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Chemical Physics Letters 403 (2005) 107–112
CHEMICAL PHYSICS LETTERS
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Dissociative electron attachment to gas phase alanine

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Received 15 November 2004; in final form 13 December 2004

Abstract

Using a high resolution electron energy monochromator the dissociative electron attachment (DEA) to the gas phase L-alanine is studied by means of the mass spectrometric detection of the product anions. Alanine and the previously studied amino acid glycine exhibit several common features due to the possibility of electron attachment to the unoccupied π* orbital of the –COOH group. The largest DEA cross-section of about 1.5×10^{-20} m^2 is observed for the production of the $(A - H)^-$ ion at the electron energy of 1.27 eV. This ion is the major reaction product at electron energies below 5 eV. At higher incident electron energies several smaller fragment anions are formed via core excited resonances at about 5.5 and 9.0 eV.

1. Introduction

L-Alanine (further alanine) belongs to the simplest α-amino acids and is often considered as a model system for properties of more complex systems, particularly in the case of ionizing radiation. The formation of radicals in single crystals of alanine exposed to energetic radiation has been the subject of investigations during the past four decades [1]. Alanine has attracted attention due to its radiation dosimetric properties and is formally accepted as a secondary standard for high-dose and transfer dosimetry [2–5]. In a dosimetric electron paramagnetic resonance (EPR) study of alanine at low temperatures [2] (temperatures of crystalline or polycrystalline sample down to 7 K) the spectra are dominated by the stable alanine radical ($CH_3CH{\cdot}COO^-$ denoted R1) which is formed via deamination of a protonated alanine radical anion [2,6,7]. Moreover, studies of alanine at room and elevated temperatures [3] indicate besides the formation of the main radical R1 (55%) also the production of the radical R2 (35%) which denotes a dehydrogenated anion or neutral radical. A number of theoretical investigations has been published on the radical formation [8–11] from alanine which support these experimental observations.

The interaction of ionizing radiation with matter leads to the production of secondary reactive species along the track of the radiation. These secondary species may in turn undergo subsequent reactions with the medium. Secondary electrons with kinetic energies below 20 eV [12] belong to the most abundant secondary particles with a yield of 5×10^4 per MeV [13] energy deposited by the primary quantum. Dissociative electron attachment (DEA) is an efficient reaction in the energy range of the secondary electrons. DEA is responsible for the formation of negative ions and radicals in the gas (and aggregate) phase and may play also an important role in the radical formation from alanine.

In this Letter, we present the first mass spectrometric study of DEA to the amino acid alanine ($A = CH_3CH(NH_2)COOH$) in the gas phase. This study contributes to the understanding of the intrinsic mechanism of the radical formation on the molecular level and gives new insight into radical formation in crystalline and

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doi:10.1016/j.cplett.2004.12.115

polycrystalline alanine upon exposure to ionizing radiation. We have to stress that there exist substantial differences for the alanine monomer in the solid state and in the gas phase. In the solid state the monomer exists in the zwitterionic form (with a proton transferred from the carboxylic acid to the amino group). Calculations suggest [14] that alanine in the gas phase adopts a large number of conformations accessible at a given temperature.

Nevertheless DEA to alanine in the gas and the condensed phase is a resonant process that proceeds in two steps:

$$\begin{aligned} e + A &\rightarrow (A^-)^{\#} \\ &\rightarrow \text{negative ion} + \text{neutral fragments} \end{aligned} \quad (1)$$

In the first step the transient negative ion (TNI) $(A^-)^{\#}$ is formed which subsequently decays into a negative ion and neutral fragments. Using the crossed electron/molecule beams technique combined with the mass analysis of the negative ions we were able to measure the ion yields for the formation of particular negative ions and for some reaction channels we could give some additional information about the formed radicals.

To the best of our knowledge there exists only one study concerning low energy electron interaction with alanine. Aflatooni et al. [15] measured the temporary anion states of selected amino acids including alanine in the electron energy range from about 0 to 6 eV. Using the electron transmission spectroscopic technique they were able to detect a resonance at an electron energy of 1.80 eV which was assigned to electron attachment into the empty π^* orbital of the –COOH group of alanine. Previous studies concerning formic acid and glycine [15–17] showed that this π^* resonance is typical for molecules containing the COOH (carboxyl) functional group. In the case of glycine these studies showed besides the π^* resonance [16,17] additional resonances at higher electron energies (around 6 and 10 eV) which were tentatively assigned to the lowest excited states of glycine. The present results of DEA to alanine are very similar to the ones obtained for glycine. Besides the low energy π^* resonance we have observed two resonances at higher energies (around 5.5 and 9 eV) and some similarity in the dissociation patterns for both molecules.

