Scientific report of the visitor including the host report

Concerning the STSM action, COST P9:

Reference Code : COST-STSM-P9-01416 / 01417

A) Purpose of the visit:

It was the aim of this short-term visit (5 days, from 21st to 25th of November 2005) to perform common experiments at the ELISA facility concerning the fragmentation of isolated and 'solvated' dipeptides, to hold scientific seminars, to discuss results obtained during and before our stay and to prepare their publication.

Scientists from 3 different laboratories have been present:

S. Brøndsted-Nielsen, Alex Streletskiy, Anne Holm and P. Hvelplund - University of Aarhus, Denmark,
P. Reinhed, H.T. Schmidt, H. Zettergren and H. Cederquist - Stockholm University, Sweden,
B. Manil, J. Rangama and B.A. Huber - CIRIL, Caen, France.

B) Description of the work and of some of the results

1) The main objective of the present experimental studies was to clarify the mechanisms provoking the C-N peptide bond cleavage in a doubly protonated dipeptide leading to the formation of the z-ion after electron capture. In the present case, we studied collisions of the doubly protonated Alanine-Lysine dipeptide ($AK\text{-}2H^+$) with sodium atoms as well as with other target gases at collision energies between 10 and 70 keV. A schematic view of the reaction is shown in Figure 1. Different mechanisms have been proposed in order to explain the C-N bond cleavage. For example, the capture of a low-energy electron to one of the NH_3^+-groups, may be followed by the migration of the formed H-atom towards the central O-atom forming OH, which will weaken the C-N peptide bond and thus cause fragmentation. Or, a direct capture to the O-atom, forming an O^- ion, may induce a similar effect.
   In order to test these theoretical predictions, different experiments have been performed. On the one hand, we changed the environment of the ammonium group to which electron capture is supposed to occur. This 'solvation' was obtained by adding 1 or 2 crown ethers to the dipeptide (see Figure 2) at both ends covering the NH_3^+ group. This 'solvation' should have a strong influence on the migration of the H-atom. On the other hand we changed the conditions for electron capture by varying the kinetic energy of the projectile and the nature of the target (Na, Ne, Xe, …). In particular, in the Ne-case, electron capture should be strongly suppressed and only collision-induced reactions are expected.
   In Fig.3 a typical mass spectrum is shown, identifying as dominant fragmentation peaks: the loss of an hydrogen atoms $[AK+H]^+$, the loss of the NH_3 group [AK+H]-

NH_3^+ and the C-N bond cleavage (formation of the z-ion). Some preliminary results, shown in Figure 4, demonstrate that the relative probabilities for these channels depend on the fact whether crown ethers are attached or not.
At present a more detailed analysis of these data is performed, including the results obtained at different collision energies and with different target gases. From the ensemble of the measured spectra we hope to clarify the mechanism causing the specific fragmentation: the cleavage of the C-N peptide bond.

2) During our stay, in addition to daily meetings on the actually performed experiments, two seminars have been organised. The first talk was given by S. Broendsted-Nielsen describing the properties of multi-peptides and bond cleavages; the second one by H. Zettergren, concentrating on the electrical properties of clusters of fullerenes and the multi-ionisation of fullerenes dimers by highly charged ions.

3) Furthermore, results obtained earlier on the fragmentation of isolated and nano-solvated AMP^- anions (see COST action P9- 00445/00446 in 2004) have been rediscussed and a manuscript has been prepared to be submitted for publication (Title: 'Collision induced dissociation of isolated and nano-solvated AMP^- anions').

4) Concerning future collaborations, we agreed with the Aarhus group to develop a new electrospray ion source which will be installed at CIRIL in Caen. This modified source will allow us to study the neutral particles emitted from the ESI ion source and to prepare charged clusters of larger biomolecules by applying a gas aggregation technique.

The collaboration between the three groups is expected to continue in 2006, also profiting from the European Infrastructure Network ITS LEIF.

