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

**Action number: CA21126**

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## Details of the STSM

**Title:** Isomer specific reactivity of the astrochemically relevant ions $H_2CO^+$ and $HCOH^+$

**Start and end date:** 14/02/2024 to 19/02/2024

## Description of the work carried out during the STSM

The research topic addressed in the activity deals with the gas phase chemistry of the astrochemically relevant C containing isomeric radical cations $H_2CO^{+\cdot}$ and $HCOH^{+\cdot}$. The aim of the STSM was to participate to an experiment planned at the DESIRS VUV beamline of the French Synchrotron SOLEIL to selectively generate both isomers and collect isomer-specific data on the reaction with a range of astrochemically-relevant neutrals, with a particular focus on reactions leading to the build-up of chemical complexity. While the most stable isomer (by ~0.3 eV) is the formaldehyde radical cation ($H_2CO^{+\cdot}$), the presence of a large isomerization barrier (~1.97 eV [1]) is predicted to lead to a tunnelling lifetime of the order of thousands of years for the higher energy hydroxymethylene radical cation ($HCOH^{+\cdot}$) [2]. Thus both ions are expected to exist as independent species in the interstellar medium, where they may react with differing cross sections (CSs) and branching ratios (BRs) of products.

### Experimental results

Experiments have been performed using the CERISES set-up associated to the DESIRS beamline: a guided ion beam tandem mass spectrometer coupling ion generation via tuneable VUV light with octupolar RF guiding and trapping of ions to measure absolute integral reactive cross sections and product branching ratios for ion-molecule reactions as a function of collision energy (in the range from meV to tens of eVs).

**Generation and reactivity of the $H_2CO^{+\cdot}$ isomer:** the ion was produced via photoionization of formaldehyde using photon energies from its ionization threshold (10.88±0.03 eV, in agreement with the 10.89 eV literature value [1]) up to 14.5 eV. To check its isomeric purity and validate our experimental technique the reactivity of the *m/z* 30 ion from photoionization of formaldehyde was studied with $C_2H_4/C_2D_4$ on which previous studies had been performed [3], and present results were in good agreement with literature data. Successively, the reactivity of $H_2CO^{+\cdot}$ was investigated with saturated ($C_2H_6$, isobutane $CH(CH_3)_3$) and unsaturated hydrocarbons (the two

[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.

$C_3H_4$ isomers allene $H_2CCCH_2$ and propyne $CH_3CCH$). The reactivity with isobutane is relevant to chemically differentiate the presence of $H_2CO^{+\cdot}$ when generating the $HCOH^{+\cdot}$ isomer. Infact, while the reaction of $H_2CO^{+\cdot}$ proceeds mainly via charge exchange (to give $CH(CH_3)_3^{+\cdot}$ in addition to dissociative charge transfer into $[C_3H_6]^{+\cdot}$ plus $CH_4$), this channel for the $HCOH^{+\cdot}$ isomer is endothermic by 1.78 eV and therefore closed at low collision energy and in the absence of internal excitation of the $HCOH^{+\cdot}$ ion.

**Generation and reactivity of the HCOH+· isomer:** two pathways have been probed to generate this isomer. The first one requires dissociative photoionization of cyclopropanol (c-$C_3H_5OH$), that, according to a literature proposal [4], should mainly give $HCOH^{+\cdot}$ with $C_2H_4$ elimination. However, a subsequent study has postulated the presence of an additional fragmentation channel giving the isobaric $C_2H_6^{+\cdot}$ ion via CO elimination [5]. To discriminate for the presence of $C_2H_6^{+\cdot}$ we have reacted the *m/z* 30 ion with $C_2D_4$, exploiting an expected difference in reactivity for charge exchange, since the reaction is exothermic for $C_2H_6^{+\cdot}$ but it is 1.6 eV endothermic for the $HCOH^{+\cdot}$ ion. A preliminary data analysis (to be completed) has revealed that the generation of $HCOH^{+\cdot}$ via dissociative photoionization of cyclopropanol is indeed unfeasible due to the presence of the $C_2H_6^{+\cdot}$ ions at all the explored photon energies. We therefore moved to the second method: dissociative photoionization of methanol, as suggested in [6]. The use of the $CD_3OH$ methanol isotopologue revealed extremely selective for the production of $DCOH^{+\cdot}$ (*m/z* 31), as demonstrated by the chemical differentiation method using $CH(CH_3)_3$, as described above. Infact the main reactive channel observed at all the explored photon energies (in the range from the appearance threshold of ~12.50±0.03 eV to 15 eV) was $C_3H_7^+$ (*m/z* 43) most likely resulting from dissociative proton transfer:

