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Dissociative Electron Attachment to ß-alanine

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A detailed study on dissociative electron attachment (DEA) to ß-alanine (ßA) in the gas phase is presented. Ion yields as a function of the incident electron energy from about 0 to 15 eV have been measured for most of the fragments. As for all α-amino acids, the main reaction corresponds to the loss of a hydrogen atom, although many other fragments have been observed involving more or less complex bond cleavages. Threshold energies have been calculated using the G4(MP2) method for various decomposition reactions. Fragmentation pathways were also investigated measuring metastable decays of the intermediate fragment anion $(ßA\text{-}H)^-$ using the mass analyzed ion kinetic energy (MIKE) scan technique. Comparisons with α-alanine and other amino acids are made when relevant.

Introduction

Amino acids are found in nature mainly as α-amino acids, i.e. with the amine group ($-NH_2$) on the first carbon after the carboxyl group (-COOH). However the amine group can be also attached to another carbon further down the chain in ß- or γ- position for example. Alanine is the only amino acid naturally found in both α- and ß- conformers. Schematic molecular structures of these two molecules are shown in Figure 1.

A recent study of the fragmentation of α- and ß-alanine upon impact of slow multiply charged ions (Ne^+, He^{2+}, O^{5+} and Xe^{20+}) reveals a strong geometry-dependence of the fragmentation process [1,2]. Both the intensity and the kinetic energy of the various ionic fragments differ from one conformer to the other.

To our knowledge no studies on fragmentation induced by low-energy electrons to ß-amino acids have been done to date. Low energy electrons are known to play a key role in radiation damage in living cells [3,4]. The mechanism (DEA) that leads to this irreversible damage involves the capture of the incident low-energy electron by the molecule forming a short lived negative ion (or transient negative ion, TNI) which then dissociates into ionic and neutral species. To better evaluate this process at the molecular level, a wide range of biologically relevant molecules has been studied in recent years such as DNA bases, constituents of the DNA backbone or α-amino acids [6-18]. These studies reveal evidence of site selective bond cleavage at very low energies. In this paper, a detailed study on the decomposition pathways of ß-alanine upon DEA will be presented; anion efficiency curves for 20 fragments have been recorded and will be discussed.

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Method

The present experiments have been performed on two different instruments to get complementary information. The first apparatus is focused on high electron energy resolution while the second setup is more sensitive for low yield fragments and provides access to investigate delayed unimolecular fragmentation reactions. Both setups have been described in previous work [19,20] and only brief details will be given here.

For the study of dissociative processes induced by low energy electrons with high energy resolution, a hemispherical electron monochromator (HEM) was used. The electron beam produced by the HEM has a typical energy resolution of 70-90 meV (FWHM) and is crossed at right angles with a neutral molecular beam. The negative ions formed in the reaction chamber are extracted by a weak electric field towards the entrance of a quadrupole mass spectrometer. Energy calibration was performed using the well known s-wave resonance in CCl_4 generating Cl^-.

A double focusing two sector field spectrometer (VG-ZAB2) equipped with a standard Nier-type ion source (FWHM ~1 eV) was utilized to probe low-intensity fragments and delayed fragmentation of the most intense products. The anions formed in the ion source are extracted by a weak electric field and then accelerated to 8 keV towards the mass spectrometer entrance slit. After passing a first field free region, the ions are mass analyzed according to their momentum per charge ratio by a magnetic sector field, and then pass a second 1.4 m long field-free region before being energy analyzed in an electric sector. The typical mass resolution m/Δm during this study was about 1500 which allows us to measure separate ion yields for isobaric anions such as $C_2H_6N^-/CO_2^-$ (see Figure 9c) or O^-/NH_2^- (see Figure10c, d). Metastable decays of the dehydrogenated parent $(ßA\text{-}H)^-$ (see Figure 4) were investigated using the mass analyzed ion kinetic energy (MIKE) scan technique. A MIKE scan is recorded by tuning the magnet to transmit $(ßA\text{-}H)^-$ and the electric sector to transmit a specific fragment ion that is produced from $(ßA\text{-}H)^-$ in the second field free region [27].

The electron energy scale was calibrated using SF_6 with the well known s-wave attachment SF_6^-/SF_6 for 0 eV and at higher energies the three resonances of F^-/SF_6 (5.5 eV, 9 eV and 11.5 eV [19]).

The ß-alanine sample, purchased from Sigma Aldrich (purity 99%) is a powder at room temperature and is heated in a home made oven in order to produce an effusive molecular beam. Typical temperatures used were 130°C for the experiment performed with the HEM instrument and 100°C for the high sensitivity sector field spectrometer. This temperature range is in principle below the thermal decomposition temperature (200°C) [26]. However, the present measurements indicate that thermal degradation of the sample can be observed at around 130°C leading to the formation of acrylic acid CH_2=CHCOOH (see discussion on production of the fragment $(ßA\text{-}NH_4)^-$, m/z=71).

The threshold energies for the various decomposition reactions have been computed using the G4(MP2) [21] method. G4(MP2) is the newest version of the Gx extrapolation methods which are widely employed for quantum thermochemical calculations. In particular, the ground state energies have been computed for various products (neutral and anions) as well as the parent neutral. The reaction threshold is then given by the difference between product and reactant energies. The thermodynamic stability of product ions with an unpaired electron has also been checked by calculating their electron affinity from B3LYP density functional calculations with the aug-cc-pvTZ basis set [22]. All calculations were performed with the Gaussian 09 program [23].

Results and Discussion

Dissociative electron attachment to ß-alanine yields various fragment anions. An overview of these anions is shown in Figure 2, where the superposition of 23 DEA mass spectra recorded from 1 to 12 eV in 0.5 eV steps is shown. This spectrum gives qualitative rather than quantitative information on the relative abundances of the fragment anions formed upon DEA.

A total of 20 fragments[1] have been investigated in the course of this study. Most fragments, with the exception of $(ßA\text{-}H)^-$, present a similar anion efficiency curve with resonances at around 3 eV, 5.5 eV and 9 eV. Exact resonance positions for each fragment are reported in Table 1.

m/z=88, 87, 86: Loss of hydrogen atom(s)

The main fragment observed upon dissociative electron attachment to ß-alanine corresponds to the loss of a hydrogen atom to form $(ßA\text{-}H)^-$ (m/z=88) via the reaction:

$$e^- + ßA \rightarrow ßA^{-*} \rightarrow (ßA\text{-}H)^- + H \qquad (1)$$

No contribution from the parent anion $(ßA)^-$ is observed in the present experiment, the peak observed at m/z=89 can be ascribed to an isotope of $(ßA\text{-}H)^-$.

