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Observation of Ultrafast Charge Migration in an Amino Acid

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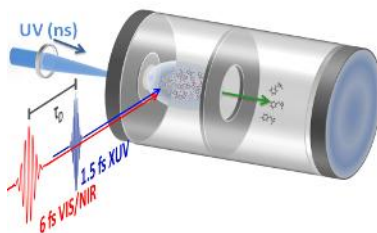
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ABSTRACT

In this communication we present the first direct measurement of ultrafast charge migration in a biomolecular building block – the amino acid phenylalanine. Using an extreme ultraviolet (XUV) pulse of 1.5 fs duration to ionize molecules isolated in the gas phase, the location of the resulting hole was probed by a 6 fs visible/near infrared pulse. By measuring the yield of a doubly charged ion as a function of the delay between the two pulses, the positive hole was observed to migrate to one end of the cation within 30 fs. This process is likely to originate from even faster coherent charge oscillations in the molecule being de-phased by bond stretching which eventually localizes the final position of the charge. This demonstration offers a clear template for observing and controlling this phenomenon in the future.

TOC Graphic



KEYWORDS

intramolecular charge migration, charge transfer, ultrafast, attosecond, pump-probe

Transfer of electronic charge within a single molecule is the fundamental initiator of many biological processes and chemical reactions. It plays a ubiquitous role in catalysis¹, DNA damage by ionizing radiation², photosynthesis³, respiration⁴, photovoltaics⁵, and for switches based on molecular nano-junctions⁶. How this process depends on the timescales, energetics, and molecular distances, has been the subject of considerable research effort⁷⁻⁹. The ability of molecules such as peptides and DNA to act as charge conduits is an intrinsic part of many biological processes. Charge can be transferred between two distant centers using covalently bonded molecules as a bridge. Given that these molecules are normally regarded as insulators, this can be a surprisingly efficient process and has led to considerable discussion of potential mechanisms such as super-exchange and charge hopping^{7,9}.

The study of intra-molecular charge transfer in isolated, complex molecules was pioneered in the 1990s by Weinkauf and co-workers. 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 could be probed using the shift in absorption of the chromophore once charged^{14,15}. With this scheme they were able to observe passage of charge through up to 12 sigma bonds in a quadrapeptide, but the temporal resolution was limited by the nanosecond laser pulse lengths. In a later experiment using pulse lengths of 200 fs and 120 fs for the pump and probe respectively, they were able to extract a 80 fs lifetime for downhill charge transfer from an ionised chromophore to the amine group in 2-phenylethyl-N,N-dimethylamine (PENNA). They suggested this was most likely due to transfer between electronic states through a conical intersection¹⁶, which is reached by the nuclear wavepacket launched from the initial ionisation.

The potential importance of even faster electron transport mechanisms mediated by electronic wavepackets which can cross multiple molecular bonds has been recognized in a number of

ground-breaking theoretical papers¹⁰⁻¹³. If an electron is suddenly removed from an orbital of the neutral, the molecule will be in a superposition of electronic states of the radical cation. The evolution of this electronic wavepacket which produces in charge oscillations, has been labeled *charge migration* to distinguish it from charge transfer mediated by nuclear motion. Depending on the cationic states contributing to the wavepacket and the conformation of the neutral molecule, charge migration across the full extent of the molecule has been predicted to take 5 fs or less for a number of different molecules¹⁰⁻¹³. This long range coherent process is believed to be due to coupling of the single hole states to excited states which have large spatial extent (2 hole, 1 particle configurations) due to strong electron correlation¹³. As these couplings are influenced by the geometry of the molecule, different initial conformations produce variations in the spatial and temporal behavior of the charge migration.

The recent development of few cycle (< 7 fs) infrared laser pulses and extreme ultraviolet (XUV) attosecond pulses has opened up the possibility of direct time domain measurements of electronic motion. This has been demonstrated for electron tunneling in atoms, photoelectron emission from surfaces, and charge oscillations in simple molecules¹⁷⁻¹⁹. However, to date there have been no experimental measurements of charge migration in complex molecules, due to the difficulty of efficiently producing these labile species and the demanding temporal and spectral light pulse specifications required. In our experimental set-up we have overcome these challenges by combining a new attosecond laser beamline with a laser induced acoustic desorption (LIAD) technique which is effective at producing clean plumes of isolated, neutral molecules for a range of biomolecular building blocks²⁰⁻²². In the present work phenylalanine molecules were irradiated by a 1.5 fs XUV pump pulse with a photon energy in the range 16-40 eV, followed at a controllable delay time by a 6 fs visible/ near infrared (500 – 950 nm,

VIS/NIR) probe pulse with an intensity of $8 \times 10^{12} \text{ Wcm}^{-2}$. The parent and fragment ions produced were then extracted into a linear time of flight device for mass analysis. Further experimental details can be found in the online Supplementary Information.

