Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 252 (2006) 228–233

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Electron impact ionization of alanine: Appearance energies of the ions

I. Ipolyi [a], P. Cicman [d], S. Denifl [d], V. Matejčík [c], P. Mach [b],
J. Urban [b], P. Scheier [d], T.D. Märk [a,d], Š. Matejčík [a,*]

[a] *Department of Experimental Physics, Comenius University, Mlynska dolina F2, 842 48 Bratislava, Slovakia*
[b] *Department of Biophysics and Nuclear Physics, Comenius University, Mlynska dolina F2, 842 48 Bratislava, Slovakia*
[c] *Faculty of Medicine, Comenius University, Špitálska 24, 81372 Bratislava, Slovakia*
[d] *Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens University, Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria*

Received 17 February 2006; received in revised form 14 March 2006; accepted 17 March 2006

Abstract

The mass spectrum and the appearance energies of the positive ions formed via electron impact ionization of L-alanine have been measured for the first time in a crossed electron-molecule beam experiment with a high-resolution electron beam. The ionization energy of the molecule and the appearance energies of the fragment ions were obtained from ion efficiency curves. Additionally, high-level quantum chemical calculations of the reaction enthalpies for dissociative ionization into positive ions and neutral radicals were performed and the results were compared with the experiment. On the basis of the calculations possible ionic structures for the measured ions were assigned. The value of the ionization energy for the parent ion with $m/z = 89$ was determined experimentally to be 9.12 ± 0.1 eV. For the principal positive fragment ions with m/z of 74, 44 and 28 the experimental values of the appearance energies are 10.74 ± 0.1, 9.10 ± 0.05 and 10.85 ± 0.1 eV, respectively.

Keywords: L-alanine; Electron impact ionization; Gas phase

---

1. Introduction

L-alanine belongs to the simplest group of the α-amino acids and is often considered as a model system for properties of more complex systems, particularly in case of ionizing radiation. The formation of radicals in single crystals of L-alanine exposed to energetic radiation has been subject of investigation during the past four decades [1]. Alanine has attracted attention due to its radiation dosimetric properties and has been formally accepted as a secondary standard for high-dose and transfer dosimetry [2–5]. The interaction of ionizing radiation with matter produces secondary reactive species along the track of the high-energy projectile. These secondary species may undergo subsequent reactions with the medium. Secondary electrons with kinetic energies below 20 eV [6] belong to the most abundant secondary particles with a yield of 5×10^4 electrons formed per MeV [7] of deposited energy. The kinetic energy of some of these secondary electrons is sufficient to induce electron impact ionization and dissociative electron impact ionization. These reactions are responsible for formation of positive and negative ions and radicals in the medium and may play important role in the radical formation of alanine. Gas phase studies may contribute to the understanding of the intrinsic mechanism of the radical formation on a molecular level.

This paper reports the results of an experimental and theoretical study of the electron impact ionization (EII) to L-alanine further only alanine, Ala – $CH_3CH(NH_2)COOH$ in the gas phase. This work is an extension of our previous experimental study of dissociative electron attachment (DEA) to this molecule in the gas phase [8] where the formation of the negative ions and corresponding radicals was investigated. Appearance energies of the ions formed upon EII and dissociative electron impact ionization (DEII) to alanine in the gas phase are determined from the threshold regions of measured ion efficiency curves:

$$e + \text{Ala} \rightarrow (\text{Ala}^+)^* \rightarrow \text{fragmention}^+ + \text{neutralfragment(s)} \tag{1}$$

In order to elucidate the studied reactions we have carried out high-level ab initio calculations of the reaction enthalpies

---

[*] Corresponding author.
E-mail address: matejcik@fmph.uniba.sk (Š. Matejčík).

1387-3806/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2006.03.009

for particular reaction channels. These calculations proved to be valuable for the interpretation of the measured results and for the assignment of the measured ions to particular ionic structures. As the size of an ionic product increases, several fragment ions may have the same mass to charge ratio and mass spectroscopic techniques often cannot identify the nature of the ion unambiguously. In this case the comparison of the measured appearance energy with the calculated ab initio reaction enthalpies gives an indication about the nature of the ion.

