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

Action number: CA21126

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Details of the STSM

Title: Fast electronic cooling in cationic complexes between PAHs and octasulfur S_8^+

Start and end date: 27/05/2024 to 31/05/2024

Description of the work carried out during the STSM

Experiments were performed at the storage ring facility DESIREE (Stockholm University), where beams of charged S_8^+ molecules were injected and trapped in the cold ring (≈ 13 K) for periods of 1s. Figure 1a shows a mass spectrum of the injected beam, which is compared with the natural abundance of S_8^+. The very good match between the two reveal that octasulfur was indeed successfully produced.

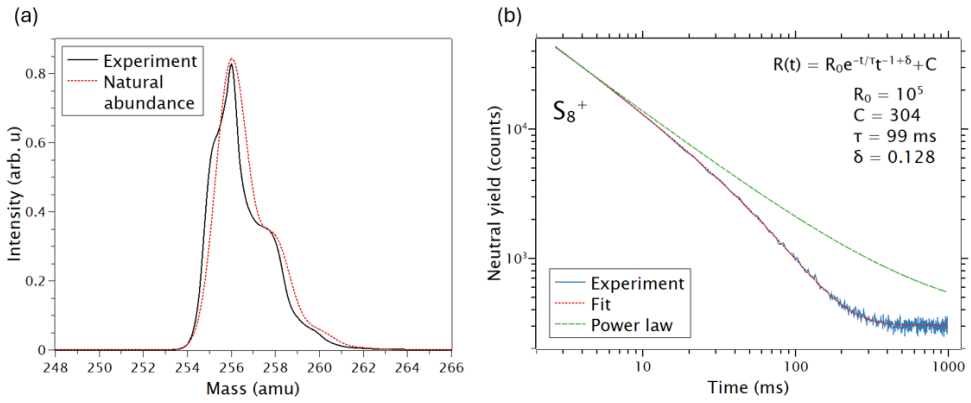


Figure 1. (a) Measured mass spectrum of S_8^+ (black), in comparison with its natural abundance pattern (red). (b) Measured neutral yield of S_8^+ as a function of stored time (blue). A quenched power law fitted to the data is depicted in red, whereas a power law in green. The parameters from the quenched power law fit are shown as inset.

The primary goal of the proposal was to measure the cooling dynamics of S_8^+. The molecular beam, which is produced in a resistively heated oven coupled to an electron cyclotron resonance (ECR) ion source, produces beams

[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.

with high and broad energy distributions. Therefore, as a function of stored time, the S_8^+ molecules cool down by competing channels, namely fragmentation and radiative cooling. In the experiment, a neutral detector was employed to measure the fragmentation of S_8^+ as a function of storing time, as depicted in Figure 1b (blue curve). If fragmentation is the only active cooling channel, the neutral yield is expected to follow a 1/t dependence (power law decay), which in a log-log plot as that in Figure 1b is seen as a linear curve. At early times of trapping, this is indeed the case, as highlighted by a fit to the experimental data by a power law (green curve). However, at later times, the neutral yield deviates from the power law, a phenomenon attributed to the appearance of radiative cooling, which competes to fragmentation. In this case, an exponentially quenched power law can be fitted to the data, as presented by the red curve, which nicely agrees with the data. From this fit, the effective radiative cooling time, τ, can be extracted (99 ms).

In addition to the measured neutral rate, a tunable OPO laser was used to induce prompt fragmentation as a function of wavelength, from which the optical absorption spectrum of S_8^+ can be extracted. These experiments were performed in the wide range from 300 to 1400 nm, although the data still needs to be analysed.

The initial plan for the proposal was to measured first S_8^+, followed by its complex with naphthalene (bare naphthalene cations have already been measured at DESIREE). Due to a lack of time during the allocated week of beamtime, however, only S_8^+ was measured. Now that these experiments were successful, plans for a follow up proposal solely dedicated to the complexes will be prepared.

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

The successful measurement of the cooling rate of S_8^+ is a major achievement, given its relevance in astrochemical models that simulate the abundances of sulfur-bearing molecules in the interstellar medium. In addition, the characterization of the optical absorption spectrum of S_8^+ will provide insights into its spectroscopic signatures, which for example, can be compared with the diffuse interstellar bands (DIBs). Currently, the measured data is being analysed, in addition with the performance of quantum chemical calculations of parameters that will be important for understanding the measured cooling dynamics, such as dissociation energies, vibrational frequencies and optical absorption spectrum. Moreover, in collaboration with astrochemists, models of the abundance of sulfur allotropes in photodissociation regions of the ISM will be adapted to include the measured effective cooling time of S_8^+.

In addition to the experiments at DESIREE, we have plans to measure the far-infrared spectrum of gaseous S_8^+ at the FELIX Laboratory in Nijmegen, The Netherlands. This will take place during the second semester of 2024, and will complement the current experiments. The vibrational modes of S_8^+ are crucial to model the competition between fragmentation, vibrational cooling and recurrent fluorescence, since they determine the energy-dependent density of states, which enter directly into the expressions for the rates of the different cooling channels. For now, these rates will be determined based on density functional theory, but soon, the calculations will have experimental verification.

Finally, there are plans for a follow up proposal at DESIREE, were complexes between S_8^+ and PAHs will be investigated. This was part of the initial plan of the current proposal, but due to a lack of time on the allocated week of beamtime, only measurements on S_8^+ were performed.