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

Action number: CA20129

Grantee name: Karolína Fárníková

Details of the STSM

Title: Excited State Photodissociation of Caesium Diiodide Ion

Start and end date: 16/07/2023 to 29/07/2023

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.

The goal of this STSM under the surpervision of Dr. Milan Ončák was to investigate gas-phase alkali-halide clusters. Specifically the Cs_2I^+ cation and CsI_2^- anion were investigated using various methods of computational chemistry. The main objective was to generate photodisociation spectra to examine the photodisociation process. The research build upon the experiments previously conducted by the group of Prof. Martin K. Beyer.

The primary focus was the Cs_2I^+ cation. For various geometries, energies of ground state and exited states have already been calculated using either CCSD(T) method (ground state) or multireference configuration interaction method (MRCI) with explicit calculation of the spin-orbit coupling (both ground and excited states). The energies of the ground states were used to calculate forces for the molecular dynamics, which were generated using the ABIN code. Using the MRCI calculations and interpolation, spectra were generated from the structures from the trajectories. These dynamics were done at various temperatures (30, 100 and 298 K).

As for the CsI_2^- anion, the first part was to find a suitable active space using MRCI to calculate the energies of the excited states. From that, the plan was similar to the one for the cation. Various geometries of the anion were optimized using the CCSD(T) method and the ground state energies were again used to calculate forces in the molecular dynamics.

We also investigated the following dissociation patterns in both ions. In Cs_2I^+, we modelled dissociation channels based on the irreducible representation of the electronic state into which the system is excited, with further dissociation to Cs^+ at higher energies. In CsI_2^-, we investigated the absorption of a second

[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.

photon to from Cs^-. To this end, we investigated the photochemistry of CsI^- that is observed in the experiment after the absorption of the first photon with the unusual electronic structure.

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.

The generated spectra, which were in agreement with the experimental results, allowed us to better understand the photochemistry of the Cs_2I^+. They show us, that in the first step, based on symmetry of the excited state, the cation dissociates either to CsI^+ and Cs, or to Cs_2^+ and I. These species can then further dissociate to Cs^+ cation. The probability of this process is highest at around 220 nm and slowly decreases all the way to about 270 nm.

As for the CsI_2^- anion, molecular dynamics were produced, which will allow for spectra to be generated in the future, when the optimal active space is found. This can lead into a further exploration of the possible dissociation channels for CsI_2^-.

The results of this STSM will be part of a publication and they will provide the basis for expanding the research into larger clusters as well as to different alkali-halide clusters, such as NaCl.

The results of this research also contribute to the objectives of the COST Action CA20129, Multiscale Irradiation and Chemistry Driven Processes and Related Technologies (MultIChem). Specifically, this project aim to explore the irradiation driven process (IDC) of the photodissociation of the caesium diiodide anion, which complies with the research coordinated objective 2, focusing on establishing a comprehensive databank of IDC-related quantities.