So far there exist only a few ionization studies for alanine in the gas phase and none of them utilizes EII. The first experiments were photoelectron spectroscopy studies (PES) where alanine was ionized with He I photons and the resulting photoelectron spectra were recorded [9–11]. Using this technique the vertical and adiabatic ionization energies of alanine have been measured, however, no information on the fragmentation of alanine has been obtained. Ion beam desorbed photo-ionization of aliphatic and aromatic amino acids has been reported by Vorsa et al. [12]. Recent experiments with synchrotron radiation were performed to measure PES of alanine [13] and to study mass selected photo-ionization (PI) [14]. In the PI experiment of Jochims et al. [14] mass spectra of α-alanine, a mixture of the L- and D-form of alanine, were obtained and the appearance energies of some selected fragment ions were determined. The present results are discussed in detail and compared with the previous gas phase photo-ionization studies of alanine.

2. Experiment

The present work is carried out using the crossed electron/molecular beam apparatus in the Bratislava laboratory. The apparatus has been described in detail previously [15]. Thus only a brief description is given here. A schematic view of the apparatus is shown in Fig. 1. The electron beam is formed in a trochoidal electron monochromator (TEM) with an electron energy resolution in the present experiment of about 140 meV. The calibration of the electron energy scale is performed by measurement of the Ar^+ ion efficiency curve for the reaction:

$$e^- + Ar \rightarrow Ar^+ + 2e^- \qquad (2)$$

that has an established value of the ionization energy of 15.759 ± 0.001 eV [16].

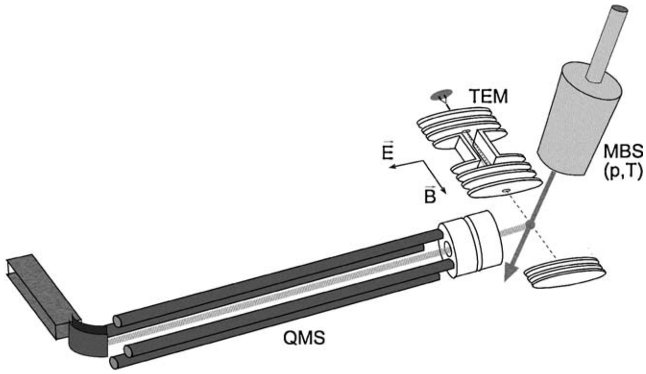

Fig. 1. The schematic view of the crossed beams experiment, TEM: trochoidal electron monochromator, MBS: molecular beams source, QMS: quadrupole mass spectrometer.

The molecular beam is produced in a temperature controlled effusive molecular beam source (EMBS). The beam is formed via effusion of gas phase alanine through a capillary (0.5 mm diameter and 4 mm long) and an external aperture. The alanine which is solid at room temperature is placed directly into the stainless steel container of the EMBS. The oven is heated to 150 °C in order to achieve a sufficiently high pressure of the alanine.

The ions formed in the intersection between the electron and the molecular beams are extracted by a weak electric field into a quadrupole mass spectrometer (QMS). The mass spectrometrically analyzed ion signal is detected as a function of the electron energy. The measured signal is accumulated for a very long time (typically a day) in order to achieve high sensitivity and accuracy and to detect reactions with very low cross sections. The stability of the experimental conditions (e.g., drift of the power supplies) was checked by the measurements of the reaction (2) at the beginning and the end of the experiment. The stability was typically about 10 meV per day. The measured ionization efficiency curves are analyzed using the data analysis described in our previous paper devoted to the measurement of appearance energies [15]. This method takes into account the finite width of the kinetic energy distribution function of the electrons in the electron beam and enables the determination of appearance energies of the ions with high accuracy. The accuracy of the experimental values of the appearance energies results from the nonlinear least square fitting procedure.

3. Theory

There exist several theoretical studies of amino acids which cover the structure and energies of individual products of fragmentation of ionized amino acids, particularly the alanine and glycine [17–23]. In all cases standard quantum chemical methods have been utilized with inclusion of correlation (MP2(FC) and CCSD(T)) and density functional methods (B3LYP functional) using basis sets 6-31G* up to the 6-311++G(2df,2pd) quality. The geometrical parameters have been obtained at the MP2 or DFT levels of the theory and energy differences have been calculated by using CCSD(T) or MP2 methods, respectively. Some contributions [24–26] are focused to the study of the behaviour of individual radicals during fragmentation.

