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Ionic fragmentation processes of core-excited α-alanine in gas phase

M. Morita, M. Mori, T. Sunami, H. Yoshida, A. Hiraya*

Department of Physical Science, Hiroshima University, 1-3-1 Kagamiyama, Higashihiroshima, 739-8526 Japan

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Abstract

Ionic fragmentation of core-excited α-alanine in gas phase was observed. The most dominant ionic species is $COOH^+$ for all core-ionizations at C 1s, N 1s, and O 1s. An increase in COO^+ and a decrease in $COOH^+$, which were observed as core-hole atom selectivity for the O 1s ionization, are explained by the enhancement of O-H bond scission. Further state-selective O-H bond scission, observed at the O 1s second peak, is attributed to the O_{OH} 1s → $3s/\sigma^*$ transition.

1. Introduction

Photochemistry of amino acids is of considerable interest in view of the origin of life and possible delivery of these molecules from space to the primitive Earth. Gaseous glycine (NH_2CH_2COOH), the simplest amino acid, is observed by radioastronomy in hot molecular cores [1] associated with the earliest phases of massive star formation. Several photoionization studies on gaseous amino acids were performed in the valence excitation region [2,3]. However, no study in the core excitation region has yet been reported. In the valence excitations of amino acids [2,3], the dominant ionic species are fragment ions with a loss of neutral COOH as well as protonated hydrogen cyanide ion ($HCNH^+$), which has great astrophysical importance [4]. The fragment ions formed by core excitations of amino acid are expected to be different from those by valence excitations. α-Alanine is selected as a target molecule because it is the next simplest amino acid after glycine, while it has higher vapor pressure than glycine.

In this letter, total ion yield (TIY) spectra in the C 1s, N 1s, and O 1s regions and mass spectra for each core-ionized state of α-alanine ($CH_3CH(NH_2)COOH$) in gas phase are presented. Then state-selective dissociation processes of the O 1s core-excited α-alanine are discussed in comparison with those of 2-methylpropionic acid (2MPA: $(CH_3)_2CHCOOH$).

2. Experimental

Experiments were performed at the soft x-ray beamline BL6 [5] constructed at the bending magnet section of HiSOR. This beamline is equipped with a Hettrick-type [6] VLS PGM (Varied-Line Spacing Plane Grating Monochromator), which covers the photon energy range from 200 to 1200 eV by switching of two gratings. The resolving powers of the monochromator, $E/\Delta E$, were ≈550 (C 1s), ≈ 800 (N 1s) and ≈ 900 (O 1s) for measurements of total ion yield (TIY) spectra. During the measurements of time-of-flight (TOF) mass spectra, the $E/\Delta E$ values were set to ≈ 300 (C 1s), ≈ 400 (N 1s) and ≈ 480 (O 1s) to gain the ion count rate. The photon energy was calibrated by measuring the TIY spectra of CO_2 in the C 1s and O 1s regions, and N_2 in the N 1s region. In the C 1s region, the intensity of the first order light was weakened especially at ≈ 290 eV by carbon contamination on optical components, and it was only 65 – 75 % of the monitored intensity that includes the higher order light and stray light.

As the vapor pressure of α-alanine is low at room temperature, a sample container equipped with a heater and a nozzle (1 mm i.d., 15mm length) was installed near the ionization region. Racemic α-alanine (Nacalai Tesque) with minimum purity of 99 % was stored in the sample container with alumina balls that homogenize the temperature distribution of α-alanine sample. Before storing α-alanine, it was heated on an oven to eliminate water. Sublimated α-alanine was passed

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*Corresponding author. Fax: +81-82-424-7489,
E-mail address: hiraya@sci.hiroshima-u.ac.jp

through the nozzle and crossed the light. The sample container was kept at 180-190 °C. Up to this temperature, a quadrupole mass analyzer set in the main chamber detected no increase in the ratio of CO_2^+ (the main product of thermal decomposition of α-alanine). The estimated vapor pressure of α-alanine was ≈ 60 Pa at 185 °C. The ultimate pressure in the main chamber was 10^{-5} Pa. During sublimation of α-alanine the pressure was about 10^{-4} Pa. Degassed 2MPA stored in a cylinder was introduced to the main chamber through a stainless steel nozzle (2 mm i.d.). This sample with 99 % purity was purchased from Tokyo Kasei Kogyo. During introduction of the sample, the pressure in the main chamber was $\approx 2 \times 10^{-4}$ Pa.

