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

Action number: CA21126

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Details of the STSM

Title: Deuteration effects in bond forming reactions of [CH2O] + radical cation isomers

Start and end date: 03/05/2026 to 09/05/2026

Description of the work carried out during the STSM

The aim of this STSM was to obtain detailed measurements of the gas-phase chemistry of the isomeric ions H_2CO^+ and $DCOH^+$ with various astrochemically relevant neutral species, including a range of both saturated and unsaturated hydrocarbons. These measurements were performed using the CERISES experiment at the DESIRS VUV beamline at the French synchrotron SOLEIL. CERISES is a guided ion beam tandem mass spectrometer where ions are generated using the tuneable VUV light. This configuration is therefore able to measure absolute reaction cross-sections as function of both the collision energy and the energy of the ionising photon (a proxy for the internal energy of the reactant ions). Importantly, control over the photon energy also enables the targeting of specific dissociative ionization pathways leading to astrochemical ions of interest that lack stable neutral equivalents.

In total, 19 reactions were studied: C_3H_8, C_3D_8, C_3H_6, C_2D_6, NH_3, and H_2O with both H_2CO^+/$DCOH^+$; CH_4 with H_2CO^+; C_2H_2, CD_4, and H_2 with $DCOH^+$; Kr with Ar^+; CH_3OH with $HCNH_2^+$; and CH_3OH with $^{12}C^+$. Full analysis of this data is still underway, but preliminary analysis has already yielded some interesting results, with a couple of highlights detailed here.

The first highlights are the differences and similarities observed when comparing the reactivity of isotopologues. In some cases, such as the reaction of $DCOH^+$ with C_2H_6, this has allowed the identification of a proton transfer product that was previously hidden under the parent ion signal. In others, such as the reaction between $DCOH^+$ and CD_4, we observed a positive kinetic isotope effect in the hydrogen atom transfer channel compared to previous measurements on the reaction with CH_4 – that is that the H atom transfer reaction $DCOH^+ + CH_4 \rightarrow DHCOH^+ + CH_3$ proceeds faster than the corresponding D atom transfer reaction. Additionally, we also observed D/H scrambling between the CD_4 deuteriums and OH hydrogen that was not visible previously, particularly at low collision energies. Finally, we note that reactions involving the larger hydrocarbons C_2H_2, C_2D_6, C_3H_6, C_3H_8, and C_3D_8 all resulted in products that involved C-C bond formation, potentially contributing to the build-up in chemical complexity in interstellar environments.

[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 other highlight was the observation that the reactions of H_2CO^+/$DCOH^+$ with NH_3 produced products corresponding to the formation of protonated formamide $[HC(O)NH_2H]^+$, an important prebiotic precursor to many organic compounds. Further, as with most of the reaction systems, we observed a significant difference between the reactivity of the two isomeric ions with NH_3. For the reaction of $DCOH^+$ with NH_3, the formation of protonated formamide was a much more significant pathway compared to the reaction of H_2CO^+ isomer, with an absolute cross-section of 7.096 ± 0.658 $Å^2$ compared to 0.331 ± 0.08 $Å^2$ (both at low photon energy and collision energy E_{cm} = 0.13 eV) . This observation is not only important for the modelling of the formation of interstellar formamide, but also highlights the limitations of treating ions as point charges (as is the case in capture models).

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

This STSM has successfully achieved its planned goal of conducting experiments to record detailed reactivity measurements of absolute cross-sections as functions of both collision energy and photon energy. The successful measurements with deuterated isotopologues have already allowed for preliminary comparison of the differences in reactivity induced by this isotopic substitution. Once fully analysed, we hope this data can not only be used to describe the reactivity of these isomeric ions in chemical network models, but also, in combination with previous data, can be used to explore potential capture modelling approaches that go beyond the treatment of ions as point charges.

These results directly address the key scientific challenges highlighted by the *NanoSpace* COST action, namely "*what is the role of nanocarbon species in non-terrestrial environments…in cosmic and prebiotic chemistry*" and "*what are the chemical pathways that lead to their [nanocarbon species] formation and destruction*". Not only have we observed pathways with the potential to contribute to the formation of protonated formamide in non-terrestrial environments, namely the reactions of H_2CO^+/$DCOH^+$ with NH_3, but we have also observed a range of pathways involving the formation of C-C and C-O bonds, thereby contributing to the build-up of increasingly complex hydrocarbon and O-containing hydrocarbon species. .

Manuscripts for the data recorded during this project are underway with computational potential energy surface calculations planned to facilitate the interpretation of the experimental data.

Personally, I have gained experience working with state-of-the-art equipment and techniques at the SOLEIL facility in collaboration with an international and interdisciplinary team. This STSM has provided me with the opportunity to develop new skills as I was able to take measurements at a beamline facility for the first time. This research has excited and inspired me and I am keen to be involved in more projects of this nature in the future.