Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA20129 MultiChem

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Details of the STSM

Title: Electron collisions with sulfamic acid: positive ion formation

Start and end date: 30/09/2024 to 04/10/2024

Description of the work carried out during the STSM

In this STSM, we investigated electron – induced dissociation of aminomethanesulfonic acid (AMS) via electron ionisation at the electron energy of 70 eV. Ionisation energies, as well as appearance energies of prominent cations are planned to be unveiled by scanning the electron energy near the threshold.

Experiments were conducted in a crossed beam set-up, installed in the CEFITEC (Centro de Física e Investigação Tecnológica – Centre of Physics and Technological research) laboratory. The apparatus consists of a trochoidal electron monochromator (TEM), a resistively heated oven, an ion guide coupled into an orthogonal time-of-flight mass spectrometer. The TEM is responsible for generating a nearly mono-energetic electron beam whereas the molecular beam is produced by sublimating a solid sample in the heated oven. Product ions generated by collisions between electrons and gas-phase molecules are extracted towards the ion guide, then to the time-of-flight extraction region, and finally detected by the MCP (microchannel plate) detectors.

Before taking measurements, the first crucial step is optimisation, in order to ensure that the apparatus is being operated at optimum performance. During optimisation, argon rare gas was employed to validate sensitivity of the machine and mass resolution of the time-of-flight mass spectrometer. On the other hand, sulphur hexafluoride (SF_6) which generates more fragments under the impact of electron ionisation was also employed to calibrate the mass spectra and avoid the effects of mass discrimination.

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

We filled the sublimation oven with the commercially purchased AMS sample, background pressures of the collision chamber and the time-of-flight chamber were at about 10^{-7} mbar and 10^{-8} mbar, respectively. We heated the sample in order to obtain sufficient AMS vapour meanwhile avoiding thermal decomposition. The heating temperature was stabilised at 130°C, we recorded electron ionisation spectra of AMS at the 70eV electron energy. Prominent fragments induced by electron impact ionisation of the AMS molecule were observed, as indicated in Figure. 01. We determined appearance energies for fragments of interest, by performing energy scans near the threshold and fitting to the Wannier function. For the appearance energy measurements, energy scale of positive ions was calibrated using argon rare gas, with the well-known Ar^+ threshold energy at 15.763 eV [1].

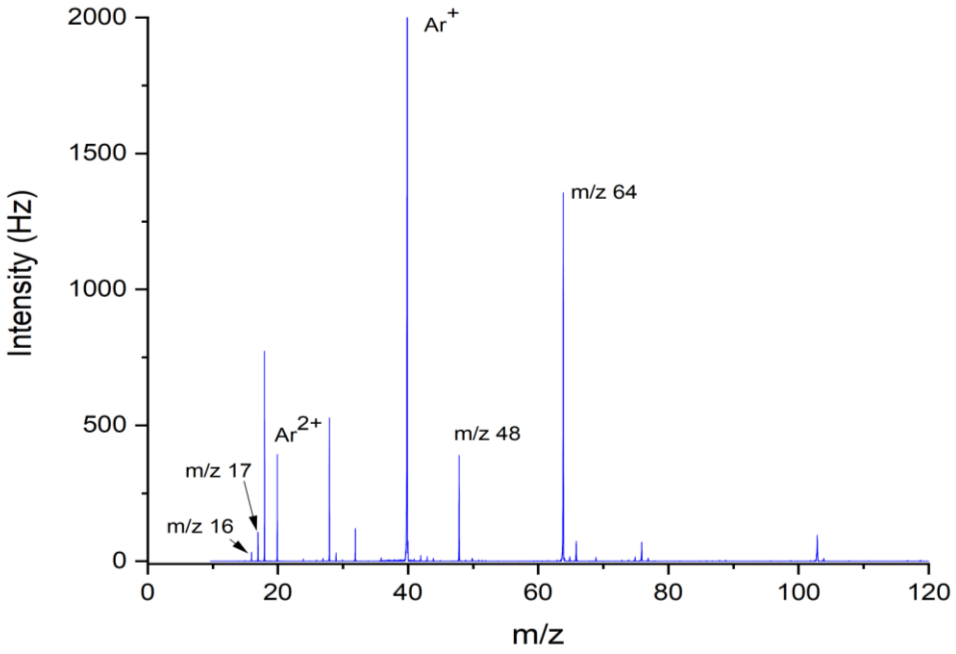

Figure 01. AMS electron ionisation spectrum recorded at the 70 eV electron energy.

