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

Action number: CA21126

Grantee name: Piyush Kalambkar

Details of the STSM

Title: Formation of Methane and Small Hydrocarbons on Carbonaceous Cosmic Dust Analogues by Hydrogen Addition

Description of the work carried out during the STSM

We followed the initial working plan described in the grant application. The experiments were performed at the LIRA laboratory (CY Cergy Paris Université) using the FORMOLISM setup (Mohamed Ibrahim et al. 2022), an ultrahigh-vacuum setup equipped with a calibrated atomic hydrogen beam, a cryogenic sample holder allowing temperature-controlled experiments, and a quadrupole mass spectrometer (QMS) for the detection of volatile products.

The samples were amorphous ^{13}C carbon films prepared at the FSU Jena. We chose ^{13}C labelled material specifically because any hydrocarbon products formed from the substrate carbon would appear at shifted mass channels $^{13}CH_4$ at m/z = 17 rather than 16, for instance making it straightforward to separate a real signal from background ^{12}C contamination. This turned out to be an important practical advantage throughout the experiments.

Before starting any hydrogenation, we measured the dissociation efficiency of the hydrogen beam by looking at m/z = 1 and m/z = 2. The dissociation efficiency was found to be approximately 33%, which gave us a reasonable estimate of the actual atomic hydrogen flux hitting the surface.

The experiments themselves fell into two parts. The first was a series of hydrogenation runs at 10 K where we varied the exposure time: 5, 10, 15, 25, 30, and 60 minutes. After each exposure we did a temperature programmed desorption run, heating from 10 to 160 K at 12 K/min while the QMS recorded signals at m/z = 1, 2, 12, 13, 15, 16, 17, 18, 26, 27, 28, 29, 30, 32, and 44. This set of masses covers atomic and molecular hydrogen, ^{13}C and ^{12}C fragments, and all the small hydrocarbons we were looking for $^{13}CH_4$, $^{13}C_2H_2$ and $^{13}C_2H$ along with CO and CO_2 as contamination checks. Some of these dose points were repeated to check that the measurements were consistent. We then repeated the same hydrogenation and TPD sequence at 25 K to see if a slightly higher substrate temperature made any difference.

The second part involved pulsed beam experiments at 100 K and 300 K. Here the hydrogen beam was switched on and off every 2 minutes over one hour, with QMS signals recorded continuously. The idea

[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.

was simple: if any hydrocarbon is forming at the surface, it should desorb at such a high temperature and its signal in the QMS should go up when the beam is on and come down when it is off. This kind of modulated signal is much easier to pick out from noise than a small steady feature in a TPD spectrum.

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

In cold and shielded regions of the interstellar medium such as dense clouds and disk midplanes, dust grains are not exposed to much UV radiation or energetic particles. What they do encounter is atomic hydrogen, which can land on grain surfaces and potentially react with the dust grain. Whether this process leads to the formation of small hydrocarbons like methane or higher hydrocarbon has not really been tested experimentally before, at least not in a controlled and systematic way (Draine 2003; Jones 2012). That was the main motivation for this work.

Across the full range of experimental conditions explored, substrate temperatures of 10, 25, 100, and 300 K, hydrogen exposure doses ranging from 5 to 60 minutes, and both continuous and pulsed irradiation modes, no clear formation of $^{13}CH_4$, $^{13}C_2H_2$, $^{13}C_2H_4$, or any other ^{13}C labelled small hydrocarbon was detected within the sensitivity limits of the QMS. Although weak and noisy features appeared in some datasets, we cannot confidently claim hydrocarbon formation. The pulsed beam experiments at 100 K and 300 K similarly showed no modulated signal correlated with beam switching at any of the hydrocarbon-relevant mass channels.

Future work will focus on turning the present non-detection into quantitative constraints. The next step will be a more detailed analysis of the QMS data, using the noise level and sensitivity of the relevant mass channels to estimate upper limits for the formation of $^{13}CH_4$, $^{13}C_2H_2$, $^{13}C_2H_4$, and other small hydrocarbons. This will make it possible to compare the experimental results more directly with the needs of astrochemical models. Further experiments will aim to improve the sensitivity of the measurements by using longer H-atom exposure times, repeating key temperature points, and refining the QMS background subtraction and calibration. In future runs, in situ FTIR spectroscopy will also be valuable, as it could reveal C–H bond formation in the solid carbon material even if volatile hydrocarbon products remain below the QMS detection limit

The results of this STSM, together with the planned follow up experiments, will form the basis of a joint publication. This collaboration between the astrochemistry group at the FSU Jena and the LIRA team at CY Cergy Paris Université including Prof. Dr. François Dulieu, Dr. Emanuele Congiu, Nour Harika, and Dr. Alexey Potapov will continue with the longer-term goal of building a comprehensive and quantitative picture of hydrocarbon formation pathways on carbonaceous cosmic dust analogues.

References: Draine, B. T. 2003, ARA&A, 41, 241.

Mohamed Ibrahim, A. S., Morisset, S., Baouche, S., & Dulieu, F. 2022, J. Chem. Phys., 156, 194307.

Jones, A. P. 2012, A&A, 540, A1.