$$DCOH^{+\cdot} + CH(CH_3)_3 \rightarrow C_3H_7^+ + CH_4 + DCO^{\cdot}$$

The reactivity of $DCOH^{+\cdot}$ was then investigated with neutrals of relevance to shape the chemistry of the interstellar medium, namely $D_2$, and some saturated ($CH_4$, $C_2H_6$) and unsaturated hydrocarbons ($C_2H_4$/$C_2D_4$, $C_2D_2$, $H_2CCCH_2$ and $CH_3CCH$). For most reacting neutral partners neat differences are observed in the branching ratios and total reactive cross sections of $DCOH^{+\cdot}$ in comparison with $H_2CO^{+\cdot}$.

One system for all: in the reaction with ethylene, the $H_2CO^{+\cdot}$ ion reacts (with a total CS at ~0.1 eV collision energy in the CM equal to ~114 Å$^2$ and roughly independent on the photon energy used to ionize formaldehyde) to give charge exchange (BR~72%), proton transfer and H atom transfer (not distinguishable since they give $C_2H_5^+$ (plus $HCO^{\cdot}$) and $HCO^+$ (plus $C_2H_5^{\cdot}$) both at *m/z* 29) (BR~26%), while the bond forming channel giving $C_3H_5O^+$ + H is a minor one (BR~2%). On the other hand, the $DCOH^{+\cdot}$ isomer has a smaller total CS (equal to ~70 Å$^2$ at ~0.1 eV collision energy in the CM, and roughly independent on the photon energy used to generate $DCOH^{+\cdot}$ from $CD_3OH$) to give proton/D transfer (BR~67%) and the bond forming channels $C_3H_4DO^+$ + $H^{\cdot}$ (BR~29%) and $C_3H_5O^+$ + $D^{\cdot}$ (BR~4%). The $DCOH^{+\cdot}$ ion is therefore more prone to lead to an increase in the chemical complexity of the reaction products, in comparison with the $H_2CO^{+\cdot}$ isomer.


[1] A.Zanchet, G. A. García et al. PCCP 22, 12886-12893 (2020) and refs therein
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[3] J. Liu, B. Van Devener, S.L. Anderson J. Chem. Phys. 121, 11746–11759 (2004)
[4] C. Wesdemiotis & F.W. McLafferty Tetrahed. Lett. 22, 3479-3480 (1981)
[5] R. Bombach, J. Dannacher et al. Chem.Phys. 82, 459-470 (1983)
[6] J. Chamot-Rooke, P. Mourgues et al. Int. J. Mass Spectrom. 226, 249–269 (2003)


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

The STSM successfully managed to achieved all of its planned goals of:

a) generating isomerically pure reagent ions for the radical cations $H_2CO^{+\cdot}$ and $HCOH^{+\cdot}$ (in its isotopic variant $DCOH^{+\cdot}$)
b) study the reactivity of the two isomers with various neutrals present in the interstellar medium, with special reference to hydrocarbons (methane, ethane, ethylene, acethylene, allene and propyne).

From the reactivity results, that we have measured in terms of absolute CSs and BRs, an interplay with theoretical treatment will allow to produce reliable estimates of the rate constants at the low temperatures relevant to model the chemistry in cold regions of the interstellar medium and planetary atmospheres. We expect that the network of ion-neutral reactions addressed in this STSM will be relevant to shape the chemistry of O-containing hydrocarbons and can contribute to the Action objectives of addressing the chemical pathways lead to the formation and destruction (e.g. via partial oxidation) of nano-carbon materials in space.

We expect that at least two publications, but hopefully even more, will result from the STSM in the near future. In terms of future prospect we plan to explore some further reactions, also using isotopic labelling to infer information about the reaction mechanisms.

Finally we note that during the beamtime we had some time to investigate some different reactions (not originally planned) for which only preliminary data had been measured in a previous beamtime, i.e. the reactions of $^{13}C^+$ with $C_2H_5OH$, $HC(=O)CH_3$ and $CH_3CN$. Additionally we also explored, in a very preliminary manner, the reactivity of $C_2D_2^{+\cdot}$ with the $C_3H_4$ isomers (allene and propyne). Such systems will require further investigation in a future beamtime.