Caen, 28.11.05

For the visitors: Bernd A. Huber

For the host institution:

I herewith confirm the above report, concerning the given dates as well as the performed experiments. The obtained experimental data are still under analysis and the results will be prepared for publication in the near future.

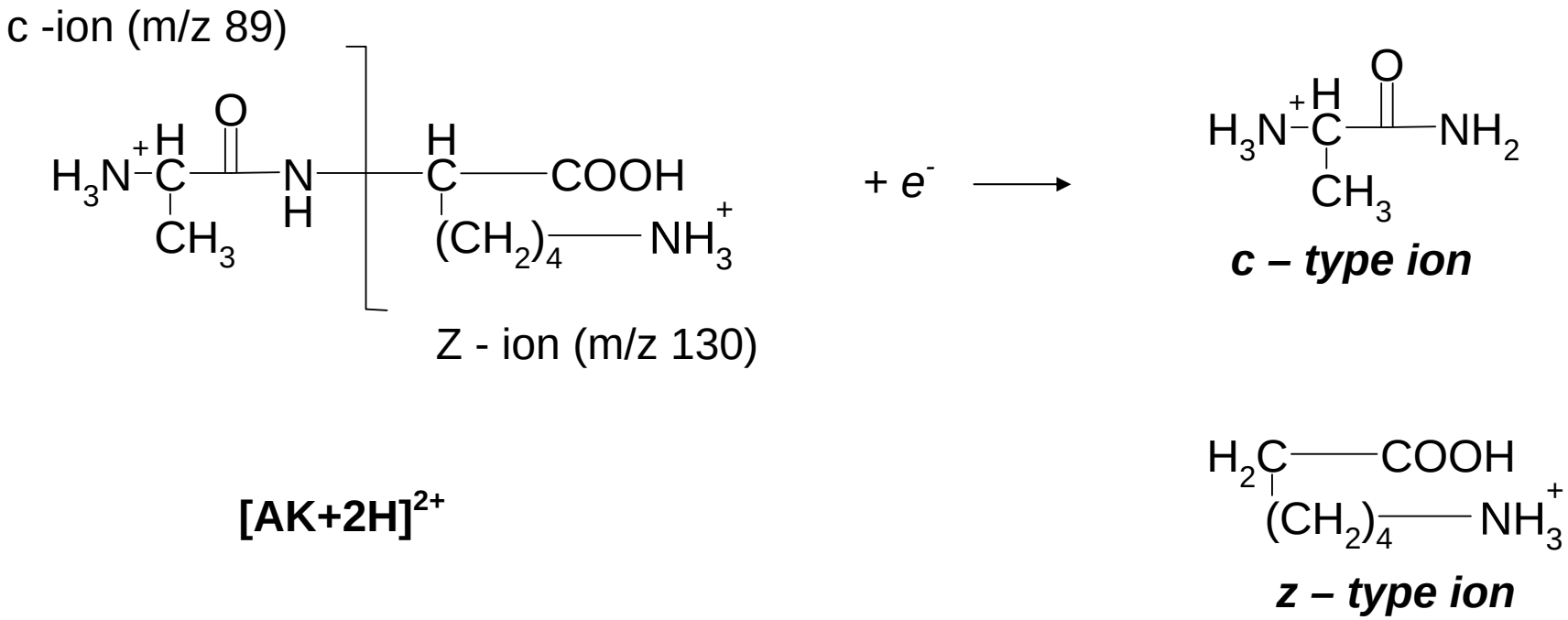
Aarhus, 28th of November 2005

Preben Hvelplund

Figure 1:

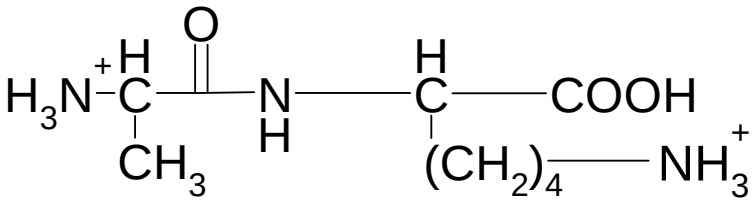
« C-N » peptide bond cleavage

Sample: Ala-Lys (AK)

