Control of Local Ionization and Charge Transfer in the Bifunctional Molecule 2-Phenylethyl-*N*,*N*-dimethylamine Using Rydberg Fingerprint Spectroscopy

Wei Cheng,[†] Narayanan Kuthirummal,[‡] Jaimie L. Gosselin,[†] Theis I. Sølling,[§] Rainer Weinkauf,[||] and Peter M. Weber*[,†]

Department of Chemistry, Brown University, Providence, Rhode Island 02912, Department of Physics and Astronomy, College of Charleston, 58 Coming Street, South Carolina 29424, The H. C. Oersted Institute, Chemical Laboratory II, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark, and Institut für Physikalische Chemie und Elektrochemie I, Heinrich-Heine-Universität Düsseldorf, 40225 Düsseldorf, Germany.

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Local photoionization pathways and charge-transfer dynamics of 2-phenylethyl-*N*,*N*-dimethylamine (PENNA) are explored using the recently developed Rydberg fingerprint spectroscopy. PENNA, a molecule that derives its biological significance from its relation to neurotransmitters, has two ionization centers that are separated by an ethyl group. We ionize the molecule in various multiphoton ionization processes using different laser wavelengths. The Rydberg fingerprint spectrum reveals the local nature of the ionization process and identifies the center of charge. We discovered that the laser wavelength provides substantial control over the activation of the individual ionization centers. The resonant (2+1) ionization with 400-nm radiation is dominated by the ejection of an electron from the amine moiety. In contrast, the resonant (1+1) ionization with 266-nm radiation leads predominantly to an ion with the charge in the phenyl group. The clean separation of the two ionization processes allows the exploration of ultrafast charge-transfer dynamics ensuing from a specific starting state characterized by a charged phenyl moiety. The width of the corresponding spectral features suggests that the charge transfer proceeds on a femtosecond time scale, suggesting a strong coupling between the two lowest-energy electronic surfaces of the PENNA cation.

Introduction

Charge transfer (CT) across molecular systems is of fundamental importance to chemistry and has ramifications in the transport of reactivity in biological systems and the energy flow in photosynthesis and the photosystems. Fundamental questions relate to the identity of the sites that eject and receive the charge and to the time scale at which charge transfer takes place. To exhibit charge-transfer dynamics, a molecule must be sufficiently large to support independent charge sites. It requires at least two functional groups that are separated by a spacer, which acts as an insulator and maintains the local character of the charge sites. Examples include some amino acids[1−4] as well as some neurotransmitters and their derivatives that contain two functional groups separated by a $-CH_2-CH_2-$ unit. Supporting the notion that the two functional groups act as separate components, classical HeI photoelectron spectra (PES) reveal that their spectral features shift independently upon methyl substitution.[5] One also finds that within the experimental accuracy (broad peaks, room temperature molecules, HeI spectral resolution $>$10 meV), the isolated functional groups in suitably small molecules have similar ionization energies (IE) as the same groups in a molecule containing two such functional groups.

Experiments exploiting the local character of functional groups have been devised to explore the charge transfer in molecules directly after ionization.[6−8] In those experiments, an intermediate electronic resonance is used as a stepping stone to ionization, and the local site concept is invoked for both the excited molecular and ionic states, to rationalize molecular fragmentation as arising from charge-transfer dynamics. Even so, there is little independent evidence to support the notion that excited molecular and ionic states are local, and alternative scenarios involving delocalized excited state orbitals could plausibly explain some of those experiments as well.[9,10]

To further unravel the charge-transfer dynamics in isolated molecules, it is important to observe charge transfer in small, biologically relevant systems, under circumstances where the charges, at the onset of the reaction, are positively localized at specific points. While for large molecules one could use a spatially resolved method, such an approach would be daunting in the mentioned molecular systems with biological activity, and in systems with multiple, closely spaced charge sites. In this report, we extend the recently developed Rydberg fingerprint method[11] to pinpoint the charge on specific points of a molecule and to observe indications for the ultrafast charge transfer that is induced by a sudden charge localization by photoionization.