A reflectron-type TOF mass spectrometer [7] located at the end of the beamline was used to analyze fragments ions. Two different extraction methods are used for α-alanine and 2MPA. For 2MPA, the photoelectron-photoion coincidence (PEPICO) method is used with detecting electrons collected by a static electric field of 800 V/cm in the ionization region. Because α-alanine sublimed from the heated nozzle is quickly solidified onto the electron detector, coincidence measurements started by an electron signal cannot be used. Therefore, pulsed extraction technique was used in this study. In this mode, a pulsed field was applied to the ionization region to extract positive ions into the TOF mass spectrometer. The electric field of 300 V/cm was applied during ≈ 780 ns with 3300 Hz repetition rate. Except for this ion extraction period, a retarding voltage of 35 V was applied to the entrance of the TOF mass spectrometer to reject ions accumulated in the ionization region during the extract-off period.

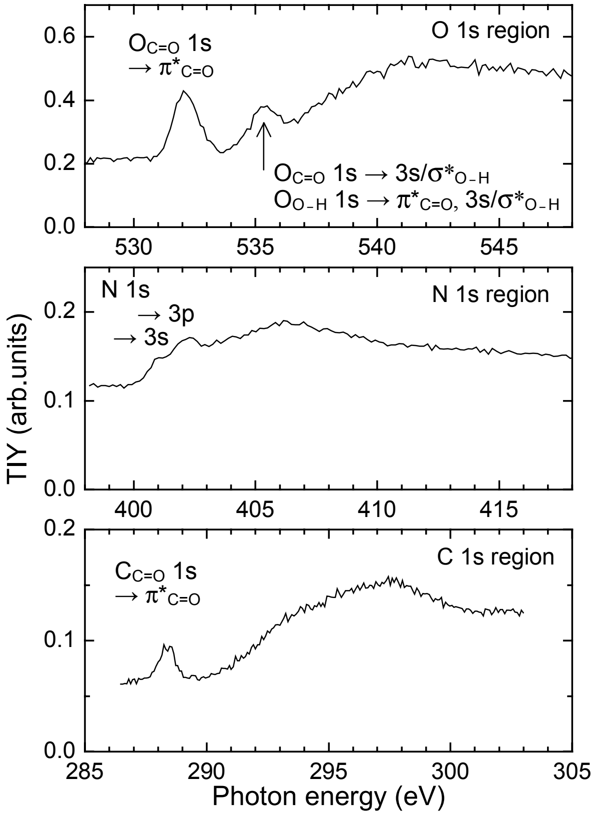

Fig. 1. TIY spectra of α-alanine measured in the C 1s, N 1s and O 1s regions.

3. Results and discussion

3.1. Total ion yield (TIY) spectrum of α-alanine

Figure 1 shows TIY spectra of α-alanine measured in the C 1s, N 1s and O 1s regions. The TIY spectrum represents the total ion counts normalized to the light intensity monitored with a gold mesh, and it can be regarded as the absorption spectrum. A sharp peak at 288.5 eV in the C 1s region was assigned to the $C_{C=O}$ 1s → $\pi^*_{C=O}$ by Cooper et al. [8]. The π* intensity of the present TIY spectrum is much weaker than that in EELS [8]. This is probably due to an overestimation of the first-order light intensity around this peak in our measurement. Though the ionization potential (IP) of the $C_{C=O}$ 1s of α-alanine has not been reported yet, it can be estimated to be ≈ 295.4 eV based on the experimental value of 295.35 eV for acetic acid [9]. The 1s IPs for other carbon atoms must be below the IP of the $C_{C=O}$ 1s, because the IP of the C_{CH3} 1s in acetic acid is 291.55 eV [9].

In the N 1s region, the structures observed at 401.0 (shoulder) and 402.5 eV are related to the N1s → 3s and 3p Rydberg transitions, respectively [8]. A broad maximum at 406.5 eV can be attributed to the σ* shape resonance as for methylamine [10]. The N 1s IP in α-alanine is estimated to be ≈ 405 eV from the value (405.15 eV) in methylamine [11]. A small edge jump at the N 1s region can be explained by the underlying valence shell and 1s ionization continua of three carbon atoms and agrees well with the estimation from mass absorption coefficients.