The anion efficiency curves of $(ßA\text{-}H)^-$ recorded with both the high energy resolution monochromator and the double focusing two sector field spectrometer are shown in Figure 3a. The signal peaks at around 1.5 eV. At that low energy it corresponds to the loss of the hydrogen from the carboxyl group -COOH (see Table 2). This low energy resonance has been observed in many amino acids [6-16] and carboxylic acids [5] but its origin is still to date a matter of controversy. In earlier studies, it was assigned to electron attachment into the π*(C=O) orbital [5-10]. It was however recently suggested that the very short lived σ*(O-H) resonance could be responsible for loss of the hydrogen directly [18] or via the coupling with a dipole bound anion state [11,15]. It is also interesting to note that the anion efficiency curve for the dehydrogenated ß-alanine is slightly different from the one for α-alanine and other α-amino acids which show a sharp peak at the energy of 1.2 eV and a shoulder at around 1.5 eV. A comparison of $(ßA\text{-}H)^-$ and $(αA\text{-}H)^-$ ion yields is made in Figure 3b. A recent study shows that the shape of the $(M\text{-}H)^-$ ion yield changes significantly with the position of the amino group ($-NH_2$) in the molecule. These results will be largely discussed in an upcoming paper [24].

A second very weak resonance has been observed at around 5 eV on many other amino acids including α-alanine [7]. This is often associated to the abstraction of a hydrogen atom from the amino group. For ß-alanine we do not observe $(ßA\text{-}H)^-$ at higher energy; however, MIKE scans recorded as a function of electron energy (Figure 4) indicate that it is indeed formed at around 3.5 eV and 5 eV but rapidly decays into the anions CH_2COOH^- or CH_3COO^- (m/z=59) and $C_3H_2O_2^-$ (m/z=71) via the reactions:

$$e^- + ßA \rightarrow ßA^{-*} \rightarrow (ßA\text{-}H)^{-*} + H$$

$$\rightarrow CH_2COOH^- + \text{neutrals} \quad (\sim 3{,}5 \text{ eV and } 5 \text{ eV}) \qquad (2a)$$

$$\rightarrow C_3H_2O_2^- + \text{neutrals} \quad (\sim 3{,}5 \text{ eV}) \qquad (2b)$$

In addition to $(ßA\text{-}H)^-$, we also observed the doubly and triply dehydrogenated anions, $(ßA\text{-}2H)^-$ and $(ßA\text{-}3H)^-$. The measured ion yields are shown in Figure 5a and 5b respectively.

In some amino acids such as valine [14], the loss of 2 hydrogen atoms was accessible at very low energy (below 1eV). This low threshold is due to the formation of molecular hydrogen in the outgoing channel which provides about 4.5 eV of energy. In the case of ß-alanine,

[1] Fragment anions of mass m/z = 25, 26 and 27, often assigned respectively to C_2H^-, $C_2H_2^-/CN^-$ and $C_2H_3^-/HCN^-$, are formed quite strongly (see Figure 2) but will not be discussed in the present work. The peak positions in the mass scans recorded at different electron energies did not allow the unambiguous assignment of these fragments. We note that in the past many discrepancies in the anion efficiency curves of CN^- and $C_2H_2^-$ (m/z=26) have been observed for various molecules such as glycine [6], proline [13] or valine [8,14]. Thus these anion yields seem to be strongly dependent on the instrument and experimental conditions used. We suspect these anions to be formed outside the interaction volume and not coming directly from the neutral beam which would explain the shifted position of the peaks in mass scans (due to a slightly different extraction voltage). Further studies will have to be undertaken in order to better understand the exact mechanism leading to the formation of these particular anions.

calculations show that the formation $(ßA\text{-}2H)^-$ is energetically accessible from 0.78 eV for the$NH_2CH_2CHCOO^-$ isomer which correspond to the loss of one hydrogen from the carboxyl group and one from the α-carbon. The lowest resonance peaks however at 2.5 eV.
The loss of 3 hydrogen atoms is observed at 5.5 eV and 9 eV. Reaction thresholds for the loss of 3 individual hydrogen atoms are estimated to be above 6 eV so the formation of the anion $(ßA\text{-}3H)^-$ also involves the formation of the hydrogen molecule in the outgoing channel. Threshold values are reported in Table 2 for the most likely isomers $NHCHCH_2COO^-$ and $NH_2CHCHCOO$-.

m/z =71, 70, 68

The anion with mass m/z =71 corresponds to the loss of mass 18 and has often been ascribed to the loss of one oxygen and two hydrogen atoms, as in studies of proline [13] or valine [14] with ion yields showing a unique resonance located at around 9 eV. In the present case we can observe 3 resonances (Figure 6a) located at 3.5eV, 5.5eV and 9eV. A close look at the high mass resolution sector field scans indicates that this anion does not correspond to $C_3H_5NO^-$ (loss of 2H and 1O) but rather to $C_3H_3O_2^-$ (loss of 4H and 1N). In a recent study, Shchukin et al. [16] also assigned, for α-amino acids alanine and valine, the loss of mass 18 to the loss of either NH_3+H or NH_2+H_2. Using enthalpies of formation, they estimated the lowest thermodynamic threshold for the formation of $C_3H_5NO^-$ to be around 1.8 eV via the formation of ammonia (NH_3) in the outgoing channel for the isomer CH_2CHCOO^-.
Similar calculations have been performed for ß-alanine using the G4(MP2) method, for each of the five $C_3H_3O_2^-$ isomers (i.e. CH_2=$CHCOO^-$, CH_2CCOOH^-, CH=$CHCOOH^-$, CCH_2COOH^- and $CHCH_2COOH^-$) and for the three following reactions:

$$e^- + ßA \rightarrow ßA\text{-}^* \rightarrow C_3H_3O2^- + NH_2 + 2H \quad (3a)$$
$$\rightarrow C_3H_3O_2^- + NH_2 + H_2 \quad (3b)$$
$$\rightarrow C_3H_3O_2^- + NH_3 + H \quad (3c)$$