In this paper, our theoretical results are based on the high-level ab initio MO calculations of the possible molecular structures occurring in the fragmentation. To obtain more reliable relative energies for studied molecules, calculations of the Gaussian-3 (G3MP2) [27] and G3MP2B3 [28] have been carried out. These methods are complex energy computations, involving several pre-defined calculations on the specified molecular system. They arose from the observation that certain ab initio methods tended to show a systematic error for predicting the energies of the ground states of organic molecules. This observation resulted in a correction equation that uses the energies from several different ab initio calculations in order to extrapolate to a very-high-accuracy result [29]. All

Table 1
List of calculated ionic and neutral structures considered in the present G3MP2 and G3MP2B3 calculations of the reaction enthalpies

$CH_3{-}CH(NH_2){-}COOH$
$CH_3{-}CH(NH_2){-}COOH^+$
$NH_2{-}C(CH_3){-}C(OH)_2{}^+$
$NH_3{-}C(CH_3){-}COOH^+$
$CH_3{-}CH{-}NH_2{}^+$
$CH_3{-}CH{-}NH_2{}^\bullet$
$COOH^\bullet$
$COOH^+$
$NH_2{-}CH{-}COOH^+$
$CH_3{}^+$
$CH_3{}^\bullet$
$CH_2{-}CH{-}NH_2{}^+$
$HCOOH$
$CH_3{-}CH{-}COOH^+$
$CH_2{=}CH{-}C(OH)_2{}^+$
$NH_2{}^\bullet$
$NH_2{-}C(CH_3){-}COOH^+$
$NH_2{=}C{=}CH_2{}^+$
$CH_2{=}CH{-}C{=}O^+$
$CH_2{=}CH{-}C^\bullet{=}O$
$CH_2{=}CH{-}NH_3{}^+$
C_2H_4
$CH_3CH_2NH_2$
HCO^+
CH_2CN^+
$NH_2{=}C{=}CH_2{}^+$
$CH_2{=}N{=}CH_2{}^+$
$CH_3{-}C{=}NH^+$
OH
NH_3
NH^+
$NH^\bullet$
$C_2H_3{}^+$
$HCNH^+$
$NH_4{}^+$
NH^+
$CH_2NH_2{}^+$
$NH_2{-}CH{=}C{=}O^+$
$CH_2{=}C{=}O^+$
$CH{=}CH{-}COOH^\bullet$
CH_3CH_2COOH
$CO_2{}^+$
CO_2
$CH_3CCNH_2{}^+$
CO^+
$HOOH$
CH_3COOH
$CH_2NH_2{}^\bullet$
$NH_2{-}CH^\bullet{-}COOH$
$C{=}C{=}O^+$

our calculations have been performed by using the Gaussian 98 program [30].

Structure and energy of the calculated molecules, are given in Table 1. The reaction enthalpies for the formation of the ions in the gas phase were calculated for the gas temperature 300 K (Table 2). Only one value for each product is presented because the results obtained on the G3MP2 and G3MP2B3 differ only in hundredths of eV. Generally, it is not easy to establish the precision of the quantum chemical method. But according to the authors of G3MP2 method [28] the average error for this method (based on the test for the collection of molecules) for ionization energies has a value of 0.06 and 0.056 eV for all types of reaction energies.

Table 2
Appearance energies of product ions upon electron impact ionization of gas phase alanine, determined from the measured ion efficiency curves, and comparison with calculated reaction enthalpies and published values of the appearance energies obtained via photo-ionization

m/z	Ions	Ab initio AE (eV)	Experimental AE (eV)	PI AE (eV) [14]
89	$NH_2CH_3CHCOOH^+$	9.07	9.1 ± 0.1	8.75 ± 0.05
74	$NH_2CHCOOH^+$	10.07	9.9 ± 0.1	9.3 ± 0.2
55	$CH_3C{\equiv}CNH_2{}^+$	11.34	11.34 ± 0.1	–
		13.68	13.1 ± 0.2	–
45	$COOH^+$	11.82	–	–
44	$NH_2CH_3CH^+$	9.51	9.1 ± 0.05	9.05
	$CO_2{}^+$	13.49	–	–
43	$NH_2CHCH_2{}^+$	9.47		
42	$NH_2CH_2C^+$	10.87	9.87 ± 0.1	9.02
28	$HCNH^+$	12.0	10.9, 12.8 ± 0.1	12.35
	$C{=}O^+$	18.83		
18	$NH_4{}^+$	10.26	12.55 ± 0.1	12.00
	H_2O^+	12.55		
15	$CH_3{}^+$	12.92	9.7, 13.50 ± 0.1	–
	NH^+	16.81		

4. Results and discussion

The electron impact ionization of alanine in the gas phase leads to the formation of a large number of positive ions. Fig. 2 shows a positive ion mass spectrum upon electron impact ionization with electrons having a kinetic energy of 70 eV. The mass spectrum is similar to the mass spectrum published in the NIST database [16]. In the present work we measure the appearance energies of the major ions in the mass spectrum with mass to charge ratios (*m/z*) 89, 74, 55, 44, 42, 28, 18 and 15. The values of the appearance energies are summarized in Table 2.

