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

Action number: CA21126

Grantee name: Alice Frustaci

Details of the STSM

Title: **Isomer Specific Reactivity of the Astrochemically Relevant Ions $H_2CO^{+\cdot}$ and $HCOH^{+\cdot}$**

Description of the work carried out during the STSM

During the STSM, the experimental campaign at the VUV beamline DESIRS of the SOLEIL Synchrotron Radiation facility (France) was focused on the experimental study of ion-molecule reactions involving the isomeric ions $H_2CO^{+\cdot}$ and $HCOH^{+\cdot}$ (in the form of the D-labelled species $DCOH^{+\cdot}$) with astrochemically relevant hydrocarbons and species containing O and N atoms. Measurements have been performed using the CERISES apparatus, a tandem guided ion beam mass spectrometer designed to measure absolute reactive cross sections (CSs) and branching ratios (BRs) as a function of the collision energy. Reactant ions are generated via photoionization via tuneable VUV light. In particular, the $DCOH^{+\cdot}$ isomer is selectively generated via dissociative photoionization of trideuterated methanol (CD_3OH), as demonstrated in [V. Richardson et al. *J. Phys. Chem. Lett.* 2024, 15, 10888−10895], while $H_2CO^{+\cdot}$ is produced via direct ionization of formaldehyde (H_2CO).

Experimental results

For the $DCOH^{+\cdot}$ isomer, reactivity was studied with H_2, CD_4, C_2H_2, C_2D_6, CH_2CHCH_3, C_3H_8, C_3D_8, H_2O and NH_3. For the $H_2CO^{+\cdot}$ isomer, measurements were taken with CH_4, C_2D_6, CH_2CHCH_3, C_3H_8, C_3D_8, H_2O and NH_3. Data with CH_4, H_2O and NH_3 will be useful to gain insights into kinetic isotope effects when compared with existing experiments performed on the reaction of $H_2CO^{+\cdot}$ with CD_4, D_2O and ND_3 [J. Liu et al. *J. Chem. Phys.* 119, 200-214 (2003); J. Liu et al. *J. Phys. Chem. A* 108, 9945-9956 (2004)].

Absolute cross sections (CS) as a function of collision energy and photon energy (as a proxy for internal energy of reagent ions) were recorded for all product channels. Attention was given to isotopic substitution effects using deuterated reagents. In particular, the reaction with C_3H_8 was also investigated using its isotopologue, C_3D_8.

Although each reactive system has some specificity, some general trends can be highlighted. The $DCOH^{+\cdot}$ isomer reacts with an MH species mainly via: *i)* proton transfer (PT), to give $MH_2^+ + DCO^{\cdot}$; *ii)* H-atom transfer (HAT), to give $DHCOH^+ + M^{\cdot}$); *iii)* hydride transfer (HT), to give M^+ plus $DHCOH^{\cdot}/DH_2CO^{\cdot}$, with bond-forming channels

[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.

sometimes observed (e.g. by detection of products at *m/z* corresponding to loss of H/CH_3/H_2O or other stable fragments from the ion-neutral adduct).

For the $H_2CO^{+\cdot}$ isomer PT and HAT channels are observed with many of the species, in addition to charge transfer (CT) giving $MH^{+\cdot}$ + H_2CO and BF channels.

Since data analysis for the various systems is still under way, we highlight in the following the main results for one system, i.e. the reactivity of both isomers with propane (C_3H_8) and its deuterated analogue (C_3D_8), as an example. For the $DCOH^{+\cdot}$ isomer reacting with C_3H_8 the most intense products are (see the mass spectra in Fig. 1): *i)* $C_3H_7^+$ (*m/z* 43) from an hydride transfer process, reaction (1), to yield either the hydroxymethyl ($DHCOH^{\cdot}$) or the methoxy radicals ($DH_2CO^{\cdot}$), both processes being exothermic, *ii)* $C_2H_5^+$ (*m/z* 29) most likely formed in association with the 1-hydroxyethyl radical ($CH_3CDOH^{\cdot}$) via reaction (2) and *iii)* the HAT transfer to give $DHCOH^+$ (*m/z* 32) plus the iso-propyl radical ($C_3H_7^{\cdot}$), reaction (3):