The first peak at 532.0 eV in the O 1s region is assigned to the $O_{C=O}$ 1s → π* [8]. The second peak at 535.2 eV has never been reported for α-alanine. The second peak of acetic acid was assigned primarily to the O_{OH} 1s → π* [12] following the assignment for formic acid [13]. However, two other transitions from $O_{C=O}$ 1s and O_{OH} 1s to the mixed 3s/σ* orbital were considered to be overlapped at the second peak of these molecules [12, 13]. From the similarity of the spectral feature of α-alanine with those of organic acid molecules, three transitions are considered to be overlapped at the second peak of α-alanine. Considering the IPs for acetic acid [9], IPs of $O_{C=O}$ and O_{OH} for α-alanine are estimated to be ≈ 538 and ≈ 540 eV, respectively.

3.2. Mass spectra for C 1s, N 1s, and O 1s ionizations

Figure 2 shows mass spectra of α-alanine obtained for the excitations above the IPs of C 1s, N 1s, and O 1s. These mass spectra contain the contribution of underlying electronic states below each edge. Fragment ions at $m/z = 45$ and at $m/z = 28$ are the main products irrespective of which atom is core-ionized. The ionic species observed at $m/z = 45$ is assigned to $COOH^+$ (carboxylium ion, $O{=}C{-}OH^+$) formed by a simple C-C bond scission, following the previous assignment in valence excitations [2]. Formation of $COOH^+$ as the dominant species following core excitations is the most evident difference from those in the valence excitations, where $COOH^+$ was only weakly [2] or hardly [3] observed. Composition of the ionic species, CO^+, CNH_2^+, and $C_2H_4^+$ at $m/z = 28$ cannot not be determined in the present measurements.

A peculiar intensity distribution of the fragment ions is observed commonly for the C 1s, N 1s and O 1s ionizations in the series of $C_2NH_x^+$ where $m/z = 43$ ($C_2NH_5^+$) is unusually weak comparing to $m/z = 41$ ($C_2NH_3^+$), 42 ($C_2NH_4^+$) and also to $C_2NH_6^+$ component in $m/z = 44$. The intensity of $C_2NH_6^+$ is estimated from the $COO^+/COOH^+$ ratio of 1/5 above the O 1s IP of 2MPA, for which COO^+ is the unique species at $m/z = 44$. On the assumption that the $COO^+/COOH^+$ ratios for 2MPA and α-alanine are equal, the fractions of $C_2NH_6^+$ in $m/z = 44$ are estimated to be ≈3/4. By using this value, the intensity ratio in the series of $C_2NH_x^+$ ($x = 3$ to 6) for the O1s ionization is estimated to be ≈2:2:1:3. In general, the yield of fragment ions with different numbers (n) of H atom is a monotonic function of n. The peculiarly weak intensity of $C_2NH_5^+$ suggests a high barrier to form $C_2NH_5^+$ or unstableness of $C_2NH_5^+$, or both.

Distributions of the fragment ions formed at 297.8 eV (C 1s) and 406.5 eV (N 1s) are nearly alike. This similarity is caused by a large contribution of the C 1s ionization continua in the N 1s region. A difference in branching ratio is found for the O 1s ionization that $COOH^+$ ($m/z = 45$) is weaker while $COO^+/C_2NH_6^+$ ($m/z = 44$) is stronger than those for the C 1s and N 1s ionization. Since the branching ratios of the $C_2NH_x^+$ series from $x = 0$ to 5 ($m/z = 38 - 43$) are nearly equal