2. Experimental

The present experiments were carried out with a crossed electron/molecule beams apparatus described in detail in the previous work [18]. Electrons from a hairpin filament were passed through a hemispherical electron monochromator that enables a maximum energy resolution of about 30 meV. However, for reasons of a higher sensitivity the present measurements were performed with the electron energy resolution of 120 meV and an electron current of 15 nA. Alanine powder was vaporized in a resistively heated oven at the temperature of 410 K. An effusing molecular beam was formed by evaporation of molecules into the reaction chamber through a 8-cm long capillary with an inner diameter at the exit of 1 mm. The electron beam was perpendicularly crossing the molecular beam in the reaction chamber. The negative ions formed there were extracted by a weak electric field towards the entrance of a quadrupole mass spectrometer. The mass selected negative ions were detected by a channeltron detector operated in the counting mode and the pulses were processed using a pulse counting technique and a computer. The intensity of negative ions was recorded as a function of the electron acceleration voltage.

The electron energy scale was calibrated by recording the ion efficiency curve of the Cl^- ion formed by DEA to CCl_4. It is very well known that this anion exhibits a s-wave resonance at 0 eV. The apparent width of the resonance was used in order to determine the electron energy resolution of the electron beam and its position to define the zero energy point of the energy scale. In the present experiment estimates for the partial cross-sections were obtained for all product anions that were generated by DEA to alanine. This was achieved by comparing the ion yields of the product ions of alanine with the ion current of Cl^- formed from CCl_4 at 0.8 eV (the known absolute partial cross-section is 5×10^{-20} m^2 [19]) measured under identical conditions, i.e., identical pressure (the reading at an ionization pressure gauge was 4.3×10^{-5} Pa) and identical electron current. The accuracy of this method is estimated to be in the range of one order of magnitude (see also discussion in [20], where also the discrimination due to the kinetic energy release in the dissociation reaction is considered).

3. Results and discussion

The dissociative electron attachment to alanine leads to the formation of at least nine negative fragment ions. In the present experiment, the parent negative ion is not observed on a mass spectrometric time scale. This is in accordance with the past (see results from electron transmission spectroscopy [15]) that alanine very likely has a negative electron affinity. The negative ions formed via DEA to alanine can be divided in two categories:

(i) negative ions formed via a simple single bond cleavage

$$e + A \rightarrow (A^-)^{\#} \rightarrow (A - H)^- + H \quad (2)$$

$$H^- + \text{neutral fragments} \quad (3)$$

$$O^- + \text{neutral fragments} \quad (4)$$

$$OH^- + \text{neutral fragments} \quad (5)$$

$$COOH^- + \text{neutral fragments} \quad (6)$$

$$(A - OH)^- + OH \quad (7a)$$

$$(A - NH_3)^- + NH_3 \quad (7b)$$

and (ii) negative ions formed via a complex rearrangement during the dissociative process

$$e + A \rightarrow (A^-)^{\#} \rightarrow CN^- + \text{neutral fragments} \quad (8)$$

$$C_2H_4N^- + \text{neutral fragments} \quad (9a)$$

$$NCO^- + \text{neutral fragments} \quad (9b)$$

$$C_3H_4NO^- + H_2O + H \quad (10a)$$

$$C_3H_2O_2^- + NH_3 + H_2 \quad (10b)$$

We have observed a number of resonances in the ion yields for DEA to alanine, they are summarized in Table 1. The DEA peaks at low electron energies 1.27, 1.42, 1.7, 2.7 and 3.2 eV have most probably their origin in the resonance associated with the π* orbital of the carboxyl functional group [15]. Additional resonances at about 5.5 and 9 eV are most probably associated with the first and second excited state of the molecule and these resonances are present in almost all measured ions.

