

Spectroscopic Observation of Conformation-Dependent Charge Distribution in a Molecular Cation

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Abstract: A prototypical case of a molecular radical cation is reported whose electrostatic charge distribution is determined entirely and uniquely by its conformational structures. Experimental observation of charge distribution in a molecular ion was for the first time demonstrated to be feasible by optical spectroscopy in the case of L-phenylalanine cation by utilizing the fact that its photodissociation propensity is entirely determined by the electronic character of its charge distribution. The cationic charge was explicitly shown to be localized in a single site or two different sites depending on the molecular conformation.

Introduction

The traditional view of electrostatic charge in a molecular ion is to assume a local site in the molecule where the charge mainly resides, as often taught in chemistry classes. The principle of charge localization,¹ as it is particularly known in the area of ion chemistry and mass spectrometry, is an empirical dictum long and strongly held. On the other hand, the elementary treatment of the H_2^+ ion demonstrates the notion of charge delocalization over the entirety of the molecule and its dependence on internuclear distance. Such is the general view of molecular charge in the framework of molecular orbital theory. These two simple, opposing viewpoints give rise to three questions:

(1) Is the electrostatic charge localized or delocalized in a moderate-size molecular ion? What is the degree of charge localization?

(2) Can the charge be localized in two different sites, rather than localized in just a single site or completely delocalized?

(3) Can one probe *experimentally* the charge distribution in a molecular ion, and if so, what kind of probe can be used?

In this article, our case study of the L-phenylalanine radical cation (**Phe**⁺) addresses the last two questions and also sheds some light on the first issue. L-Phenylalanine (**Phe**) is one of 20 natural amino acids occurring in living organisms, whose photophysical and chemical properties depend entirely on its molecular conformation that can be classified into two distinct subgroups.^{2–5} Theoretical calculation has found that, in one of these conformational subgroups, the charge is “split” between

two cationic cores of comparable local ionization energies (IEs),⁵ as was also observed previously by Weinkauff et al. in the radical cation of 2-phenylethylamine (PEA⁺).⁶ On the other hand, in the other conformational subgroup of **Phe**⁺, the charge was found localized in a single site. In the present study, we note that such distinct charge distributions are associated with totally different electronic characters of their optical chromophore, which is utilized to demonstrate the feasibility of experimental probing of charge distribution and to verify the possibility of charge division between two local sites of a molecular cation.

Methods

The experimental setup used in this study has been previously described in detail.⁷ Briefly, the **Phe** vapor was obtained by heating the sample powder to 190 °C in the source oven and expanded supersonically through a pulsed nozzle with a 0.8-mm hole by using a neon carrier gas at 1 atm. Care was taken to minimize thermal fragmentation of **Phe** by optimizing various beam generation conditions (temperature, nozzle opening duration, stagnation pressure, etc.). The molecular beam was sampled by a skimmer and irradiated by the fundamental or frequency-doubled output of Nd:YAG-pumped dye lasers. The photoionized species were accelerated and detected in a linear time-of-flight mass spectrometer.

The geometries of **Phe** and **Phe**⁺ were optimized at the B3LYP/6-311+G(d,p) level using Gaussian 98 software.⁸ We reproduced the geometries of the six **Phe** conformers as recently reported by Lee et al.,⁹ who revised the structures of the two conformers (A and E in Figure 1) from the original assignment by Snoek et al.² Each neutral structure was chosen as the initial point in calculating the stable geometry of **Phe**⁺, which can be regarded as the ultimate structure of the cation produced by vertical photoionization of the corresponding neutral conformer.

