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

Action number: CA21126

Grantee name: Chiara Beldi

Details of the STSM

Title: Hidden Charge States: Infrared Signatures of Anionic Fullerene Species in Planetary Nebulae

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.

During this STSM at the Instituto de Astrofísica de Canaria (IAC), the properties of anionic metallofullerenes were investigated to explore the possible role of these systems in circumstellar environments.

The first stage of the project consisted in the selection of the target species. Following previous work published by the host group, it was decided to consider negatively charged exohedral metallofullerenes (Mg-C_{60} and Fe-C_{60}) as a first instance. These species have been proposed to exist in circumstellar regions where metals, fullerenes and smaller metal-containing organic molecules also are present and have been linked to several still unidentified IR features observed in these environments.

During the first stage of the STSM, the harmonic IR spectra of neutral and cationic [Mg-C_{60}] were simulated to benchmark different levels of theory and to ensure a consistent treatment for the different charge states. The calculated spectra and a preliminary analysis of the interaction between Mg and C_{60} were compared to the work previously carried out by the host group to assess the robustness of the methods, considering that a different quantum chemistry package and a different computational framework were going to be used to model the anionic systems. Different multiplicities and different placements of the Mg atom were also tested at this stage. The results agreed with the previous work.

Having validated our computational approach for the negatively charged species, optimisation of the anionic C_{60} system were carried out. Isolated anionic C_{60} poses significant computational challenges due to its triply degenerate LUMO. Since the size of the system means that a multireference treatment is unfeasible, DFT treatment of this species is necessary but requires careful method selection. We employed B3LYP-D3, CAM-B3LYP and ωB97x-D functionals with the 6-31G(d) and 6-31+G(d) basis sets, testing the combinations previously validated on the neutral system. Convergence difficulties prompted us to implement Fermi smearing for fractional

[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.

occupations. Due to the complexity and novelty of the systems being studied, we are currently verifying the robustness of these preliminary results, which suggest that the [Mg-C_{60}] system can form a bound anion. To test the validity of the methods on different systems, a first set of optimisation calculations at the same levels of theory have been carried out on [Fe-C_{60}] and [Indene-C_{60}] adduct and are currently being analysed.

The calculations initiated during the STMS will help establish a comprehensive and reliable computational protocol to treat anionic fullerene derivates using accessible DFT techniques. Due to the difficulties in producing and validating the optimised geometry for these molecules, the evaluation of the anions' stability and the production of the IR spectra has been moved to a later time.

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 STSM achieved its principal objectives by addressing a fundamental gap in astrochemical research, which is the absence of studies on the role of anionic fullerene derivatives in environments where fullerenes have been detected and electron attachment processes are favourable.

The project highlighted the challenges associated with the computational treatment of anionic metallofullerenes. The scarcity of data on these species highlights the need for a more rigorous development of relevant computational methodologies and for the validation of the computational frameworks used to model these species. As the project progressed, it therefore became apparent that the initial priority should have shifted from the production of the reference IR spectra to a systematic study to investigate best practices for the computational treatment of anionic fullerene derivatives. A plan has been outlined to verify the robustness of the output of the calculations, including a thorough testing of the SCF convergence and a detailed comparison between the different levels of theory. Further testing on different fullerene-based anionic species will allow to verify the performance of the established protocol, and calculations are already underway for exohedral [Fe-C_{60}] and [PAH-C_{60}] adducts. The results of this project will enable to refine the computational treatment of these overlooked but potentially significant species in astrophysical environments.

Preliminary results indicate that the Mg-C_{60} system can form a bound anion, and the IR spectra will therefore be produced for comparison with the other charge states. The production of IR spectra for the other species of interest will be evaluated on a case-by-case basis, after the existence of a bound anion has been established via the optimisation calculations. In particular, the plan is to extend the current work to the anion of [Fe-C_{60}] and the anions and cations of [Indene-C_{60}] and [Anthracene-C_{60}]. At this stage it will also be possible to perform a preliminary evaluation of the stability of the anionic complexes via electron affinity calculations. Additionally, we are planning to investigate the bonding type and strength, which will help us to better understand the interactions underpinning these interesting systems.

This project will contribute to the scope of the Action by improving the computational methodologies for the treatment of important carbonaceous astrochemical species, along with the production of computational molecular data for comparison with astronomical observation and/or experimental data. Additionally, it will help with the understanding of the chemical networks of space by considering the formation and stability of negatively charged fullerene derivatives. Fullerene anionic chemistry is complex and largely unexplored, and the extension of computational protocols to anionic fullerenes will be of significant interest for the astrochemical community. The STSM helped establish a collaboration between the two research groups, laying a foundation for future collaborative work.