SCIENTIFIC REPORT

Short Time Scientific Mission within the COST scientific programme on

Radiation Damage in Biomolecular Systems

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Date: 7.10.2004 – 16.10.2004

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Scientific programme followed the proposed working plan. The calculation of ionization energies at the present state of the theory offers reliable data that can be compared with experimental results.

Literature search revealed relatively few works dealing with relevant subject. Published theoretical approaches to the study of alanine and glycine [1-7] used wave-function based quantum chemical methods with inclusion of electron correlation (MP2(FC) and CCSD(T)) and density functional methods (B3LYP functional) with basis sets ranging from 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 at CCSD(T) or MP2 level. Some contributions [8-10] are oriented to the study of the behavior of individual radicals occurring in the process of fragmentation.

Our results are based on the calculations performed at the Gaussian-3 (G3MP2) [11] and G3MP2B3 [12] levels (RMS deviation for ionization energies in G2/97 test set is ~0.1 eV). During calculations special attention was paid to find most stable nuclear conformation for any given species. All calculations have been performed using the Gaussian 98 and Gaussian03 program packages[13].

List of molecules for which structure and energy have been calculated is given in Table 1. From calculated enthalpies at 298 K energy differences determining the energy trshold for appearance of given ions have been evaluated. They are summarized in the Table 2. It can be seen from experimental results [14,15] that some cations appears at the energy that is below the ionization energy of parent molecule. This is probably the case

of the ion formation running through the fragmentation of the neutral alanine species followed by the ionization of fragments; which means the process of the fragmentation is not always connected with the parent ion.. The formation of $COOH^+$, $NH_2CHCH_2^+$ and NH_4^+ cations are the examples of such a processes. $COOH^+$ cation is formed by the rupture of the C-C bond followed by ionization of COOH radical. The formation of $NH_2CHCH_2^+$ cation is energetically favourable via fragmentation of neutral alanine with successive ionization of formed fragment.

In a short time the all necessary calculation will be finished. Obtained values will be published together with the experimental data obtained in Innsbruck and Bratislava laboratories.

Our stay in Innsbruck was good organized. We had access to all necessary resources both computer power and latest literature.

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TABLES

Table1. List of calculated molecules, radicals and ions

CH3-CH(NH2)-COOH	NH2=C=CH2(+)
CH3-CH(NH2)-COOH(+)	CH2=N=CH2(+)
NH2-C(CH3)-C(OH)2 (+)	CH3-C=NH(+)
NH3-C(CH3)-COOH(+)	OH
CH3-CH-NH2(+)	NH3
CH3-CH-NH2(°)	NH(+)
COOH(°)	NH(°)
COOH(+)	C2H3(+)
NH2-CH-COOH(+)	HCNH(+)
CH3(+)	NH4(+)
CH3(°)	NH(+)
CH2-CH-NH2(+)	CH2NH2(+)
HCOOH neut.	NH2-CH=C=O(+)
CH3-CH-COOH(+)	CH2=C=O(+)
CH2=CH-C(OH)2(+)	CH=CH-COOH(°)
NH2(°)	CH3CH2COOH
NH2-C(CH3)-COOH(+)	CO2(+)
NH2=C=CH2(+)	CO2
	CH3CCCNH2(+)

Table 2. Alanine fragmentation (all energies in eV)

m/z	ion assignments [1]	ion assignments [2]	Appearance Energy [1]	Appearance Energy[2]	our results
89	$NH_2CH_3CHCOOH^+$	the same ion	8.75±0.05	9.12±0.2	9.07
74	$NH_2CHCOOH^+$	the same ion	9.3±0.2	10.74±0.2	10.07
55	$CH_3C{\equiv}CNH_2^+$	$CH_3C{=}C{=}O^+$	9.3±0.2	11.34	b
45	$COOH^+$		9.3±0.2		9.22
44	$NH_2CH_3CH^+$	the same ion	9.05±0.1	9.10±0.05	9.51
43	$NH_2CH_2CH^+$		9.05±0.1		9.41
42	$NH_2CH_2C^+$	$CH_2{=}C{=}O^+$	9.05±0.1	9.87	11.07[a]
40		$C{=}C{=}O^+$	9.35		
30	$NH_2CH_2^+$		9.05±0.1		9.57
29	NH_2CH^+		9.05±0.1		
28	$HCNH^+$	$C{=}O^+$	12.35	10.85,12.8	12.0
27	$C_2H_3^+$		11.5±0.2		13.28
18	NH_4^+	the same ion	12.0	12.55	10.26
15	CH_3^+	NH^+	12.0	9.4,13.5	

[a] $CH_3C{\equiv}NH^+$ cation represents the most stable structure for this stechiometry

[1] H-W. Jochims et al. Chem. Phys. 298 (2004) 279.
[2] Š. Matejčík (unpublished results)

b- calculation not yet finished