Using photoelectron spectroscopy via resonant Rydberg states, it was recently shown that the energies of Rydberg states are subliminally sensitive to the structure of the molecular ion core and that they can therefore be used to fingerprint the chemical structures of molecules.[11] Rydberg states arise when an electron is promoted to a highly excited level, where it orbits the ion core at a large average distance. Despite the extended size of the Rydberg wave function, the Rydberg energy levels are sensitive to the geometry of the ion core because the electron

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* To whom correspondence should be addressed. E-mail: Peter_Weber@brown.edu.

[†] Brown University.

[‡] College of Charleston.

[§] University of Copenhagen.

[||] Heinrich-Heine-Universität Düsseldorf.

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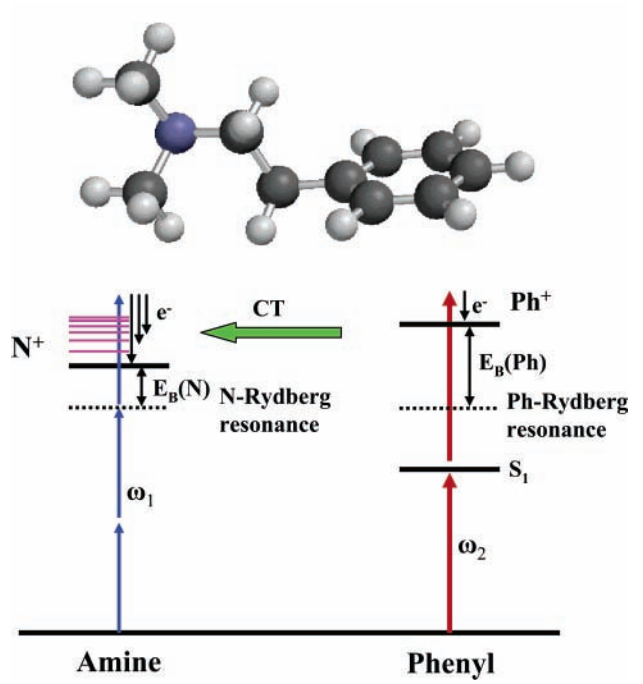

Figure 1. Photoionization schemes used to explore the local ionization and charge transfer (CT) in 2-phenylethyl-*N*,*N*-dimethylamine (top). Ionization with 400-nm photons (ω_1) proceeds in a nonresonant or partially resonant three-photon process, while ionization with 266-nm photons (ω_2) is on- or near-resonant with the S_1 electronic state of the phenyl ring. The kinetic energy of the ejected electrons (e^-) is observed in the photoelectron spectrum and analyzed to obtain the binding energy, E_B.

wave function experiences a phase shift upon each orbit around the molecular ion core. This phase shift is dependent on the atomic composition, the size, and the chemical and geometrical structure of the ion core. Thus, the entire three-dimensional shape of the electron wave function is affected by the internal chemical structure of the ion core. This leads to an adjustment of the energy of the Rydberg levels which is reflected in the size of the quantum defect (see below).[12] Hence, for a given principal quantum number n, the Rydberg state energy, that is, the quantum defect, is specifically correlated to its ion core structure.

Structure, as reflected in the Rydberg level energies, relates to the distribution of atoms and charges, in relation to the center of the charge around which the Rydberg electron revolves. It therefore stands to reason that if a molecule of specific structure has multiple possible charge centers, the Rydberg fingerprint spectra corresponding to each of those charge centers should be distinctly different. In the present work, we test this concept on a molecule with two potential charge centers. Because in PENNA the phenyl and the amine group charge centers are very different in composition, size, and chemical as well as geometrical structure, we expect that the photoelectron fingerprint spectra, and the quantum defects corresponding to each of those charge centers, should be distinctly different. This suggests that Rydberg fingerprint spectra provide a new methodology to identify charge centers in small, medium-sized, as well as extended molecules.

