use of a short train of attosecond pulses to explore the ultrafast dynamics in an amino acid [12]. In this work, the evolution of various ionic fragments of phenylalanine was followed in time after prompt single-photon ionization of the molecule by the XUV attosecond pulses. More recently, the authors of the present paper have reported the first experimental demonstration of charge migration in the same amino acid. It was found that this process is characterized by sub-4.5 fs oscillations appearing in the quantum yield of a specifically doubly charged fragment [13].

Charge migration refers to a charge transfer mechanism occurring on a temporal scale that precedes notable nuclear motion [14], [15]. The first experimental glimpse of an extremely efficient and ultrafast charge transfer within polypeptide molecules, was reported by Schlag and co-workers [16], [17]. They showed that if an electron is selectively ionized from a chromophore at the C-terminal end of a peptide, the location of the charge can be probed by using the shift in absorption of the chromophore once charged. By employing this technique, they were able to observe a charge transfer over more than 10 σ-bonds. They interpreted their experiments in terms of a very fast charge-transfer process, which can efficiently compete with fast intra-chromophoric rates. They also showed that this charge transfer was directly correlated with the properties of individual amino acids.

The ultrafast dynamics of charge transfer processes initiated in complex biologically relevant molecules by sudden photoionization have been investigated in various theoretical papers [14], [15], [18], [19]. It was suggested that if an electron is suddenly removed from a molecular orbital, the molecule will be in a superposition of electronic states of the radical cation. The temporal evolution of this electronic wavepacket, producing charge oscillations, has been referred to as charge migration to distinguish it from charge transfer mediated by nuclear motion. For example, a hole generated by prompt ionization of the highest-occupied molecular orbital (HOMO) of the tetrapeptide Trp-Leu-Leu-Leu (Trp and Leu are the amino acids Tryptophan and Leucine, respectively) and localized on the Trp chromophore migrates to the N terminus (or amino-terminus) of the peptide in 0.75 fs [15]. Direct experimental access to such sub-femtosecond processes is mandatory to image electronic dynamics in complex molecules and requires of attosecond measurement techniques.

In this work, we report experimental measurements and a detailed theoretical analysis of the first application of isolated attosecond pulses to phenylalanine. In Section II, the pump-probe experimental setup is described. Experimental results are discussed in Section III, where we first present the mass spectrum of phenylalanine produced upon photoionization by isolated attosecond pulses, followed by the pump-probe measurements that reveal the signature of ultrafast charge migration along the molecular skeleton. The theoretical data and interpretation are given in Section IV. Finally, Section V presents a summary of the most significant results.

II. EXPERIMENTAL SETUP

For the experiments a Ti:sapphire laser system was used (FemtoPower PRO HE CEP, Femtolasers) with the following characteristics: 6-mJ pulse energy, 25-fs pulse duration and 1-kHz repetition rate. The carrier-envelope phase (CEP) was stabilized by two feedback loops: a fast loop acting on the oscillator and a slow loop acting on a glass wedge placed in the stretcher before the preamplifier. The residual CEP fluctuation was about 200 mrad (rms), measured in-loop with a f-to-2f interferometer using an integration time of 1 ms. We then compressed the pulses using the hollow-fiber compression technique [20], [21] in combination with a broadband chirped-mirror dispersive delay line. Due to the high energy of the laser pulses, the pressure gradient scheme has been employed [22]. We used a 1-m-long hollow fiber with an inner diameter of 320 µm, filled with helium: the pressure at the input of the fiber was kept to <5 mbar and 2 bar at the output. The beam position at the input of the hollow fiber was actively stabilized [23]. A pulse energy of 3.3 mJ was obtained at the output with no gas in the fibre, and 2.3 mJ with gas. After 8 reflections on the chirped mirrors, pulses as short as 4 fs were achieved. The pulse duration was measured by using a single-shot Self-Referenced Spectral Interferometry method [24] implemented with Cross-Polarized Wave (XPW). By using a novel single-shot interferometric technique, allowing in situ measurement of intensity-dependent phase changes experienced by ultrashort laser pulses upon nonlinear propagation, we have demonstrated that CEP stability is substantially preserved by the hollow fiber compression technique [25].