References:

[1] Weitzel, K.-M.; Mahnert, J.; Penno, M., *ZEKE-PEPICO investigations of dissociation energies in ionic reactions*, **Chem. Phys. Lett.**, 1994, 224, 371.

Description of the STSM main achievements and planned follow-up activities

Figure.01 illustrates the electron ionisation (EI) spectrum of AMS molecule (with argon gas being used for energy calibration purpose, resulting in Ar^+ m/z 40 and Ar^{2+} m/z 20 peaks) at the 70 eV electron energy. As can be seen, there is no observation of parent cation at m/z 111, exhibiting strong agreement with the EI spectrum of AMS molecule available on the NIST webpage [2].

The most intense cation generated by electron ionisation of AMS molecule is assigned to SO^{2+} at m/z 64, followed by the second most abundant fragment at m/z 48 with a further neutral loss of one oxygen, forming the SO^+ cation.

The m/z 48 peak could also be the O_3^+ cation. Cleavage of the OH group directly from the precursors leads to the formation of the OH^+ cation at m/z 17, which is also considered as a prominent fragment in the EI spectrum of AMS. Similarly, product cation observed at m/z 16 can be assigned to either the cleavage of the NH_2 group or to a single loss of an oxygen molecule, resulting in the NH_2^+ or O^+ cations, respectively. According to the molecular structure of AMS, other fragments of interest could be S^+ or O_2^+ at m/z 32 and CO^+ at m/z 28. However, air molecules in the gas line might also contribute to the aforementioned peaks.

We performed near–threshold energy scans and Wannier fits for all prominent fragments in order to determine appearance energies experimentally. Fitting procedure is carried out with the help of integrated Python software developed at the CEFITEC laboratory. Figure. 02 and Figure. 03 illustrate the ionisation efficiency curves of the AMS fragments. Experimental data are depicted as blue dots, whereas the green dashed line represents the Wannier fitting curve. Experimental appearance energies of AMS fragments are summarised in the Table. 01.

The STSM has investigated the fragmentation mechanisms of gas-phase aminomethanesulfonic acid in isolated conditions and appearance energies of prominent fragments experimentally, thereby contributing to a deeper understanding on basic reactions of the AMS molecule under electron collisions. As a followed step of this STSM, for a better understanding as well as a stronger connection between two laboratories, interaction experiments between electrons and hydrated AMS clusters are planned to be performed at the Innsbruck group. On the other hand, we are planning to draft scientific articles from the results of this STSM: electron-driven fragmentation of AMS molecules with the formation of positive ions, and those of the upcoming cluster measurements. Publications are expected to be submitted by the end of the year.

Cation	m/z	Experimental appearance energy (eV)
SO_2^+	64	12.85 ± 0.11
SO^+/ O_3^+	48	16.33 ± 0.10
OH^+	17	11.20 ± 0.10
NH_2^+ / O^+	16	17.00 ± 0.13

Table 01. List of prominent fragments generated by electron collisions with AMS molecules via electron ionisation mechanism and their experimental appearance energies.