The ion yield for the formation of the negative ion $(A - H)^-$ with mass to charge ratio (MCR) 88, i.e., DEA associated with an abstraction of the H atom, is presented in the Fig. 1. The DEA cross-section for this negative ion has a maximum value of about 1.5×10^{-20} m^2 at the electron energy of 1.27 eV. The magnitudes of the ion yields for all of the negative ions presented in this Letter are normalized with respect to this dominant peak in the $(A - H)^-$ yield. The careful data analysis (Gaussian peak fitting) shows that this resonance consists of two peaks located at 1.27 and at 1.42 eV, respectively. According to the ETS study [15] there exists a resonant formation of the TNI with a center at 1.8 eV due to the temporal occupation of the π* orbital of the carboxyl group in alanine. The two peaks observed in the $(A - H)^-$ ion yield at these low electron

Table 1
The positions of the peak resonances of negative ions formed via DEA to alanine

Ion	MCR	Electron energy (eV)				
$(A - H)^-$	88	1.27	1.42		5.5	
$(A - OH)^-/(A - NH_3)^-$	72		1.7		4.9	9.1
$C_3H_4NO^-/C_3H_2O_2$	70				5.5	8.8
$COOH^-$	45			2.7	5.67	9.0
C_2H_4 N^-/NCO^-	42			2.7	5.75	9.0
CN^-	26				5.95	9.3
OH^-	17			3.2	5.45	9.2
O^-	16				5.9	9.6
H^-	1				5.7	9.0

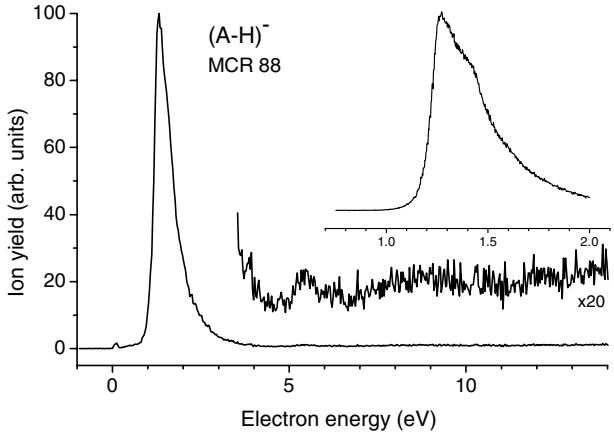

Fig. 1. The ion yield for the $(A - H)^-$ ion formation via DEA to alanine.

energies have their origin in this resonance and may correspond to different isomers of the $(A - H)^-$ ion (i.e., an abstraction of H from O (2a), α-C (2b), N (2c) and C (2d)). In analogy to DEA to glycine [16] we assume that the energetically most favorable channel is (2a). This assignment is supported by the thermodynamical data existing for the $(A - H)^-$ anion in the solution which corresponds to the (2a) form of $(A - H)^-$ ions (i.e., $\Delta_f H_g((A - H)^-) = -518.8 \pm 9.6$ kJ/mol and EA(A − H) = 3.42 ± 0.13 eV [21]). These data indicate a threshold for $(A - H)^-$ formation at about 1.2 eV which is in a good agreement with our experimental results. We tentatively assign the feature at 1.42 eV (see inset in Fig. 1 showing details of the low energy peak) to the (2b) isomer.

A very important characteristic of a reaction proceeding via different reaction channels is the *branching ratio R*. For three reaction channels A, B, C with a concentration of products n_A, n_B, and n_C, the branching ratio for a reaction A is defined by

$$R_A = n_A/(n_A + n_B + n_C). \quad (11)$$

The branching ratio (11) expresses the relative population of the reaction channel A. In the case of DEA to alanine we have at least nine reaction channels. Fig. 2 presents the branching ratios for the three most abundant negative ions. $(A - H)^-$ is the dominant product in the low electron energy range from 0 to about 4 eV. The cross-section for the formation of the $(A - H)^-$ decreases rapidly at higher energies and the ratio for this ion at about 6 eV amounts to 1% of the 1.27 eV resonance.

The negative ion yield of H^- (Fig. 3a) formed via reaction (3) shows two resonances located at 5.7 and 9.0 eV, respectively. The formation of the H^- anion is not observed at electron energies below 5 eV which is in agreement with our previous observation for glycine. We do not have any information about the neutral fragments for this reaction channel.

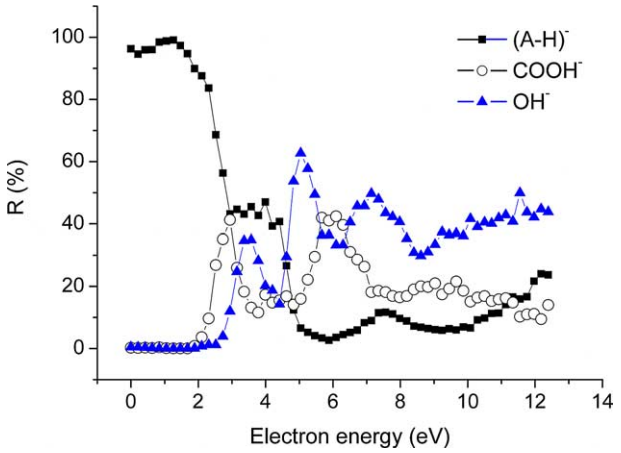

Fig. 2. The branching ratio R (see text) for the formation of $(A - H)^-$, OH^- and $COOH^-$ via DEA to alanine.