We chose phenylalanine as a model molecule for charge migration since its radical cation has two charge acceptor sites with approximately the same binding energy located on the phenyl and amine groups²³, separated by two singly bonded carbons (Figure 1). Figure 2 shows the mass spectra obtained individually from the XUV (a) and VIS/NIR (b) pulses. The main contributions correspond to the parent ion M^+ (165 Dalton), loss of the carboxyl group yielding the immonium ion ($M\text{-COOH} = 120$), and breakage of the $C_{\alpha}\text{-}C_{\beta}$ bond with the charge residing on the amine ($M\text{-R} = 74$) or phenyl groups ($R = 91$, $R\text{+H} = 92$). The XUV pulse is capable of ionizing all valence and some inner shell orbitals resulting in a wide range of fragment ions as seen in Figure 2a. We particularly note peaks at 103 ($M - \text{COOH, NH}_3$), 77 (C_6H_5^+), 65 (C_5H_5^+) which correspond to charge localized on the phenyl ring, and a small peak at 60 which is due to the doubly charged immonium ion. In order to probe localization of the charge at the phenyl or amine sites, we have exploited differences in the excitation and ionization rates of these groups using the VIS/NIR pulse, as explained in the following paragraphs.

Figure 3 shows the yield of a number of different fragment ions relative to the largest peak in the spectrum at mass 74. While there is no temporal dependence in the parent (165) and immonium (120) ions, fragments corresponding to charge residing on the phenyl group (65, 77, 91, 103) increase gradually for positive delays. Within statistical uncertainties the time constants for each of these fragments are consistent and give an overall weighted average of 80 ± 20 fs. This temporal evolution can be attributed to an internal conversion process into the π_1 state of the phenyl radical cation following initial ionization of a different orbital by the XUV pulse. It is

known that the π_1 state of the phenyl radical cation absorbs strongly in the visible while the neutral phenyl and neutral and charged amine groups do not¹⁵. Therefore, increasing population of this state opens up absorption by the broadband VIS/NIR pulse through resonant 1 photon transitions thus enhancing production of fragments corresponding to charge on the ring.

Figure 4 shows that the doubly charged immonium ion (mass 60) has a very sharp rise at $t = 0$ followed by an exponential decay with a short time constant of 30 ± 5 fs. The identification of this peak as a doubly charged ion is confirmed by the peaks at 60.5 (an isotopologue) and 59.5 (H loss) which have similar temporal behavior. There is no indication in the literature that double ionization of neutral amino acids can lead to a stable doubly charged parent ion. However, it is evident that loss of neutral COOH helps stabilize the doubly charged immonium ion allowing it to have holes at both the amine and phenyl sites. Carboxyl loss is common following ionization of amino acids and is mediated by an alpha cleavage mechanism from charge residing on the amine group²⁴. In contrast to the XUV pump pulse, the VIS/NIR probe pulse is only capable of ionizing the lowest lying orbitals (phenyl π_1 , amine n_N) due to its moderate intensity. The delocalized nature of the π_1 phenyl orbital leads to a reduced rate of tunnel ionization due to the large dipole moment induced in the ring by the strong laser field. In organic molecules this behavior manifests itself as higher saturation intensities for single ionization than would be expected for atoms with similar ionization potentials²⁵. Therefore, it is more probable that the atomic-like n_N orbital is ionized by the VIS/NIR pulse than the π_1 orbital²⁶.

The yield of immonium dications is a particularly sensitive probe of charge location since the local ionization potential will increase as the hole approaches the amine group causing ionization by the VIS/NIR pulse to be suppressed. It is worth noting that fluctuations in the data close to time zero visible in the inset of Fig. 4 might be produced by charge oscillations to and from the

amine site with a period close to the duration of the probe pulse (about 6 fs), although this needs to be confirmed by additional experiments with improved statistics. Although such electronic motion is faster than nuclear re-arrangement, the electron wavepacket would be expected to lose coherence as bonds are stretched resulting in the charge finally settling at the amine site. We propose that the measured 30 fs time constant is therefore a consequence of the sensitivity of charge migration to the nuclear dynamics. This is consistent with the model of charge migration in PENNA described by Lünmeman et al.¹² who showed that charge oscillations between the phenyl and amine sites are strongly influenced by the $C_{\alpha} - C_{\beta}$ bond length.

