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Dynamics of Glycine Dications in the Gas Phase: Ultrafast Intramolecular Hydrogen Migration versus Coulomb Repulsion

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Ⓢ *Supporting Information*

ABSTRACT: We present a combined experimental and theoretical study of the complex dynamics of excited doubly ionized glycine molecules in the gas phase. Multicoincidence mass spectroscopic techniques together with ab initio molecular dynamics simulations and density functional theory calculations allow us to show that an ultrafast intramolecular hydrogen migration (∼30 fs) appears in competiton with the expected Coulomb repulsion.
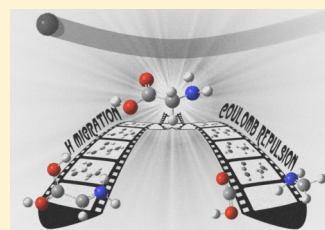
SECTION: Kinetics and Dynamics

The stability of multiply charged molecular ions in the gas phase has attracted large attention as they play an important role in gas-phase chemistry[1−4] and their stabilities challenge fundamental concepts of chemical bonding.[5,6] In general, a multiply ionized molecule becomes less stable than its neutral parent due to the extraction of electrons from the bonding regions and the charge−charge repulsion forces acting inside of the molecule. The breaking of the molecule into charged fragments, often referred to as Coulomb explosion, usually leads to more stable structures. Therefore, only a limited number of molecules are thermochemically stable as dications in the gas phase.

In addition to these fundamental aspects, in the case of biomolecules, understanding the behavior of doubly charged species is also important to shed light on the radiation damage mechanisms as swift ions can induce multiple ionizations and subsequent fragmentations. With the advent of an ion-beam-based cancer treatment, the hadron therapy,[7] it is necessary to better understand the radiation damage at the molecular level.[8,9]

The detection of stable doubly charged species has also interesting consequences for astrochemistry; the enhanced reactivity shown by dications (superelectrophile effect[10,11]) has been proposed as a key feature to explain the formation of relevant new species in interstellar space[12] and planet atmospheres.[13] The search for prebiotic molecules, such as glycine, in interstellar media has been a hot topic in the last decades, centering much on experimental[14−16] and theoretical efforts.[17−19]

It is thus relevant to understand how biomolecules evolve toward the stabilization of the electrostatic repulsion forces when two or more electrons have been removed.[5,20,21] The dynamics of such multiply charged molecular species can be finely probed using physical techniques, giving insight into ultrafast chemical processes at the femtosecond (fs) time scale.[22] In this respect, the isomerization dynamics of simple molecular cations, such as acetylene[23,24] and methanol,[25] has been recently reported. It has been shown that in such simple systems, hydrogen transfer may occur within a few tens of fs, being responsible for the ultrafast decay of the excited dications. Hydrogen transfer has also been suggested to play a role in the dissociation of protonated oligonucleotides[26] and in the formation of H_3^+ from small molecular ions.[27−29]

In this work, we have used a combined experimental and theoretical study to show that in doubly charged excited glycine molecules, an ultrafast hydrogen migration process appears in competition with the expected Coulomb explosion (that leads to fission into two singly charged cations). We demonstrate that the ultrafast intramolecular hydrogen transfer is followed by a subsequent loss of neutral moieties and that this is the only plausible mechanism that explains the detection of stable dicationic species.