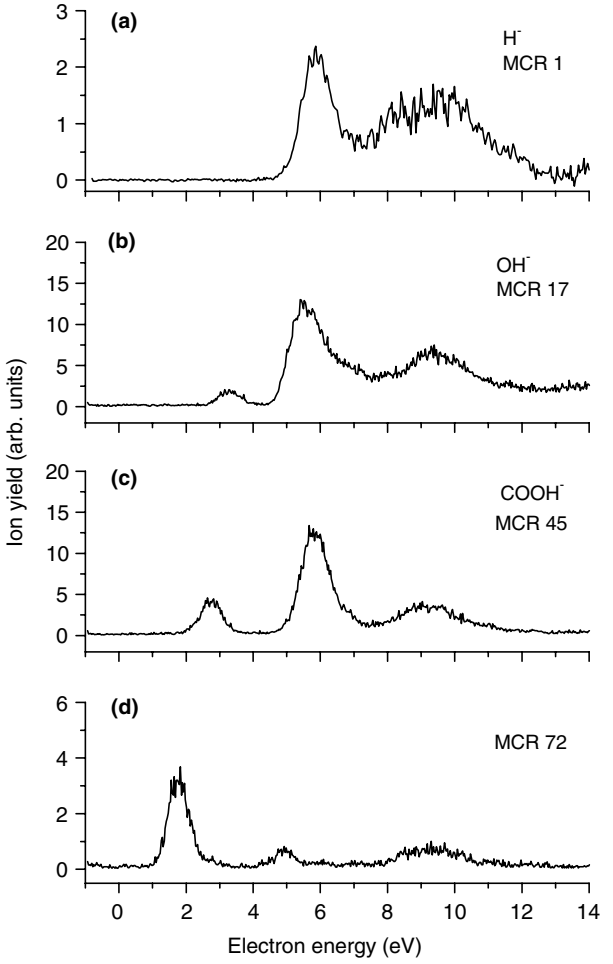

Fig. 3. The ion yields for different fragment anions (MCR 1, 17, 45 and 72) obtained from alanine and normalized to the $(A - H)^-$ yield in Fig. 1.

The formation of the OH^- ion (MCR 17, Fig. 3b) was observed at three distinct resonances at 3.2, 5.45 and 9.2 eV. MCR 17 may correspond to NH_3, but the assignment MCR 17 as OH^- is unambiguous as the ammonia molecule has a negative electron affinity. The most efficient formation of this anion occurs at 5.45 eV with the ion yield amounting to 15% of the $(A - H)^-$ at 1.27 eV. At electron energies above 5 eV the OH^- ion is the dominant reaction channel of the DEA to alanine (with a branching ratio of 60% at about 5 eV, see Fig. 2), with an exception of a narrow interval at the electron energy around 6 eV where the $COOH^-$ reaction channel is the dominant one. The $COOH^-$ ion is formed at three resonances, which are located at 2.7, 5.67 and 9 eV. The $COOH^-$ ion yield at 5.67 eV reaches 15% of the $(A - H)^-$ peak at 1.27 eV and in the narrow interval around this energy $COOH^-$ has a branching ratio of 40% (Fig. 2). The OH^- and $COOH^-$ ions are formed also at 3.2 and 2.7 eV, respectively. These resonances could be still associated with the π^* resonance of the carboxylic group which is localized at 1.8 eV and has an appreciable width [15].

The negative ion with a MCR 72 may exist in at least two forms $(A - OH)^-$ (7a) and $(A - NH_3)^-$ (7b), moreover, each of these forms may have several isomers. On the basis of the present mass spectrometric study, we are not able to identify the forms of this ion and of the neutral products. In the databases [22,23] we cannot find the necessary thermodynamical data for these ions and corresponding radicals. The strongest appearance of the ion with the MCR 72 is at 1.7 eV, the magnitude of the ion yield at this energy amounts to 4% of the $(A - H)^-$ reference peak. The peak is located within the π^* resonance of the COOH group, that may be an indication for the existence of the $(A - OH)^-$ form of the MCR 72 ion in this energy range. Additional resonances at 4.9 and 9.1 eV are much less significant with magnitudes of about 1%. The branching ratio for this ion reaches 10% in narrow intervals of energies around the 1.7 and 4.9 eV resonances.

