Sub-4-fs Charge Migration in Phenylalanine

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Abstract: Charge migration initiated by attosecond pulses was experimentally observed in an amino-acid. An oscillatory pattern in the yield of a doubly-charged fragments was measured with periods of 3.7 fs and 2.6 fs.
OCIS codes: (320.7150) Ultrafast spectroscopy; (300.6560) Spectroscopy, x-ray.

1. Introduction

The process of electron transfer in molecular complexes is of crucial importance in biochemistry since it triggers the first steps in a number of biochemical processes such as photosynthesis, cellular respiration and electron transport along DNA [1]. Theoretical studies have pointed out that very efficient charge dynamics can be driven by purely electronic effects, which precede any rearrangement of the nuclear skeleton and which can evolve on a temporal scale ranging from few femtoseconds down to tens of attoseconds [2-4]. This ultrafast charge dynamics, essentially driven by electron correlations, has been referred to as charge migration.

Here we report on a clear experimental measurement of charge migration in the amino acid phenylalanine, after attosecond excitation. Charge migration was evidenced in phenylalanine as an oscillatory evolution in the yield of a doubly-charged molecular fragment. Two main oscillations were measured, with periods of 3.7 fs and 2.6 fs, thus confirming the purely electronic origin of the measured dynamics. Numerical simulations of the temporal evolution of the charge wave-packet created by the attosecond excitation pulse strongly support the interpretation of the experimental data in terms of charge migration.

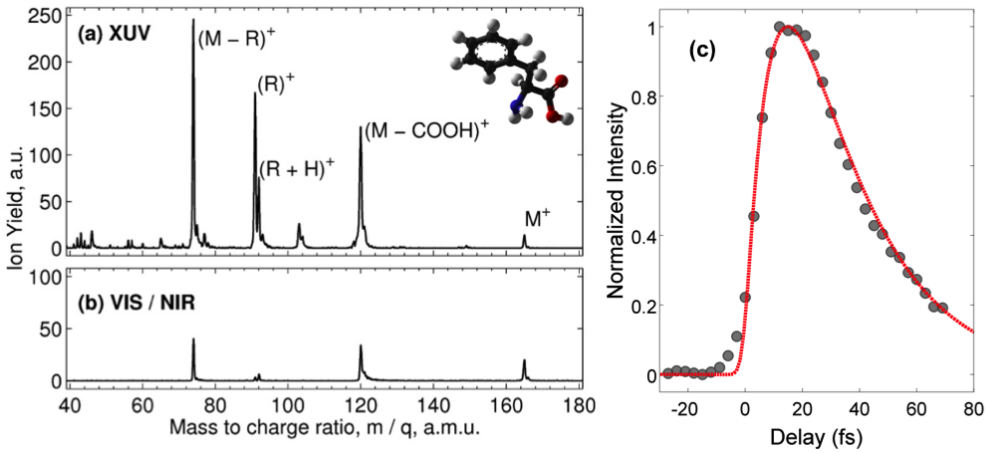

Fig. 1: Mass spectra measured from ionization of phenylalanine by (a) XUV pulses only and (b) NIR pulses only. M is the parent ion, R is the side-chain group. (c) Yield of doubly charged immonium ion (mass/charge = 60) vs. pump-probe delay. The dotted red line is a fitting curve with an exponential rise time of 10 fs and an exponential relaxation time of 25 fs. The inset of panel (a) shows the structure of phenylalanine.

2. Results and discussion

In our experiments, charge migration was measured by using a two-color, pump-probe technique. Charge dynamics was initiated by isolated sub-300-as pulses [5], with photon energies in the spectral range between 17 eV and 35 eV and subsequently probed by 4-fs, waveform-controlled near infrared (NIR) pulses, with central wavelength of 720 nm. A clean plume of isolated and neutral molecules of phenylalanine was generated by evaporation of the amino acid from a thin metallic foil heated by a CW diode laser. The parent and fragment ions produced by the interaction

of the molecules with the pump and probe pulses were then collected by a linear time-of-flight device for mass analysis, where the metallic foil was integrated into one of the end electrodes [6]. Figures 1(a) and 1(b) shows the mass spectra measured by excitation with attosecond pulses only and NIR pulses only, respectively

We have then measured the evolution of the yield of the doubly charged immonium ion (mass/charge = 60) as a function of the delay between the attosecond pump pulse and the NIR probe pulse (the immonium ion is formed by loss of the –COOH group). Figure 1c shows the measured dication yield as a function of the pump-probe delay, on a 100-fs time scale. The experimental data display a rise time of 10±2 fs and an exponential decay with time constants of 25±2 fs (in agreement with the results reported in Ref. [7]). We then we increased the temporal resolution of the measurement by reducing the delay-step between pump and probe pulses from 3 fs to 0.5 fs. Figure 2 shows a 25-fs-wide zoom of the exponential decay, where an oscillation of the dication yield is clearly visible. The corresponding fitting curve (red line in Fig. 2), which closely follows the measured points, is given by the sum of an exponential function (with a time constant of 25 fs) and two sinusoidal functions, with frequencies of 0.27 PHz (3.7-fs period) and 0.38 PHz (2.6-fs period), obtained from the Fourier transform of the experimental data. This ultrafast dynamics can only be associated with purely electronic processes, thus constituting the first experimental measurement of charge migration in a biomolecule.

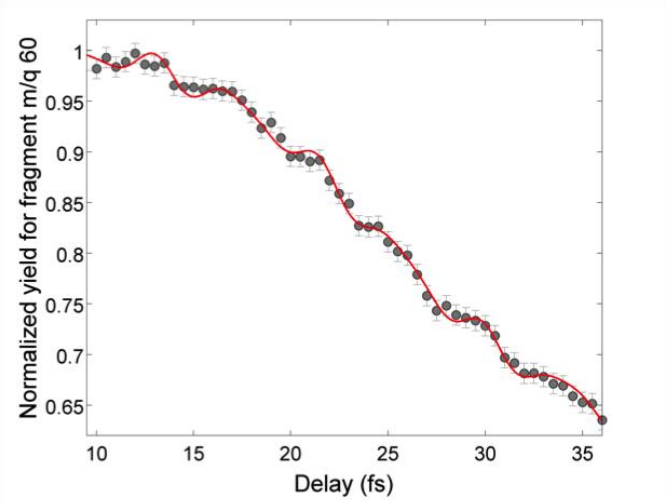

Fig. 2: Generation yield of doubly charged immonium ion (mass/charge = 60) as a function of the pump-probe delay measured with 0.5 fs temporal steps. The red line is the fitting curve discussed in the text.

We have also performed theoretical calculations to describe the hole dynamics induced by an attosecond pulse similar to that used in the experiment. Due to the large bandwidth of the pulse, a manifold of ionization channels are open, thus leading to a superposition of many cationic states, i.e., to an electronic wave packet. For all open channels, the ionization amplitudes have been quantitatively determined. The evolution of the electronic wave packet has then been described by using a standard time-dependent density matrix formalism. The results of the numerical simulations clearly show the production of an ultrafast electron dynamics, characterized by oscillation frequencies in good agreement with the experimental result. We notice that, at variance with previous work, only valence and inner-valence electrons are efficiently ionized by our XUV pulse, so that the observed dynamics is that of a delocalized hole.

3. References

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