We have recently employed a similar combined experimental and theoretical strategy to investigate the fragmentation dynamics of γ-aminobutyric acid, excited and ionized in
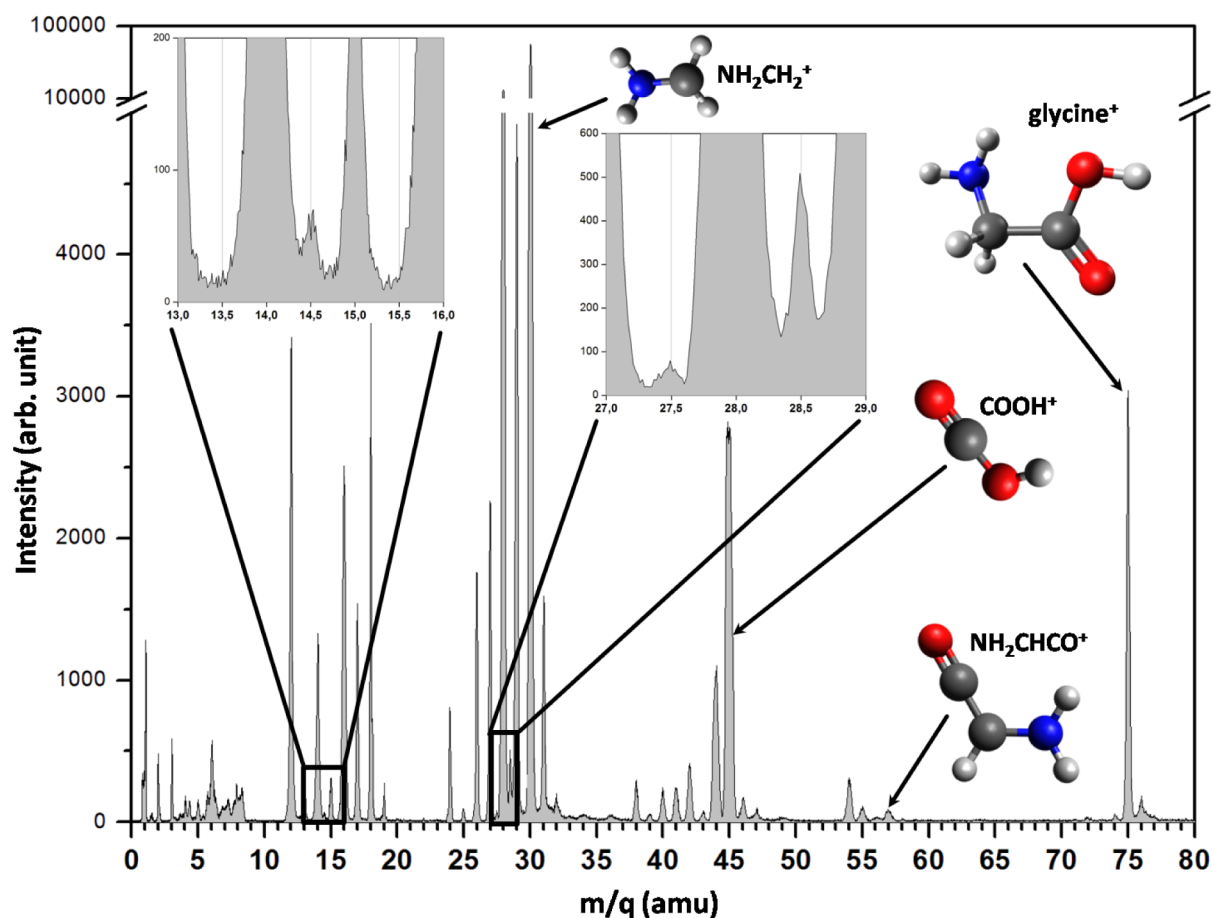
Figure 1. Mass spectrum of the cationic products of the interaction of Xe^{25+} ions with neutral glycine at the energy of 387.5 keV. Zoom-ins show the presence of doubly charged cations at m/q = 14.5, 27.5, and 28.5.