In this letter we have identified two separate ultrafast processes in isolated phenylalanine molecules. Following ionization of phenylalanine with an XUV photon, transfer into the π_1 state of the phenyl group in around 80 fs was measured through enhanced absorption of the VIS/NIR probe pulse, which we attribute to an internal conversion processes from higher lying states in the cation. In contrast, since the probe pulse preferentially ionizes the n_N orbital, we have demonstrated that the double ionization yield is a very sensitive test for proximity of charge to the amine group. This was demonstrated by a dramatic increase in production of doubly charged immonium ions when the XUV pulse just precedes the VIS/NIR pulse, which reduces for longer delays with a time constant of 30 fs due to migration of charge towards the amine group. Such a fast process is consistent with the model of ultrafast coherent charge oscillations to and from the amine site being terminated by nuclear re-arrangement. The use of attosecond pump pulses and few-optical cycle VIS/NIR probe pulses together with the implementation of the double ionization technique, provide a powerful scheme capable of studying charge migration which will allow this phenomenon, and its consequences for a range of biological processes, to be more fully understood. In the future such dynamics could be coherently manipulated with additional

ultrashort pulses so that the final destination of the charge could be steered, giving unprecedented quantum control over any subsequent chemical reactivity.

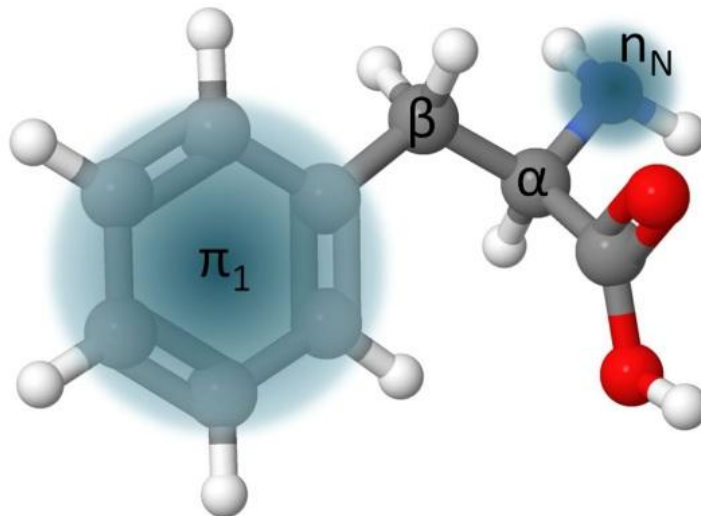


Figure 1: 3D structure of phenylalanine. The location of the two highest occupied molecular orbitals are shown. These correspond to the n_N lone electron pair on the nitrogen of the amine group and π_1 of the phenyl group, separated by a bridge of two carbon atoms (α, β).

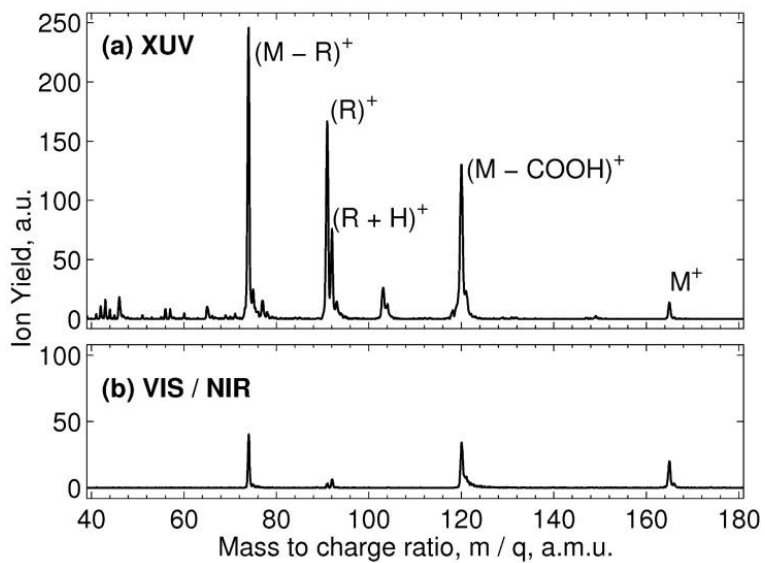


Figure 2: Mass spectra from ionisation of phenylalanine. (a) XUV pulse only, (b) VIS/NIR pulse only. M is the parent ion, with major fragments corresponding to loss of the carboxyl group (immonium ion M-COOH) and cleavage of the $C_\alpha - C_\beta$ bond (side chain group R and M-R).