The parent ion Ala^+ is detected with a very weak intensity (less then 0.6% of the strongest peak in the mass spectrum with *m/z* 44). The weak intensity of the molecular ion is due to its low stability against dissociation. The appearance energy of the Ala^+ ion is according to present experimental data 9.10 ± 0.1 eV (Fig. 3). This value exceeds the recently measured adiabatic ionization energies of alanine determined: (i) in a synchrotron radiation photo-ionization experiment by Jochims et al. [14] of 8.75 eV and (ii) in the PES experiments by Debies and Rabalais [9], Klasinc [10] of 8.8 and 8.88 eV, respectively. Cannington and Ham [11] determined in their PES experiment the vertical ionization energy of alanine to be 9.85 eV. The present ab initio calculations of the reaction enthalpy (which is closely related to the adiabatic ionization energy and which includes the effect of the gas temperature) of alanine yield for the adiabatic ionization energy a value of 9.07 eV, which corresponds very well with the present experimental value.

The parent molecular ion dissociates on the microsecond time scale in a number of positively charged fragment ions and radicals which indicates presence of a low barrier against dissociation. The ion with *m/z* of 74 is most probably formed via

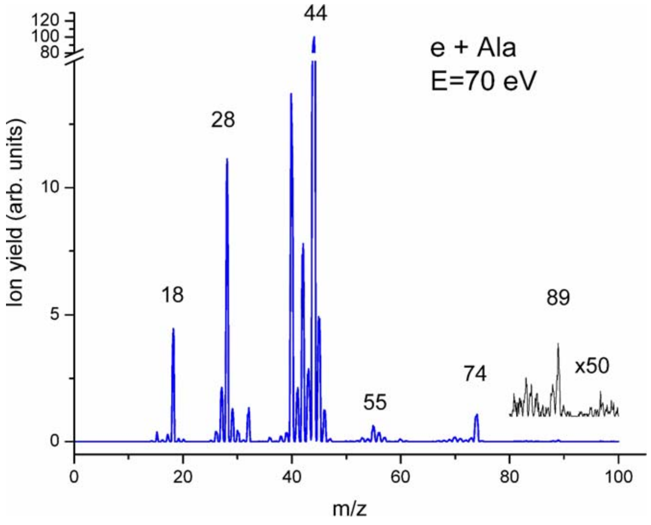

Fig. 2. Mass spectrum of the L-alanine measured at an electron energy of 70 eV. Note the weak molecular peak of alanine and that *m/z* = 40 is enhanced due to the presence of Ar that is used for calibration purposes.