collisions with energetic multiply charged ions.[30] In the present work, we improved it by including, in addition to the standard exploration of the PES, ab initio molecular dynamics simulations, which are crucial to obtain a complete picture of the problem. The mass spectrum of the cationic products measured after collisions of highly charged Xe^{25+} ions with glycine molecules at the energy of 387.5 keV is shown in Figure 1 (experimental details are given in the Supporting Information, SI). The intact molecule survives the interaction with a certain probability, and a corresponding peak is visible at m/q = 75 amu attributed to the $NH_2CH_2COOH^+$ radical cation. However, the spectrum is dominated by molecular dissociation with the main peaks at m/q = 30, 28, and 45 amu. These peaks correspond to the fragments produced by cleavage of the $C_{carboxyl}-C_\alpha$ bond leading to the formation of $NH_2CH_2^+$, $HNCH^+$, and $COOH^+$, respectively. In general, these ions are the characteristic features obtained in the fragmentation of ionized α-amino acids.[31−34] Note that the survival yield for the intact molecule is higher after interaction with multiply charged ions compared to electron-impact ionization or photoionization due to a lower energy transfer.[34] Interestingly, we clearly identify the formation of doubly charged molecular cations at m/q = 28.5, 27.5, and 14.5 amu (see zoom-ins in Figure 1). Except from the 28.5 amu peak, recently observed in electron impact experiments,[35] none of these peaks were previously detected.