Reaction (3b) will lower the threshold by 4.54 eV due to the formation of a hydrogen molecule and reaction (3c) by 4.61 eV due to the formation of ammonia in comparison with reaction (3a). The threshold energies are reported in Table 2. From these values it is clear that $C_3H_3O_2$- at 5.5 eV and 9 eV might come from any of the five isomers. The lower resonance at around 3.5 eV is the result of a sequential loss of a hydrogen and NH_3 as shown in the MIKE scan vs. electron energy in Figure 4a. According to our calculation the isomers formed could either be CH_2=$CHCOO$- or CCH_2COOH- via reaction (3a).
The ion yield measured with the HEM (Figure 6b) exhibits another resonance at around 1.4 eV which also corresponds to the $C_3H_3O_2$- anion. However, it is not energetically possible to form this anion from ß-alanine at this low energy (see Table 2). Thus we believe this lower resonance is due to the higher temperature (around 130°C) used with this instrument. Even though in the literature the thermal decomposition temperature is found to be above 200°C it seems that the sample is already decomposing at this lower temperature. Previous studies [25] showed that one product of the thermal decomposition of ß-alanine is acrylic acid (CH=CH_2COOH, i.e. $ßA\text{-}NH_3$). We suggest that the anion observed at low energy corresponds to the loss of a hydrogen atom from the carboxyl group of acrylic acid via the reaction

$$e^- + CH{=}CH_2COOH \rightarrow CH{=}CH_2COOH^{-*} \rightarrow CH{=}CH_2COO^- + H \quad (4)$$

This reaction (4) has a threshold of 1.25 eV (see Table 2). The shape of the peak further supports this explanation as it is characteristic for a dehydrogenated anion from carboxylic acids [5] with a steep rise and a step like structure on the right hand side of the peak.
In addition to m/z=71, we also observe in this range the masses m/z=68, 70 and 72. For the latter, isotope correction shows that the signal is only partly due to the isotopic form of $ßA\text{-}NH_4$ anion (m/z=71) and thus formation of the fragment anion $(ßA\text{-}OH)^-$ or $(ßA\text{-}NH_3)^-$ should be considered. For many α-amino acids, this anion formation is quite a dominant channel and

is usually assigned to the loss of OH; it is surprisingly low for ß-alanine. No ion yield has been recorded for this fragment due to poor signal to noise ratio.
The ion with m/z=70 can correspond to either $C_3H_2O_2^-$ or $C_3H_4NO^-$. Only one peak is visible in the mass scan, extrapolation with its neighbouring anions indicates it is $C_3H_4NO^-$ (ßA-H_3O). The formation of this anion has been interpreted in the past as a sequential loss of a hydrogen atom (from the N or C site) and a water molecule [9]. As for α-alanine, the ion yield peaks at around 5.5 eV and 9 eV (see Figure 7b) but the signal is weaker.
Finally, a weak signal is found at m/z=68 which corresponds to the loss of H_5O, probably H_2O+_3H or H_2O+H+H_2. It peaks at the energy of about 9 eV with a small peak between 5 eV and 7 eV (Figure 7a).

m/z =59, 58: C_α-$C_ß$ bond cleavage

CH_2COOH^- (m/z=59) is the second most abundant fragment observed, it corresponds to the cleavage of the C_α-$C_ß$ bond; although we cannot exclude the presence of this anion in the form CH_3COO^-. Collisions with multiply charged ions [1,2] induce fragmentation preferentially into the cations H^+ and $NH_2CH_2^+$ (m/z=44), the latter involving the scission of the same C_α-$C_ß$ bond. This particular bond appears to be weakened by ionization according to calculations performed by Bari et al [1]. The ion yield for CH_2COOH^-, shown in Figure 8a, peaks at 5.5 eV and another weak resonance is visible at around 8.8 eV. The threshold for the formation of this fragment is estimated to be around 1.62 eV (see Table 2), so one could expect fragmentation at lower energies than observed experimentally. It might indicate that there is no favorable coupling between some lower resonance such as the π*(C=O) and the dissociative C_α-$C_ß$ state. However, as mentioned above, CH_2COOH^- is observed at 3.5 eV as a product of the metastable decay of $(ßA-H)^-$ (see Figure 4b). CH_2COOH^- seems to decay further by dissociation (likely into $COOH^-$ or $HCOO^-$) at this electron energy as it is not observable in the yield formed in the ion source (Figure 8a).
One mass lower (m/z=58) we observe quite weakly the anion CH_2COO^-. The anion efficiency curve, shown in Figure 8b, exhibits the same two resonances at 5.5 eV and around 9 eV but with similar strength in this case.
Other fragments such as $C_2H_5O^-$ (m/z=45), $C_2H_3O^-$ (m/z=43) and C_2HO^- (m/z=41) involve the C_α-$C_ß$ bond cleavage as part of a more complex dissociative process. Formation of these anions is discussed in the following paragraph.

m/z =40 to 45

A group of anions is formed from mass m/z=40 up to 45 with the dominant fragments at m/z = 41, 42 and 44. Due to the high mass resolution of the double focusing two sector field spectrometer, we were able to separate isobaric anions allowing a better peak assignment for these masses. A zoom of Figure 2 in the mass range of interest is shown in Figure 9a. Each peak is labelled with the proposed chemical compounds.
In Figure 9b the ion yield of $COOH^-$ or $HCOO^-$ (m/z=45) is plotted showing resonances at 3.2 eV, 5.7 eV and 8.7 eV. The lowest resonance is assigned to the formation of HCOO- rather than $COOH^-$ due to the lower formation threshold (see Table 2). For α-alanine [7], formation of $COOH^-$ or $HCOO^-$ (m/z=45) was one of the most dominant channels, while for ß-alanine it is a rather weak channel. An explanation for this molecule-specific observation may be given by the study from Bari et al [1,2] where the C-C_α bond cleavage (leading to formation of the $CH_3CH(NH_2)^+$ cation) was the predominant fragmentation channel. We note that in DEA to α-alanine the C-C_α bond cleavage can only lead to the formation of $COOH^-$ as C_2H_6N ($CH_3CH(NH_2)$) has a negative electron affinity according to the calculation performed with the G4(MP2). For ß-alanine the C-C_α bond cleavage seems to lead preferentially to the formation of $C_2H_6N^-$ (m/z=44) rather than $COOH^-$. $C_2H_6N^-$ ($NH_2CH_2CH_2^-$) is formed only at 5.3 eV (Figure 9c).

