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X-ray initiated photodissociation of glycine molecule

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We investigated the charge distribution and dissociation dynamics of glycine (NH2CH2COOH) molecule irradiated with 310 eV x-rays from the Advanced Light Source synchrotron. With simultaneous measurements of the fragment ion yield, dissociation angle, and kinetic energy, we were able to reconstruct a three-dimensional image of the x-ray initiated molecular dissociation. Using coincidence and correlated analysis and applying a systematic comparison of properties of ion species, we partially disentangled the fragmentation pathways and identified the most probable fragmentation channels that lead to the observed fragment ions. In addition, we showed anisotropic angular distributions of dissociation subsequent to core-level photoionization and Auger decay and found an association between the initial bond breaking sites and the kinetic energies of the final fragment ions.

I. INTRODUCTION

Molecular fragmentation is one of the fundamental phenomena in photoreactions. The nuclear dynamics subsequent to the photoionization plays a key role in determining charge redistribution and transfer, and hence the final ionic products [1–3]. The understanding of the fragmentation of the molecular ions subsequent to the initial photoionization may provide the foundation for the ultimate photo-control of charge dynamics. Photo-induced charge re-distribution and molecular dissociation of diatomic or triatomic molecule has been investigated vigorously [4–7]. Difficulties in disentangling different fragmentation pathways soar as the number of atoms in the molecule increases. Ion-ion coincidence technique has been used as a common method to distinguish ions of the same species originating from different fragmentation channels [8–10]. The correlations between different observables have enabled tools for further deconvolving the dissociation processes.

In this work, we investigated the fragmentation of glycine (NH2CH2COOH) molecules subsequent to core-level ionization. With momentum-imaging time-of-flight (TOF) spectroscopy and position-sensitive measurements, we were able to directly determine the kinetic energy (KE), the emission angle (in laboratory frame), and dissociation angle (between the final momentum vectors of the departing fragments) and thus reconstruct a three-dimensional image of the fragmentation. By comparing the correlated measurements of multiple observables, such as the KEs and the emission and dissociation angles for various coincidence channels, we determined the dominant fragmentation pathways that led to the observed fragment ions. With the information of partially disentangled fragmentation pathways, we further studied the trends in the energetics of the ion fragments and found associations between particular bond cleavages and the fragments’ KEs. We also determined the momentum angular distributions that imply a transient change in the geometry of the fragment molecular ions.

II. EXPERIMENTAL SETUP

The experiment was carried out at beamline 8 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory [11]. The nominal photon energy was 308 eV. Based on photon energy calibration using NEXAFS data, the actual photon energy was found to be 310 eV. Throughout this work, we use the calibrated value for the photon energy. Ion signals were collected and recorded by a TOF spectrometer equipped with a delay-line detector (RoentDek GmbH) for both time and position measurements, allowing resolving the dissociation angle and the KE simultaneously [12, 13]. Gas phase glycine was delivered by a heated oven assembly at an oven temperature of 130 - 150 C. The base pressure of the chamber is ∼1x10^{-8} torr. The x-ray beam intersects with the molecular beam at 90°, forming a plane that is parallel to the detector plane. The polarization of the x-ray beam is along the TOF spectrometer axis. With simultaneous measurements of ion positions on the detector plane and TOF, a 3-D distribution of angle and velocity can be directly obtained: the velocity projection on the detector plane is obtained from the ion position measurement and the velocity along the direction perpendicular to the detector plane is obtained from the TOF measurement. The dead time of the detector is ∼10 ns.

III. EXPERIMENTAL RESULTS

In the current work, the predominantly C 1s photoionization and the subsequent Auger decay lead to dications
of the polyatomic molecule which mostly dissociate in a concerted (simultaneous) or sequential manner. It is typical for an amino acid molecule, such as glycine, to lose neutral H pairs [14] and the dissociation can also release other neutral fragments that are not detectable in the current experiment. The photon energy used was above the 1s binding energy of C (292.3eV) and below that of N (405.6eV) or O (538.2eV) atomic site in glycine molecule [15]. We confirmed that the first step of the dissociation is dominated by the bond breaking between the carboxyl (COOH) and the amino (NH₂CH₂) groups, as reported in previous work [14]. The resulting large fragment ions can undergo further, secondary dissociation. We have observed fragment ions of large (m/q ≥ 38 amu), medium (32 amu ≥ m/q ≥ 24 amu), and small (m/q = 12-18 amu) sizes (see Fig. 1).