A deeper analysis of the fragmentation dynamics has been carried out by means of coincidence measurements of the emitted cationic fragments from a single collision (see details in the SI and in ref 30). Figure 2 shows a so-called "correlation or coincidence map" obtained in collisions of Xe^{25+} projectiles with the glycine molecule. It displays the time-of-flight of the heavier cationic fragment (TOF2) as a function of the time-of-flight of the lighter cationic fragment (TOF1), thus reflecting the fragmentation of the glycine dication into two charged fragments. The insets in Figure 2 give more details in the regions of interest. The most intense islands observed in the coincidence measurements correspond to the cleavage of the $C_{carboxyl}-C_\alpha$ bond (island $30^+/45^+$ in Figure 2b) and subsequent neutral moiety emissions from the two singly charged fragments, H or H_2 from $NH_2CH_2^+$ and O or OH from $COOH^+$ (islands $30^+/29^+$, $30^+/28^+$, and $29^+/28^+$ in Figure 2a). Table 1 in the SI gives the identification of the fragments produced with their relative intensities. As can be seen, in the coincidence map and in the corresponding "two stops" mass spectrum (see the SI), the doubly charged species (at 14.5, 27.5, and 28.5 amu) are absent. Thus, the analysis of the coincident mass spectra shows that these doubly charged fragments are not measured in coincidence with any other charged fragment, that is, they are formed by neutral moiety emission from the doubly ionized glycine molecule. In addition, our coincidence measurements show also a quite interesting feature. We identify an island corresponding to $18^+/57^+$ amu (see insets c and d in Figure 2). The typical $C_{carboxyl}-C_\alpha$ bond cleavage does not explain the observation of this fragmentation channel.
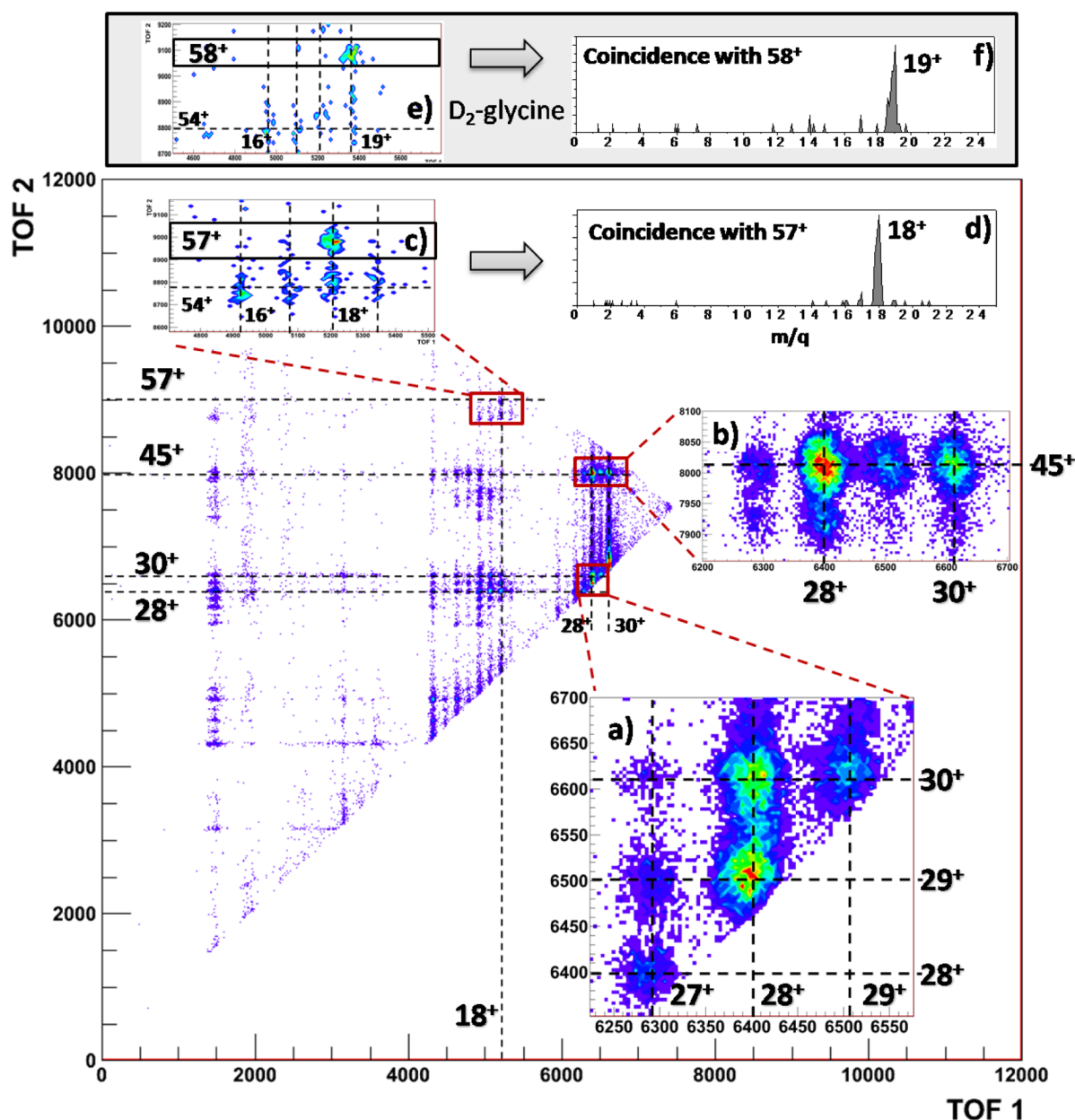
Figure 2. Coincidence map for the fragmentation of the glycine dication in two charged fragments after the interaction of neutral glycine with Xe^{25+} ions at the energy of 387.5 keV. The time-of-flight (in ns) of the heavier fragment (TOF2) is plotted as a function of the time-of-flight of the lighter one (TOF1). Insets show (a−c) zoom-ins of the regions of interest, (d) the mass spectrum of the light cationic fragments emitted in coincidence with NH_2CHCO^+, (e) zoom-ins of the coincidence map for the fragmentation of the deuterated glycine NH_2CD_2COOH, and (f) the mass spectrum of the light fragments emitted in coincidence with NH_2CDCO^+ in collision with deuterated glycine.