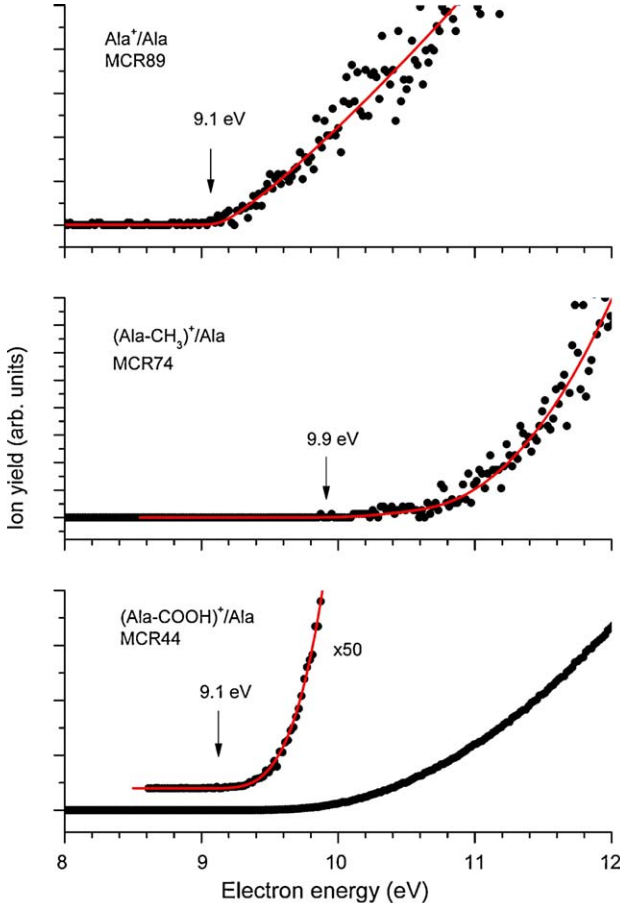

Fig. 3. Ion efficiency curves for the ions with $m/z = 89$, 74 and 44 close to the respective thresholds. The solid lines indicate the fits and the arrows the estimated thresholds.

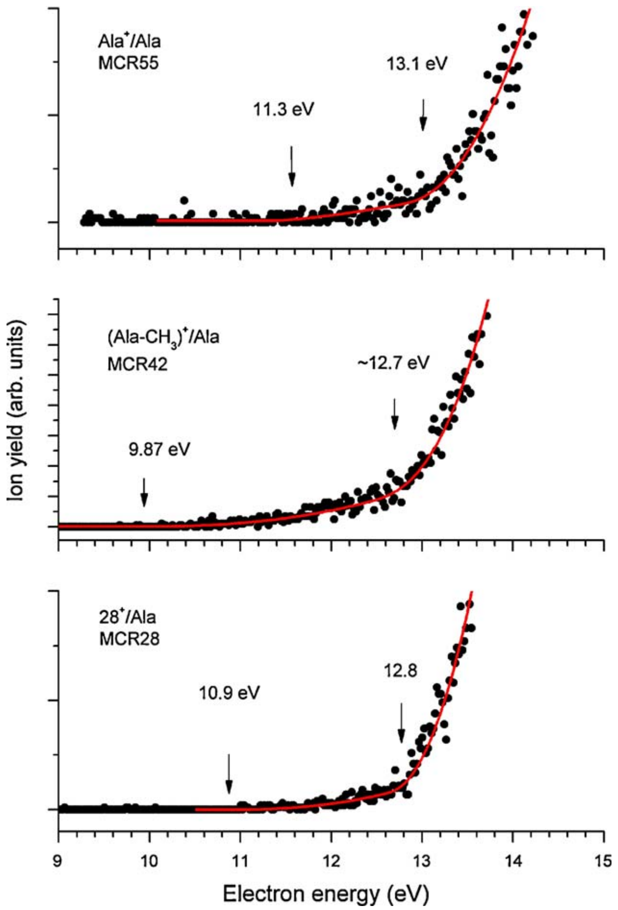

Fig. 4. Ion efficiency curves for the ions with $m/z = 55$, 42 and 28 close to the respective thresholds. The solid lines indicate the fits and the arrows the estimated thresholds.

reaction:

$$\mathrm{Ala}^{+*} \rightarrow \mathrm{NH_2CHCOOH}^{+} + \mathrm{CH_3}^{\bullet} \qquad (3)$$

where $NH_2CHCOOH^+$ is the glycyl radical cation. The appearance energy for this reaction is determined from the present experiment with 9.9 ± 0.1 eV. Jochims et al. [14] observed in the PI experiment the formation of a fragment ion with m/z of 74 already at 9.3 eV. The presently performed ab initio calculations give a reaction enthalpy for reaction (3) of 10.07 eV and thus support the experimental value obtained here. The difference between the PI value of the appearance energy and the present value is significant and it is difficult to explain it without knowing all experimental conditions, however, a possible explanation could be associated with the resolution of the mass spectrometer. The mass 73 associated with the formation of CH_4 and the ion with $m/z = 73$ could have lower appearance energy then the ion with $m/z = 74$.