At mass m/z=44, we distinguish another small peak assigned to CO_2 anions (C_2H_4O also corresponding to m/z= 44 does not seem to be produced). Formation of CO_2 requires two bonds to cleave. The corresponding ion yield is weak and peaks around 10 eV (see Figure 9c).
Two and four masses lower we observe $C_2H_4N^-$ (m/z=42) and $C_2H_2N^-$ (m/z=40) anions which involve again a C_α-C bond cleavage and the removal of respectively 2 and 4 hydrogen atoms from the chain. The smaller fragment (m/z=40) is mainly formed at 9 eV as the cleavage of two more C-H bonds requires too much energy (see Figure 9h).
Mass m/z=42 features a second peak, which belongs to the NCO anion although we can not exclude completely the presence of $CH_2C{=}O^-$. Formation of NCO^- requires few bond cleavages and a quite complex rearrangement. It is formed via both 5.5 eV and 9 eV resonances.
The negative ions with m/z=43 and m/z=41 are assigned to $C_2H_3O^-$ and C_2HO^-. The anion efficiency curves are reported in Figure 9d and 9g respectively. Once again we observe that the removal of extra hydrogen from the carbon site requires more energy and the fragmentation is mainly accessible via the 9 eV resonance for C_2HO^- (m/z =41). No threshold energies have been calculated however for these reactions.

m/z =17, 16, 15

Finally, the lightest fragments observed upon DEA to ß-alanine are OH- (m/z=17), O^- and NH_2^- (m/z=16) and NH^-/ CH_3^- (m/z=15). Anion efficiency curves of these four fragments are shown in Figure 10.
The isobaric anions NH_2^- and O^- (m/z=16), are in fact separated by around 0.0238 amu and can be well distinguished with the high mass resolution sector field instrument. The two anions efficiency curves are shown in Figure 10c and 10d respectively. The NH_2^- fragment is formed preferentially at low energies (5.5 eV) and O^- at higher energies which is in good agreement with previous studies [10,14]. However, the intensity of the ion yield for O^- is surprisingly low for ß-alanine.
At mass m/z=15, we were not able to assign with certitude the nature of the fragment, it might be NH^-, CH_3^- or both. The study by Mauracher et al [10] on glycine assigned the lowest resonance (5.5 eV) to CH_3^- and the highest (8 eV) to NH-; this is not so clear in the present work.

Conclusion

In the present paper we have reported a detailed DEA study on the amino acid ß-alanine. The high mass resolution of the sector field instrument allows us to assign most of the peaks to specific compounds and distinguish some isobaric anions. The fragmentation is overall strong and is mediated via resonances located at around 3 eV, 5.5 eV and 9 eV with the exception of the $(ßA\text{-}H)^-$ anion which appears at lower energy (1.5 eV). The two dominant fragments observed were $(ßA\text{-}H)^-$ and CH_2COOH^-, which corresponds respectively to the loss of an hydrogen atom from the carboxyl group and to the cleavage of the C_α-$C_ß$ bond. This observation is consistent with a study on fragmentation of ß-alanine upon impact with multiply charged ions where the main fragments were found to be the cations H^+ and $NH_2CH_2^+$.

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Figure 1. Schematics of: a) α-alanine and b) ß-alanine

Figure 2. Sum of 23 anion mass spectra of ß-alanine recorded from 1 to 12 eV in 0.5 eV steps recorded with the double focusing two sector field spectrometer

Figure 3. Anion efficiency curves for $(ßA\text{-}H)^-$: a) comparison between the high energy resolution monochromator (FWHM~100meV) and the double focusing two sector field spectrometer (FWHM~1eV), b) comparison between α- and ß-alanine.

Figure 4. Mass analyzed ion kinetic energy scans as a function of the incident electron energy for the metastable decay of the intermediate anion $(ßA\text{-}H)^-$ into: a) $(ßA\text{-}H\text{-}NH_3)^-$ (m/z=71) and b) CH_2COOH- or CH_3COO- (m/z=59).

Figure 5. Anion efficiency curves for: a) $(ßA\text{-}2H)^-$ and b) $(ßA\text{-}3H)^-$. Both ion yields have been recorded with the double focusing two sector field spectrometer.

Figure 6. Anion efficiency curves for $(ßA\text{-}NH_4)^-$: a) recorded with the double focusing two sector field spectrometer with an oven temperature of 100°C and b) recorded with the HEM instrument with an oven temperature of 130°C.

Figure 7. Anion efficiency curves for: a) $(ßA\text{-}H_5O)^-$ and b) $(ßA\text{-}H_3O)$-. Both ion yields have been recorded with the double focusing two sector field spectrometer.

Figure 8. Anion efficiency curves for: a) CH_2COOH^- or CH_2COO^- (m/z =59) recorded with both instruments and b) CH_2COO- (m/z =58) recorded with the double focusing two sector field spectrometer only.

Figure 9. Anion efficiency curves for: b) COOH-/$HCOO^-$, c) $C_2H_6N^-$ and CO_2^-, d) $C_2H_3O^-$, e) NCO^- , f) $C_2H_4N^-$, g) $CHCO^-$ and h) $C_2H_2N^-$. a) represents a zoom of Figure 2. All ion yields have been recorded with the double focusing two sector field spectrometer.

Figure 10. Anion efficiency curves for: a) NH^- / CH_3^- (m/z =15), b) OH^- (m/z =17), c) NH_2^- (m/z =16) and d) O^- (m/z =16). All ion yields have been recorded with the double focusing two sector field spectrometer.

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A rich fragmentation upon low energy electron impact is observed for the amino acid ß-alanine. It involves simple or multiple bond cleavage (see Figure) mediated for most fragments via resonances located at around 3 eV, 5.5 eV and 9 eV.

Table 1. Mass, chemical composition and peak positions for all investigated anions formed via DEA to ß-alanine.

m/z	Fragment Anion	Resonance Positions (eV)		
88	ßA-H	1.5		
87	ßA-2H	2.5	6.8	9.1
86	ßA-3H		5.7	9.2
71	$C_3H_3O_2$ ↔ ßA-NH_4	3.5	5.5	9.5
70	C_3H_4NO↔ßA-H_3O		4.8	8.6
68	C_3H_2NO↔ßA-H_5O			9.4
59	CH_2COOH		5.5	8.8
58	CH_2COO		5.5	8.5 / 9.5
45	HCOO / COOH	3.2	5.7	8.7
44	$NH_2CH_2CH_2$		5.3	
	CO_2			10
43	C_2H_3O		5.5	9.5
42	C_2H_4N		6	9.5
	NCO		5.5	9
41	CHCO	3.5		9.5
40	C_2H_2N			10
17	OH		5	9
16	O	4		9 / 11
	NH_2		5.5	8
15	NH / CH_3		6	9

Table 2. Threshold energies calculated using G4(MP2) method for DEA from ß-alanine and acrylic acid (a product of thermally decomposed ß-alanine). For each reaction the threshold energies have been calculated for different isomers of the fragment anion.