The reason for these unexpected findings lies in an ultrafast intramolecular hydrogen migration, as explained by our quantum chemical calculations (see details in the SI). First, starting from the geometry of the most stable conformers of neutral glycine (within less than 1.5 kcal/mol with respect to the most stable one), we have carried out ab initio molecular dynamics simulations. We mimic the experimental conditions by extracting two electrons from the neutral conformers and introducing a certain amount of excitation energy ($E_{exc} \approx 0.1-4$ eV) randomly distributed among the internal (vibrational) degrees of freedom of the molecule. In this way, we reproduce the sudden ionization and excitation produced in the collision of neutral gas-phase glycine molecules with highly charged ions. In this respect, it is worth mentioning that for two-fold

ionization of Na clusters in collisions with Xe^{25+}, the minimum energy transferred is on the order of 1−2 eV.[36] This energy range is a lower bound for the excitation energy in the glycine case because the ion might come closer to the molecule (collision at smaller impact parameters) to capture/remove the electrons. The main fragmentation channel observed in the first steps of the dynamics leads to fission of the dicationic glycine, Gly^{2+} (**1**) into $NH_2CH_2^+/COOH^+$ (at $t \approx 30$ fs; see Figure 3a), which corresponds to the measured $30^+/45^+$ coincidence peak. However, the simulations also show an ultrafast intramolecular H transfer (on a similar time scale $t \approx 30$ fs) leading to two stable doubly charged isomers (see Figure 3b,c) [$NH_2CHC-(OH)_2$]$^{2+}$ (**2**) and [$NH_3CHCOOH$]$^{2+}$ (**3**); both of them correspond to a minimum on the potential energy surface
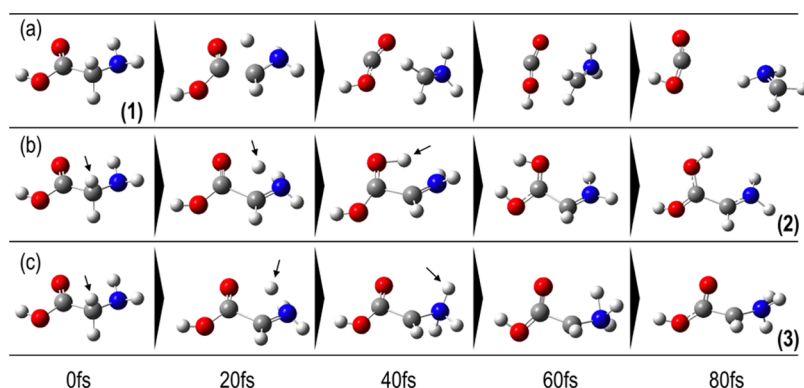
Figure 3. Snapshots of molecular dynamics simulations of a glycine dication (**1**) with (a) 2.18 eV of internal energy, giving a fission process leading to fragments $NH_2CH_2^+/COOH^+$, and (b) 2.45 and (c) 2.72 eV, leading the isomerization by H-transfer in diol $[NH_2CHC(OH)_2]^{2+}$(**2**) and $[NH_3CHCOOH]^{2+}$ (**3**), respectively. Arrows indicate the hydrogen migration.

(PES), as shown further below. This occurs only starting from certain conformers and for a given range of internal energies. Coulomb explosion is the dominant channel in the energy range considered in this work. The importance of this channel slowly decreases with energy, especially above 1.5 eV (see the SI for details), while that of isomerization slightly increases. At 4 eV, the latter channel represents 5% of the observed dynamics, in reasonable agreement with the fact that H-transfer channels in Figures 1 and 2 are associated with peaks of very low intensity (see below). Our statistical study, performed over a total of 1700 trajectories, shows that the Coulomb explosion is indeed the dominant process. H migration is thus statistically less likely. Because both processes occur at the same time scale, the reasons for the dominant Coulomb explosion are two-fold: (i) energetic: the exit channel in the Coulomb explosion is more stable than that for the isomer produced in the H migration; and (ii) entropic: the two fragments produced in the Coulomb explosion lead to a larger increase in entropy than the single isomer produced in the H migration.