We have also detected in the present experiment the O^- fragment ion (Fig. 4a) with a broad resonance formed with a center at about 9.6 eV. The ion yield of this anion does not exceeds 1% of the magnitude of the $(A - H)^-$ peak and the branching ratio does not exceed 0.5%. It is possible that O^- is formed also at about 5 eV (there is a slight increase of the signal) but the sensitivity of the present experiment is not sufficient to see a clear resonance at this energy.

The negative ion with a MCR 26 is assigned to the CN^- ion produced via reaction (8). This ion cannot be produced via single bond cleavage, at least five bonds have to be broken prior the CN^- formation. The energy necessary for that has to be gained from the rearrangement of the neutral products and from the high electron affinity of the CN radical of 3.862 eV [22]. The maximum for the CN^- formation appears at 9.3 eV (Fig. 4b) and a weak signal is already present at about 6 eV. The formation of the ions with a MCR 42 via (9a,b) fol-

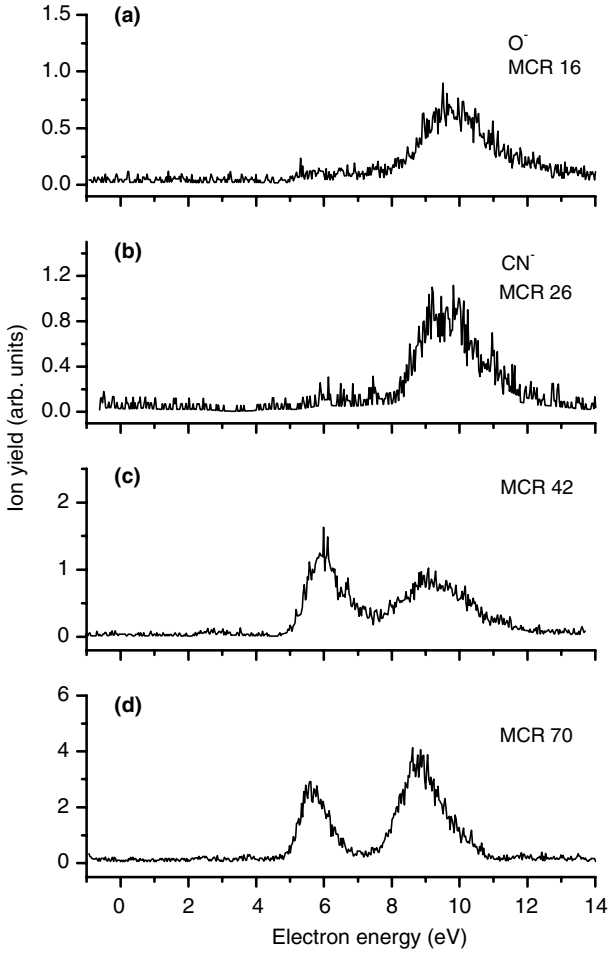

Fig. 4. The ion yields for different fragment anions (MCR 16, 26, 42 and 70) obtained from alanine and normalized to the $(A - H)^-$ yield in Fig. 1.

lows a complex reaction path. There exist several isomeric forms (NCO^-, CNO^-, $CH_2{=}NCH_2^-$, $CH_2{=}CHNH^-$) but on the basis of present experiments we are not able to elucidate the nature of the ions formed during DEA reactions. The ions with the MCR 42 are formed at two resonances (5.75 and 9.0 eV) and possibly at 2.7 eV (Fig. 4c). Fig. 4d shows the ion yield for the ions with a MCR 70 produced via reactions (10a,b) with resonances located at 5.5 and 8.8 eV. The nature of this ion is not clear, two possible ions can be produced: the $C_3H_4NO^-$ ion with a formation of H_2O and H neutral fragments of the $C_3H_2O_2^-$ ion with a formation of NH_3 and H_2 neutrals.