For the next major fragment ion having an m/z of 55 two thresholds are observed in the ion yield at 11.34 ± 0.1 and at 13.1 ± 0.2 eV, respectively (Fig. 4). Jochims et al. [14] suggested that the ion with this m/z could be the propargylamine cation $CH_3C{\equiv}CNH_2^+$. Present calculations indicate that the formation of $CH_3C{\equiv}CNH_2^+$ and HOOH (reaction enthalpy of 11.34 eV) can be associated with the first threshold (11.34 eV) of the ion yield and the energy of the second threshold corresponds very well to the reaction enthalpy of a process where two OH radicals are formed:

$$\mathrm{Ala}^{+*} \rightarrow \mathrm{CH_3{-}C{\equiv}C{-}NH_2}^{+} + \mathrm{HOOH} \qquad (4a)$$

$$\mathrm{Ala}^{+*} \rightarrow \mathrm{CH_3{-}C{\equiv}C{-}NH_2}^{+} + 2\mathrm{OH}^{\bullet} \qquad (4b)$$

The mass spectrum of the alanine is dominated by the ion having an m/z of 44 (Fig. 3). This ion was assigned by Jochims et al. [14] to the immonium ion $NH_2CHCH_3^+$ which is most probably formed via

$$\mathrm{Ala}^{+*} \rightarrow \mathrm{NH_2CHCH_3}^{+} + \mathrm{COOH} \qquad (5)$$

The present experimental appearance energy of 9.10 ± 0.04 eV is identical within the error bars with the thermo-chemical value for the reaction threshold for this ion, being 9.12 eV [31]. It is important to note, that this ion has an appearance energy, which corresponds within the error bars with the present experimental value of the appearance energy of the molecular ion Ala^+. This indicates the instability of the C–COOH bond in the molecular ion Ala^+ formed upon electron impact ionization. The calculated enthalpy of the formation for this ion with 9.51 eV is high in comparison with the experimental appearance energy. The difference between the experimental and the calculated value is about 0.4 eV which is much larger then the error bars for both, the experiment and the theory.

The ion with *m*/*z* 42 has an experimental appearance energy of 9.87 ± 0.1 eV (Fig. 4). This value disagrees with the very low value obtained in the photo-ionization study by Jochims et al. [14] of 9.05 eV. Jochims et al. suggested that this ion has the structure $NH_2CH_2{=}C^+$. Present calculations, however, indicate that the most stable structure for this stoichiometry is $CH_3C{\equiv}NH^+$, which is formed via the following reaction process:

$$\mathrm{Ala}^{+*} \rightarrow\ CH_3C{\equiv}NH^+ + HCO^- + H_2O \qquad (6)$$

The present calculations give a rather high value of the reaction enthalpy of 10.87 eV which exceeds the present experimental value by 1 eV. We calculated also further possible structures for this stoichiometry (see Table 1), however, for all of them the reaction threshold is higher. The low experimental value of the appearance energy for the ion with $m/z = 42$ of 9.87 eV could originate from the neighbouring ion $NH_2CHCH_2^+$ with an *m*/*z* of 43. This ion has according to present calculations appearance energy of 9.47 eV. In the present experiment we are not able to exclude an overlap between the masses 42 and 43. The appearance energy of the ion with $m/z = 43$ has not been measured in present study.

The ion with *m*/*z* 28 belongs also to the principal ions formed via DEII to alanine. The ion was identified by Jochims et al. [14] as $HCNH^+$ and this assignment is also supported by the present calculations. This ion can be formed via dissociation of the glycyl radical cation:

$$\mathrm{Ala}^{+*} \rightarrow\ (NH_2CHCOOH)^{+*} + \text{fragments},$$

$$(NH_2CHCOOH)^{+*} \rightarrow\ HCNH^+ + HCOOH \qquad (7)$$

The reaction enthalpy for $HCNH^+$ is according to present calculations 12.00 eV. The ion efficiency curve for this mass of 28 shows two distinct thresholds, i.e., a first one at 10.85 ± 0.1 eV and a second one at 12.8 ± 0.2 eV, $m/z = 28$ is also the mass per charge ratio of the CO^+ ion. The enthalpy of formation of this ion is in the energetically most favourable case via reaction:

$$\mathrm{Ala}^{+*} \rightarrow\ (COOH)^{+*} + \text{fragments},$$

$$(COOH)^{+*} \rightarrow\ CO^+ + OH \qquad (8)$$

according to present calculations 18.83 eV. This high threshold energy suggests that both experimentally measured thresholds correspond to the formation of the $HCNH^+$ ion with different neutral fragments.