To test the validity of this conjecture, we explored the photoionization dynamics of 2-phenylethyl-*N*,*N*-dimethylamine. The excitation scheme of the experiment is laid out in Figure 1. PENNA has two functional sites that can harbor a charge, namely, a phenyl and an amine group, separated by a $-CH_2-CH_2-$ spacer. Density functional calculations suggest that the lowest energy conformer of PENNA has an extended structure.[13] The methylation shifts the local ionization energy of the amine group site down by about 0.7 eV, compared to the hydrogenated amine, placing it well below the ionization energy of the phenyl ring.[5] Ionization at the phenyl is therefore expected to lead to the first excited state of the cation. This state can undergo CT to the lower-energy amine site. In this CT step, electronic energy is converted into vibrational energy, which opens up a dissociation channel after the ionization. In a recent paper by Weinkauf and co-workers, a fragmentation of PENNA directly after ionization was observed and taken as an indication for a local ionization at the phenyl group and a subsequent charge transfer to the amine site.[13] The use of mass spectrometry did not allow, however, to directly monitor and identify the initial or the final charge centers. The present report provides the first unambiguous identification of a local charge center upon ionization by comparing the Rydberg spectra of PENNA with those of smaller molecules containing the amine and phenyl groups individually. In addition, we are able to control the localization of the ionization process by choosing ionization laser wavelengths that are resonant with specific Rydberg levels. Finally, the spectrally resolved photoionization experiment allows us to infer the time scale of the charge-transfer process that arises from the ion that has the charge pinpointed at the phenyl group.

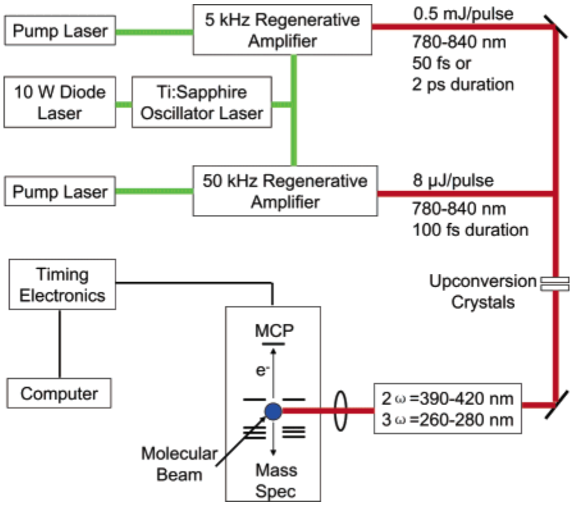

Figure 2. The experimental apparatus. A combined femtosecond/picosecond laser system consisting of a femtosecond oscillator and two regenerative amplifiers generates pulses with a wide range of pulse characteristics (see text). Upon upconversion to the second and third harmonic using BBO-crystals, the light pulses ionize molecules that are seeded in the molecular beam. The photoelectron kinetic energy spectrum is recorded using fast pulse-counting timing electronics.

Experimental Details

While the main features of our experiment have been described in detail elsewhere,[14] several new features were implemented in the present experiment. A brief description of the apparatus, shown in Figure 2, is therefore warranted. The laser pulses originate in a femtosecond Titanium-Sapphire laser (Spectra-Physics, Tsunami), and are amplified either in a 5 kHz or in a 50 kHz regenerative amplifier (both Positive Light, Spitfire). The output of the 50 kHz amplifier is tunable in the range of 810 ± 30 nm and has pulse durations of 100 fs. The 5 kHz output can be tuned over a similar range. Its pulse duration can be selected to be in the picosecond range or in the femtosecond range. For the present experiments, the 2-ps output,