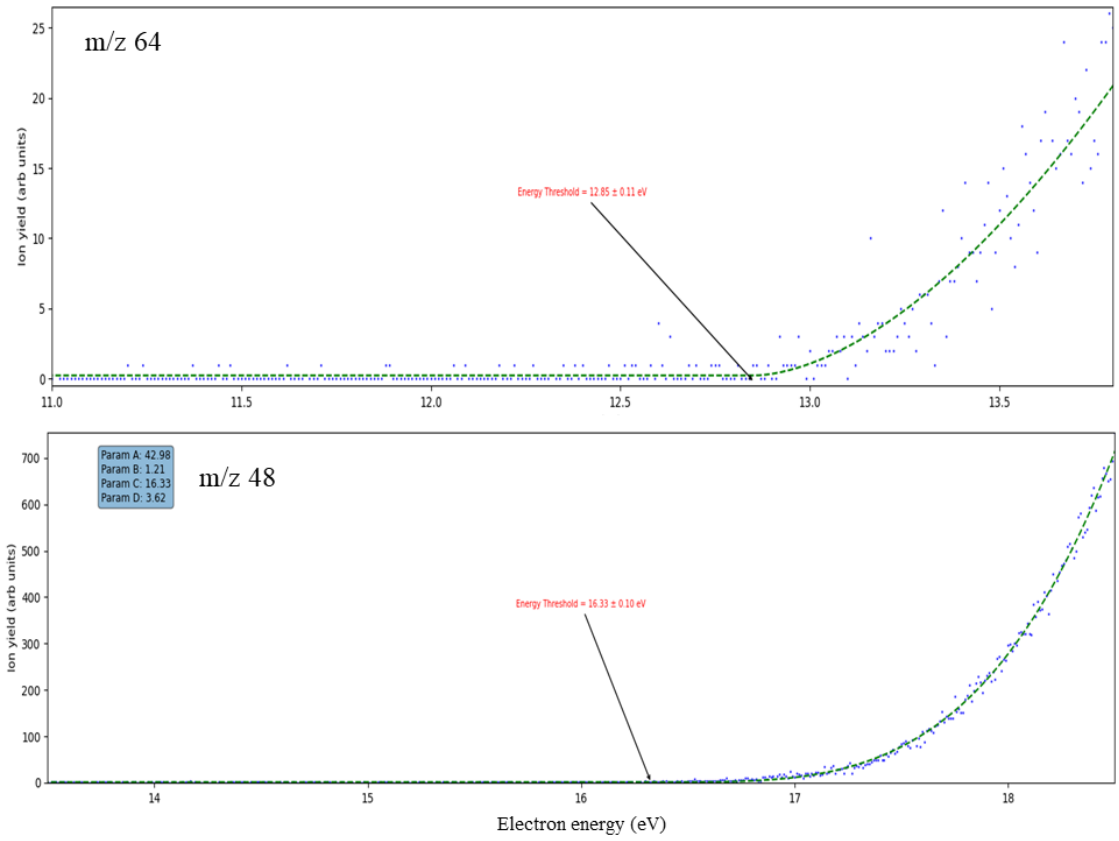

Figure 02. Experimental threshold energies for prominent fragments at m/z 64 and m/z 48.

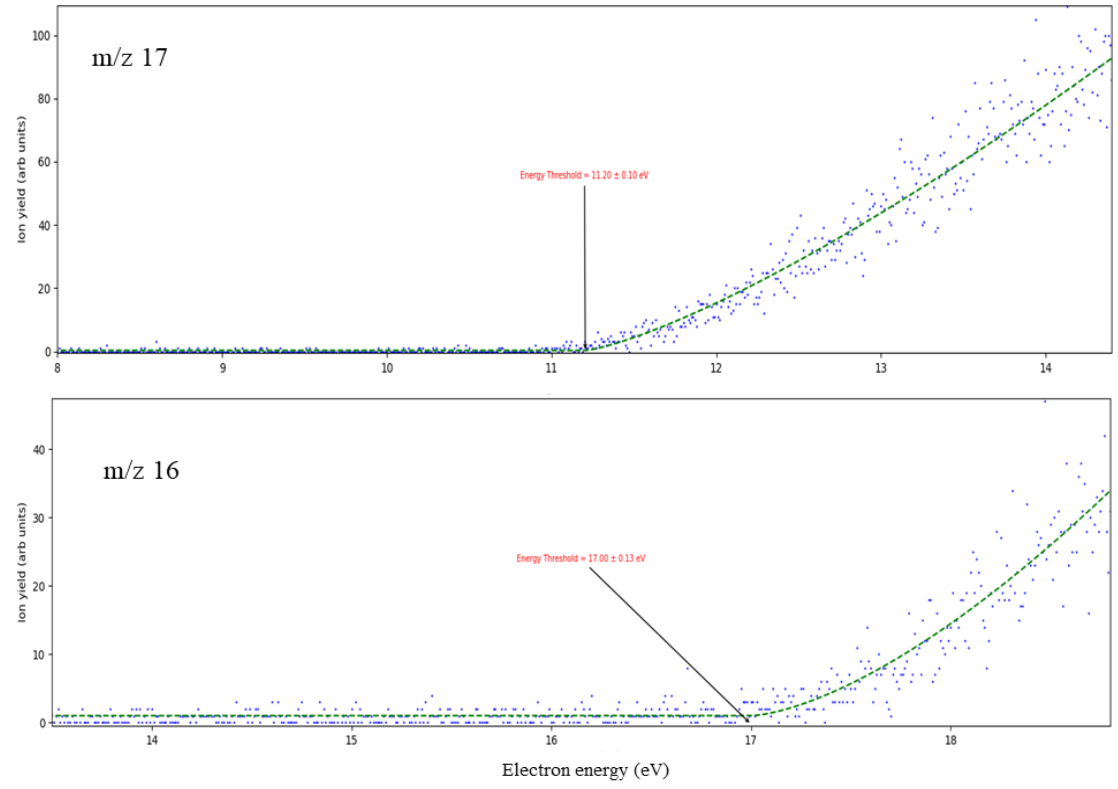

Figure 03. Experimental threshold energies for prominent fragments at m/z 17 and m/z 16.

References:

[2] Aminomethanesulfonic acid (nist.gov)