For the ion with $m/z = 18$ the NH_4^+ and H_2O^+ are the two possible compositions. The ab initio calculation for the production of an NH_4^+ ion and HC=CHCOOH (these products were suggested by Jochims et al. [14]) gives for the reaction threshold a value of 10.26 eV. However, the measured ion yield at $m/z = 18$ (Fig. 5) has a threshold at 12.55 ± 0.1 eV. This value corresponds within the error bars to the ionization energy of water (12.62 ± 0.002 eV [32]). On the basis of these facts we believe that this ion yield results from the ionization of water released from the alanine sample at elevated temperatures and that the formation of the NH_4^+ ion is not observed in the present experiment, most probably due to fact that the cross section for this reaction is very low.

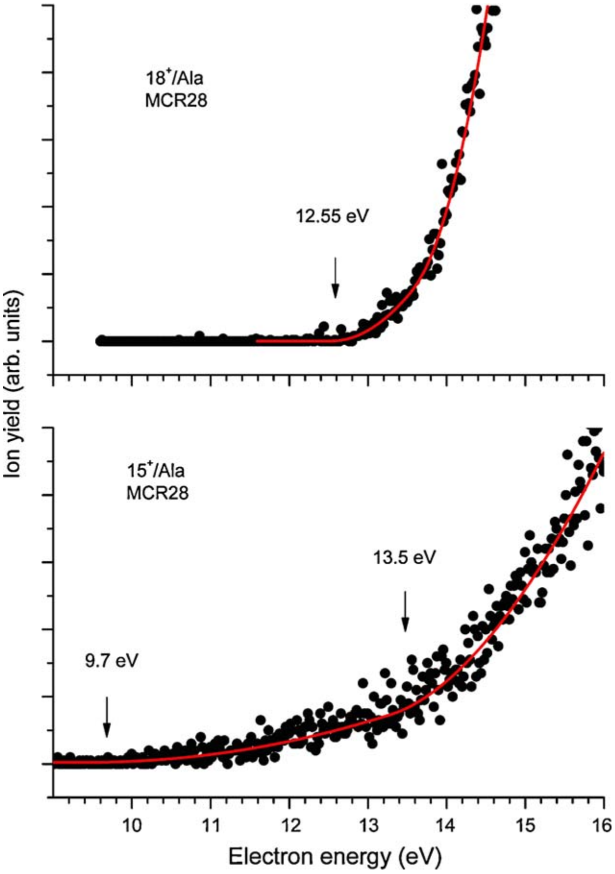

Fig. 5. Ion efficiency curves for the ions with $m/z = 18$ and 15 close to the respective thresholds. The solid lines indicate the fits and the arrows the estimated thresholds.

The ion yield for the smallest recorded ion ($m/z = 15$) is presented in Fig. 5. Two thresholds are present in the ion yield the first one at 9.7 ± 0.1 eV and the second one at 13.5 ± 0.1 eV. We assign the 13.5 eV threshold to the CH_3^+ ion. The calculated reaction enthalpy for formation of CH_3^+ from the alanine cation via:

$$\mathrm{Ala}^{+*} \rightarrow\ CH_3^+ + NH_2CHCOOH$$

has a value of 12.92 eV. The $m/z = 15$ can also be interpreted as the NH^+ ion. However, the formation of this ion from alanine is energetically less favourable. According to present calculations the reaction enthalpy is 16.81 eV. We are not sure about the origin of the first threshold at 9.7 eV, however, as the ionization energy of the CH_3 is 9.84 ± 0.01 eV [16] and the intensity of this ion very low, we assume that the first threshold is due to electron impact ionization of the CH_3 radical, which is formed in trace amounts in the molecular beam source.

5. Conclusions

Electron impact ionization of alanine in the gas phase results in strong fragmentation. The reason for this phenomenon is the instability of the alanine molecular ion against dissociation. The dominant reaction channel is the formation of the immonium ion $NH_2CHCH_3^+$ and a COOH radical at electron energies close to the ionization threshold of the parent ion. Further fragment ions formed via electron impact ionization to alanine are interpreted on the basis of quantum chemical calculations. For a large number of neutral and ionized fragments the most probable structures are assigned based on the calculated reaction enthalpies for possible pathways and the experimentally determined appearance energies.

Acknowledgments

This work was supported by Slovak Science and Technology Assistance Agency under the contract no. APVT-20-007504, the FWF Wien, Austria and the European Commission, Brussels.

References

[1] I. Miyagava, K.J. Itoh, Chem. Phys. 36 (1936) 2157.