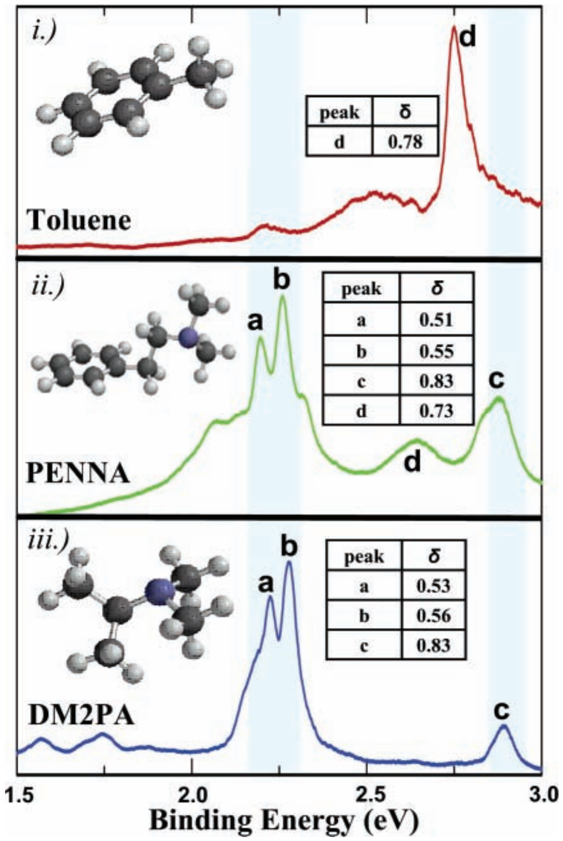

Figure 3. Local ionization at the amine chromophore: Binding energy spectra of (i) toluene, (ii) 2-phenylethyl-*N*,*N*-dimethylamine (PENNA), and (iii) dimethyl-2-propylamine (DM2PA), obtained by analyzing the kinetic energy spectrum of the photoelectrons as described in the text. The electrons are ejected from the molecules in multiphoton processes using laser pulses of about 130-fs duration, with a wavelength of 400 nm.

with pulse energies of 0.5 mJ, was used. Both the femtosecond, 50 kHz pulses, and the picosecond, 5 kHz pulses, are up-converted by sequential BBO crystals, providing pulses at the second harmonic (2ω) at 400 nm or at the third harmonic (3ω) near 266 nm.

The laser beams are directed to a molecular beam apparatus that is equipped with a time-of-flight photoelectron spectrometer and ultrafast timing electronics. This apparatus has been described in detail before.[14] 2-Phenylethyl-*N*,*N*-dimethylamine was purchased from Aldrich (98%) and used without further purification. Care was taken, however, to eliminate all sources of trapped water by dehydrating with a molecular sieve. The sample was entrained in a stream of helium carrier gas at 1.3 bar by bubbling the helium through the liquid held at 70 °C. The comparison samples of toluene and *N*,*N*-dimethyl-2-propanamine were purchased from Aldrich and used as obtained. For generating the molecular beams, those samples were held at room temperature and −30 °C, respectively.

Results and Discussion

The Rydberg fingerprint spectrum of the bifunctional PENNA, obtained with laser pulses with a wavelength of 400 nm, is compared in Figure 3 with the equivalent spectra of small molecules containing only one of the active photoionization sites. Toluene serves as the comparison with only the phenyl chromophore, while *N*,*N*-dimethyl-2-propanamine (DM2PA) is used as a model containing the tertiary amine. The spectra plot the binding energies of the excited electronic orbitals from where the electron is ejected by the last laser photon. This binding energy, E_B, is the energy difference between a high-lying electronic state, most often a Rydberg state, and the ionization energy corresponding to that particular level. In our experiment, we determine the binding energy as

$$E_B = E_{h\nu} - E_{e-}$$

where $E_{h\nu}$ is the energy of the photon and E_{e}- is the kinetic energy of the ejected photoelectron. Since the potential energy surfaces of the higher Rydberg levels and the ion levels are almost identical, there is no change of vibrational energy or quantum number, so vibrational energy does not enter the equation.[21] For Rydberg levels, the binding energy is related to the principal quantum number n (an integer) and the quantum defect δ (a number most often between 0 and 1) by the relation

$$E_B = \frac{\text{Ry}}{(n - \delta)^2}$$

where Ry is the Rydberg constant, 13.6 eV. Analysis of the Rydberg fingerprint spectrum therefore allows us to determine both n and δ. The values obtained for the quantum defects are included in Figure 3.

The Rydberg fingerprint spectrum of PENNA, Figure 3ii, is comprised of a small set of intense peaks and several minor peaks and shoulders. The dominant peaks, a, b, and c, with binding energies of 2.20, 2.26, and 2.88 eV, can be attributed to Rydberg states with a principal quantum number of 3 and quantum defects δ of 0.51, 0.55, and 0.83, respectively. Those dominant peaks have almost identical analogues in the spectrum of DM2PA, Figure 3iii, where the quantum defects are 0.53, 0.56, and 0.83. Those peaks in the PENNA spectrum are therefore associated with an ionization process localized at the amine center. The one feature with a binding energy of 2.64 eV (peak d in Figure 3ii) is more likely associated with the phenyl ionization center: the quantum defect in the PENNA spectrum is 0.73, whereas in the toluene spectrum (Figure 3i) it is 0.78. The intensity of this feature is only about 2.4% of the total ionization signal, indicating that the (2+1) photoionization with 400 nm is almost exclusively centered at the amine site.