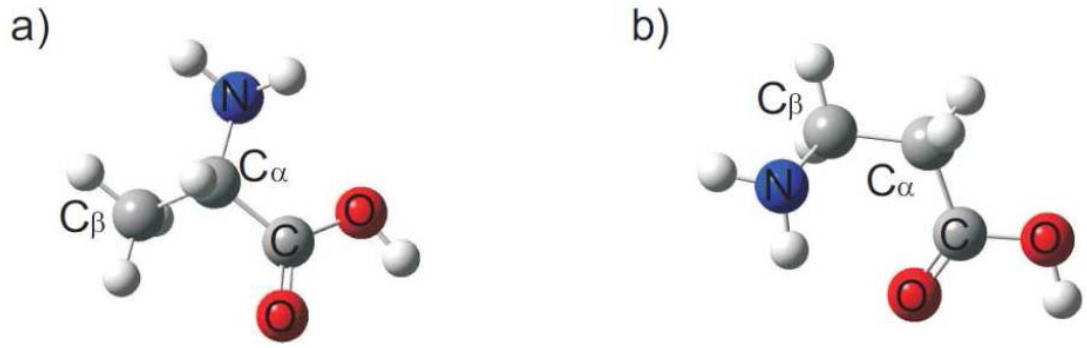
ßalanine ↔ $C_3H_7NO_2$ ↔ $NH_2CH_2CH_2COOH$

Fragments	Anion Isomers	Threshold energy (eV)
$C_3H_6NO_2^-$ + H	$NH_2CH_2CH_2COO^-$	1.23
	$NHCH_2CH_2COOH^-$	3.33
	$NH_2CHCH_2COOH^-$	3.83
	$NH_2CH_2CHCOOH^-$	2.26
$C_3H_6NO_2^-$ + 2H [a] + H_2 [b]	$NH_2CH_2CHCOO^-$	5.31[a] / 0.78[b]
$C_3H_6NO_2^-$ + 3H [c] + H_2 + H [d]	$NHCHCH_2COO^-$	6.58[c] / 2.04[d]
	$NH_2CHCHCOO^-$	6.85[c] / 2.31[d]
$C_3H_3O_2^-$ + NH_2 + 2H [e] + NH_2 + H_2 [f] + NH_3 + H [g]	CH_2=$CHCOO^-$	6.38[e] / 1.84[f] / 1.77[g]
	CH_2CCOOH^-	8.04[e] / 3.50[f] / 3.43[g]
	CH=$CHCOOH^-$	8.39[e] / 3.85[f] / 3.78[g]
	CCH_2COOH^-	8.42[e] / 3.89[f] / 3.82[g]
	$CHCH_2COOH^-$	8.85[e] / 4.31[f] / 4.24[g]
$C_2H_3O_2^-$ + NH_2CH_2	CH_2COOH^-	1.62
CHO_2^- + $NH_2CH_2CH_2$	$HCOO^-$	1.03
	$COOH^-$	2.51

Acrylic acid ↔ ßA-NH_3 ↔ $C_3H_4O_2$ ↔ CH_2=$CHCOOH$

Fragments	Anion Isomers	Threshold energy (eV)
$C_3H_3O_2^-$ + H	CH_2=$CHCOO^-$	1.25
	CH=$CHCOOH^-$	3.26
	CH_2=$CCOOH^-$	2.90

Figure1



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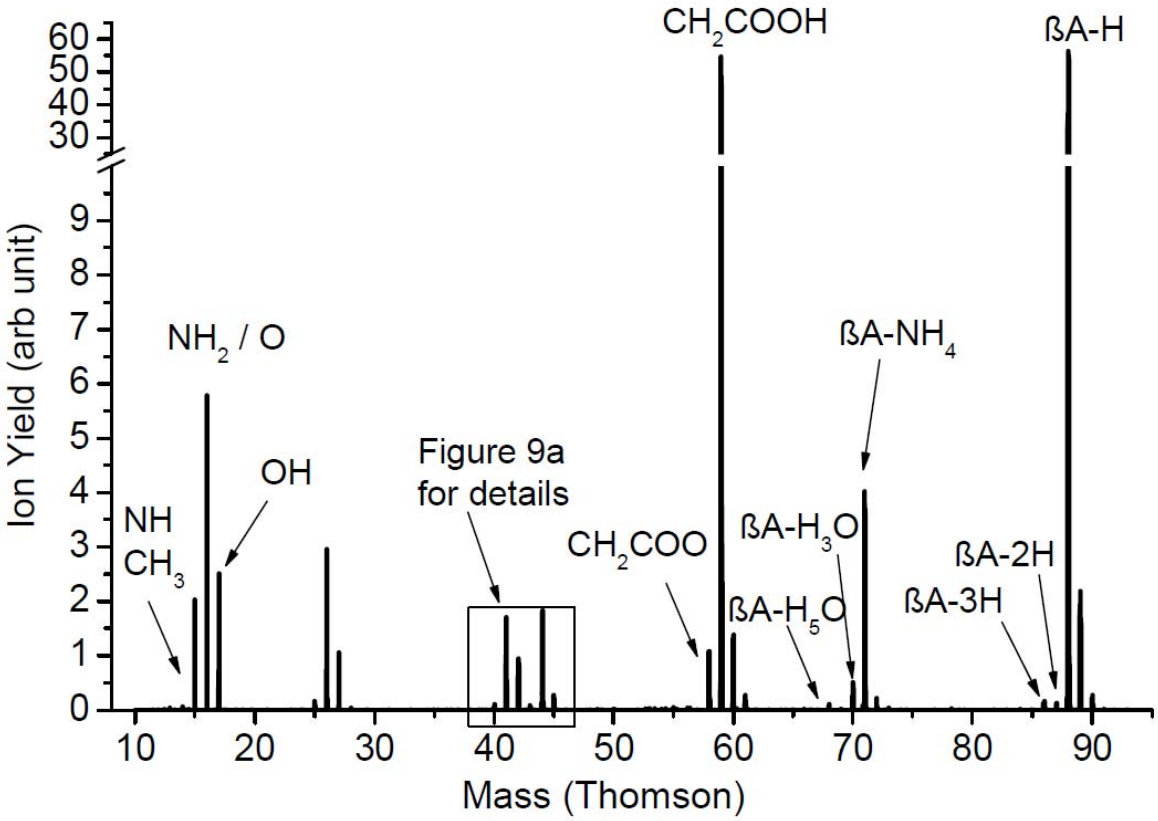
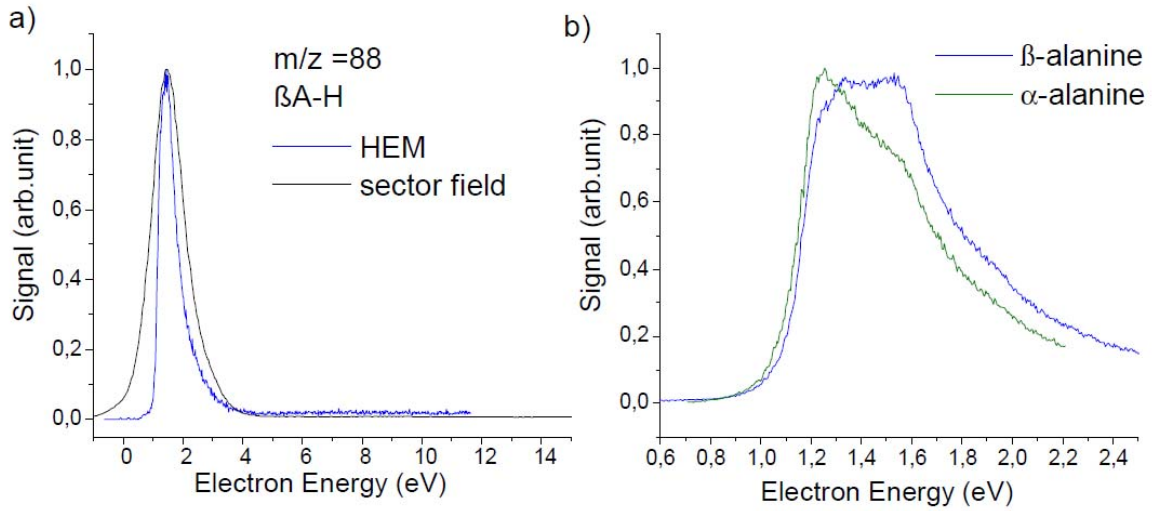