$$DCOH^{+\cdot} + C_3H_8 \rightarrow C_3H_7^+ + DH_2CO/DHCOH \quad (1)$$

$$DCOH^{+\cdot} + C_3H_8 \rightarrow C_2H_5^+ + CH_3CDOH^{\cdot} \quad (2)$$

$$DCOH^{+\cdot} + C_3H_8 \rightarrow DHCOH^+ + C_3H_7^{\cdot} \quad (3)$$

Absolute cross section data recorded at a fixed photon energy of 13.07 eV are given in Fig. 2. It is relevant to note that all product channels show CSs increasing with decreasing collision energies, indicative of processes that do not present energy barriers (at least in the energy range explorable in our experiments) and proceed via complex mediated pathways.

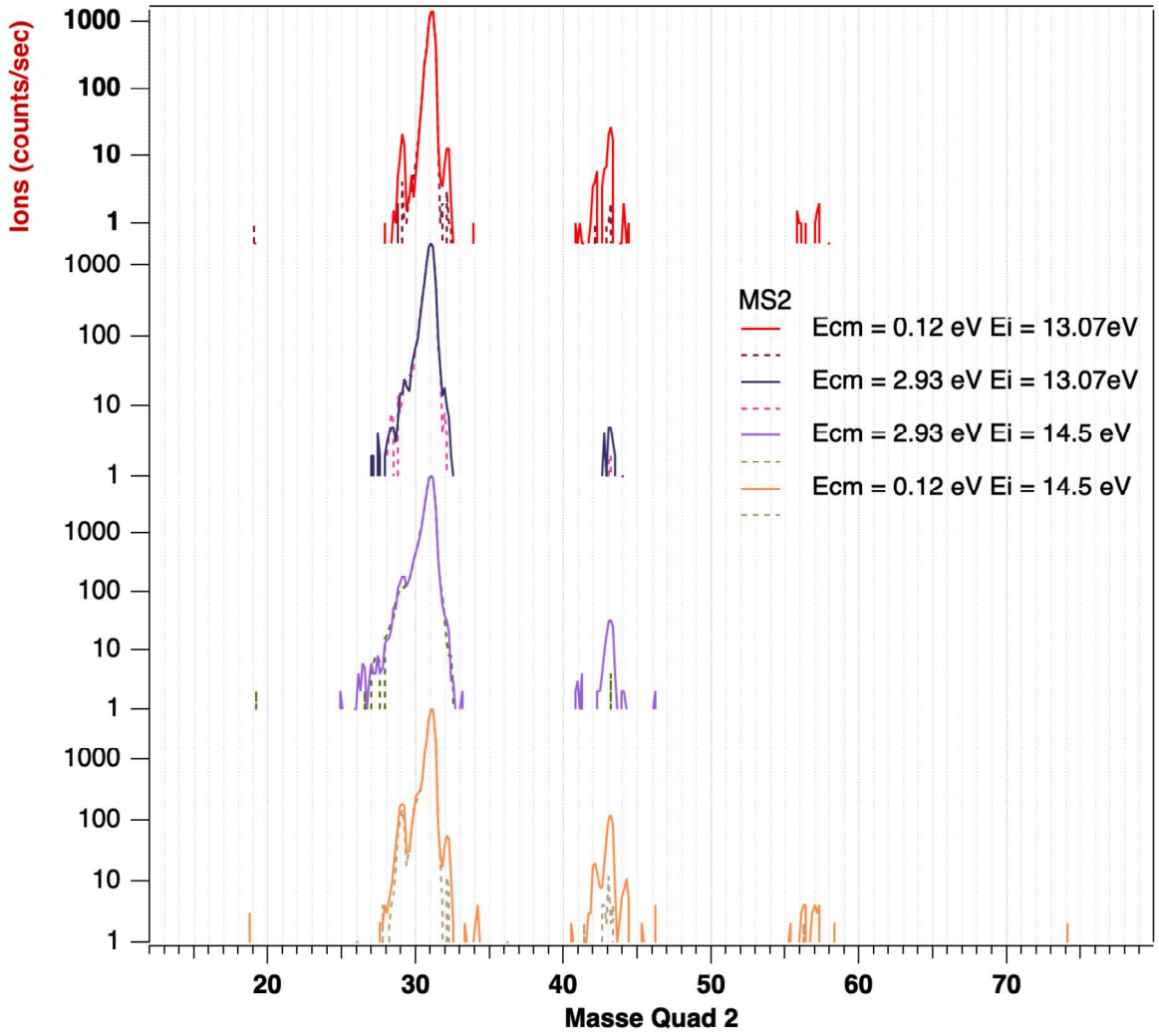


Figure 1 Mass spectra of the products for the reaction $DCOH^{+\cdot} + C_3H_8$ recorded for different collision and photon energies: a) E_{CM} =0.12 eV, E_{phot} =13.07 eV; b) E_{CM} =2.93 eV, E_{phot} =13.07 eV; c) E_{CM} =0.12 eV, E_{phot}=14.5 eV; d) E_{lab} = 2.93 eV, E_{phot}=14.5 eV.