FIG. 1. (Color online) Time of flight (TOF) spectrum of glycine irradiated with x-ray at 310 eV.

To show the different dissociation channels of the ion fragments, ion-ion coincidence analysis was applied and the results are shown in Fig. 2 as a photoion-photoion coincidence (PIPCICO) map, where each panel shows coincidences between ions of different m/q ranges. The TOF of the ion species depends on their mass-to-charge ratio. In this work, we only investigate the ions with the charge of +1, and therefore will refer to all ions and their positions in the TOF spectra and in PIPICO maps by their mass only. All masses will be given in atomic mass units.

As seen in Fig. 1, mostly, mid-size and small fragment ions, e.g. CO⁺, NCH₃⁺ and atomic ions, were produced. Only a small amount of NH₂CH₂C⁺ (around m=42) was produced. Figure 3 shows the integral ion yield of the dominant coincidences, exhibiting that a large number of C⁺ and O⁺ ions were produced.

As seen in Fig. 2(a), in the first step of the fragmentation, the amino group is likely to lose two H atoms resulting in the main contribution of m=28; the carboxyl group is more stable at 45 amu. There is, however, also subsequent dissociation of the carboxyl group which produces CO⁺ or COH⁺ and leads to a strong correlation between m=28 and m=28 or 29, as shown in Fig. 2(c). Continued dissociation of the carboxyl group also releases an O⁺ ion or OH⁺ ions, contributing to the strong correlation between m=28 and m=16 or 17 as shown in Fig. 2(d). Another fragmentation pathway that leads to coincidences between intermediate ions, such as those of m=16-18 and m=28, is bond breaking and charge separation that lead to doubly charged carboxyl group. This channel with asymmetric charge distribution, i.e., the two charges are localized at one fragment, was determined to be the dominant pathway to producing intermediate fragment ions.

In the coincidence map of the smallest ions, shown in Fig. 2(e), the coincidence events between m=16 (O⁺) and m=6 (C2⁺) likely originate from the dissociation of glycine in the trications state due to shake-up or shake-off processes [16]. Double Auger decay can also lead to trications and result in doubly charged fragment ions [17, 18]. The coincidence events between m=14 and m=7 and the coincidence between m=16 and m=8 are contributions by the residual gas of O₂ and N₂. A particularly interesting peak is that of the coincidence between m=16 and m=12 (O⁺ and C⁺), as plotted in Fig. 2(f). As shown in Fig. 3, this coincidence account for a large contribution to the observed fragment ion abundance. We assigned m=16 as O⁺, because much less coincidence with m=13-15 from CH₃⁺ or NH₃⁺ were observed. The “twisted bowtie” shape of this coincidence island indicates that angle be-
tween the momenta of these two ions differed significantly from the antiparallel (180°). The abnormal shape is a result of sequential dissociations where the third fragments that carry away momenta are either not detected or not shown in a PIPICO map of two-body coincidence. As mentioned earlier, dissociating glycine molecular ions are likely to lose two H atoms, as indicated by the dominant peak at m=28, either in self-coincidence or with the COOH$_2^+$ cation. However, in the dissociation that leads to NCCH$_4^+$ (m=\sim 40) and O$^+$ (m=16), H atoms seem likely to remain attached.

In the coincidence map shown in Fig. 2, the slope of the pattern indicates ratio of momenta of the faster and slower ions. A slope of -1 corresponds to equal momenta associated with a tail-to-tail two-body break-up, as shown by all the coincidences in Fig. 2(a). Widening of the island is due to the momentum gained by both ions in the coincident pair from the previous step in the sequential bond cleavages, typically due to releasing H atoms. Bond cleavages leading to large and intermediate fragments (Fig. 2(a-d)) are dominantly associated with characteristics of two-body break-ups. The pattern of coincidence between m=12 and m=16 (Fig. 2(f)) shows a large deviation from the -1 slope, indicating secondary dissociation after the initial charge separation. The angle of the slope for the coincidence island can be obtained by linear fitting or by rotating the island patch for narrower projection [14]. We applied both methods and present the values with smaller error bars. We selected the strongest coincidence islands in Fig. 2 and present the obtained angle of slopes for these coincidences in Table I.