Figure 3



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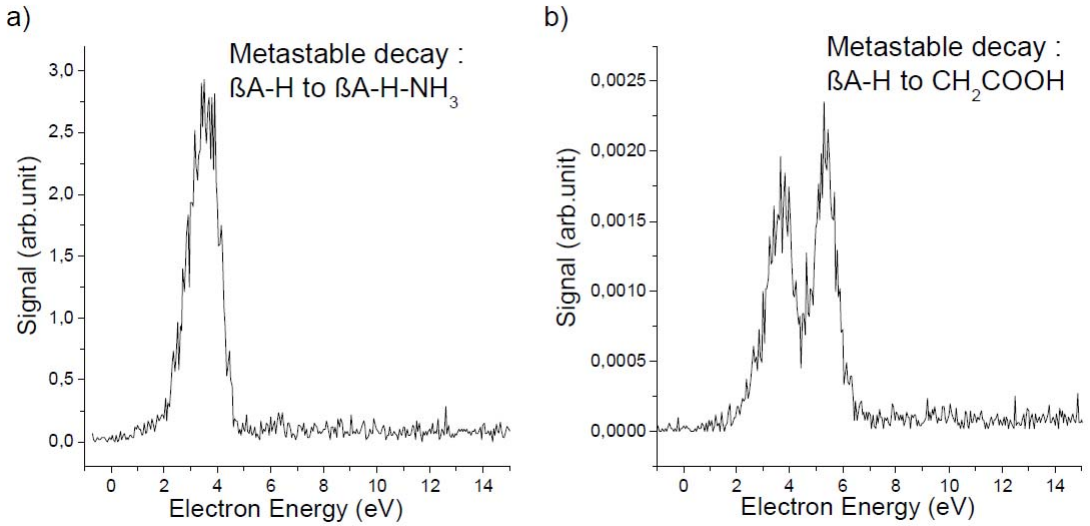

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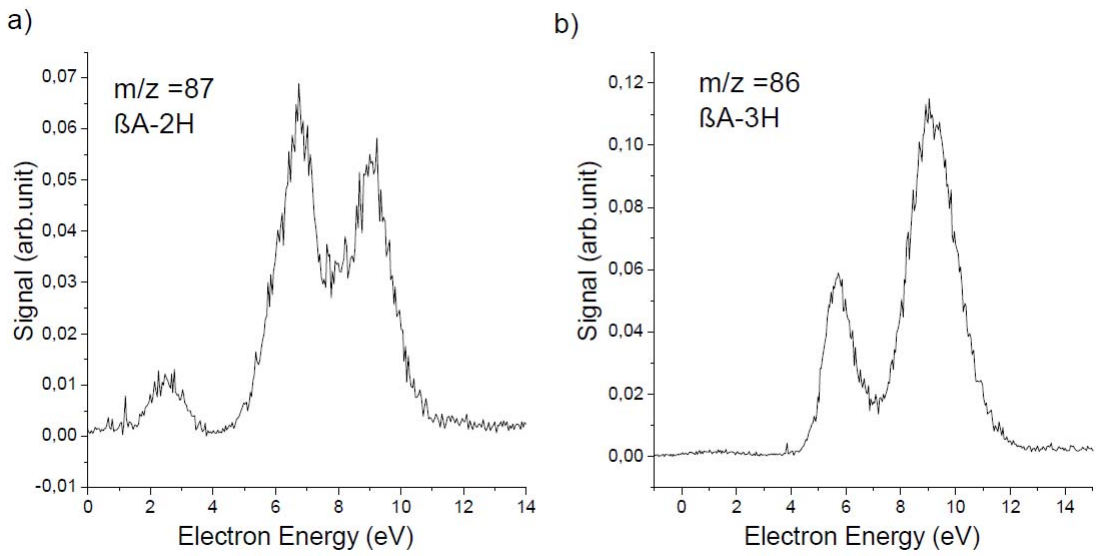