A further theoretical analysis of fragmentation has been performed by a thorough exploration of the PES of the doubly charged glycine molecule obtained from density functional theory calculations (see Figure 4 and the SI). From doubly charged glycine (**1**), the most exothermic channel is dissociation into $NH_2CH_2^+/COOH^+$ (island $30^+/45^+$ in Figure 2b; see the right-hand side of Figure 4). Both ions are produced with enough internal energy to follow subsequent fragmentation, $NH_2CH_2^+$ by loosing either H or H_2 (islands $45^+/29^+$ and $45^+/28^+$ in Figure 2b) and $COOH^+$ by loosing either OH or O (islands $30^+/28^+$ and $30^+/29^+$ in Figure 2a; see the four fragmentation pathways starting from $NH_2CH_2^+/COOH^+$ in Figure 2 of the SI). Our exploration of the PES reveals that the corresponding transition states and final products are below the energy of Gly^{2+}, explaining why these are the most intense islands observed in the experiment. Note that Gly^{2+} is produced in a collision with an energetic ion; therefore, it is reasonable to assume that the produced fragments have enough internal energy to overcome the barriers needed to reach the $45^+/28^+$, $45^+/29^+$, $30^+/28^+$, and $30^+/29^+$ fragments. Further evolution of these channels into smaller fragments is not likely because the resulting products are significantly higher in energy (see Figure 2 of the SI). Our molecular dynamics simulations show that Coulomb explosion into $NH_2CH_2^+/COOH^+$ represents ∼98% of the trajectories. This process occurs in ∼30 fs, while further fragmentation of the singly charged $NH_2CH_2^+$ and $COOH^+$
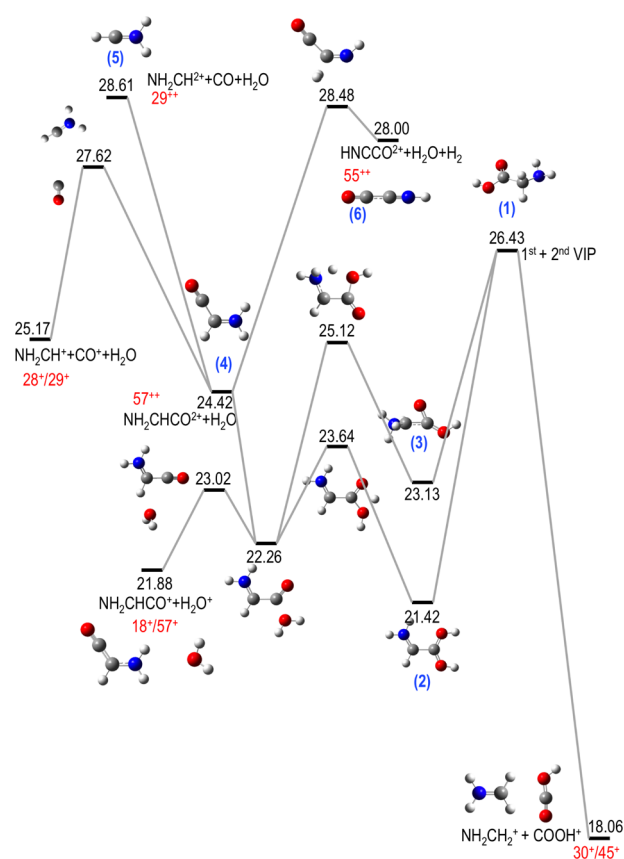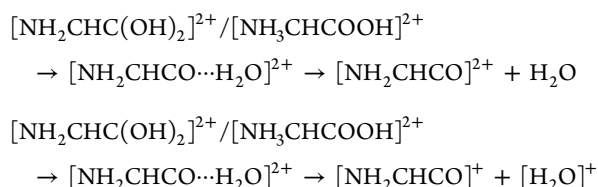

Figure 4. Fragmentation pathways for doubly positively charged glycine. Only the most relevant stationary points of the PES are shown. Relative energies, ΔE, are given in eV at the DFT-B3LYP/6-311++G(d,p) level of theory including the zero-point energy correction with respect to the most stable isomer of the neutral molecule. Key structures are labeled as (**1**), (**2**), and so forth. Coincidence notation is also included, for example, $30^+/45^+$.
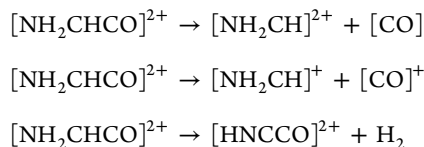
requires longer times than those considered in the present simulations (200 fs).