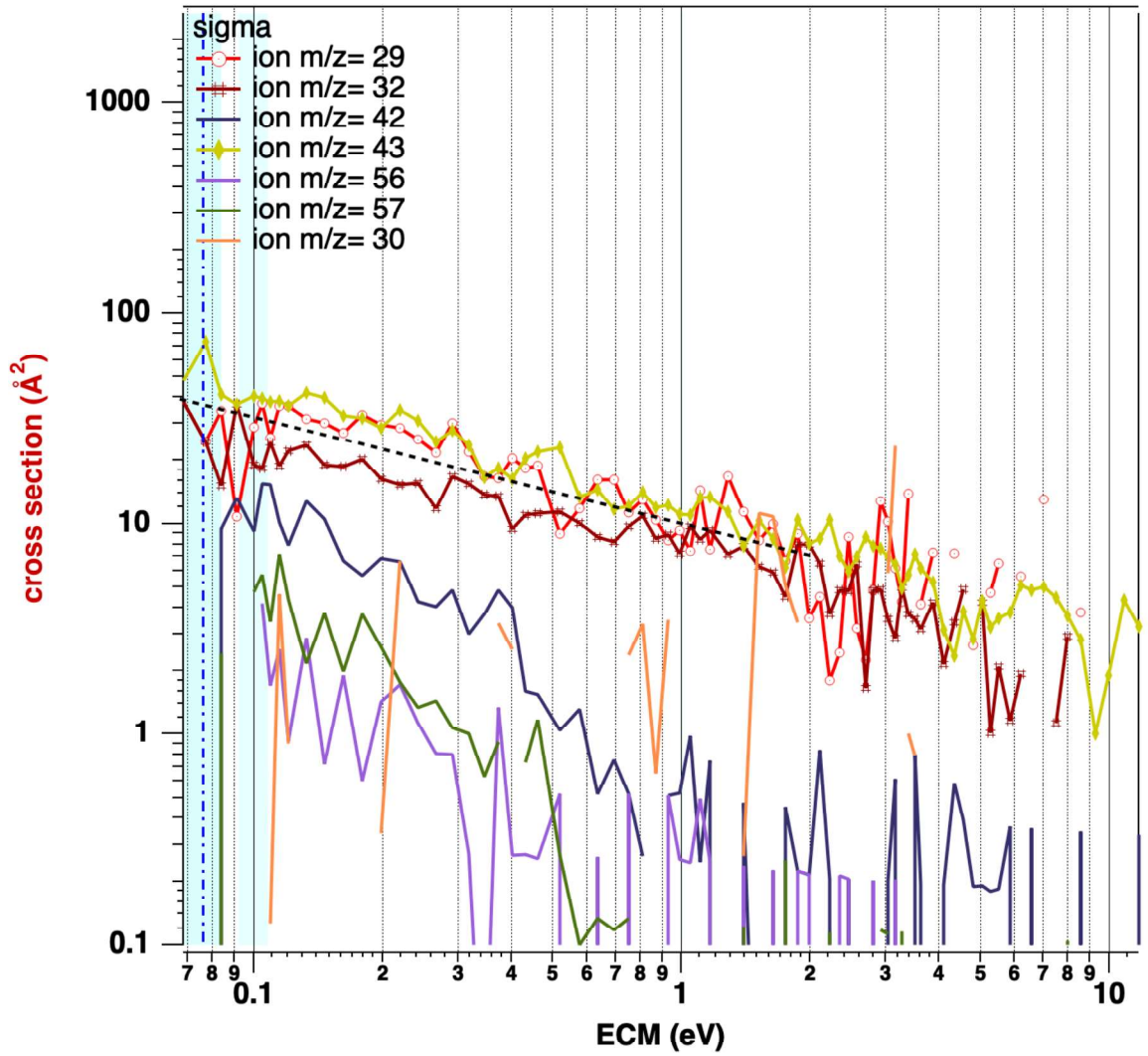


Figure 2 Absolute cross section as a function of the collision energy in the center of mass $DCOH^{+\cdot} + C_3H_8$. The photon energy is 13.07 eV. The dashed black line is a guide for the eyes indicating a Langeving trend of the CSs with collision energy. The data are corrected for the natural isotopic abundance of ^{13}C to discriminate its contribution at masses M and M+1.

The product assignment is confirmed from the experiments performed with C_3D_8, for which the corresponding products are observed as (see mass spectra in Fig. 3: *i)* $C_3D_7^+$ (*m/z* 50), ii) $C_2D_5^+$ (*m/z* 34) iii) D_2COH^+ (*m/z* 33) .

