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

Action number: CA21126

Grantee name: Vincent Richardson

Details of the STSM

Title: Formation of aromatic hydrocarbons through low energy ion-molecule reactions

Description of the work carried out during the STSM

Description of the activities carried out during the STSM. Any deviations from the initial working plan shall also be described in this section.

This STSM involved a two-week research trip to the NanoBio Physics group at the University of Innsbruck to perform mass spectrometry and IR spectroscopic measurements. These measurements focused on characterizing the products formed by ion-molecule reactions within helium nanodroplets (HNDs), which have been suggested as an effective facsimile for the conditions present on the surface of astrochemical ice and dust grains. While a range of experimental approaches have been developed to study the bulk processing of astrochemical ices (by photons, electrons, and ions), the reactivity of low-energy ions with ices has avoided detailed experimental investigation despite being highlighted as a subject of significant interest by theoreticians.

The first set of measurements investigated the formation of the benzene cation inside ionized HNDs containing different mixtures of C_2H_2 and H_2O. In a previous study [10.1021/jacs.6c04278], we demonstrated that the benzene cation can form efficiently inside HNDs following the sequential addition of C_2H_2. However, as astrochemical ices are rarely mono-component, we wanted to investigate whether the addition of H_2O inhibited this process. Mass and IR spectra of relevant ions were therefore recorded for different ratio mixtures of C_2H_2:H_2O, with the impact of simultaneous vs sequential addition also explored.

The second set of measurements involved a series of preparatory test measurements towards the ultimate goal of being able to obtain kinetics parameters for reactions within HNDs. This involved the recording of mass spectra for a range of different reaction systems (including systems where no reaction is expected) and at a range of different pressures. The goal of these measurements is to determine the impact of mass, dipole moment, and polarizability on the rates of both droplet evaporation and reactant complex formation. Finally, as we had additional time left, we also performed a set of measurements on

[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 Grant Holder Manager to verify the grant documents compliance and proceed with the payment.

the reaction of C_{70}^+ with H_2O, with a particular focus on potential $C_{70}O^+$ and $C_{70}OH^+$ products. These ions were formed through sequential pick-up and again probed through both mass spectrometry and IR action spectroscopy.

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

Description and assessment of whether the STSM achieved its planned goals and expected outcomes, including specific contribution to Action objective and deliverables, or publications resulting from the STSM. Agreed plans for future follow-up collaborations shall also be described in this section.

Regarding the first set of measurements, we recorded a series of mass of mass spectra of C_2H_2:H_2O mixtures with water fractions ranging from 5%-50%. As the water fraction increased, the relative population of acetylene complexes/hydrocarbon ions decreased sharply, with the mass spectra at the higher water fractions dominated by water solvation. An example of the change in mass spectrum between two different water fractions can be seen in Fig. 1.