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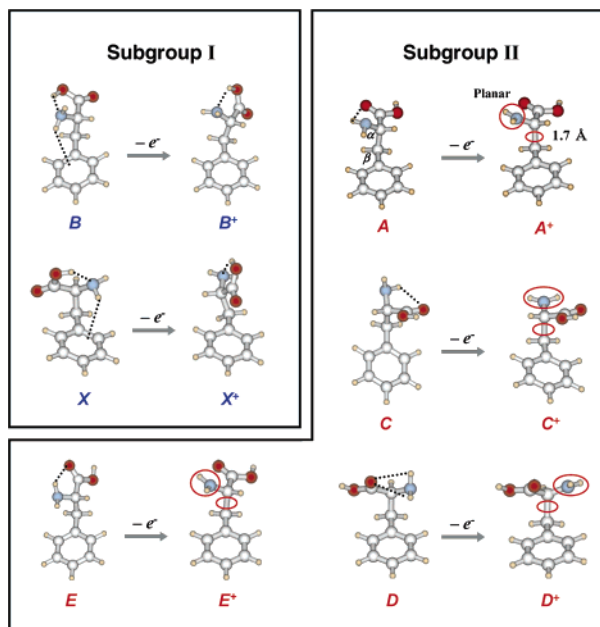


Figure 1. Six lowest-energy conformers of **Phe** and **Phe⁺**. The geometry of each conformer was optimized at the B3LYP/6-311+G(d,p) level. The neutral structure of conformers E and A was recently redetermined by Lee et al.,⁹ while those of the other four were determined by Snoek et al.² Only the six lowest-energy conformers of the neutral **Phe** were chosen as the input geometries for the optimization of **Phe⁺**. For conformers A⁺, C⁺, D⁺, and E⁺ that belong to subgroup II, two notable structural features that suggest charge division, i.e., the planarity of the C_α-NH₂ group and the elongation of the C_α-C_β bond, are represented by the circles.

Results and Discussion

The new findings of this article are based on our earlier work on conformation-dependent properties of **Phe**,^{3–5} in which the supersonic jet technique was used to cool the floppy, multi-conformer molecule so that it can be locked into only a few most stable conformations. Such a technique has recently been employed in many microscopic studies of biologically important molecules in the gas phase.^{10–16} The conformational structures of the neutral **Phe** in a supersonic jet were first proposed by Snoek et al.,² the bulk of which was confirmed by us^{3–5} and also by Lee et al.⁹ Briefly, the six lowest-energy conformers were found to be classifiable into two different subgroups according to the intramolecular hydrogen-bonding scheme. Subgroup I includes the conformers labeled B and X and involves sequential hydrogen bonds COOH → NH₂ → π (phenyl ring), while subgroup II contains the conformers A, C, D, and E, which all have a hydrogen bond in the reverse direction NH₂ → COOH, with no interaction with the phenyl ring.^{2–5}

Figure 1 shows the conformational structures of the neutral **Phe** as well as the cationic **Phe⁺** optimized from its neutral form, which were reported in our earlier article⁵ and are shown here for expedient reference in slightly revised structures.⁹ Some

Table 1. Molecular Parameters for the Six **Phe⁺** Conformers^a

	subgroup I		subgroup II			
	B ⁺	X ⁺	A ⁺	C ⁺	D ⁺	E ⁺
θ (C _α -NH ₂) (deg)	143	133	176	165	179	177
R (C _α -C _β) (Å)	1.58	1.56	1.70	1.70	1.71	1.70
R (C _α -N) (Å)	1.42	1.44	1.39	1.39	1.38	1.38
R (C _β -C _π) (Å)	1.48	1.50	1.47	1.47	1.46	1.47
net charge ^b of -NH ₂	0.15	0.14	0.29	0.30	0.29	0.31
	0.17	0.09	0.34	0.34	0.33	0.35
dipole moment (D)	6.37	4.49	2.37	2.94	2.77	2.37

^a The molecular parameters were obtained from the six conformers of the **Phe⁺** radical cation that are geometry-optimized at the B3LYP/6-311+G(d,p) level (Figure 1). It is to be noted that the conformers of subgroup II have a highly planar C_α-NH₂ group and an anomalously long C_α-C_β bond, which is in agreement with a high degree of charge division, as manifested by the large partial charge on the amino group. The cationic conformers of subgroup II also exhibit a smaller dipole moment because the cationic charge is split between the amino and phenyl groups. There is also a notable decrease in the bond lengths of the C_α-amino bond (denoted by C_α-N) and the C_β-phenyl bond (C_β-C_π), which goes along with the elongation of the C_α-C_β bond. ^b The “net” charge is calculated from the difference between the partial charges of **Phe⁺** and **Phe** obtained by the Mulliken (upper) or NBO (lower) population analysis.