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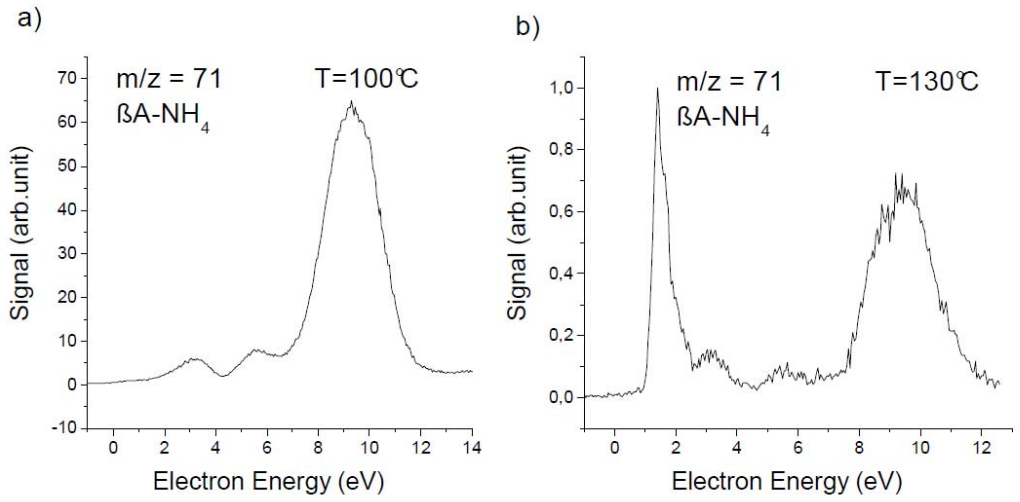

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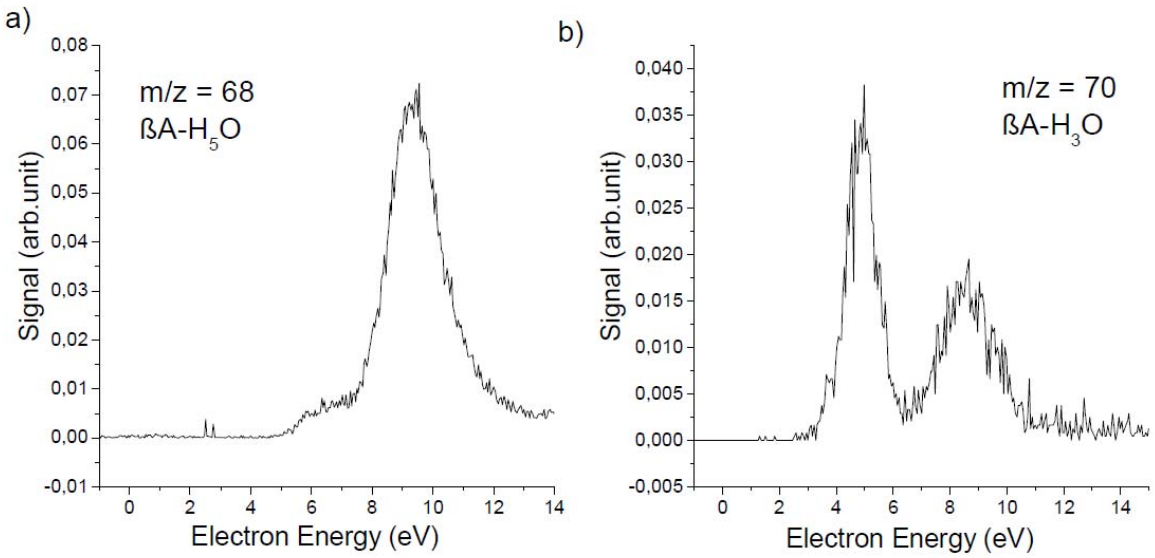

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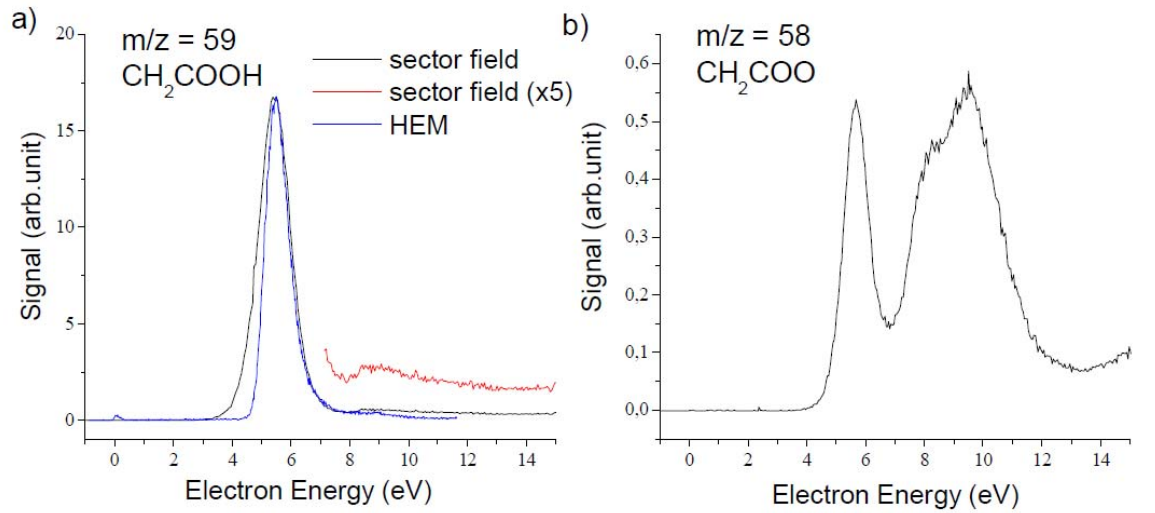


