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

Action number: CA21126

Grantee name: Tom Douglas-Walker

Details of the STSM

Title: Stability of functionalized PAHs in space: Cyanobiphenyl

Start and end date: 20/05/2024 to 24/05/2024

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)

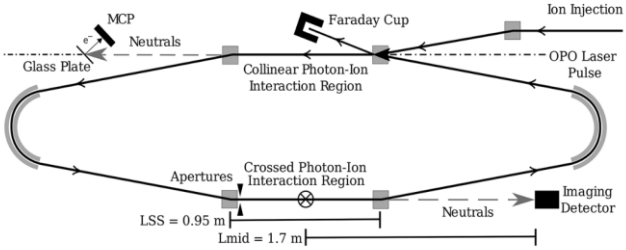


Figure 1: Schematic of the DESIREE apparatus[1]

The goals of this STSM were to obtain time-resolved dissociation and radiative cooling rates of two isomers of cyanobiphenyl ($C_{13}H_9N^+$) at the Double ElectroStatic Ion Ring ExpEriment (DESIREE) facility at Stockholm University. A schematic of the apparatus used can be seen in Figure 1.

For these experiments, ions were produced from an electron cyclotron resonance (ECR) source. The singly-charged cations were accelerated to 34 keV and mass selected by a bending magnet before being injected into the asymmetric ring. The ions were stored in the ring for multiple rotations, and upon dissociation, produced neutral fragments. These fragments were no longer bound by the electrostatics of the ring and were detected by either the MCP detector or an imaging detector which are positioned at tangents to the ring. These two detectors counted the absolute number of neutral fragments and the position of the fragments, allowing dissociation rates and kinetic energy release (KER) distributions to be obtained.

[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 the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

The number of ions entering the storage ring was increased by use of an oven to heat the sample and regulated by opening/closing slits in the ion-beam path between the source and the ring. This ensured sufficient ions to record a high signal-to-noise scan, but also prevented saturating the imaging detector.

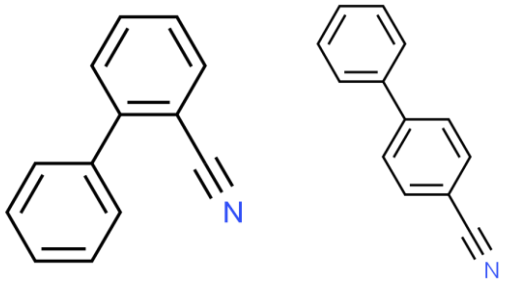


Figure 2: 2-cyanobiphenyl (left) and 4-cyanobiphenyl (right)

Initial test measurements showed that there was a sudden drop-off in the number of neutral fragments detected during the first few cycles of the storage ring. This was believed to be due to a poor injection angle of the ion beam into the ring. Subsequent optimisation of the ion beam through a 10mm aperture helped improve the injection angle and remove this phenomenon.

The photo-induced dissociation rate of 4-CyBP+ (Figure 2) was measured utilising a 1KHz OPO (EKSPLA NT242, reduced to 250Hz by a frequency divider to prevent overlapping of decay measurements). No photo-induced fragments were observed in the visible range; however, a small number of fragments were present at 380nm. The number of fragments were maximised by fine adjustment of the OPO alignment through the stored ions.

The electron-impact and photo-induced dissociation rate experiments were then repeated for the -ortho isomer, 2-CyBP+. After changing the sample, the ion-beam required very little optimisation. We completed the electron-impact dissociation rate measurements as well as photo-induced dissociation measurements again using both 380nm and 370nm light from the OPO for comparison of the dissociation rate.

In addition to this, we obtained the spontaneous cooling rates of the 2-CyBP+ molecules with loss of hydrogen ($C_{13}H_8N^+$). The detectors are insensitive to detection of H, yet, this molecule could form by loss of H from the parent ion and stay bound in the ring due to its similar mass-to-charge ratio. Hence, we measured the cooling rates of this molecule to estimate the contribution of this fragmentation pathway in the overall experiments.

[1]J. W. L. Lee et al. *J. Chem. Phys* **158**:174305 (2023)

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.

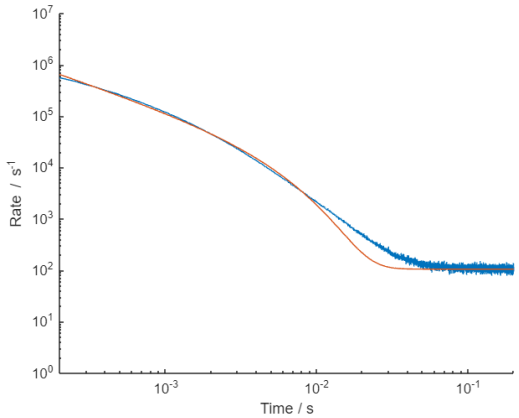


Figure 3: Determination of dissociation rate coefficient from the measured count rate

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This STSM was overall highly successful from an experimental point of view. We were able to achieve the aims set out in the STSM proposal to determine the dissociation rate of two cationic isomers of cyanobiphenyl, 2-CyBP+ and 4-CyBP+. These data were collected over many hours and typically averaged over 100,000+ cycles ensuring high quality statistics. Analysis is still ongoing; however, initial results have made it possible to extract preliminary rate constants for the spontaneous decay of both isomers.

An example of this can be seen in Figure 3, where the measured count rate of 2-CyBP+, averaged over many storage cycles, is modelled by $R(t) = r_0 t^{-1} e^{-kt} + B$ where

B is a constant background, r_0 is the signal amplitude and k is the rate constant where dissociation is quenched by IR and RF cooling. Initial modelling suggests this molecule is able to cool by RF, similar to other cyano-functionalised PAHs. Further analysis with data from stored $C_{13}H_8N^+$ (loss of H from 2-CyBP) may help improve the accuracy of the determined constants.

The next steps for data analysis are to investigate the photo-induced dissociation rate of these isomers and to fully analyse the KER distributions. This work is planned for June 2024, with video calls already arranged between myself, Mark Stockett, Ugo Jacovella and Arun Subramani to discuss and delegate the remaining analysis. We hope to be able to publish the collected data in the future. The only information we were not able to obtain were the KER distributions for photo-induced dissociation rates of 2-CyBP+. However, we were able to obtain KER information from electron-impact dissociation rates of both isomers, as well as for photo-induced measurements on the -para isomer.

This STSM has also been highly successful from other perspectives. For example, the project has been a fantastic opportunity for my personal development as a young researcher, providing me the opportunity to work at a new laboratory and collaborate with other researchers in the field. The project provided me with hands-on experience of working at a user facility and understanding the variety of experiments that can be undertaken at DESIREE. Additionally, the STSM funding helped facilitate the first collaboration between researchers at University of Edinburgh and the DESIREE facility at Stockholm University. We hope that this greater knowledge of the laboratory may help us write our own proposals and work together on collaborations in the future.