important molecular parameters for the radical cation are summarized in Table 1. The cationic structures were found to be quite different from those of the corresponding neutrals they derive from, which explains the gradual rise in the experimental photoionization efficiency curves.^{4,6} The neutral conformers B and X of subgroup I undergo a drastic change in their backbone-residue structure upon ionization since the attractive interaction between the amino hydrogen and phenyl group in the neutral turns into a repulsive one in the cation due to the newly formed positive charge on the phenyl ring. The backbone structure (COOH → NH₂) itself, however, is retained to a large part. On the other hand, the backbone structure (NH₂ → COOH) of subgroup II conformers is destroyed with a total loss of hydrogen bond in the cation as shown in Figure 1. Moreover, two notable structural changes are observed in common in the conformers of this subgroup: (1) the pyramidal C_α-NH₂ group in the neutral becomes nearly flat in the cation, and (2) the C_α-C_β bond is markedly elongated to 1.7 Å.

The planarity of the C_α-NH₂ group is usually associated with the loss of a nonbonding electron from the nitrogen atom, just as in the case of the ammonia cation (NH₃⁺).¹⁷ It is also borne out in our calculation of partial charges in the cationic conformers using the Mulliken and natural bond orbital (NBO) population analyses (Table 1), which are to be regarded as qualitative but not quantitative indicators of molecular charge distribution. On the other hand, the elongation of the C_α-C_β bond indicates a decrease in the effective bond order of this particular bond, which may result from the withdrawal of its electron density by the adjacent amino and phenyl groups that assume partial positive charge upon ionization. According to a known empirical relation,¹⁸ the bond energy for the C-C bond of 1.7 Å length is predicted to be ~0.9 eV (20 kcal/mol), which is much smaller than the bond energy of a regular C-C single bond (88 kcal/mol). Both of the above structural changes strongly suggest that the positive charge produced by ionization mainly resides in the two cationic charge sites in all subgroup II conformers, in strong contrast to subgroup I conformers.

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It appears that a split charge distribution is hindered in subgroup I conformers B^+ and X^+ by their $\text{COOH} \rightarrow \text{NH}_2$ hydrogen bond because the carboxyl hydrogen holds the nonbonding electron of the amino nitrogen tightly in their hydrogen bond. Therefore, in these conformers, the electron is removed solely from the phenyl ring, leaving behind a nearly whole cationic charge there. There might be an alternative explanation for the failure of subgroup I conformers to attain a split charge distribution. The $\text{COOH} \rightarrow \text{NH}_2$ hydrogen bond stabilizes the nonbonding orbital of the nitrogen atom and would thus lead to a significant increase in the effective IE of the amino group. Consequently, the local IE values of the two cationic charge sites would no longer be comparable. The ionization will take place mainly from the phenyl ring that has a lower IE, and thus the cationic charge will end up there instead of being divided between the two sites. In either case, the carboxyl group may be viewed as a molecular “switch” that opens or closes the electronic circuit for charge localization. The presence of the carboxyl group in **Phe** is the most distinctive and crucial feature that leads to its conformation-dependent charge distribution, the likes of which does not exist in a PEA^+ radical cation.⁶

It came to our attention, after realizing the marked weakening of the $\text{C}_\alpha\text{--C}_\beta$ bond, that the electron impact ionization mass spectra of **Phe** and other such molecules that contain a similar $\text{C}_\alpha\text{--C}_\beta$ bond exhibit an extensive fragmentation pattern for that particular bond.¹⁹ This prompted us to comparatively examine the dissociation pattern for different conformers of the Phe^+ radical cation produced in a conformer-selective way by resonant two-photon ionization (R2PI).^{3,4} In other words, when a certain amount of energy is deposited to the cation by an additional photon after R2PI, the cations of subgroup II were anticipated to show a higher degree of fragmentation than those of subgroup I since the $\text{C}_\alpha\text{--C}_\beta$ bonds of the former are already much weakened by charge division.