The visible/near infrared (VIS/NIR) beam was divided into two portions by using an ultrabroadband beam splitter with 30% reflection. The transmitted beam part was focused by a 1-mm radius of curvature mirror into a 3-mm-thick cell filled with xenon at static pressure to produce extreme ultraviolet (XUV) radiation by high-order harmonic generation (HHG). Isolated attosecond pulses, with energy in the nanojoule range, were produced by employing the ionization gating technique, which
is a temporal gating scheme based on sub-cycle ionization dynamics in a gas cell driven by few-optical-cycle pulses with above-saturation intensity and stable CEP [26], [27]. A 100-nm-thick aluminium filter was used to filter out the fundamental radiation and the low order harmonics. An indium foil has been also used in a few measurements described in the text. The temporal duration of the XUV pulses (290±20 as) was measured by using the Frequency Resolved Optical Gating for Complete Reconstruction of Attosecond Bursts (FROG CRAB) technique [28], [29]. The remaining part of the VIS/NIR beam was collinearly recombined with the XUV beam by using a mirror with a central hole. The temporal delay between VIS/NIR and XUV pulses was adjusted with attosecond resolution by using a piezoelectric translation stage. The pump and probe pulses were collinearly focused into the mass spectrometer, as shown in Fig. 1, by using a gold-coated toroidal mirror, with unit magnification, which provided an almost aberration-free image of the XUV source with negligible temporal smearing of the attosecond pulses [30]. The peak intensity of the VIS/NIR probe pulse in the sample was about $5 \times 10^{12}$ W/cm$^2$.

Gas-phase molecules were produced by employing the laser induced thermal desorption method. Phenylalanine was deposited on a 10-μm-thick stainless steel foil, mounted onto the repeller electrode of a time of flight (TOF) mass spectrometer [31]. To evaporate the sample, the reverse side of the foil was irradiated with a CW diode laser operating at a wavelength of 960 nm, with a spot diameter of 6 mm and power in the range 0.3 – 0.4 W. The distance from the foil to the focal point of the ionizing laser pulses was approximately 3 mm.

The temperature of the sample was estimated by assuming equilibrium heat conduction along the foil to the repeller electrode and that 30% of the incident radiation was absorbed by the foil at this wavelength [32]. Radiative heat losses were negligible for the calculated temperatures. For the lowest laser power used, the temperature at the centre of the foil was estimated to be 430 K and about 410 K at a radius of 2 mm.

### III. EXPERIMENTAL RESULTS

#### A. Fragmentation Results

We investigated the phenylalanine molecule, one of the essential amino acids for human life. It is an α-amino acid, consisting in a central carbon atom (α carbon), linked to an amine (-NH$_2$) group, a carboxylic group (-COOH), a hydrogen atom and a side chain (-R). The side chain is specific for each amino acid and for phenylalanine is formed by a methylene (-CH$_2$-) group (β carbon) terminated by a phenyl ring. We have chosen it as a model molecule for charge migration because it contains two electron-acceptor sites with approximately the same binding energy located on the phenyl and amine groups, and separated by two singly bonded carbon atoms. The molecule was first irradiated with the XUV attosecond pulse which has a photon energy bandwidth of $\sim$19 eV, from 16 eV to 35 eV. The parent and fragment ions produced were then extracted into the TOF spectrometer for mass analysis. Figure 2 shows the measured mass spectrum, where the main contributions correspond to the parent ion M$^+$ (165 Da), loss of the carboxyl group yielding the immonium ion (M-COOH at 120 Da), and breakage of the C$_{6}$C$_{6}$C$_{6}$ bond with the charge residing on the amine (M-R at 74 Da) or phenyl groups (R at 91). We observe a small peak with a mass to charge ratio $m/q = 60$, which is due to the doubly charged immonium ion. The XUV pulse is capable of ionizing all valence and some inner shell orbitals, resulting in a wide range of fragment ions. It was observed that using only the 4-fs VIS/NIR pulses to ionize the molecule produced predominantly parent ions in the mass spectrum.

#### B. Pump-Probe Measurements

The temporal evolution of the ionic fragments produced in phenylalanine has been investigated by means of two-color pump-probe measurements, using attosecond pump pulses and 4-fs VIS/NIR probe pulses at a variable temporal delay. To obtain the zero of the experimental data we have removed the 100-nm-thick aluminium filter and we have measured as a function of time the fragment yields produced by the VIS/NIR-pumpVIS/NIR-probe interaction. This defines our zero time position to an accuracy better than 1 fs.