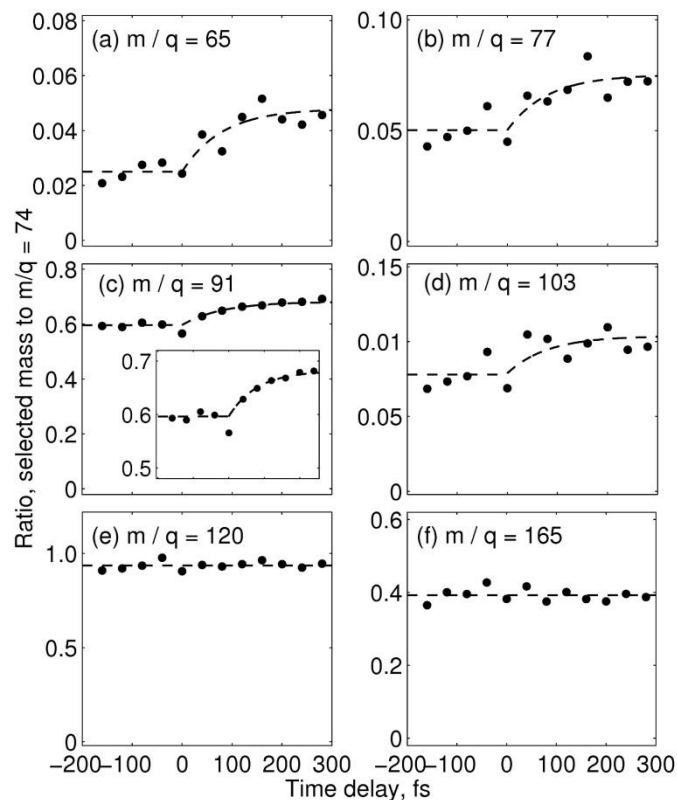


Figure 3: Yields of ions relative to the dominant ion in the spectrum (M-R) as a function of pump(XUV) – probe(VIS/NIR) delay. (a) mass 65 – phenyl ring with 1 C eliminated; (b) 77 - phenyl ring; (c) 91 side chain ions R ; (d) 103 - M-COOH,NH₃; (e) 120 - immonium ions M – COOH; (f) 165 – parent ion M. Dotted lines in (a), (b), (c) and (d) panels are simple exponential fits to the data with a time constant of 80 fs. The inset in (c) provides a magnified view for data close to time zero.

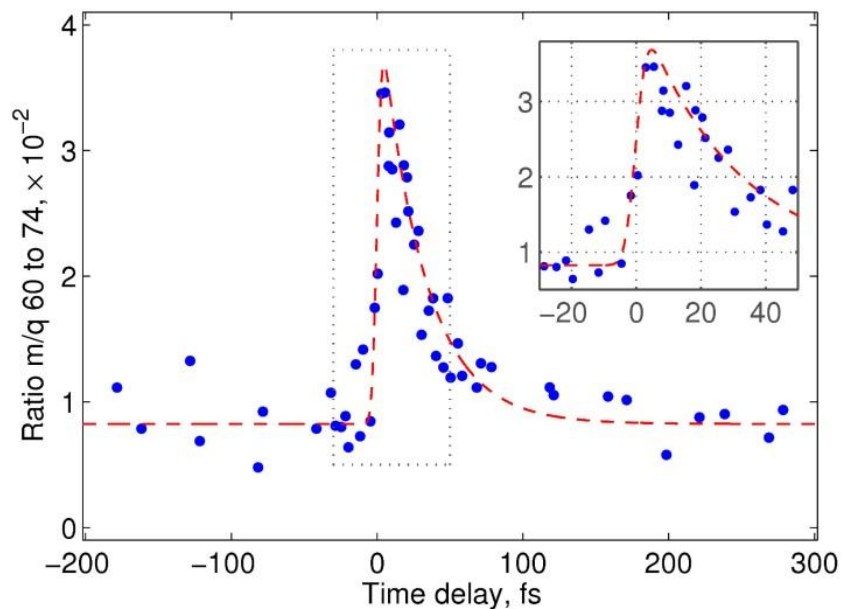


Figure 4: Yield of doubly charged immonium ion (mass 60) relative to the dominant ion in the spectrum (M – R, mass 74) as a function of pump(XUV) – probe(VIS/NIR) delay. The dotted line is a fit using a simple exponential decay convolved with a Gaussian with a width corresponding to the cross correlation of the two pulses (~6.2 fs). The time constant of the fit is 30 fs. The inset shows an expanded view of the points close to zero delay.

ASSOCIATED CONTENT

Supporting Information

Contains Supplementary Figures and Legends; Supplementary Methods; Supplementary Discussion; Supplementary References. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interests.

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