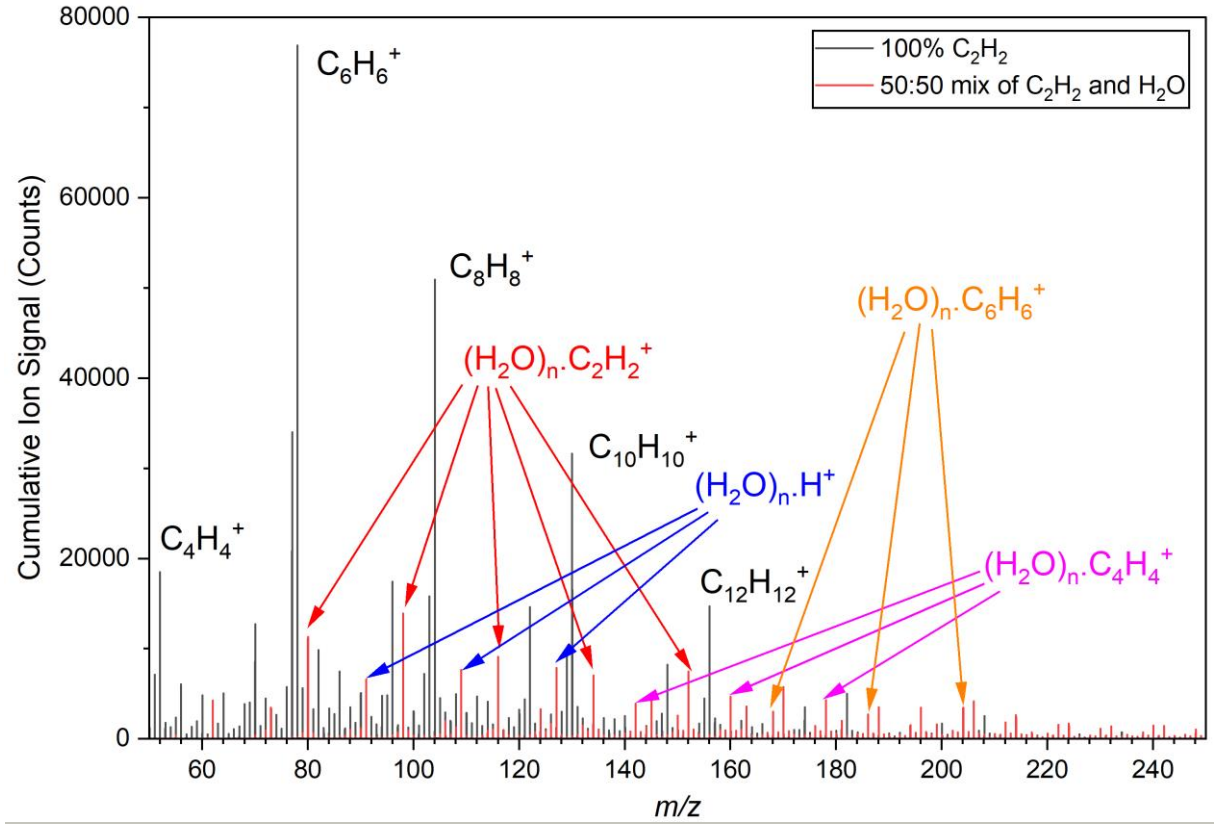


Fig. 1: Mass spectra of the ions formed following pick-up of two different C_2H_2:H_2O mixtures by ionized HNDs.

IR spectra of the $[C_4H_4]^+$ and $[C_6H_6]^+$ ions formed were recorded in the 760-1400 cm^{-1} region, in good agreement observed with the spectrum recorded previously for the $[C_4H_4]^+$ ions formed from a pure C_2H_2 sample. However, the lack of extensive IR features in this region for either of these ions makes conclusive identification challenging. Further measurements with a UV/VIS laser system are planned, where extensive characteristic lines have been observed for both $[C_4H_4]^+$ and $[C_6H_6]^+$ previously. Long-term, further measurement will explore the impact of additional common components of interstellar ice (e.g. CO).

Mass spectra were recorded as a function of pressure in the $5E^{-9}$-$2E^{-7}$ mbar range following the sequential addition of two reactants at two different pressures for seven different reaction systems. This

is to explore the impact of mass, complex binding energy, dipole moment, and polarizability on the rates at which species accumulate around charge centres and at which solvated ions are lost during transmission through the instrument. Characterization of these effects is required to determine the distribution of chemical environments under which reactions occur, the first step toward a kinetic description. Analysis of these results is underway. The long-term goal is to combine the results from these characterization measurements with the reactivity studies described above to enable the effective modelling of low-energy ion-neutral reactivity on astrochemical dust and ice grains.

Finally, while $C_{70}OH^+$ and $C_{70}O^+$ ions were observed in the mass spectra following the sequential addition of C_{70} and H_2O to ionized HNDs, with corresponding IR spectra recorded in the same range as earlier, no intense spectroscopic features were observed. While some minor features were noted, the comparatively low intensity of the product peaks and the available laser power in the relevant region led to very poor signal-to-noise levels. While the efficient formation of $C_{60}OH^+$ from the reaction of C_{60}^+ with H_2O has been noted previously [https://doi.org/10.1021/acs.jpca.2c01329], either the equivalent reaction with C_{70}^+ is significantly less efficient or such pathways are suppressed under the reaction conditions present within HNDs.

Two primary aims of the NanoSpace COST action are: *What are the chemical pathways that lead to their formation and destruction?* And *What nanocarbon species are present in space and how can we identify them?* The measurements performed as part of this STSM directly address these questions, both by exploring potential mechanisms for polyaromatic hydrocarbon formation on interstellar dust and ice, and by recording reference ion spectra that can employed for astronomical observations.