In a previous work [12] we observed dynamics in a number of fragments with a time constant of 80 ± 20 fs, which we attributed to an internal conversion process. In this work, which has much better statistics, the fractional yields of nearly all the singly charged fragments vary as a function of pump-probe delay. However, there is a marked difference when the XUV beam is filtered with an aluminium foil, generating an XUV spectrum from 16 to 35 eV, compared to an indium foil, which produces a XUV spectrum with a 3-eV (full-width at half maximum) peak centred around 15 eV, followed by a broad and weak spectral component extending up to 25 eV. This is demonstrated in Fig. 3 for the fragment $m/q = 28$ (NH$_2$C). It can be seen that in the case of XUV pulses transmitted by the aluminium filter (see Fig. 3(a)), the...
fragment yield increases with pump-probe delay, with a time constant of 80±2 fs. Other fragments also increase with time constants in the range from 50 fs to 100 fs at the expense of the parent \( m/q = 165 \) and immonium ions \( m/q = 120 \) which decrease. By contrast, in the case of XUV pulses transmitted by the indium filter (see Fig. 3(b)), a sudden increase in the yield of the fragment \( m/q = 28 \) can be observed with no subsequent dynamics. This result suggests that when only a valence electron can be ionized (XUV pulse filtered by indium), no temporal dynamics of the singly charged ions are observed, but the presence of hole in the valence shell allows the VIS/IR pulse to be absorbed. For instance, it is known that absorption by the phenyl chromophore shifts from the ultraviolet to the green when there is a hole in the highest occupied molecular orbital [17]. This increases the yield of smaller fragments when the XUV pulse precedes the VIS/IR pulse with a concomitant reduction in parent and larger fragment ions. When an inner valence orbital is ionized (by the XUV pulse filtered with aluminium), there is initially no resonant absorption of the probe but an internal conversion to a lower electronic state generates a hole in the valence shell opening up absorption of the probe and hence further fragmentation. The measured timescale of 50-100 fs is compatible with an internal conversion mechanism as it is mediated by nuclear motion on potential energy surfaces.

On the other hand, the immonium dication \( m/q = 60 \) shows a faster temporal evolution, as shown in Fig. 4, where the data points have been acquired by using 3-fs step in pump-probe time delay. The experimental data has been fitted by the convolution, \( F(t) \), of a Gaussian pulse of 4-fs full-width at half maximum (FWHM), with the following function:

\[
R(t) = A(e^{-t/\tau_1} - e^{-t/\tau_2})
\]

where \( \tau_1 = 10\pm2 \) fs and \( \tau_2 = 25\pm2 \) fs. Upon decreasing the delay-step between pump and probe pulses from 3 fs to 0.5 fs, an oscillation of the dication yield is clearly visible in the pump-probe measurement. Figure 5 displays the measured data, acquired with delay-step between pump and probe pulses of 0.5 fs, after subtraction of the fitting curve \( F(t) \) (assuming \( \tau_1 = 10 \) fs and \( \tau_2 = 25 \) fs).

As reported in [13], we have performed a Fourier analysis of the experimental data. Time-dependent Fourier transforms have been calculated by using a sliding Gaussian window function

\[
g(t-t_d) = \exp\left[-(t-t_d)^2/t_0^2\right]
\]

with \( t_0 = 10 \) fs and peak at \( t_d \) (gate delay time). As shown in Fig. 6 at short pump-probe delays \( t < 10 \) fs two main frequency components are present, around 0.14 PHz and 0.3 PHz. Therefore in this temporal window the pump-probe data have been fitted by the sum of two sinusoidal functions:

\[
S(t) = A_1 \sin(2\pi\nu_1 t + \phi_1) + A_2 \sin(2\pi\nu_2 t + \phi_2)
\]

The calculated frequencies are: 0.14 PHz (lower and upper
phenylalanine with energy peak around 0.24 PHz is visible in the Fourier spectrogram.

For this reason the data have been fitted with a sinusoidal function of frequency 0.234 PHz (oscillation period of 4.3 fs), with lower and upper confidence bounds of 0.229 and 0.238 PHz, respectively.

Fig. 6. Fourier sliding-window analysis of the experimental data.