Figure 2 shows the mass spectra for different conformers of Phe^+ and their fragments produced by one-color R2PI followed by photofragmentation with the additional photon. Using R2PI via the band origin of the $\pi\text{--}\pi^*$ transition (Figure 3a), we selectively ionized each conformer. By R2PI alone with no additional photon (Figure 2a), no fragment peak was observed other than those from thermal decomposition in the nozzle (marked by asterisks). With an additional photon of visible (Figure 2b) or UV (Figure 2c) wavelength, photofragmentation of Phe^+ is seen to occur. The delay between the ionization pulse and the photodissociation pulse was about 20 ns to ensure that the newly produced cation finds itself equilibrated within the excess energy from ionization by the time the photodissociation pulse arrives. The most remarkable feature of Figure 2b is that only B^+ and X^+ (subgroup I) yield a significant amount of photofragments of mass 74, 91, 92, and 120 amu upon absorption of a visible photon (700 nm in this case), whereas no photoinduced fragment peak was observed for A^+ , C^+ , D^+ , and E^+ (subgroup II). This result is totally contrary to what we expected earlier: the cationic conformers A^+ , C^+ , D^+ , and E^+ with their weaker $\text{C}_\alpha\text{--C}_\beta$ bond were predicted to fragment but turn out to remain intact, whereas the conformers B^+ and X^+ with a regular C--C bond actually undergo fragmentation. Interestingly, when we raised the energy of the third photon

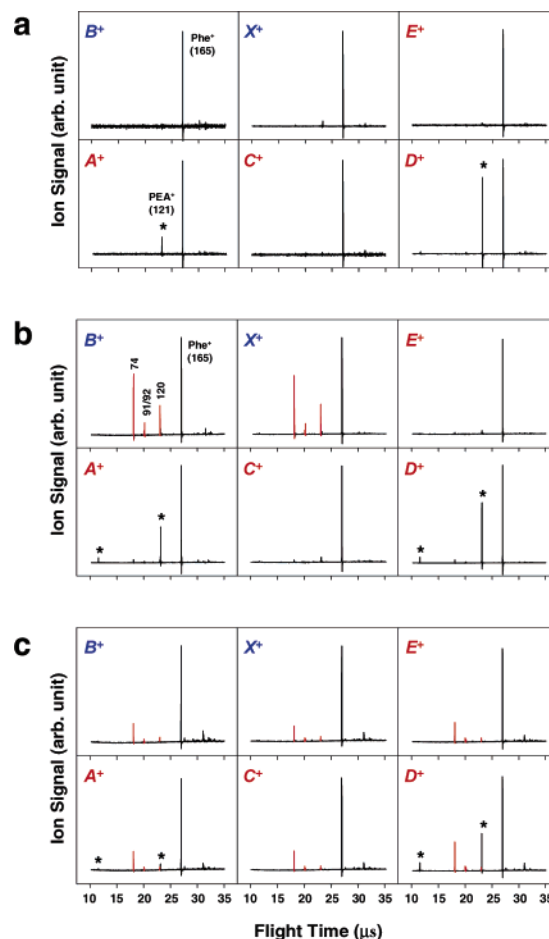


Figure 2. Time-of-flight mass spectra of Phe^+ and its fragment ions. The mass spectra were obtained by R2PI alone (a) and by R2PI with subsequent excitation at 700 nm (b) and 335 nm (c). The peaks marked by asterisks represent a thermal fragment of **Phe**, i.e., 2-phenylethylamine (PEA, 121 amu), produced in the heated nozzle and its photofragment (30 amu). The masses of the photofragments correspond to $[\text{C}_6\text{H}_5\text{CH}_2\text{CH--NH}_2]^+$ (120 amu), $[\text{C}_6\text{H}_5\text{CH}_2]^+$ (91 amu), $[\text{C}_7\text{H}_8]^+$ (92 amu), and $[\text{HOOC--CH--NH}_2]^+$ (74 amu). A power-dependence test indicated that these fragments resulted from one-photon absorption.

further into the UV region (335 nm in this case), the fragmentation becomes indiscriminate; all conformers of both subgroups I and II undergo fragmentation in virtually the same way (Figure 2c).