While the PENNA spectrum displayed in Figure 3ii is well defined by the measurement of both the photon and the electron kinetic energies, it should not be interpreted as a spectrum of energy levels of the molecule above the ground state. Rather, the binding energy is the amount of energy needed to eject an electron from a corresponding Rydberg state. Nevertheless, the binding energies can be converted to energies belonging to the states, provided the ionization energy to which the Rydberg series converges is known. From the experiments described below, we estimate that the ground state of the PENNA ion is about 7.3 eV above the ground state of the neutral molecule. It follows that the peaks associated with the amine ion core are at energies of 5.1, 5.04, and 4.42 eV, respectively. On the basis of the magnitudes of the quantum defects,[15] and the theoretical studies on DM2PA by Sølling et al.,[16] we assign these levels to two of the 3p states and the 3s state, respectively. The combined energy of the two laser photons that are used to access these states is about 6.2 eV, significantly higher than the adiabatic energy of the Rydberg states above the ground state. The geometrical structure associated with the amine ion is highly displaced from the neutral ground-state geometry,[13] which is expected to enhance the Franck−Condon factors for vertical transitions to those surfaces at the laser photon energy.

The ionization energy to the phenyl local charge center of PENNA is not precisely known. From HeI photoelectron spectra,[5] by analogy to the toluene molecule, and from our work described below, we put that energy to about 8.8 eV. It follows that the Rydberg peak most likely associated with the phenyl group, the one with a binding energy of 2.64 eV, is about 6.16 eV above the ground state. It might be conceivable that the two-photon absorption brings the PENNA molecule to the second excited singlet valence state of the phenyl moiety and that the 2.64 eV feature would be due to a valence state. However, such highly excited valence states have very short lifetimes.[17] We performed photoionization experiments on PENNA using the picosecond light pulses from the 5 kHz laser system and found that the spectra are indistinguishable from those taken with the femtosecond laser.[18] Thus, the peak with a binding energy of 2.64 eV persists on a picosecond time scale and is therefore likely associated with a long-lived Rydberg state. On the basis of its large value of the quantum defect, we assign this level to the 3s Rydberg state belonging to the phenyl ion core.

From the assignment of the peaks observed in Figure 3, it follows that there are *two* levels that can be identified as 3s Rydberg levels: one belonging to the ion core at the amine site and one with the ion core at the phenyl site. Regardless of these assignments, the spectral features observed for the amine and the phenyl ion cores are very different, both regarding their energy above the molecular ground state and the binding energy of the Rydberg electron. The Rydberg fingerprint technique is therefore not only sensitive to the molecular structure but also toward the location of the charge center. It clearly provides a new methodology to identify charge centers within isolated molecules.

We applied this new method to explore the dependence of the charge localization on the laser wavelength. At a wavelength of 266 nm, which is resonant with the origin transition of the S_1 state in phenyl,[13] we found an ionization spectrum that is dramatically different from the one at 400 nm. The 266-nm spectrum of PENNA, along with the one-center comparison molecules, is shown in Figure 4. The DM2PA molecule now shows only a single sharp peak near the ionization energy of the molecule, which stems from a resonant two-photon ionization process involving the previously discussed 3s level. The toluene spectrum has a series of closely spaced, sharp peaks, which arise from the resonant two-photon ionization via the S_1 level. The individual peaks are readily identified as vibrational modes of the toluene ion. The PENNA spectrum is very broad and reveals only one small peak on top of a broad hump, at an energy that is similar to the peaks of the toluene spectrum.

The 266-nm spectrum of the PENNA molecule has several important features that allow us to draw interesting conclusions. Most important are the position of the band maximum and the width of the peak, which causes the spectrum to reach down far below the ionization energy of the phenyl site.