IV. THEORETICAL METHOD AND DISCUSSION

We have then performed numerical simulations in order to analyse the ultrafast charge evolution after attosecond excitation. Due to the low intensity of the attosecond pump pulses used in the experiment, time-dependent first-order perturbation theory has been employed for the calculation of the ionization amplitudes at the end of the pulse (t = T):

\[ c_{atom}(T) = -i \langle \Psi_{atom}(\varepsilon, \vec{r}) | \vec{e} \cdot \vec{r} | \Psi_0(\vec{r}) \rangle \int_{-\infty}^{T} E(t) e^{i(E_{\alpha} - \varepsilon - E_0)t} dt \]  

(4)

where \(\Psi_0\) is the all-electron (called N-electron) ground state of phenylalanine with energy \(E_0\), \(\Psi_{atom}(\varepsilon)\) is the N-electron continuum state, describing a photoelectron ejected from the \(\alpha\) molecular orbital with kinetic energy \(\varepsilon\) and angular quantum numbers \(l\) and \(m\) (\(|m| \leq l\)), \(E_\alpha\) is the energy of the corresponding cationic species and \(E(t)\) is the electric field of the XUV pulse polarized along the \(\vec{e}\) direction. \(\Psi_0\) and \(\Psi_{atom}(\varepsilon)\) wave functions have been evaluated in the framework of the fixed-nuclei approximation by using the static-exchange density functional theory (DFT) [33] method, which makes use of the Kohn-Sham DFT to describe molecular bound states and of the Galerkin approach to evaluate continuum wave functions in the field of the corresponding Kohn-Sham density. The LB94 functional [34] has been employed to account for exchange and correlation effects. In order to obtain reliable values of the ionization energies \(E_\alpha\), we have employed the VWN [35] local density approximation (LDA) functional within the Slater transition state procedure [36] using the ADF commercial program [37], [38] with a TZP basis set (taken from the ADF library). Bound and continuum states are evaluated in a multicentric basis set built with products of B-splines and spherical harmonics, as widely described in previous works [39], [40]. We use a large one-center expansion (OCE) placed at the center of mass of the molecule to accurately describe the asymptotic behavior of the continuum states. To improve the convergence of the calculation for the description of the more localized bound states, the OCE is supplemented with N (number of atoms) small non-overlapping off-center expansions located at the nuclear positions. For phenylalanine, we obtain converged results using as radial parameters a OCE with a 30 a.u. radius and 23 off-center expansions extended up to 1 a.u. of radius. Because of the large size and the lack of symmetry in the phenylalanine molecule, we have included an angular expansion of 484 spherical harmonics (equivalently, angular momentum \(l \leq 20\) in Eq. 4). The initial guess for the electronic density was generated with ADF [37], [38], and the molecular geometries of the different conformers were optimized at the DFT-B3LYP [41], [42] level with the 6-311+g(3df,2p) basis set employing Gaussian09 computational package [43].

The electronic density of the (N-1)-electron cation can be calculated as [44], [45]

\[ \rho_{ion}(\vec{r}, t) = \sum_{\alpha} \left( \sum_{\alpha' \neq \alpha} \right) \gamma_{\alpha \alpha'}^{(ion)} \varphi_{\alpha}(\vec{r}) + \right. \]

\[ \left. - \sum_{\alpha' \neq \alpha} \gamma_{\alpha \alpha'}^{(ion)} e^{i(E_{\alpha' \alpha} - E_\alpha)t} \varphi_{\alpha'}(\vec{r}) \varphi_\alpha(\vec{r}) \right) \]  

(5)

where \(\varphi_{\alpha}(\vec{r})\) is the \(\alpha\) molecular orbital and \(\gamma_{\alpha \alpha'}^{(ion)}\) is the reduced density matrix element defined as:

\[ \gamma_{\alpha \alpha'}^{(ion)} = \sum_{lm} \int c_{\alpha lm}(\varepsilon) c_{\alpha' lm}^{*}(\varepsilon) d\varepsilon \]  

(6)