The conformers that yield the fragments can be more clearly identified by comparing the R2PI excitation spectra monitored at different mass channels in the absence and in the presence of the third photon. Figure 3a shows the mass-resolved R2PI excitation spectrum for the parent mass peak of Phe^+ (165 amu) in the origin region of the $S_0\text{--}S_1$ transition ($\pi\text{--}\pi^*$), which was also reported in our previous articles.^{3,4} The first six labels designate the band origins of the six lowest-energy conformers, while the band X' corresponds to a low-frequency vibration of the conformer X. We then fixed the third photon wavelength at 700 nm and recorded the R2PI excitation spectra at the three major fragment mass channels of 74, 92, and 120 amu (Figure 3b). Only the excitation bands that correspond to the conformers B and X were observed, which clearly indicates that all the photofragments originate from the cations of B and X upon absorption of a visible photon (700 nm). On the other hand, when we changed the wavelength of the fragmentation laser to UV (335 nm), every conformer band was detected at all

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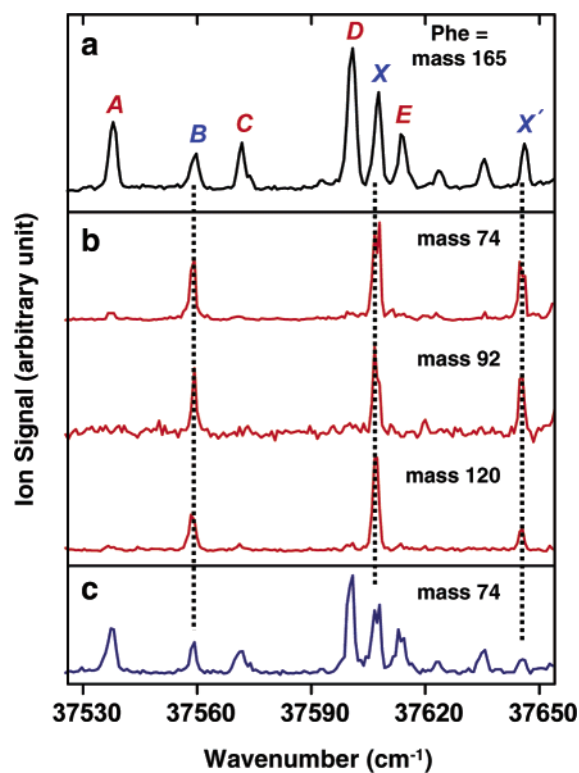


Figure 3. Origin of photofragments. (a) Mass-resolved R2PI excitation spectrum of **Phe**. (b) R2PI excitation spectra at a given mass of the photofragments obtained by scanning the wavelength of the R2PI laser while fixing the wavelength of the photodissociation laser at 700 nm. (c) Same as b except that the wavelength of the photodissociation laser is now fixed at 335 nm.

fragment mass channels, a typical case of which is shown in Figure 3c for a major photofragment at 74 amu. It is clear that fragmentation occurs indiscriminately in all six cationic conformers when they absorb a UV photon.

It is indeed a baffling and counterintuitive finding that the cationic conformers with a weaker C–C bond survive the photofragmentation while the other conformers with a stronger bond undergo extensive fragmentation. But it can be explained by noting that what governs photodissociation is not just the strength of a chemical bond. In fact, for photodissociation to occur, the molecule (or the ion, in the present case) has to absorb a photon in the first place. Therefore, the disparate fragmentation propensity shown in Figures 2 and 3 between the conformers of subgroups I and II may be because they absorb the light quite differently, which may in turn result from the difference in the character of the absorption chromophore for optical transition between the two subgroups of **Phe**⁺.