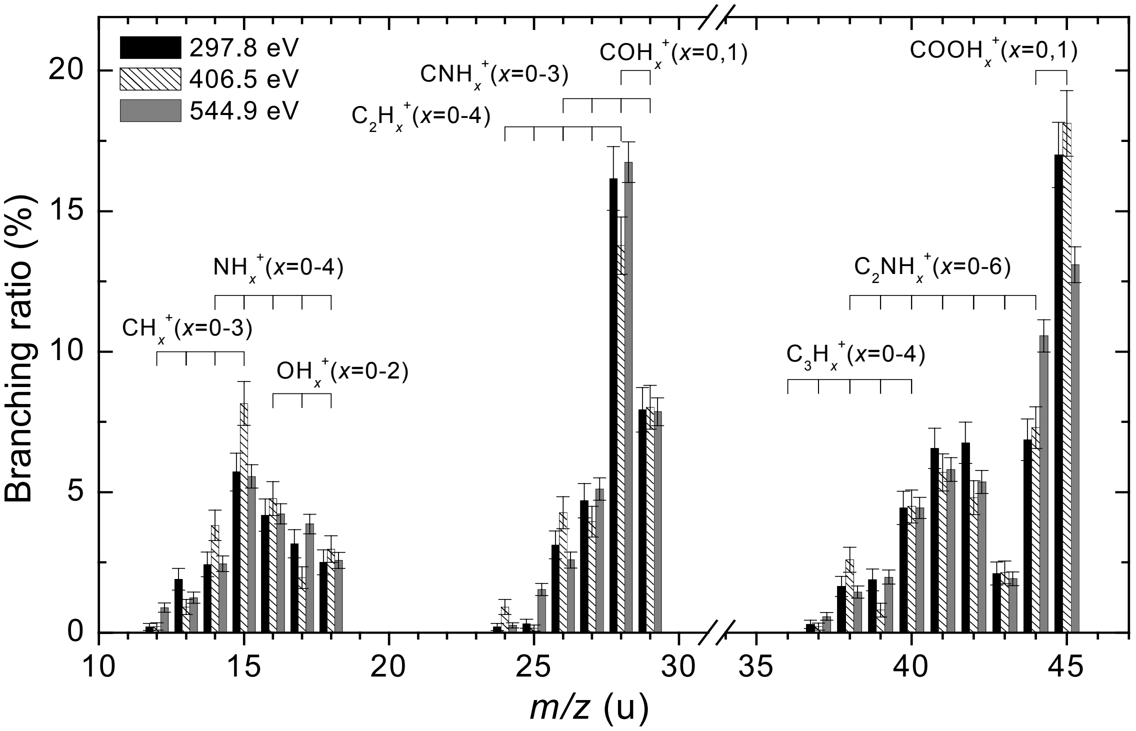

Fig. 2. Mass spectra of α-alanine obtained for excitations above 1s IP's of C, N and O atoms.

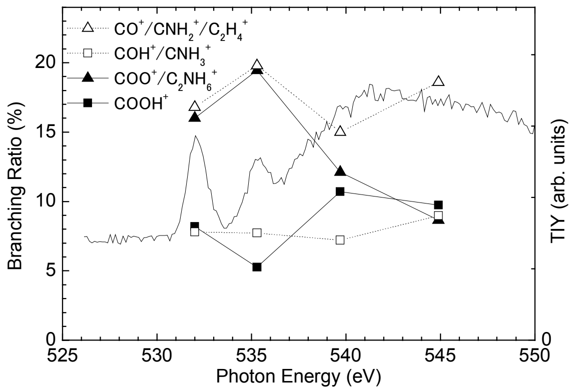

Fig. 3. Branching ratio spectra for selected fragment ions and TIY spectrum of α-alanine in the O 1s region.

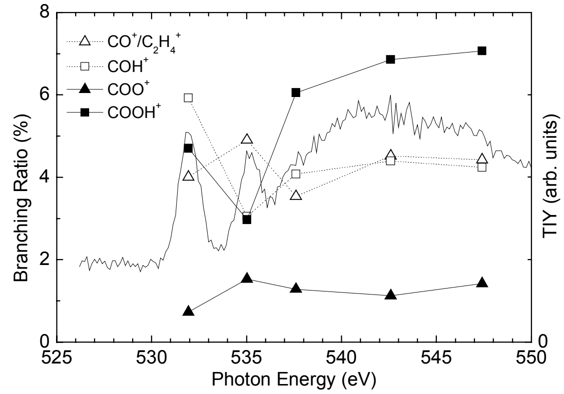

Fig. 4. Branching ratio spectra for selected fragment ions and TIY spectrum of 2MPA in the O 1s region.

for the C, N and O 1s, the ionic species that increases at the O 1s ionization is assigned to COO$^+$. The amount of increase in COO$^+$ from the C and N 1s ionizations to the O 1s ionization counterbalanced well to the amount of decrease in COOH$^+$. The observed core-hole atom selectivity above the 1s IPs of O$_{C=O}$ and O$_{OH}$ can be explained by a preferential O-H bond scission in these core-hole states.

3.3. Dissociation processes at the O 1s resonances

Figure 3 shows the branching ratios of the fragment ions with *m/z* = 28, 29, 44, 45 together with the TIY spectrum of α-alanine in the O 1s region. These branching ratios are obtained after subtraction of the TOF spectrum at the O1s pre-edge from the TOF spectra at each energy position. At the second peak, COO$^+$/C$_2$NH$_6^+$ (*m/z* = 44) and CO$^+$/CNH$_2^+$/C$_2$H$_4^+$ (*m/z* = 28) are enhanced while COOH$^+$ (*m/z* = 45) is suppressed. As two or three ionic species are overlapped at *m/z* = 28 and 44, it is not clear which fragment ion is responsible for the observed state selectivity. To clarify this, the ion branching ratio in the O 1s region was measured for 2MPA, for which the fragment ions at *m/z* = 44 can be uniquely assigned to COO$^+$.

