Scientific Report about the short term visit COST-STSM-P9-03139

The present studies aim to better understand electron-capture induced fragmentation processes occurring after collisions of complex molecules with a Cs vapour, which means processes which are induced by the capture of 'quasi-free' electrons. This type of experiments has been performed, although we did not apply the so-called FAIMS technique, as originally planned, as experimental difficulties prevailed a successful run during the short visiting period. Instead, the performed experiments have concentrated on

1. the formation of positive and negative fragments in collisions of protonated nucleobases with Cs.
2. the competition between different fragmentation channels, when protonated dipeptides collide with Cs-vapour and capture electrons.

Ad 1): The fragmentation of neutral nucleobases by ion and electron impact has been studied by several groups. Particularly in the latter case, the formation of negative fragments has been analysed at low electron energies by the Innsbruck group. In the present case, we start out with the protonated system (singly positively charged ions), thus requiring the capture of two electrons (in subsequent collisions) in order to form negative fragments. After the first capture process a neutral system is formed which might decay in a fast process or which might be metastable. In the second collision either the still intact molecule or the fragments may capture the second electron. Here the lifetime of the intermediate neutral system and the average time between two collisions is important. Indeed we have measured the distribution of negative fragments for the different nucleobases. We hope to get some insight into the mechanisms and the statistical and prompt decay processes by a detailed comparison of the obtained fragment spectra with the Innsbruck results. The analysis of the data is going on.

Ad2): Concerning the fragmentation of a dipeptide, we have studied protonated glycine-alanine, either in its isolated form or nanosolvated in a small number of different solvent molecules (water, methanol, acetonitril or crown ether). The dominant fragmentation processes concern the loss of an H-atom, of ammonia or the formation of c- or z-ions. The latter process corresponds to the cleavage of the N-C_α bond and requires either the electron capture close to this bond or the migration of an H-atom from the ammonium group towards this bond. We have measured the ratio of two channels, namely the loss of ammonia and the formation of the z-ion, as a function of the number of solvent molecules. It turned out that this ratio increases strongly when one water molecule is attached, it increases further when this number is increased and reaches finally a saturation after further adding of water molecules. This effect is similar in the case of a methanol solvent. However, when adding one molecule of CH_3CN, the measured ratio does not change essentially. These phenomena are tentatively interpreted as a change of the conformation of the dipeptide when a solvent molecule is added. This change of conformation is expected to be different for different solvents. In order to support this hypothesis, calculations of the geometry are on the way, based on the use of the Gaussian package. Basically, our technique allows us to address the conformation of the peptide cation from the fragmentation pattern after double electron capture.

Aarhus, 28th of September 2007

B.A. Huber

I herewith certify that these experiments have been performed at the ELISA-facility of the Department for Physics and Astronomy of the University of Aarhus within the STSM project.

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