Figure 4 suggests that the cationic conformers B⁺ and X⁺ of subgroup I should absorb a light rather like the benzene cation since their positive charge is localized in the phenyl ring. They should therefore exhibit an absorption spectrum in the visible region just like the absorption spectrum of the benzene radical cation that begins at ~550 nm.²⁰ The actual absorption spectrum can be red-shifted even to the near-IR region due to the small energy gaps between bonding orbitals, as is generally the case with many aromatic cation systems.²¹ On the other hand, the

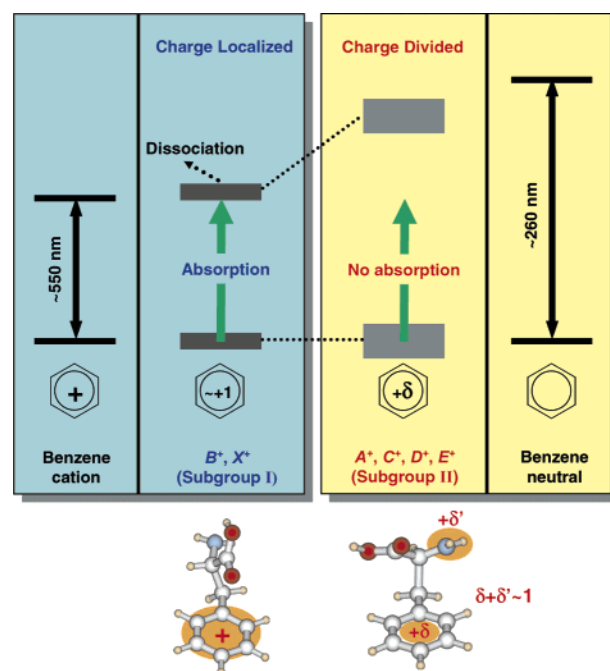


Figure 4. Relationship between charge distribution in the **Phe**⁺ radical cation and the character of its optical chromophore. In conformers B and X that belong to subgroup I (shown in the left panel), the cationic charge is primarily localized in the phenyl ring so that the character of their optical chromophore strongly resembles that of the benzene radical cation whose absorption lies in the visible region. In contrast, for conformers A, C, D, and E of subgroup II (in the right panel), the cationic charge is nearly equally divided between the phenyl ring and the amino group. The optical chromophore of **Phe**⁺ in this case is characterized by “mixing” of the electronic traits of the neutral and cationic benzene, with an absorption spectrum considerably blue-shifted from that of B⁺ and X⁺. Use of a visible or near-IR photon following R2PI results in the photoexcitation and fragmentation of only B⁺ and X⁺, whereas a UV photon below 350 nm leads to the indiscriminate photofragmentation of all the conformers.

cationic conformers of **Phe**⁺ that belong to subgroup II must suffer from the partial withdrawal of the cationic charge from the phenyl ring to the amino group due to the charge division between both charge sites. As a result, the cationic phenyl ring becomes partially neutralized, and the optical absorption should be considerably blue-shifted. When a UV light of sufficiently short wavelength is irradiated on the **Phe**⁺ radical cation, both conformeric subgroups will absorb the light and eventually undergo fragmentation with the excess energy (Figures 2c and 3c). On the other hand, when a visible photon is used, subgroup I conformers may still absorb the light and give rise to fragmentation, but subgroup II conformers whose absorption is considerably blue-shifted may no longer absorb the light and thus are allowed to remain intact (Figure 2b).

To verify our charge division model rather succinctly represented by Figure 4, we obtained the action spectra for the ion intensity of the fragment at 74 amu as a function of the third photon wavelength. The result, given in Figure 5, shows that only the cations of subgroup I fragment with the absorption of a visible or a near-IR photon, while both subgroups of cations commonly undergo fragmentation with a UV light below 350 nm. Similar action spectra obtained at other fragment masses reveal nearly identical spectral profiles. Given that the fragmentation occurs only after the cations absorb the third photon, the action spectra shown in Figure 5 can be regarded as the absorption spectra of the cations produced by conformer-selective R2PI. From Figure 5, it is evident that the cations of

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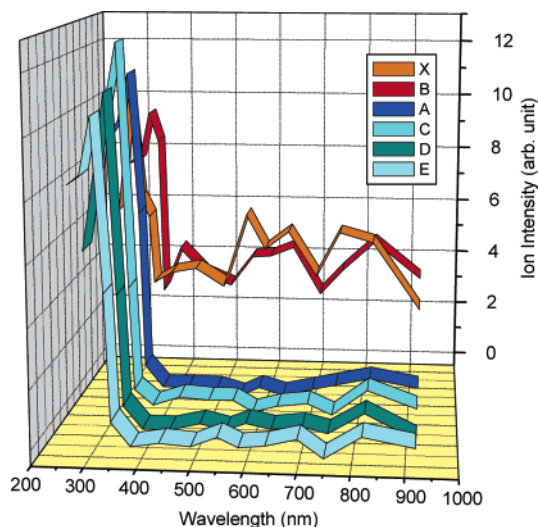


