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Reference: Short visit Grant EIPAM Beneficiary: Helga Dögg Flosadóttir, Raunvísindastofnun Háskóla Íslands, Reykjavík, Iceland Host: professor Paul Scheier, Institut für Ionenphysik und Angewandte Physik Period: 27.11.06-08.12.06, 12 days, Innsbruck, Austria Reference code: EIPAM 1530

SCIENTIFIC REPORT

Purpose of visit

The underlying processes and the mechanics of damage and repair of biological molecules such as DNA and proteins are subject to increasing interest in the research community. Interaction of ionizing radiation with living organisms is complex but one of the dominant mechanism in the induction of radiation damage is believed to be due to secondary electrons. It has been shown that low energy electrons (<20 eV) are able to induce substantial damage in various complex biomolecules. [1,2]

Dissociative electron attachment (DEA) to valine was recently studied experimentally in a crossed electron/molecule beam apparatus in the range from 0-14 eV. DEA to valine leads to the formation of fragments with the mass to charge ratio (m/Z): 116, 100, 72, 56, 45, 26 and 17. Most of these m/Z ratios may be assigned to more than one elemental composition and some may be formed through direct dissociation as well as through complex rearrangement. When comparing DEA to valine with DEA to glycine [1] and alanine [2] it is clear that this is also the case for the other two amino acids. They show similar fragmentation patterns where we see the m/Z that may not be unambigiously assigned from the current data. This is also the case for glycine and alanine wich show similar fragmentation patterns. Furthermore in many cases the origin of the fragments is not definite i.e., the question is open if some of the fragments are the result of metastable decay of mother fragments such as [M-H]⁻.

The purpose of the visit was to clarify these questions, first of all to unambiguously identify the elemental composition to be assigned to m/Z ratios where there were two or more possabilities. Second we planned to look at the metastable decay of major fragment ions to clarify the role of formation of secondary fragments.

Work carried out

During the period of the Short Term Visit the comprehensive study on the stability and exact composition of the anionic fragments of the aminoacid L-Valine was conducted. A high resolution double focusing sector field MS (mass resolution for anions up to 10000) was used for the experiment. Unimolecular fragmentation was studied with MS-MS techniques.

The electron energy scans of all the fragments (except for one) studied in Bratislava [3] were measured again at two different temperatures, 390 K and 400 K. These were the mass to charge ratios 17, 26, 45, 56, 100 and 116. In addition to these masses the mass to charge ratios 1, 16 (O- and NH₂- seperately), 44, 70 and 74 were also measured at these temperatures.

The m/Z ratios 16, 26 and 56 amu, wich may not unambiguously assigned to one molecular composition, were measured with high mass resolution. All of these have the possibility of at least 2 different chemical compositions. The mass 16 amu can possibly be O⁻ or NH₂⁻. We separated the mass peaks for O and NH2 and measured their electron energy scan. To clarify the elemental composition behind the m/Z 26 and 56 electron energy scans of were taken of individual components of their isotopic distribution. The isotope intensity of the fragments of masses 26 and the 56 amu and their electron energy resonances were measured since seperating the peaks seamed to be more complicated in those cases. These measurements show that the m/Z ratio 16 wich could clearly be seperated into O and NH2 wich both show distinct resonance profiles, however from those it is likely that the O contribution results from residual water. The m/Z 26 is composed of two elemental composition, CN and C₂H₂ wich both show distinct resonance profiles. From those only CN shows a low energy resonance as C_2H_2 is only formed at higher energies. The elemental composition of m/Z 56 could not be clarified.

The metastable decay of the most intensie anion, [V-H]⁻ was measured, within two different



timeframes wich bracket metastable decay in the first field free region and metastable decay in the second field free region of the double focusing sector field MS. The [V-H] was found to decay into two different fragments (m/Z 45 and m/Z 70 amu) [Figure 1].

It is interesting to note that there is an extra resonance at 7.4 eV for the metastable formation of 70 amu from [V-H]⁻ wich does not show at the [V-H] electron energy scans. This resonances intensity is about 14% of the intensity of the 5.3 eV resonsance also seen in the [V-H]⁻ but when the metastable decay is measured at shorter times (at the first field free region in the VG) this resonance increases in intensity relative to the lower one. up to 28%. When the m/Z 70 amu is measured directly as formed in the ion source the higher energy resonance amounts to the 37.5% of the lower energy resonance [Figure 2]. This shows that the higher energy resonance of the metastable decay is the faster one and also takes place in the ion source before extraction.

The metastable decay of $[V-H]^{-}$ leading to the formation to the m/Z 45 was only observed in the second field free region i.e. at longer delay times as no signal for metastable decay leading to the formation of 45 was seen from the fist field free region but 45 is observed with considerable intensity directly from the ion source we must conclude that there are two distinct processes leading to the m/Z 45 whereby the ion source formation must be attributed to the fragmentation of the transient molecular ion.



The electron energy scan of the m/Z 70 amu appearing from the ion source decay, first field free region and the metastable decay

There appeared so many questions and so many interesting things in the L-Valine that measurements are still being conducted by Stephan Denifl, Institut für Ionenphysik und Angewandte Physik in Innsbruck working for Paul Scheier. These include Collission Induced Dissociation, Metastable Decay, as well as further verification of elemental composition of individual m/Z ratios. As next steps we plan to measure alanine and glycine and to get a better overview of the processes, similar resonances or fragmentation pathways and other important features of the most basic aminoacids. Complementary to the studies conducted in Innsbruck we carry out Metastable Decay and Collission Induced Dissociation exeriments on the same amino acids by Laser Disorption Ionisation. This is important in order to understand any fragmentation in bigger

biomolecules such as proteins and peptides that use peptide bonds as the main backbone.

Collaborations

Collaboration in the field of charge induced fragmentation on biochemicali relevant molecules has now been established between Prof. Paul Scheier, Institut für Ionenphysik und Angewandte Physik, Leopold-Franzens-Universität Innsbruck, Austria, and Prof. Oddur Ingólfsson, Science Institute, University of Iceland, Reykjavík, Iceland

Publications

A publication of the results during this visit is in preparation. Oral presentation will be given at the University of Iceland and conference contribution in oral or poster form might result from this work.

Citations

[1] Gohlke S. et al. Journal of Chemical Physics 116 (23) 10164-10169 (2002)

[2] Ptasinska S. et al. Chemical Physics Letters, 403 (1-3): 107-112 (2005)

[3] Transient negative ions of valine; formation and decay, J. Kočíšek, D. Kubala, M. Stano, Š. Matejčík and Ingolfsson