As mentioned above, the system may also evolve by intramolecular H migration, keeping the two charges on the molecule. H can be transferred from C_α to produce either the geminal diol form $[NH_2{=}CH{-}C(OH)_2]^{2+}$ (**2**) or the $[NH_3{-}CH{-}COOH]^{2+}$ isomer (**3**) (see Figure 4). For singly charged glycine Gly^+, previous studies[37] have shown that the relative

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dx.doi.org/10.1021/jz4020234 | J. Phys. Chem. Lett. 2013, 4, 3903–3909

stability of these isomers is similar to that found in this work for the doubly charged ones. However, the transition states connecting them lie above the lowest fragmentation channel of Gly$^+$ (NH$_2$CH$_2^+$/COOH); thus, the isomerization processes are not accessible channels in singly charged glycine.[38] Indeed, the mass spectra of Gly$^+$ are quite different from those of the singly charged dienol isomer because in the latter case, the loss of neutral water is the dominant channel.[39,40] In contrast, the calculated PES for the doubly charged glycine shows that both isomers can be directly obtained from Gly^{2+} without energy barriers. This is confirmed by the observation of these conformers in the molecular dynamics simulations. Moreover, not only cleavage of the C$_{carboxyl}$−C$_\alpha$ bond but also loss of water is observed in the experiment (see Figure 1). From conformers (**2**) and (**3**), at several points of the PES, competition between fission producing two singly charged species and atomic rearrangement leading to dicationic stable molecules is possible. The left-hand side of Figure 4 shows the most important stationary points in the PES that explain the doubly charged species detected in the mass spectrum and the 18$^+$/57$^+$ amu island measured in the coincidence map. In more detail, from the two species produced in the H transfer, [NH$_2$=CH−C(OH)$_2$]$^{2+}$ (**2**) and [NH$_3$−CH−COOH]$^{2+}$ (**3**), we observe the formation of an intermediate complex in which H$_2$O is loosely bound to NH$_2$CHCO; from this intermediate species, competition between the loss of a neutral water molecule and the loss of a singly charged one can be seen

$$[NH_2CHC(OH)_2]^{2+}/[NH_3CHCOOH]^{2+}$$
$$\rightarrow [NH_2CHCO\cdots H_2O]^{2+} \rightarrow [NH_2CHCO]^{2+} + H_2O$$

$$[NH_2CHC(OH)_2]^{2+}/[NH_3CHCOOH]^{2+}$$
$$\rightarrow [NH_2CHCO\cdots H_2O]^{2+} \rightarrow [NH_2CHCO]^+ + [H_2O]^+$$

From the amino ketene dication obtained after evaporation of a neutral water molecule, [NH$_2$=CH−C=O]$^{2+}$ (**4**), loss of CO, CO$^+$, and H$_2$ is possible

$$[NH_2CHCO]^{2+} \rightarrow [NH_2CH]^{2+} + [CO]$$

$$[NH_2CHCO]^{2+} \rightarrow [NH_2CH]^+ + [CO]^+$$

$$[NH_2CHCO]^{2+} \rightarrow [HNCCO]^{2+} + H_2$$

The dehydration process explains the peak at m/q = 28.5 amu (**4**), whereas CO and H$_2$ losses from the amino ketene dication explain the peaks at m/q = 14.5 (**5**) and 27.5 amu (**6**), respectively. Previous studies observing the peak at 28.5 amu[35] proposed a direct loss of OH and H from Gly^{2+}; this route would require much more energy than the two-step mechanism proposed here, isomerization + neutral water loss. It is worth noting that (**4**) presents an energy that makes it accessible from the entrance channel (**1**), but its possible dissociation pathways appear above this energy. Formation of (**6**) and (**5**) becomes accessible channels if we assume that part of the population of the initial Gly^{2+} is formed with an internal energy of ∼2.2 eV. Thus, the computational study shows that for the formation of the observed doubly charged species, the excited amino ketene dication [NH$_2$=CH−CO]$^{2+}$ (**4**) plays a central role.