Figure 5. Action spectra for photofragmentation that yields the 74-amu fragment. The spectra were obtained by scanning the wavelength of the photodissociation laser while fixing the wavelength of the R2PI laser at the band origins of the conformers specified. The signals were scaled by the intensity of the parent ion (Phe^+ , mass 165 amu) and the laser power. At wavelengths longer than 350 nm, only B^+ and X^+ (subgroup **I**) absorb a photon and dissociate, while all six conformers undergo fragmentation below 350 nm. The threshold of optical absorption is ~ 350 nm for subgroup **II** of Phe^+ , which suggests that its optical chromophore, the phenyl ring, is significantly neutralized by charge division. We could not reach the absorption threshold for subgroup **I** down to 920 nm, which was the longest wavelength covered by our dye laser.

the two subgroups have distinctly different wavelength ranges of optical absorption: the onset of absorption for subgroup **I** is beyond 920 nm and that of subgroup **II** is ~ 350 nm. Of course, these values must have been considerably red-shifted from the band origins of their cold cations since we deposit ~ 1 eV of energy to the cation above the adiabatic IE in the process of one-color R2PI.⁵ The absorption threshold of 350 nm of our experiment for subgroup **II** would amount to 295 nm for a cold cation, if we arbitrarily assume that our cation has $\sim 70\%$ of the initial excess energy as its internal energy.²²

It is noteworthy that the two cationic subgroups retain their own electronic characters with little mixing between them despite the considerable excess energy deposited by R2PI (~ 0.7 eV for subgroup **I** or ~ 1.0 eV for subgroup **II**).⁵ This may indicate that the distinct charge distributions between the two subgroups represent two different electronic states of Phe^+ accessible by the conformer-selective ionization. In the present case, the coupling between the two states should be rather weak

and the excess energy is apparently not high enough to induce internal conversion, leading to a negligible degree of conformational mix involving charge redistribution between the two subgroups. The excess energy after ionization should then be quickly dissipated into vibrational and rotational degrees of freedom within the given electronic state.

In summary, we first found theoretically that four of the six cationic conformers of Phe^+ have their charge divided between the two cationic charge sites of comparable local IEs, the amino group and the phenyl ring. Two major structural signs of charge division were also observed for these conformers: the planarity of the $\text{C}_\alpha\text{-NH}_2$ group and the marked elongation of the $\text{C}_\alpha\text{-C}_\beta$ bond to an unprecedented length of 1.7 Å. We attempted to prove the occurrence of charge division by directly testing whether the fragmentation propensity is more enhanced for these cationic conformers on account of their weakened $\text{C}_\alpha\text{-C}_\beta$ bond. The result turned out to be totally counterintuitive: those conformers with a split charge and thus elongated bond do not fragment while the others with a localized charge undergo facile fragmentation upon absorption of a visible or near-IR photon. The culprit was the change in the character of the optical chromophore of the cation as charge becomes localized in a single site or divided between two different sites. The cationic conformers with a charge localized on the phenyl ring absorb a low-energy photon because of the cationic character of their optical chromophore, whereas those with a split charge do not absorb the same photon because their optical absorption is considerably blue-shifted due to the partial neutralization of the cationic phenyl group. Such conformation dependency of charge distribution was experimentally verified in this study by the conformation-dependent absorption spectra of Phe^+ obtained by photodissociation. It is quite remarkable that the striking difference in the charge distribution between the two subgroups goes parallel with our previous classification of these conformers based on their hydration propensity,³ ionization energy,⁴ and cation structure.⁵ All these aspects are intimately and consistently related to the intramolecular hydrogen bonds, which determine the conformational landscapes of neutral and cationic Phe .

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Supporting Information Available: Complete ref 8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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