[2] D.F. Regulla, U. Deffner, Int. J. Appl. Radiat. Isot. 33 (1982) 1101.

[3] M.Z. Heydari, E. Malinen, E.O. Hole, E. Sagstuen, J. Phys. Chem. A 106 (2002) 8971.

[4] V. Nagy, J.M. Puhl, M.F. Desrosiers, Radiat. Phys. Chem. 57 (2000) 1.

[5] S. Ebraheem, W.B. Beshira, S. Eid, R. Sobhy, A. Kovacs, Radiat. Phys. Chem. 67 (2003) 569.

[6] C.Y. Fongillo, J.P. Patau, T. Goulet, M.J. Fraser, Jay-Gerin J.P., Radiat. Phys. Chem. 51 (1998) 229.

[7] International Commission on Radiation Units and Measurements, ICRU Report 31 (ICRU, Washington, DC, 1979).

[8] S. Ptasinska, S. Denifl, P. Candori, S. Matejcik, S.P. Scheier, T.D. Mark, Chem. Phys. Lett. 403 (2005) 107.

[9] T.P. Debies, J.W. Rabalais, J. Elec. Spectrosc. Relat. Phenom. 3 (1974) 315.

[10] L. Klasinc, J. Elec. Spectrosc. Relat. Phenom. (1976) 161.

[11] P.H. Cannington, N.S. Ham, J. Elec. Spectrosc. Relat. Phenom. 32 (1983) 139.

[12] V. Vorsa, T. Kono, K.F. Willey, N. Winograd, J. Phys. Chem. B 103 (1999) 7889.

[13] I. Powis, E.E. Rennie, U. Hergenhaahn, O. Kugeler, R. Bussy-Socrate, J. Phys. Chem. A 107 (2003) 25.

[14] H.-W. Jochims, M. Schwell, J.-L. Chotin, M. Clemino, F. Dulieu, H. Baumgartel, S. Leach, Chem. Phys. 298 (2004) 279.

[15] M. Stano, S. Matejcik, J.D. Skalny, T.D. Märk, J. Phys. B: At. Mol. Opt. Phys. 36 (2003) 261.

[16] NIST Chemistry WebBook, NIST Standard Reference Database Number 69 – March, 2003 Release, http://webbook.nist.gov.

[17] I. Powis, E.M. Rennie, U. Hergenhahn, O. Kugeler, R. Bussy-Socrate, J. Phys. Chem. A 107 (2003) 25.

[18] S. Simon, M. Sodupe, J. Bertran, J. Phys. Chem. A 107 (2002) 5697.

[19] F. Rogalewicz, Y. Hoppiliard, Int. J. Mass Spectrom. 199 (2000) 235.

[20] P. Selvarengan, P. Kolandaivel, J. Mol. Struct. (Theochem) 671 (2004) 77.

[21] R.A.J. O'Hair, S. Blanksby, M. Styles, J.H. Bowie, Int. J. Mass Spectrom. 182/183 (1999) 203.

[22] M.J. Polce, C. Wesdemiotis, J. Mass Spectrom. 35 (2000) 251.

[23] F. Tureček, E.A. Syrstad, J.L. Seymour, L. Chen, C. Yao, J. Mass Spectrom. 38 (2003) 1093.

[24] F. Tureček, F.H. Carpenter, M.J. Polce, C. Wesdemiotis, J. Am. Chem. Soc. 121 (1999) 7955.

[25] T.L. Petrenko, J. Phys. Chem. A 106 (2002) 149.

[26] P. Lahorte, F. De Proft, G. Vanhaelewyn, B. Masschaele, P. Cauwels, F. Callens, P. Geerlings, W. Mondelaers, J. Phys. Chem. A 103 (1999) 6650.

[27] L.A. Curtiss, K. Raghavachari, P.C. Redfern, V. Rassolov, J.A. Pople, J. Chem. Phys. 109 (1998) 7764.

[28] A.G. Baboul, L.A. Curtiss, P.C. Redfern, K. Raghavachari, J. Chem. Phys. 110 (1999) 7650.

[29] D.C. Young, Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems, John Wiley & Sons Inc., 2001.

[30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98 (Revision A.11), Gaussian Inc., Pittsburgh, PA, 1998.

[31] S.G. Lias, J.E. Bartmess, J.F. Libman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988).

[32] CRC Handbook of Chemistry and Physics, CD edition, CRC Press, 2004.