The broad peak in the PENNA spectrum is centered at the same energy as the series of peaks in the toluene spectrum. Multiphoton ionization spectra of PENNA by Weinkauf et al. revealed that the initial one-photon excitation, the transition from S_0 to S_1, is local to the phenyl component.[13] From the fact that the ionization spectrum out of the S_1 state shows a dominant signal near the toluene group signal, we conclude that at 266 nm the ionization is almost entirely localized at the phenyl part. Apparently, there is very little or no crossing from the phenyl moiety to the amine moiety during the ionization process: only a very small amount of signal at 7.5 eV is observed, and even that is attributed to the nonresonant two-photon ionization at the amine part of the molecule (for comparison see PES of DM2PA in Figure 4iii). This component has an intensity of only 1% of the total signal. We conclude that whereas ionization with 400 nm is predominantly local to the amine group, the ionization with 266-nm photons is almost entirely local to the phenyl group!

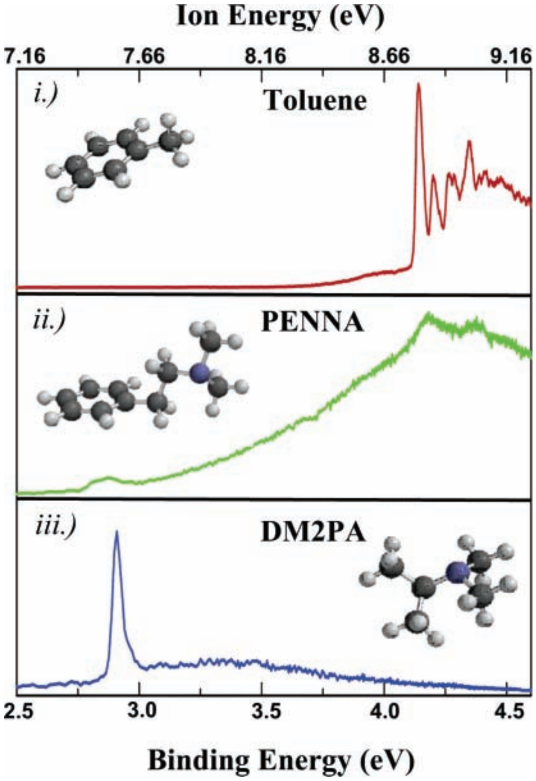

Figure 4. Binding energy spectra of (i) toluene, (ii) PENNA, and (iii) DM2PA, as in Figure 3, but obtained by ionization with 266-nm laser pulses of about 160-fs duration. The spectra are cut off at the high energy end by the combined laser photon energy.

A second interesting feature of the PENNA spectrum of Figure 4 is the width of the band. The observed spectral feature is limited at the high-energy side by the energy of the laser photons. Even so, the band exhibits a width about 1 eV. This is in marked contrast to the corresponding bands in toluene, where the bandwidth is limited by the spectral resolution of the instrument, about 0.02 eV. The ionization proceeds via the vibrationless origin level of the S_1 state. Spectra published in the literature show that this origin peak of S_1 is sharp, within the resolution of a nanosecond laser.[13] Thus, any dynamics of this state must be slow on a nanosecond time scale. Since our experiment is on a femtosecond time scale, any dynamics in the intermediate resonance is therefore too slow to contribute to the photoionization dynamics. Instead, the broadness of the band must arise from properties of the ion states. Several possible reasons for the broadness need to be discussed: (i) lifetime broadening, (ii) a geometry change upon ionization, and (iii) vibronic coupling.

(i) The spectrum is very smooth and structureless. This suggests that at least some contribution to the width of the PENNA band arises from an ultrashort lifetime of the ion that is born with the charge at the phenyl site. The ionic state created by ejecting an electron from the phenyl group is about 1.5 eV higher in energy than the state with the charge at the amine. It is likely then, that immediately following the generation of the positive charge at the phenyl group by electron ejection, an electron is transferred from the amine to the phenyl moiety. If the spectral band was broadened only homogeneously by the ultrashort lifetime of this charge-transfer process, one should conclude that the charge transfer proceeds on a time scale of 1 fs. However, other broadening factors may contribute, so that this number is likely a lower bound.