We determined the KEs of all ions and their dissociation angles and emission angles based on the TOF and position measurements. The dissociation angle is defined as the angle between the momentum vectors of the two coincident fragment ions and the emission angle is defined as the angle in the laboratory frame, between the ion’s momentum and the polarization direction of the radiation. Even with the same mass, ions from different dissociation channels may carry different KEs. Figure 4 exhibits the KE distribution for ions of two selected masses (m=28 and 16) originated from various dissociation channels as labelled in the figure legend. For m=28 (CO$^+$ or NCH$_2^+$), the KEs are similar and of about a few eVs for different channels. The channel that involves H$_2$O formation, i.e., releasing H$_2$O$^+$ ions is associated with smaller KEs and a narrower KE distribution compared to the others (see Fig. 4(a)). The KEs of O$^+$ ions possess a much stronger dependence on the dissociation channels, as seen in Fig. 4(b). Among the three selected channels, the KE of O$^+$ from coincidence [O$^+$, CO$^+$] has the smallest peak value and the narrowest distribution, while the KEs for the atomic coincidence channels [O$^+$, O$^+$] and [C$^+$, O$^+$] are significantly larger, associated with broad distributions. The dissociation channel of [O$^+$, CO$^+$] leads to a component of highly energetic O$^+$ ions and a very broad KE distribution.
The distributions are normalized to peak values at 180°. Figure 5 shows the emission angular distributions for ions of m= 28 originated from different dissociation channels. The emission angular distributions for channel \([\text{NCH}_2^+, \text{COOH}^+]\) and \([\text{NCH}_2^+, \text{CO}^+]\) are broader than that for channel \([\text{O}^+, \text{CO}^+]\), which has a characteristic of tail-to-tail dissociation of \(\text{COOH}^+\). As expected, the emission angular distributions of the fragments of the same dissociation channel are similar due to conservation of momentum at the earlier dissociation stage, as seen in the angular distributions of \(\text{NCH}_2^+\) and \(\text{COOH}^+\) exhibited in Fig. 6(a). For coincidence fragments that went through multiple dissociation steps and were produced at the late stage of the dissociation, the emission angular distributions are likely to be different, as in the case shown in Fig. 6(b). The \(\text{O}^+\) ions seem to preferentially emitted along the x-ray polarization vector compared to the \(\text{C}^+\) ions. As shown in Table I, \(\text{O}^+\), \(\text{CO}^+\), and \(\text{COOH}^+\) are produced, the dissociation angular distributions are likely to be different, as in the case shown in Fig. 6(b). The \(\text{O}^+\) ions seem to preferentially emitted along the x-ray polarization vector compared to the \(\text{C}^+\) ions. As shown in Table I, \(\text{O}^+\), \(\text{CO}^+\), and \(\text{COOH}^+\) are produced at an earlier dissociation stage than \(\text{C}^+\) for this fragmentation channel.

The emission angular distribution between two coincident ions exhibits a strong dependence on the dissociation channel and on the stage of the dissociation, as seen from Figure 7. At the initial stage of the molecular dissociation where \(\text{NCH}_2^+\) and \(\text{COOH}^+\) were produced, the dissociation angle of the two ions is preferential around 180°, indicating a two-body break-up. At the intermediate stage where fragments, such as \(\text{NCH}_2^+\) or \(\text{CO}^+\), are released,
the smaller angles start to contribute to the distribution. At the final stage, the atomic ions, such as C$^+$ and O$^+$ are produced, and the dissociation angular distribution extends significantly below 90°. The angular distribution of the dissociation of COOH$^{2+}$ into [O$^+$, CO$^+$], through an intermediate stage, is the most closely confined around the 180°, just as its parent channel that produces the ion of COOH$^{2+}$.

![Diagram](https://example.com/diagram.png)

**FIG. 6.** (Color online) Emission angle distribution of ion-ion coincidence between m=28 and m=45 and coincidence between m=12 and m=16. The distributions are normalized to peak values at 180°. The legends show the ion species of the dominant contribution to fragment ion yields.