4. Conclusion

DEA to gas phase alanine leads to the formation of at least nine fragment anions. Like in the case of many other biological important molecules M (M = formic acid, acetic acid, thymine, cytosine, uracil [16,17,24]) the most abundant anion is the closed shell anion $(M - H)^-$. In the case of DEA to alanine, the formation of the $(A - H)^-$ anion and the H radical is the dominant reaction path in the electron energy range below 3 eV. The appearance of the negative ions in this energy range results from the decay of the π^* resonance of the COOH group [15]. The cross-section for the $(A - H)^-$ ion formation has a value of about 1.5×10^{-20} m^2 at 1.27 eV. Additional DEA channels are associated with core excited resonances at about 5.5 and 9 eV. In the electron energy range above 5 eV the OH^- and $COOH^-$ are the most abundant products of DEA to alanine with branching ratios up to 60% and 40%, respectively. For some reaction channels we are not able to identify unambiguously the structure and to assign the negative ions and neutral fragments or radicals produced via DEA to alanine.

The present experiment shows that low energy electrons below 15 eV can effectively produce anion radicals of alanine. Thus studies of simple amino acids may serve as a model for radiation damage to larger biocomplexes like proteins, and also in relation to the interactions of radical anions in the vicinity of water molecules and the DNA helix in a living cell.

Acknowledgements

This work was supported by the FWF, ÖAW and ÖNB, Wien, Austria, and the European Commission, Brussels, Austria-Slovakia project 39s8 and Slovak grant agency VEGA (Project No. 1/1009/2004).

References

[1] I. Miyagawa, K. Itoh, J. Chem. Phys. 36 (1962) 2157.
[2] D.F. Regulla, U. Deffner, Appl. Radiat. Isotopes 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. Beshir, S. Eid, R. Sobhy, A. Kovacs, Radiat. Phys. Chem. 67 (2003) 569.
[6] E. Sagstuen, E.O. Hole, S.R. Haugedal, W.H. Nelson, J. Phys. Chem. A 101 (1997) 9763.
[7] G.C.A.M. Vanhaelewyn, S.A. Amira, W.K.P.G. Mondelaers, F.J. Callens, Spectrochim. Acta A 56 (2000) 387.
[8] A.A. Bugay, V.A. Onischuk, T.L. Petrenko, V.V. Teslenko, Appl. Radiat. Isotopes 52 (2000) 1189.
[9] T.L. Petrenko, J. Phys. Chem. A 106 (2002) 149.
[10] F. Ban, S.D. Wetmore, R.J. Boyd, J. Phys. Chem. A 103 (1999) 4303.
[11] P. Lahorte, F. De Proft, G. Vanhaelewyn, B. Masschaele, P. Cauwels, F. Callens, P. Geerlings, W. Mondelaers, J. Phys. Chem. A 103 (1999) 6650.
[12] International Commission on Radiation Units and Measurements, ICRU Report 31 ICRU, Washington, DC, 1979.
[13] V. Cobut, Y. Frongillo, J.P. Patau, T. Goulet, M.J. Fraser, J.P. Jay-Gerin, Radiat. Phys. Chem. 51 (1998) 229.

[14] M. Cao, S.Q. Newton, J. Pranata, L. Schafer, Theochem. J. Mol. Struct. 332 (1995) 251.
[15] K. Aflatooni, B. Hitt, G.A. Gallup, P.D. Burrow, J. Chem. Phys. 115 (2001) 6489.
[16] S. Gohlke, A. Rosa, E. Illenberger, F. Brüning, M.A. Huels, J. Chem. Phys. 116 (2002) 10164.
[17] S. Ptasinska, S. Denifl, A. Abedi, P. Scheier, T.D. Märk, Anal. Bioanal. Chem. 377 (2003) 1115.
[18] D. Muigg, G. Denifl, A. Stamatovic, O. Echt, T.D. Märk, Chem. Phys. 239 (1998) 409.
[19] S.C. Chu, P.D. Burrow, Chem. Phys. Lett. 172 (1990) 17.
[20] P. Cicman, M. Francis, J.D. Skalny, T.D. Märk, Int. J. Mass Spectrosc. 223/224 (2003) 271.
[21] M.J. Locke, R.T. McIver, Jr., J. Am. Chem. Soc. 105 (1983) 4226.
[22] NIST Chemistry Webbook, Available from: <http://www.webbook.nist.gov/chemistry/>, NIST Standard Reference Database Number 69 – March, 2003 Release.
[23] CRC Handbook of Chemistry and Physics, 83rd edn., CDRom.
[24] S. Denifl, S. Ptasinska, M. Cingel, S. Matejcik, P. Scheier, T.D. Märk, Chem. Phys. Lett. 377 (2003) 74.