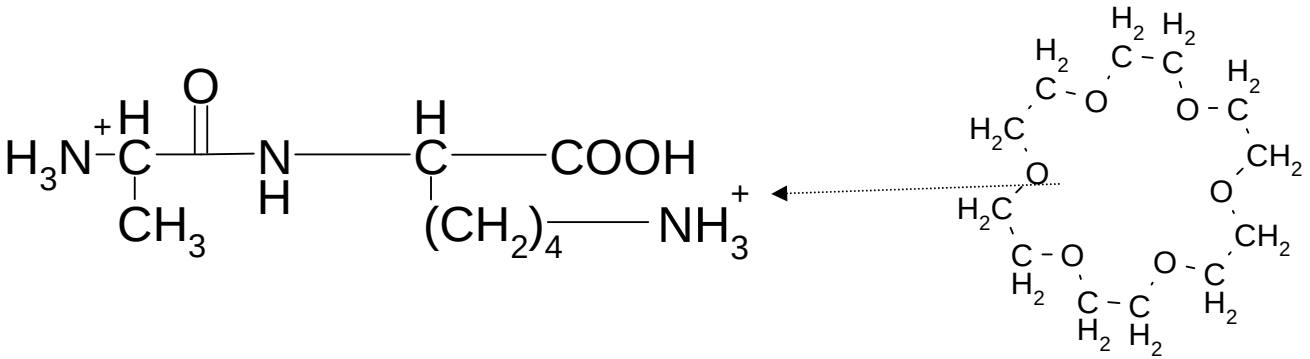


[AK+2H]$^{2+}$

1



2



3

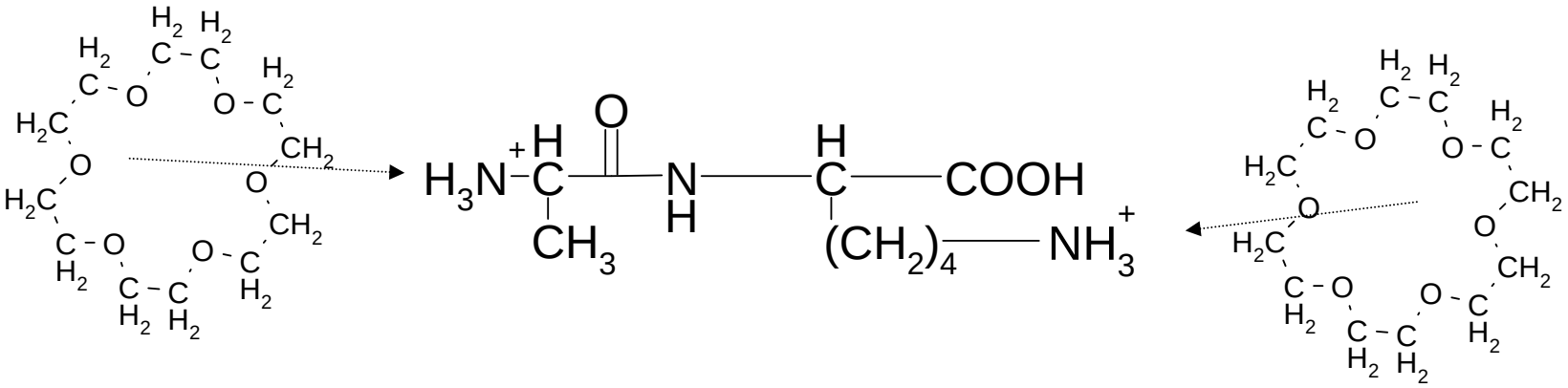


Figure 2

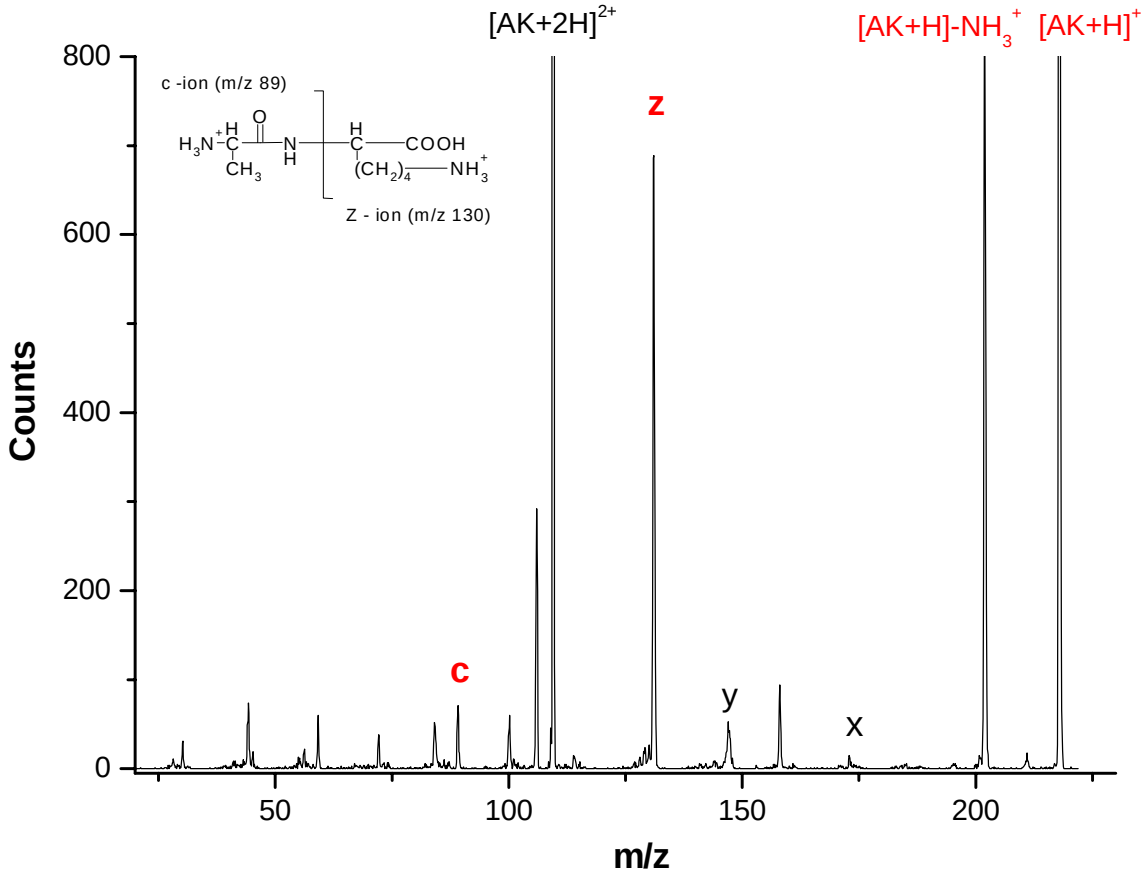


Figure 3

Probability of N-C_α cleavage = Int (z)/ Σ (Int(z, c, $[AK+H]^+$, $[AK+H-NH_3]^+$)

Probability of H loss = Int ($[AK+H]^+$)/ Ó (Int(z, c, $[AK+H]^+$, $[AK+H-NH_3]^+$)

Probability of NH_3 loss = Int ($[AK+H-NH_3]^+$)/ Ó (Int(z, c, $[AK+H]^+$, $[AK+H-NH_3]^+$)