As mentioned above, several observables, such as the ion abundance in a coincidence channel in comparison with that in adjacent coincidence channels, the KE, and the angular distribution, provide information indicating their fragmentation pathways. Combining these measurements, we determined the most probable fragmentation pathways and summarize the KE and the widths of the angular distribution of the associated ions in Table I for the major channels. The ambiguity of the determination of species with a particular mass is minimized by considering the consistency in properties such as ion abundance and angular distribution of the ions differing by one or two H atoms only. For example, the mass of 16 in the coincidence between m=16 and m=12 can be assigned to O$^+$ or NH$_2^+$. Since the coincidence between m=12, 14 or 15 is much weaker and does not have the twisted shape in the coincidence map (see Fig. 2), we presume that O$^+$ dominantly accounts for the ion signal of...
m=16 in this coincidence. Similarly, for the coincidence between m=16 and m=16, O$^+$ is considered as the main contribution because the adjacent channels of coincidence between m=14 and m=15 or 16, are associated with low signal rates, different KE for m=16, and different island slopes in the PIPICO map. The ion signal of m=28 can represent a CO$^+$ contribution or a NCH$_2^+$ contribution. Based on the observation that the coincidence between m=26 or 27 and m=16 is almost absent (see Fig. 2), the dominant contribution to coincidence between m=28 and m=16 is likely to be [O$^+$, CO$^+$]. For this coincidence a few possible assignments of the dissociation pathways are (the release of neutral H atoms is not included):

Sequential:
1. NCH$_2$COOH$\rightarrow$(asymmetric charge distribution)
   \[\text{NC}($H_n$) + COOH($H^2$)$\rightarrow$NC($H_n$)+O$^+ + CO^+\]
2. NCH$_2$COOH$\rightarrow$(symmetric charge distribution)
   \[\text{NCH}_2^+ + COOH($H^2$)$\rightarrow$NCH$_2^+ + O^+ + CO\]

Concerted:
3. NCH$_2$COOH$\rightarrow$NC($H_2$)+O$^+ + CO^+$
4. NCH$_2$COOH$\rightarrow$NCH$_2^+ + O^+ + CO$

Since the dissociation angle of the two ions is associated with a narrow distribution along 180° indicating a tail-to-tail dissociation, (2)-(4) are less likely the responsible pathways than (1). The determination of concerted or sequential bond cleavage and the fragment assignment are also further supported by the estimated slopes for particular dissociations. For instances, for the pathway leading to [C$^+$, O$^+$], the first bond breaking results in equal momenta of the large fragment NH$_2$CH$_2$COH$^+$ and the lighter O$^+$, and the subsequent bond breaking of the large fragment will release a C$^+$ ion (and a neutral fragment) that carries part of the total momentum, proportional to the ratio of the mass of C to that of the total mass of the large fragment NH$_2$CH$_2$COH. This mass ratio was calculated and found matching the measured slope tangent of the coincidence island, as shown in Table I. A similar argument can be made for coincidence between m=28 and m=12. The energy due to the release of a neutral element at an earlier stage of the dissociation was also estimated based on the width of the island along the shorter side in the coincidence map, as presented in Table I.

IV. DISCUSSION

Direct photoionization can lead to preferential ionization with radiation polarized along a particular molecular axis reflecting the shape of the ionized molecular orbitals [19, 20]. Without molecular alignment, this angular preference relative to the molecular axis appears to be a preference relative to the photo beam polarization direction. Anisotropic ion angular distribution is not expected for core-level ionization due to the symmetric shape of the 1s orbital. Auger decay processes is also not expected to affect the ion emission angle in the laboratory frame, since these processes do not involve photons. Isotropic angular dependence in the laboratory frame was observed in small molecules, such as methane, following core-level ionization [21]. The dissociation angle between two fragments, on the other hand, reflects the original geometry of the molecule and is further affected by specific fragmentation pathways. The deviations in the dissociation angle from the geometry of the neutral molecules or parent ions are linked to the time scale of sequential processes during the dissociation and the transient geometry changes of the intermediate fragment ions [22].

The anisotropic emission angular distribution of coincident ions NCH$_2^+$ and COOH$^+$, shown in Fig. 6(a), is not expected for core-level ionization. For low energy ions such as those from the coincidence of [NCH$_2^+$, COOH$^+$], the angular dependence of the detection efficiency is weak, since the TOF spectrometer is expected to
The molecule and possibly a geometry change of COOH

of OH (see Table I). The two coincidence channels share

an emission angular distribution dominant along the po-

beam polarization due to resonant excitation of C at 311
eV photon energy [23]. However, our data taken at dif-

ferent photon energies also show anisotropic angular dis-

tributions.