Figure 9

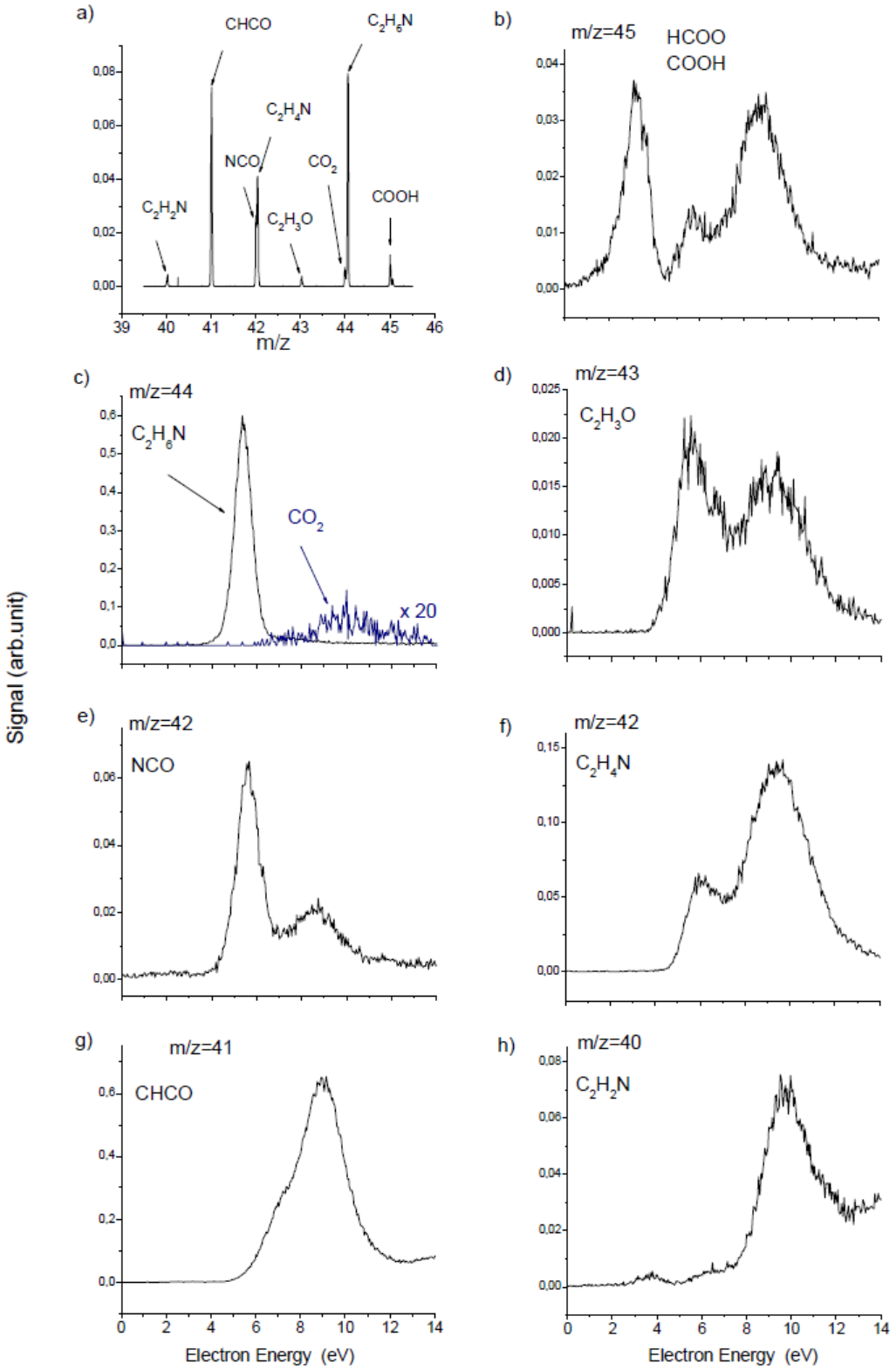
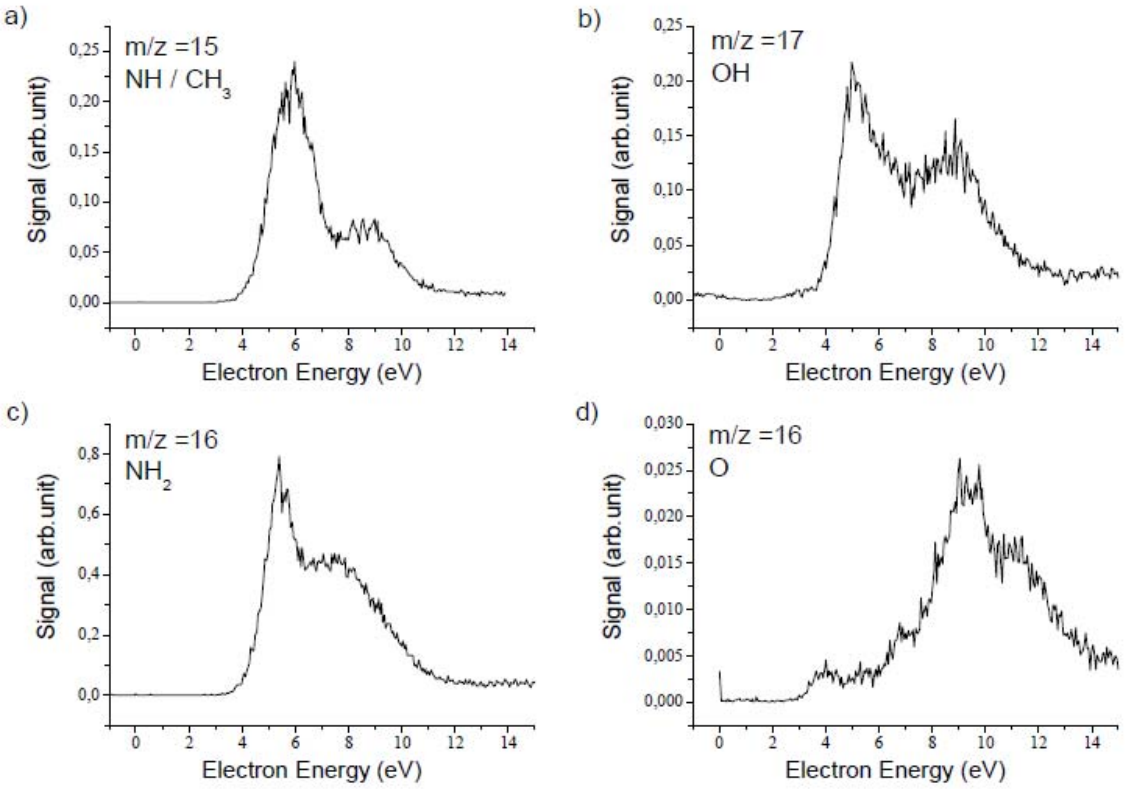

a)
CHCO
C_2H_5N
C_2H_4N
NCO
CO_2
C_2H_3O
C_2H_2N
COOH
m/z
b)
m/z=45
HCOO
COOH
c)
m/z=44
C_2H_6N
CO_2
x 20
d)
m/z=43
C_2H_3O
e)
m/z=42
NCO
f)
m/z=42
C_2H_4N
g)
m/z=41
CHCO
h)
m/z=40
C_2H_2N
Signal (arb.unit)
Electron Energy (eV)
Electron Energy (eV)

Figure 10


a)
m/z =15
NH / CH3
Signal (arb.unit)
Electron Energy (eV)
b)
m/z =17
OH
Signal (arb.unit)
Electron Energy (eV)
c)
m/z =16
NH2
Signal (arb.unit)
Electron Energy (eV)
d)
m/z =16
O
Signal (arb.unit)
Electron Energy (eV)