We have neglected the interaction of the photoelectron with the remaining (N-1)-electron cation. The hole density is given by the difference between the electronic density of the neutral molecule, which does not depend on time, and the electronic density of the ion, \(\rho_{hole}(\vec{r}, t) = \rho_{neutral}(\vec{r}) - \rho_{ion}(\vec{r}, t)\), and can be written as follows:

\[ \rho_{hole}(\vec{r}, t) = \sum_{\alpha} \left( 1 - \sum_{\alpha' \neq \alpha} \gamma_{\alpha \alpha'}^{(ion)} \right) \varphi_{\alpha}^{2}(\vec{r}) + \right. \]

\[ \left. + \sum_{\alpha' \neq \alpha} \gamma_{\alpha \alpha'}^{(ion)} e^{i(E_{\alpha' \alpha} - E_\alpha)t} \varphi_{\alpha}(\vec{r}) \varphi_{\alpha'}(\vec{r}) \right) \]  

(7)

where

\[ \rho_{neutral}(\vec{r}) = \sum_{\alpha} \varphi_{\alpha}^{2}(\vec{r}) \]  

(8)
Figure 7 shows the calculated ionization energies of all open channels for the most abundant conformer of phenylalanine, according to previous theoretical work [46]. These energies are approximately given by the Kohn-Sham orbital energies resulting from the VWN-transition state calculations. For a given photon energy, all channels below that energy will be populated. We are thus creating a wave packet containing all ionic states with ionization potentials below 35 eV. As illustrated in Fig. 7, 35 eV is the largest photon energy contained within the bandwidth of the attosecond pulses used in the experiment. Their relative contributions to the total wave packet are given by both the pulse profile and the dipole couplings from the ground state of the neutral.

In order to test the validity of our description of the ionization process, we have first calculated the photoelectron spectra of phenylalanine for photon energies of 21.2 and 45 eV, by using the computed dipole transition matrix elements and ionization potentials, and we have compared our results with synchrotron [47] and He(I) [48], [49] radiation experiments. We have convoluted our infinite resolution lines with a Gaussian function of 0.3-eV width at half maximum to account for the vibrational broadening and experimental energy resolution, which is rather limited in this and earlier experiments (the experiments cannot resolve the individual peaks). The comparison between theory and experiment is shown in Fig. 8. As can be seen, the agreement is reasonably good. We notice however that the experiment of Plekan et al. was performed at a photon energy of 100 eV, which is substantially higher than ours. Other two earlier experiments were performed at a photon energy of 21.2 eV [48], [49]. Our results are in better agreement with the most recent experiment, especially for binding energies below 15 eV, which includes the most relevant cationic states in the hole dynamics reported in the present work.

The electronic wave packet generated by the attosecond pulse was then calculated from the ionization amplitudes, by using the experimental frequency spectrum of the pulse (shown in Fig. 7). Time zero in the simulation corresponds to the end of the attosecond pulse and the wavepacket evolution is calculated for positive times immediately after the prompt ionization. The evolution of the electronic wave packet was then evaluated by using a standard time-dependent density matrix formalism [50], in which the system is described by a sum of single-particle Hamiltonians. Since in this work we consider ionization from the ground state, which has a pronounced single-determinant character, the effects related to 2holes-1particle (2h1p) states are expected to be much smaller. In ground state photoionization, 2h1p states are nevertheless not negligible in inner-valence shell ionization, as has been extensively studied by Cederbaum and coworkers [51], but they are of minor importance in outer-valence ionization, which is the dominant process in our work. The latter conclusion is supported by photoelectron spectroscopy experiments in this and similar molecules, in which satellite lines associated to 2h1p states are always much weaker that those associated to 1h states. It is also supported by new theoretical calculations that we have carried out for glycine [52], in very good agreement with the results obtained by Kuleff et al. [53]. Therefore, in the range of photon energies leading to the cationic states relevant for the observed dynamics, we can safely conclude that 2h1p states do not play a significant role.

Every ionic state is related to a single Slater determinant.
with doublet spin multiplicity. However, this single determinant is not built from Hartree-Fock (HF) orbitals but from Kohn-Sham (KS) orbitals arising from DFT calculations. In complex non-symmetric molecules it often happens that there is a kind of “orbital rotation” upon ionization, expressed as a mixing of HF orbitals. This is reported e.g. in the paper by Lünnemann et al. [19]. However, this does not mean a breakdown of the one particle (1h) approximation for such states, just that the Dyson orbital, still of norm close to 1, is a linear combination of ground state HF orbitals. Since some correlation is built in the KS orbitals, they are generally closer to the correct Dyson orbitals than the HF ones. As mentioned above, this has been tested by reproducing the results by Kuleff et al. [53] for glycine outer valence ionizations [52].