The angular distribution of the subsequent dissociation in comparison with that of the previous step may

reflect the natural geometry of the molecule or indicate changes in the geometry of the initial fragment ions. As

shown in Fig. 6(a) and Table I, the first step of dissociation leading to NCH$_2^+$ and COOH$^+$ is associated with

an emission angular distribution dominant along the polar-

ization direction of the x-ray beam or a dissociation angle of 180°. Secondary dissociation of the NCH$_2^+$ and

COOH$^+$ mainly contributes to the coincidence of [C$^+$, CO$^+$]. The [NCH$_2^+$, CO$^+$] coincidence originates from a

similar initial dissociation but likely with an early release of OH (see Table I). The two coincidence channels share

similar characteristics: a dissociation angular distribution peaking at around 180° and a similarly broader dis-

tribution. The preferred dissociation angle between CO$^+$ and C$^+$, mainly produced from the secondary dissociation of NCH$_2^+$+COOH$^+$, reflects the initial geometry of the molecule and possibly a geometry change of COOH$^+$, and the broad distribution indicates that during the time of the secondary dissociation when each of the large frag-

ment ions released a neutral constituent, the fragment ions had rotated away from their earlier orientation. The

next bond breaking can also, though not dominantly, lead to C$^+$ and O$^+$, which could partially account for the dis-

sociation angle around 90° for the coincidence [C$^+$, O$^+$] (see Fig. 7 ). In case of the first dissociation that leads to a neutral NCH$_2$ and a doubly charged carboxyl group COOH$_2$$^+$, this channel is responsible for the coincidence of [OH$^+$, CO$^+$], [H$_2$O$^+$, CO$^+$], and [O$^+$, CO$^+$]. The disso-

ciation angular distribution, almost identical for [OH$^+$, CO$^+$] and [H$_2$O$^+$, CO$^+$], shows a peak at 180° which is

larger than the original geometry $\sim$120° between the C-

OH and C=O bonds [24]. The broad distribution could be an indication of the spread of a geometry change dur-

ing the dissociation. In contrast, the coincidence of [O$^+$, CO$^+$] is associated with a narrow dissociation distribu-

tion around 180°, differing by 60° from the neutral molec-

ular geometry and resembling that for channel [NCH$_2^+$, COOH$^+$]. This may indicate that this channel is a fast disso-

ciation channel associated with a quick geometric re-orientation than the other two channels involving isomerization and water formation. As shown in Table I, the coincidence of [C$^+$, O$^+$] is determined to be mainly from a unique dissociation pathway of molecular ions that lost an O$^+$ first. The dissociation angle between O$^+$ and C$^+$ peaks around 180°, which is larger than the angle, about 120°-130°, between C-C and C-

OH or C=O bond direction in the geometry of neutral glycine [24, 25]. The much broader angular distribution implies that this dissociation channel is a slower process than other channels. Since C$^+$ and O$^+$ were produced at the last dissociation step, it is also possible that contributions from other pathways broadened the angular distribution as mentioned above.

Bond cleavage between the amino and carboxyl groups results in small ionic fragment KEs (see Table I). The

large ion KEs are associated with a deferred charge separation: an initial asymmetric charge distribution that

leads to a neutral amino group and doubly charge carboxyl group, in which case either the bond between the

two groups or within the carboxyl group breaks first (see coincidence between m=16 and m=12) and coincidence between m=16 and m=16). The observation of highly ener-

getic O$^+$ ions in the [O$^+$, O$^+$] channel (see Fig. 4(b)) is not easily explained. A point charge model of Coulomb repulsion between the two O$^+$ ions, would render an ini-

tial separation of less than one angstrom. Hence, we

consider the bond cleavage may occur in a short range regime of the potential surface, resulting in the large dis-

sociation energy.

V. CONCLUSION

We reported the investigation of charge distribution and molecular fragmentation pathways of glycine molecules irradiated with x-rays at a photon energy above the 1-s ionization threshold of carbon. With the simultaneous measurements of the angle and KE and by the application of the ion-ion coincidence technique, we determined the dominant fragmentation pathways that led to the observed fragment ions. We found that the pathway leading to the dominant atomic ions starts with the cleavage of the double bond of oxygen atom within the carboxyl group. We also found the pathway resulting in water formation is associated with a bond-breaking between the amino group and the carboxyl group and an asymmetric charge distribution between the two large fragments. The determined dissociation pathways enabled us to investigate further how various events along the dissociation pathway affect the energet-

ics of the fragment ions and their angular correlations. First major bond cleavage between the amino and car-

boxyl groups and dissociation involving water formation typically yields small KEs; whereas stripping off a doubly bound oxygen likely leads to highly energetic fragment oxygen ions. The changes in the dissociation angular distribution of the ions between the subsequent steps of bond cleavage indicates changes in the internal geometry of the fragment ions. This work also indicated unexpected anisotropy in the emission angular distributions of the fragmentations subsequent to core-level photoion-

ization and Auger decay.
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