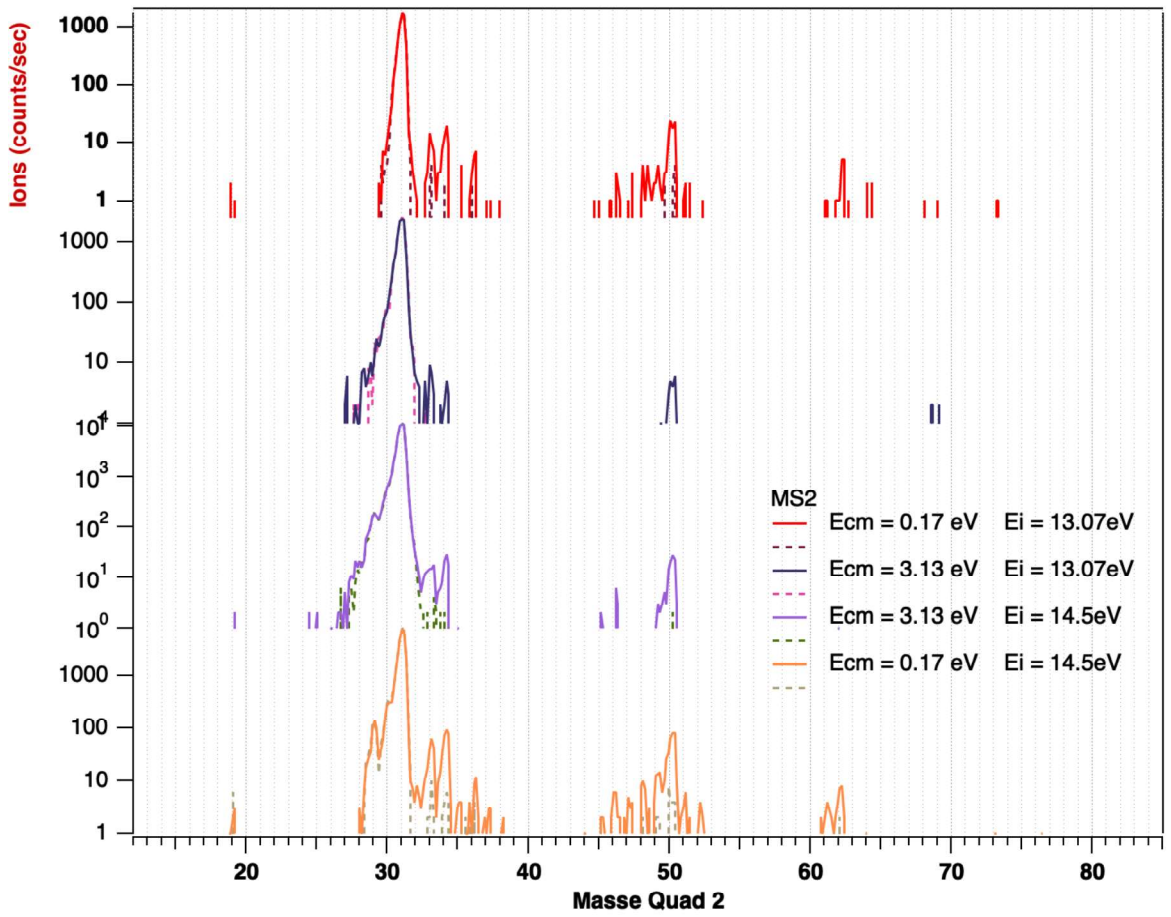


Figure 3 Mass spectra of the products for the reaction $DCOH^{+\cdot} + C_3D_8$ recorded for different collision and photon energies: a) E_{CM} =0.17 eV, E_{phot} =13.07 eV; b) E_{CM} =3.13 eV, E_{phot} =13.07 eV; c) E_{CM} =0.17 eV, $E_{pho\,t}$=14.5 eV; d) E_{CM} = 3.13 eV, E_{phot}=14.5 eV.

In the second part of the beamtime, the ion source was fed with formaldehyde vapours (generated by heating paraformaldehyde in a water bath kept at about 30 °C) to generate the $H_2CO^{+\cdot}$ isomer via photoionization, and the reaction with C_3H_8/C_3D_8 gave the following results.

With C_3H_8, four main products are observed: *i)* HAT transfer to give H_2COH^+ (*m/z* 31) plus the iso-propyl radical (C_3H_7·), reaction (4); *ii)* hydride transfer (HT) to give $C_3H_7^+$ (*m/z* 43) plus DHCOH·/ DH_2CO·, reaction (5) *iii)* $C_3H_8^+$ (*m/z* 44) plus H_2CO via charge transfer reaction (6) and *iv)* $C_4H_8^+$ (m/z 56) plus H_2O, reaction (7):

$$H_2CO^{+\cdot} + C_3H_8 \rightarrow H_2COH^+ + C_3H_7^{\cdot} \quad (4)$$

$$H_2CO^{+\cdot} + C_3H_8 \rightarrow C_3H_7^+ + DH_2CO\cdot/DHCOH\cdot \quad (5)$$

$$H_2CO^{+\cdot} + C_3H_8 \rightarrow C_3H_8^+ + H_2CO \quad (6)$$

$$H_2CO^{+\cdot} + C_3H_8 \rightarrow C_4H_8^+ + H_2O \quad (7)$$

Absolute cross section data recorded at a fixed photon energy of 11.0 eV are given in Fig. 4. Also in this case, all product channels show CSs increasing with decreasing collision energies, with the exception represented by the CS at *m/z* 44 which increases with collision energy, in agreement with the fact that the process is slightly endothermic (only by ~0.1 eV).

