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

Action number: CA21126

Grantee name: Vincent Richardson

Details of the STSM

Title: In-situ Spectroscopic Characterisation of O-C Bond Formation via Ethanol Proton-Bound Dimers

Start and end date: 21/07/2024 to 26/07/2024

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.

(max. 500 words)

For this STSM, measurements were performed using the FELion cryogenic 22-pole ion trap instrument at the FELIX laboratory in Nijmegen, where the widely tuneable FELIX free electron laser has been used to obtain IR spectra of various systems.

The ions relevant to the current study were generated via electron impact ionization of ethanol vapour (in some instances diluted with He) in a storage ion source (SIS). Ions formed in this way are mass selected by a quadrupole mass filter and inserted into the cryogenic 22-pole trap, where they are cooled to the trap temperature by a He pulse. For most of the measurements performed during this project, this pulse was doped with either Ne or H_2 to form “tagged” ion-dopant complexes. The contents of the ion trap following this pulse can then be monitored using a second quadrupole mass filter to give a mass spectrum of the trapped ions before and/or after irradiation.

Spectra can, in theory, be obtained in one of two ways. IR-MPD measurements involve the dissociation of the target ion through the absorption of multiple resonant photons. In such cases, no tagging is required with spectra being recorded either through the depletion of the bare ion mass or the enhancement of the fragment mass channel as a function of wavelength. Alternatively, spectra can be recorded through the dissociation of the tagged complexes through the absorption of a single resonant photon. In this case, spectra are recorded through the depletion of the tagged complex mass as a function of the wavelength.

[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.

For this project we have focused on the following process:

$C_2H_5OH_2^+$ (*m/z* 47) plus $C_2H_5OH \rightarrow [C_4H_{13}O_2]^+$ (*m/z* 93) $\rightarrow [C_3H_{11}O]^+$ (*m/z* 75) plus H_2O (1)

As well as the following secondary reaction of the m/z 75 product:

$[C_3H_{11}O]^+$ (*m/z* 75) plus M $\rightarrow [C_3H_9O]^+$ (*m/z* 73) plus H_2, M (2)

To do this we have recorded mass spectra of the ions formed both in the SIS and in the trap following the reaction of the mass selected *m/z* 47 ion from the SIS with ethanol seeded in the He cooling pulse. This allows for the discrimination between processes which are the direct result of the reaction of the *m/z* 47 ion from the trap with ethanol, and those which are the result are subsequent secondary and/or tertiary reactions.

Additionally, spectroscopic characterisation has been performed for not only the *m/z* 75 product of the primary reaction (1), but also the *m/z* 47 reactant ion, the *m/z* 93 intermediate complex(es) and the *m/z* 73 secondary product ion. In each case, comparison of the measured spectra with either computed spectra or previously recorded spectra for a given ionic structure, or both, allows for identification of the isomer(s) present.

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.

(max. 500 words)

The main achievements of the STSM are as follows:

- Spectroscopic characterization of the Ne-tagged *m/z* 47 ion formed in the SIS as $C_2H_5OH_2^+$ through comparison with both calculations and previously recorded spectra of both $C_2H_5OH_2^+$ and $CH_3O(H)CH_3^+$, the other feasible *m/z* 47 ion.
- Mass spectrum of the products of the reaction of the *m/z* 47 ion from the SIS with Ethanol seeded in He, showing both the *m/z* 75 primary product and the *m/z* 93 adduct complex, with the lack of *m/z* 73 signal allowing for the identification of this ion formed in the source as the result of secondary processes
- IR spectra of the Ne-tagged *m/z* 75 product ion in the 350 to 1600 cm^{-1} range, showing good agreement with the spectra predicted by calculations for the $C_2H_5O(H)C_2H_5^+$ ion, though further data analysis is required before a final spectrum can be presented. Saturation depletion measurements, however, are consistent with the exclusive formation of a single isomer
- IR spectra of the H_2-tagged *m/z* 93 intermediate complex(es) formed during the reaction. These show good agreement with previous measurements of the bare ions performed using the CLIO light source, though further work is required to understand the deviations from calculated line positions observed in both cases.

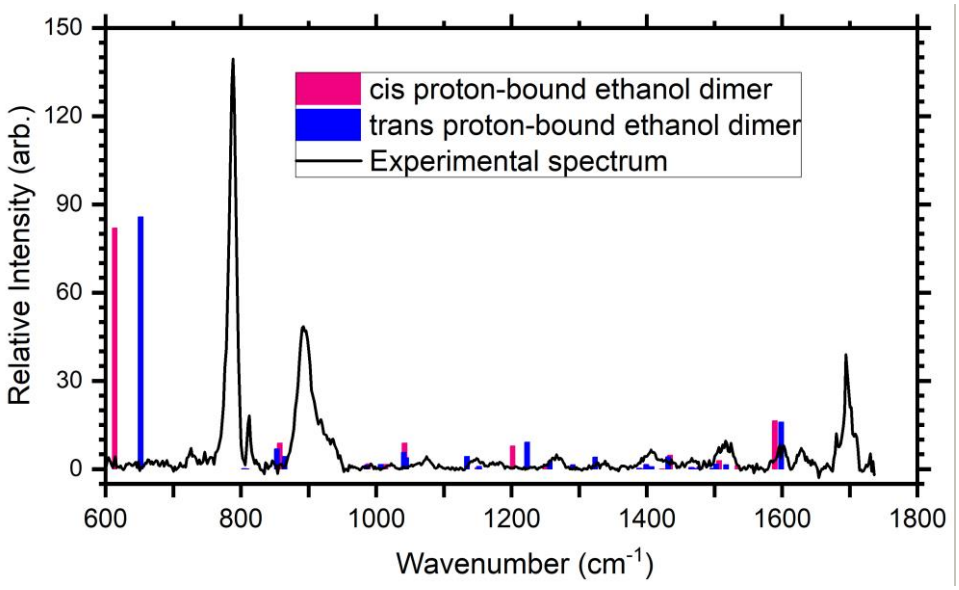


Fig. 1. Comparison of experimental spectrum of H_2-tagged *m/z* 93 intermediate complex (black line) with computational predictions of the line positions and intensities for the *cis* (pink) and *trans* (blue) proton-bound dimers of ethanol.

- IR spectra of the Ne-tagged *m/z* 73 product of the secondary reaction of the *m/z* 75 ions in the SIS. Due to the weakly-bound nature of the tagged complexes, accurate depletion saturation measurements were hindered by off-resonant heating effects, but the recorded spectrum is in good agreement with the predicted spectrum of the $CH_3CHOC_2H_5^+$ ion.

Data analysis for the measurements is still underway, but this project will help elucidate the mechanisms behind the build-up of oxygen-containing hydrocarbons under astrochemical conditions. The coupling of spectroscopic measurements of this type with widely used mass spectrometry-based kinetics measurements allows for isomer-specific reactivity information that can then be used in increasingly complex astrochemical models.

We expect this project to result in a publication once data treatment and interpretation has been completed, with further follow-on projects on a range of other systems of astrochemical relevance also being anticipated as part of this collaboration. In particular, discussions are underway to develop proposals relating to both O- and S-containing hydrocarbons.