We turn now to the island at 18$^+$/57$^+$ amu (see insets c and d in Figure 2). This is explained by the fission from the dications (**2**) and (**3**) into NH$_2$CHCO$^+$ + H$_2$O$^+$ (see Figure 4). Additional neighboring islands in the map correspond to subsequent dissociations of these cations. Again, these species can only be produced if one considers atomic rearrangement before Coulomb explosion. Thus, the detection of the 18$^+$/57$^+$ island is additional experimental evidence of the intramolecular H transfer. To further confirm this mechanism, we have performed experiments with the doubly deuterated glycine molecule in the central carbon atom (NH$_2$CD$_2$COOH). In this case, as expected, we observe the coincidence NH$_2$CDCO$^+$/HDO$^+$ island at 19$^+$/58$^+$ amu (see insets e and f in Figure 2). Although in the fragmentation of singly charged enol glycine it was shown that dehydration involves the amine group,[41] our study of the PES (Figure 4) predicts the formation of the complex [NH$_2$CHCOH$\cdots$H$_2$O]$^{2+}$ after H migration from (**2**) and from (**3**) prior to the fission into NH$_2$CHCO$^+$ + H$_2$O$^+$.

Finally, we want to stress that methylenimine (CH$_2$NH)[42] and cyanoformaldehyde (CNCHO)[43] have been detected as neutral species in star-forming regions; they are isomers of the doubly charged species NH$_2$CH^{2+} and HNCCO^{2+} detected in the present work. Reaction of these dicationic species with neutral CO and H$_2$, respectively, can lead to the formation of H$_2$NCHCO^{2+} (**4**), which in turn can react with water to form the diol isomer of Gly^{2+} (**2**). These reactions are exothermic, and the energy involved in the process would be enough to obtain Gly^{2+} (**1**). Although, according to our results, alternative routes may also lead to the formation of H$_2$NCHCO$^+$ + H$_2$O$^+$ or HNCCO$^+$ + H$_2$O$^+$ + H$_2$; the mechanism proposed here suggests that this path might lead to the spontaneous synthesis of glycine in the interstellar media.

In summary, we have studied the fragmentation dynamics and different de-excitation pathways characterizing the decay of glycine dications in the gas phase. Experimentally, excited molecular dications are produced in collisions with Xe^{25+} ions, and the fragments are identified by coincident time-of-flight mass spectrometry. We find that two types of processes occur in competition. On the one hand, charge separating processes are leading to the coincident detection of two singly charged fragments. On the other hand the formation of smaller stable dications is produced by evaporation of neutral fragments following ultrafast intramolecular hydrogen migration (∼30 fs). Only a few percent (typically 5−10%) of the detected processes correspond to H migration, in agreement with the ab initio molecular dynamics simulations in which the internal energy of the molecule is larger than ∼2 eV. These processes are expected to occur in other biomolecules and therefore should be considered when trying to obtain a complete picture of their complex fragmentation dynamics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of the experimental procedure and of the theoretical simulations together with some complementary results, including assignment of the correlation islands corresponding to the regions of interest in the coincidence map, a mass spectrum of the cationic products obtained by fragmentation of the glycine dication, fragmentation pathways for doubly positively charged glycine, isomerization pathways for doubly positively charged glycine, statistics for each value of the excitation energy, and the percentage of processes as a function of the internal excitation energy. This material is available free of charge via the Internet at http://pubs.acs.org.

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