The nature of the Dyson orbital can only be probed by evaluating dynamical properties, like photoionization cross sections, or electron momentum spectroscopy. This is additionally supported by the vast number of published studies of photoionization cross sections performed with the present approach, also in molecules of comparable complexity [54]-[63].

Due to the random orientation of the phenylalanine molecule, we calculated the hole dynamics resulting from excitation by pulses with the electric field polarized along three orthogonal directions, and the results were then averaged. Although no electron selection rules strictly apply, due the lack of global symmetry elements, of course approximate local symmetries will apply, depending on the localization of the initial orbital. E.g., for an initial orbital of mainly \( \sigma \) ring character, a parallel polarization excites it to \( \sigma \) ring states, while a perpendicular one drives it to \( \pi \) final states, and similar considerations apply to initial orbitals mainly localized on other moieties (-NH\(_2\), -COOH, etc). This explains why the results obtained for the different polarization directions, x, y and z, are different.

We note that, in the particular case considered in this work, the Lebedev sampling method to average over molecular orientation [64], would lead to the same final result. Indeed, the reduced density matrix elements \( \gamma_{\alpha\alpha} \) (reported in Eq. 6) can be written as a function of the electron ejection direction (\( \Omega_e \)) and the orientation of the molecule (\( \Omega_\alpha \)). For randomly oriented molecules and non-resolved electron ejection angles, one would have to integrate over both \( \Omega_e \) and \( \Omega_\alpha \). However, this integration would only affect the \( \gamma_{\alpha\alpha} \) terms in Eq. 7, which contain products of amplitudes with the same angular momentum \( \ell \), but different \( \alpha \) and \( \alpha' \). So, if the symmetry of the channels \( \alpha \) and \( \alpha' \) is the same for all states (as in phenylalanine), the algebra to integrate the angular part of \( \gamma_{\alpha\alpha} \) is exactly the same as the usual one to derive integrated cross sections (see [65] and references therein). This means that, in practice, it is enough to average the results obtained for three arbitrary but orthogonal orientations.

![Fourier power spectra of the calculated hole density integrated over various atoms of the phenylalanine molecule for the most abundant conformer.](Image 309x234 to 570x261)

Fig. 9. Fourier power spectra of the calculated hole density integrated over various atoms of the phenylalanine molecule for the most abundant conformer.

![Fourier sliding-window analysis of the calculated temporal evolution of hole density integrated over the amine group for the most abundant conformer of phenylalanine.](Image 41x55 to 302x84)

Fig. 10. Fourier sliding-window analysis of the calculated temporal evolution of hole density integrated over the amine group for the most abundant conformer of phenylalanine.

We have integrated the hole density around particular portions of the molecule. Figure 9 shows the Fourier power spectra of the calculated hole density over various atoms of the molecule: the nitrogen atom of the amine group, the double bonded oxygen atom of the carboxylic group, two carbon atoms of the phenyl group and a non-aromatic carbon atom. Beating frequencies in agreement with the experimental observations were observed when the charge density was integrated around the amine group. The hole densities at different positions in the molecules do not show clear and clean frequency components (with the exception of the double bonded O atom in the carboxyl group, which however cannot be observed in the doubly-charged immonium fragment, which results from the loss of the carboxyl group).
We note that the VIS/NIR probe pulse is not locally absorbed only by the amine group, but also by other sites of the molecule. However, the simulations indicate that the periodic modulations observed in the experiment are mainly related to the absorption of the probe pulse by the amine group. The charge dynamics around the amine group is then imprinted in the probe absorption. As shown in Fig. 9, a clear peak at 0.25 PHz is visible in Fourier power spectrum of the calculated hole density integrated around the amine group, in very good agreement with the pump-probe measurement. As discussed in [13], the sliding-window Fourier analysis of the numerical simulation, shown in Fig. 10, demonstrated that the main peak at 0.25 PHz forms in about 15 fs and disappears after about 35 fs, in agreement with the results of the Fourier analysis of the experimental data. A higher frequency component is visible around 0.36 PHz in the delay intervals below 15 fs and above 30 fs. The temporal evolution of the main Fourier components is a consequence of the complex interplay among several beating processes initiated by the broad band excitation pulse. We note that the oscillation periods obtained from the experimental data and from the numerical simulations are shorter than the fastest vibrational

### Table I

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Wavenumber (cm$^{-1}$), frequency (PHz) and corresponding periods (fs) of vibrational modes for the lowest cationic state of phenylalanine.