The branching ratios of selected fragment ions and the TIY spectrum of 2MPA in the O 1s region are shown in Fig. 4. The TIY spectrum is similar to that of α-alanine. Also, the branching ratios of CO$^+$/C$_2$H$_4^+$, COO$^+$, and COOH$^+$ show similar dependencies on the excitation energy with each of the corresponding mass in α-alanine. As an increase in the COO$^+$ is observed at the second peak of 2MPA, the increase in COO$^+$/C$_2$NH$_6^+$ at the second peak of α-alanine can be attributed to that of COO$^+$. This is also supported by that no selectivity is observed for C$_3$H$_7^+$ corresponding to C$_2$NH$_6^+$ in α-alanine. The increase in COO$^+$ and the decrease in COOH$^+$ at the second peak of α-alanine and 2MPA can be explained by the state selective enhancement of the O-H bond scission. As three transitions of the O$_{OH}$ 1s → π*, 3s/σ* and the O$_{C=O}$ 1s → 3s/σ* are overlapped at the second peak, it is necessary to consider which excited state or states are responsible for the observed selectivity.

Based on the sum rule for oscillator strength, we assume that the partial sum of the oscillator strengths over the two peaks is nearly equal for the O$_{C=O}$ 1s and O$_{OH}$ 1s electrons. Under this condition, the contribution of the O$_{C=O}$ 1s → 3s/σ* excitation to the second peak should be less than those of the two transitions from the O$_{OH}$ 1s to account for the essentially equal integrated intensities of the first and the second peak. The intensities of the O$_{OH}$ 1s → π* and 3s/σ* transitions can be estimated from the N 1s EELS of HCONH$_2$, in which transitions from the N 1s to π* and 3s/σ* orbitals are resolved with the intensity ratio of ≈ 3:2 [13]. Accordingly, the two transitions from the O$_{OH}$ 1s to the π* and 3s/σ* orbitals are likely to have a comparable intensity. Between these two transitions, transition to the 3s/σ* orbital is expected to cause an enhancement of O-H bond scission because of the O-H antibonding character of the excited orbital not only in the core-excited state but also in the Auger final states, because the spectator Auger decay where an electron remains at the excited orbital is dominant for the O 1s core-excited organic molecules [12]. Actually, state selective suppression of OH$^+$ and COH$^+$ that is explicable by the enhancement of the O-H bond scission has been observed for alcohol molecules at their O 1s first resonance (O 1s → 3sa'/σ*) [14, 15] corresponding to the O$_{OH}$ 1s → 3s/σ* in organic acids. On the other hand, no contribution of the π* orbital to the O-H bond scission has yet been known experimentally nor expected theoretically. From these facts, the observed selectivity in α-alanine and 2MPA can be attributed to the O_{OH} 1s → 3s/σ* that carries appreciable intensity in the second peak. A similar argument was made on the broadness of the second peak of formic acid [16].

Though the decrease in COH^+ and increase in $CO^+/C_2H_4^+$ at the second peak of 2MPA can be explained consistently by the preferential O-H bond scission, the ionic species responsible for the selectivity still remains unidentified even for COH^+ due to the possibility of the structural isomer HCO^+. Regarding COH^+ in α-alanine that shows no state selectivity, a decrease in COH^+ at the second peak, if occurs, may be cancelled by an increase in CNH_3^+.

4. Conclusion

Total ion yield spectra and mass spectra of fragment ions of the C 1s, N 1s, and O 1s core-ionized α-alanine in gas phase were presented. The dominant ionic species formed in the soft x-ray region is $COOH^+$, which is known to be hardly formed in the VUV region. From comparison of mass spectra above IPs of the C 1s, N 1s, and O 1s, a pronounced core-hole atom selectivity was observed at the O 1s ionization as an increase in COO^+ and a decrease in $COOH^+$.

In addition to the core-hole atom selectivity, the excited-state selectivity at the second peak in the O 1s region was observed as the increase of COO^+ and decrease of $COOH^+$ with a further extent than those above the O 1s IP. The observed excited-state selectivity in α-alanine can be attributed to the O_{OH} 1s → 3s/σ* that carries appreciable intensity in the second peak.

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