(ii) A change of geometry upon ionization, coupled with a high density of vibrational states, can lead to inhomogeneous broadening, as was previously observed in photoelectron spectra of flexible molecules.[9,10,19,20] In most of these cases, stabilizing interactions between the charge site and a second functional group within the molecule cause considerable neutral-to-cation structural changes, leading to a shift of the IE and an excitation into a dense set of vibrational states of the radical cation. Stabilization of the charge by intramolecular interactions should lead to a red shift of the IE, which we do not observe for the center of the peak. In addition, PENNA quite likely retains its extended structure upon ionization.[13] We conclude that such interactions should be of lesser importance and therefore exclude them as a broadening mechanism.

(iii) After the reasoning of ii, the fact that when ionizing via the phenyl S_1 state some molecular ions are populated at energies below the IE of toluene still merits an explanation. A vibronic coupling of high vibrations of the amine-ion state to the optically accessible phenyl state could account for a broad spectrum and signal that is at the red side of the phenyl IE. In such a case, these amine vibrations would gain intensity by borrowing oscillator strength from the phenyl-ion state. Because the $N-(CH_3)_2$ bending vibrations that are involved in a change of the charge at the amine site have a low energy, the photoelectron spectrum is expected to be rather dense.

In conclusion, the fact that the maximum of the photoelectron spectrum of PENNA is situated at the position of the toluene spectrum indicates a local ionization at the phenyl site. The broadness of the spectrum is likely due to a combination of a short lifetime and an intensity borrowing of vibrations of the amine charge state from the phenyl charge state. On the basis of the above arguments, we understand the spectrum as a clear indication for a very fast charge transfer after ionization. Even so, it is likely that the time scale for the charge transfer is larger than given by the spectral width.

The small peak in the 266-nm spectrum of PENNA can be used to obtain the ionization energy of the molecule. While the spectrum of Figure 4ii provides an upper bound of 7.5 eV, a better value can be obtained by observing the spectrum as it varies with the laser wavelength. We were able to observe this spectral feature in a spectrum with laser wavelengths as long as 273.3 nm. In that spectrum, we observe a threshold for the onset of signal at 7.3 eV.[18] This suggests that the adiabatic ionization energy of PENNA is at 7.3 eV.

The photoionization of PENNA via the phenyl site is remarkable in several further aspects. In many other molecular systems that were recently investigated,[11,21,22,23] photoionization is associated with a pathway that involves superexcited valence states that quickly convert to highly excited Rydberg states. In PENNA, we see no evidence for such ionization pathways. Most likely, the charge transfer out of the superexcited state is so efficient and fast that photoionization of these states is not observable.

Concluding Remarks

The methodology developed here opens up new opportunities to observe ultrafast charge transfer from specific sites. In contrast to competing methods requiring vibrationally resolved spectra of tracer groups,[24] the Rydberg technique is applicable to all molecules and works well in conjunction with very fast processes on femtosecond time scales. The method to identify highly localized charge centers could be extended to molecular systems with multiple charge sites. This allows the study of the rugged potential energy landscape that governs charge transfer in peptides. Weinkauf et al. modeled the energy landscape of peptide chains on the basis of local functional peptide groups (N terminal, C terminal, amide groups, aromatic chromophores).[7] They found the local model to be a good first-order description of the energetics in large systems that are not accessible to a full global calculation. In their systems, however, ionization was leading to the lowest-energy charge sites, and ionization was assumed to be local, on the basis of the trivial reason that no other site was energetically accessible for two-photon ionization at the wavelength used. Our experiments on PENNA are the first direct experimental proof of a local ionization to an excited valence state of a molecule. In retrospect, they justify the experiments of Levy and co-workers,[6] who assumed, without direct testing, that resonant ionization in a bi-chromophoric molecule allows to prepare the charge in the site of the higher ionization energy. To model the charge transfer in peptide systems, one not only needs to know the energy landscape, but also the charge-transfer dynamics between the different local charge sites. The experimental methodology developed here, coupled with the important finding of highly local ionization, may now open the way for observing the time scales of charge transfer between multiple sites of extended systems.[25]

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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