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

Action number: CA 21126

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Details of the STSM

Title: **IR action scpectroscopy of the astrochemically-relevant HCCS+ and H2CCS+ ions**

Start and end date: 07/05/2023 to 12/05/2023

Description of the work carried out during the STSM

The experiments (IR-action spectroscopy of $HCCS^+$ and H_2CCS^+ ions) were carried out at the FELIX Laboratory in Nijmegen (NL) by using 22-pole FELion cold ion trap. We aimed to generate $HCCS^+$ via the dissociative electron impact (EI) ionization of both thiophene (c-C_4H_4S) and 2,5-dibromothiophene (c-$C_4H_2Br_2S$). The rationale for looking to generate $HCCS^+$ from two different precursors is that, while the fragmentation of the non-halogenated thiophene is also expected to lead to the formation of an intense m/z 58 ion (H_2CCS^+), its larger vapour pressure makes it a more widely applicable potential source for future reactivity studies.

Though no isomers of $[C_2H_2S]^+$ have yet been detected in the ISM, neutral H_2CCS has recently been identified. We therefore aimed to collect the vibrational spectra of the m/z 58 ions formed from the dissociative ionization of thiophene, as this would allow for an identification of the $[C_2H_2S]^+$ isomers present, potential observation of these ions on the basis of their IR spectra and, should only one isomer be detected, identification of a method of ion generation for future reactivity studies.

Finally, we also planned to generate $HCCS^+$ through the reaction of S^+ with C_2H_2 in order to compare the spectrum of the ion generated from this reaction with that formed by dissociative ionization of the cyclic precursors. This would not only allow us to confirm the assignment of the m/z 57 product of this reaction to $HCCS^+$ but also to determine whether ions formed in this way are exclusively in the ground triplet state or if there is some contribution from the low-lying singlet excited state.

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

[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.

$HCCS^+$ and $[C_2H_2S]^+$ ions were efficiently produced via dissociative ionization of 2,5-dibromothiophene and thiophene respectively. Although Ne-tagging was attempted, this proved to be highly inefficient (this might have been a technical problem or a result of the low binding-energy of the target ions) and so we instead tagged both species with H_2.

For the $HCCS^+$ ions, IR-PD scans of the H_2-tagged m/z 59 complexes were performed in the 515-945 cm^{-1}. From this, we observe a single main feature at 593 cm^{-1}, which we assign to the C-C-S bending mode predicted at 607 cm^{-1} line in the calculated spectrum of the ground state. From depletion measurements, we infer that 80% of the tagged ions correspond to the ground state. However, due to time lost due to FEL-2 instability, we were unable to scan the higher wavenumber region.

For the $[C_2H_2S]^+$ ions, IR-PD scans of the H_2-tagged m/z 60 complexes were performed in the 325-450 and 740-1790 cm^{-1} regions. From this, we observe four primary features at 341, 843, 871, 1362 and 1560 cm^{-1} as well as a potential further feature at 984 cm^{-1}. However, due to time constraints we were unable to get sufficient signal-to-noise of the region covering the main bands for a clear assignment, with the higher wavenumber region also not being probed despite computed bands for the main isomer occurring at 3163 and 3285 cm^{-1}.

As a conclusion and on the basis of the results obtained so far, these investigations promisingly allow for boosting the knowledge of C-based, S-bearing molecular species in space. Even if still under analysis, the spectroscopic data collected will then give room to the study of the reactivity of such species in space, that could result in different channels also giving carbonaceous materials as products. With new ongoing plans on future measurements involving different systems (e.g. CCS^+), this mission definitely contributed to promote the creation of interdisciplinary research teams to develop future laboratory experiments that will probe the formation, spectroscopy and reactivity of nC.