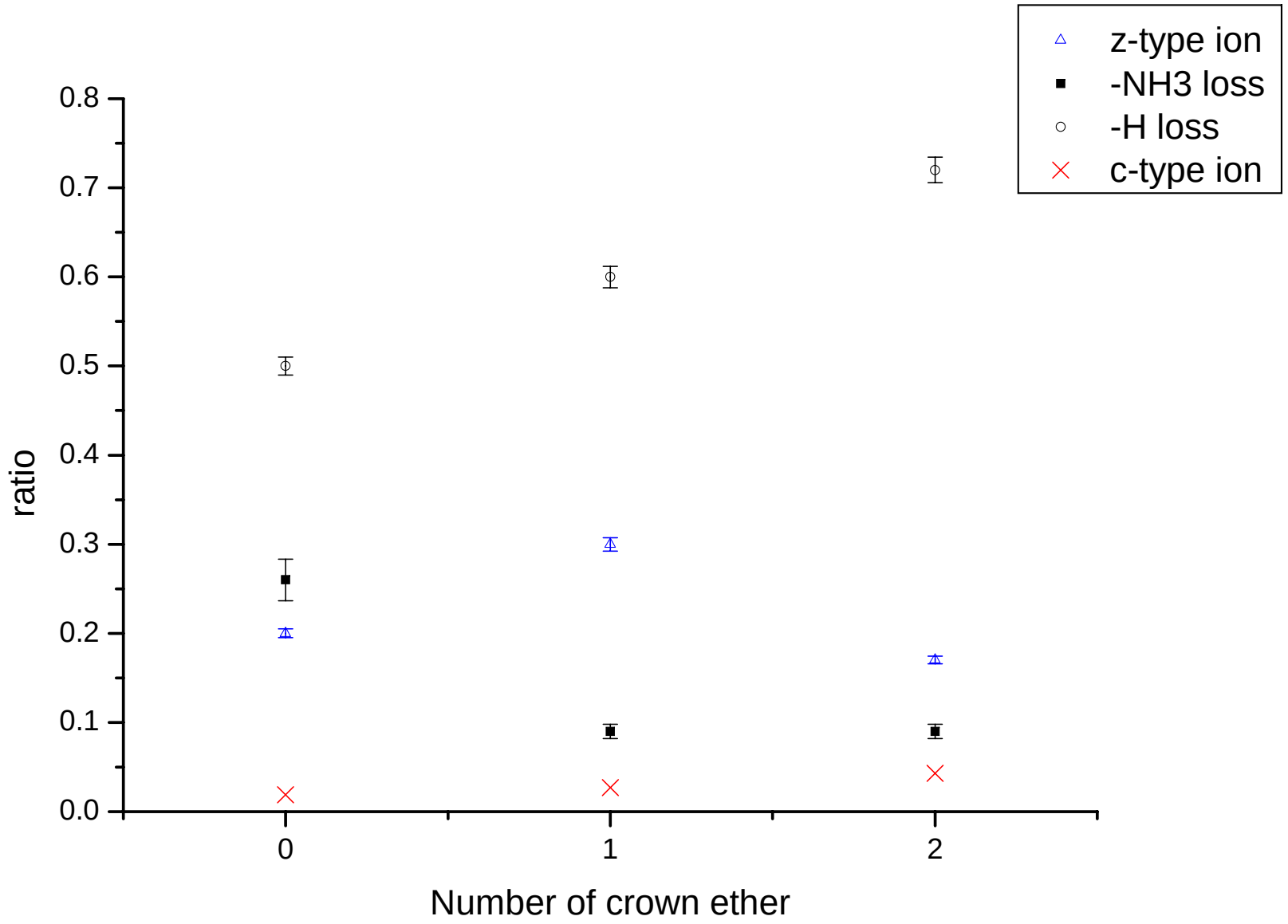

z-type ion
-NH3 loss
-H loss
c-type ion
ratio
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
1
2
Number of crown ether

Figure 4