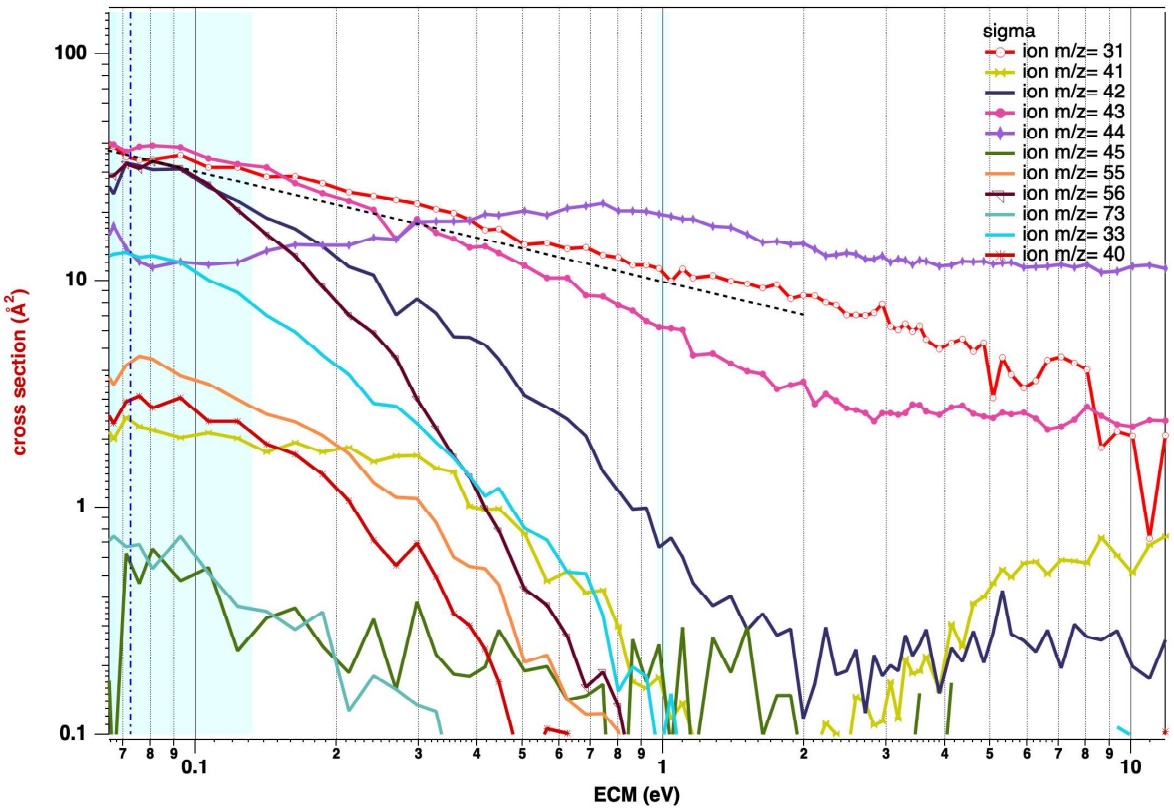


Figure 4 Absolute cross section as a function of the collision energy in the center of mass for the reaction $H_2CO^{+\cdot} + C_3H_8$. The photon energy is 11 eV. The dashed black line is a guide for the eyes indicating a Langeving trend of the CSs with collision energy. The data are corrected for the natural isotopic abundance of ^{13}C to discriminate its contribution at masses M and M+1.

Also for this isomer, product assignment is confirmed from the experiments performed with C_3D_8, for which the corresponding products are observed as: *i)* H_2COD^+ (*m/z* 32), *ii)* $C_3D_7^+$ (*m/z* 50), *iii)* $C_3D_8^+$ (*m/z* 52) and *iv)* $C_4H_2D_6^+$ (*m/z* 62).

The experimental programme was completed with only minor deviations from the original plan. Measurements involving C_2H_3CN, CH_3CHO and HCOOH were not performed due to time constraints and prioritization of the hydrocarbon reaction systems for isotope-comparison studies.

Additionally, charge transfer (CT) processes between Ar and Kr in their first excited energy states were investigated, along with the reaction between $HCNH_2^+$ and CH_3OH and the reaction of $^{12}C^+$ with CH_3OH, were $^{12}C^+$ was generated from CO.

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

Overall, the STSM enabled the acquisition of a substantial dataset covering a wide range of ion–molecule reactions. The comparison between deuterated and non-deuterated systems provides valuable insight into the underlying reaction dynamics and fundamental gas-phase processes. The measured reactivity, expressed in terms of absolute cross sections and branching ratios, will be combined with theoretical modelling to derive reliable rate constants at the low temperatures relevant for the chemistry of cold regions of the interstellar medium and planetary atmospheres.The network of ion–neutral reactions investigated during this STSM is expected to play a significant role in shaping the chemistry of oxygen-containing hydrocarbons and to contribute to the objectives of the COST Action, particularly in elucidating the chemical pathways leading to the formation and destruction of nano-carbon materials in space. Planned follow-up activities include theoretical investigation of the studied reactions through calculation of the potential energy surface (PES).

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