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Fig. 11. Fourier power spectra of the hole density integrated over the amine group for the most abundant conformer of phenylalanine; we have identified the ionic states that are responsible for the most important beatings.

Fig. 12. Calculated Kohn-Sham orbitals of phenylalanine whose beating is mainly responsible of the Fourier peaks at 0.25 PHz (A25-A28) and 0.36 PHz (A41-A44).
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period for the lowest cationic state of phenylalanine, which we have calculated by employing standard DFT-B3LYP quantum chemistry calculations (same procedure as for the geometry optimizations). The calculated vibrational frequencies are shown in Table I. Of course we cannot claim that the relative intensities of the relevant beatings observed in the experiment can be explained by a theoretical calculation in which the probe step is not included (this may explain the discrepancies between measured and calculated peak intensities), but we can clearly identify that the observed beatings are unambiguously associated to charge fluctuations around the amine group, which in turn are associated to a small number of cationic states among all the accessible ones. Indeed, another important result of the numerical simulation is that it is possible to identify the ionic states that are responsible for the most important beatings. These are identified in Fig. 11, for the most abundant conformer. From the simulation it is possible to conclude that the main frequency peak around 0.25 PHz originates from a beating between two states that contain a hole in a molecular orbital that is highly delocalized (A25) and a second one that is more localized on the amine group (A28), shown in Fig. 12. Similarly, the frequency component around 0.36 PHz arises from an interference between two states (A41 and A44) that contain hole density on the amine and the carboxyl groups (see Fig. 12), which allows charge migration between the two sites. These interferences manifest as fluctuations in the electronic density on the amine group.

We have performed calculations for the 6 most populated conformers (see Fig. 13) at the temperature of the experiment (430K), according to previous theoretical work [46]. The corresponding Fourier spectra are shown in Fig. 14, together with the results for the thermal average (bottom panel in Fig. 14) obtained by taking into account the relative populations given in [46]. For the most populated conformers (and therefore for the averaged results), the frequencies at which the dominant peaks appear are in good agreement with those observed experimentally.

From the pump-probe measurements and the numerical simulations it is possible to conclude that charge fluctuations moving across the molecular chain, which ultimately lead to charge localization, are extremely fast even for a molecule as large as phenylalanine; therefore, charge localization (spontaneous or forced by external factors) can occur in a similar or even shorter time scale. Moreover, we have demonstrated that these fluctuations, which are required for an ulterior localization of the charge, can be induced by an attosecond pulse in spite of its broad bandwidth and, therefore, its low selectivity. The consequence is that one does not need to start from a localized charge state to induce charge fluctuations over the whole molecule (as done in most previous theoretical works). All this shows that attosecond pulses not only have the appropriate temporal resolution to study charge transfer, but also induce the necessary charge fluctuations that are needed to force localization in a particular molecular site (e.g., by using an external electromagnetic field). The only remaining issue is how to extract more precise information about this last step (localization) by using a probe pulse as the one employed in the present work or others. Certainly this requires further investigations from the experimental and theoretical points of view.

V. CONCLUSION

The observation of charge migration in complex molecular structures and, in particular, in biologically relevant molecules is one of the main targets of attosecond science. The investigation of charge evolution in these structures initiated by prompt ionization by attosecond pulses is important per se
and for a better understanding of the interaction process between light and complex molecules. We adopted a novel methodology for the measurement of the charge migration process: we found that the yield of immonium dications is a particularly sensitive probe of charge location. Indeed, a clear ultrafast oscillation of the dication yield was measured, following the attosecond excitation, which we have unambiguously associated to the charge migration process within the investigated amino acid molecule. The results obtained in the case of phenylalanine can be seen as the first experimental confirmation that attosecond pulses and techniques are essential tools for understanding of dynamical processes on a temporal scale that is relevant for the evolution of crucial microscopic events at the heart of the macroscopic biological response of molecular complexes.

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