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

Action number: CA21126

Grantee name: Boutheïna KERKENI

Details of the STSM

Title: Anharmonic frequency calculations and computational refinement of PAH molecular spectroscopy for astrophysical applications

Description of the work carried out during the STSM

During the STSM at the Astrophysics sub-department of the University of Oxford, the work developed along two complementary directions: anharmonic vibrational spectroscopy of polycyclic aromatic hydrocarbons (PAHs) and modelling of their charge distribution and stability under astrophysical conditions.

A systematic series of quantum-chemical calculations was initiated for PAHs of increasing molecular size, starting from benzene (C6) and extending progressively to larger systems up to coronene (C24). Geometry optimisations and anharmonic vibrational-frequency calculations were performed at the ωB97X-D/6-311+G(d,p) level, using a long-range corrected density functional including dispersion and a basis set containing diffuse and polarization functions. The same computational framework was adopted for the different PAH charge states to ensure a consistent description of molecular structures, vibrational properties and charge-dependent energetics. The calculations submitted during the STSM constitute the basis for assessing anharmonic effects and their computational feasibility as PAH size increases, with the longer-term objective of improving molecular spectroscopic data relevant to infrared astronomical observations.

In parallel, the molecular calculations were connected to the astrophysical question of PAH charge states in different environments, motivated particularly by observational evidence for predominantly neutral PAHs in AGN/outflow environments and more strongly ionised PAHs in star-forming regions. A Python-based charge-balance model was developed and numerically validated for coronene. Photoionisation rates were calculated using molecular photoabsorption data and astrophysical radiation fields, and their numerical robustness was tested against radiation-field scaling, ionisation-threshold variations, alternative numerical integration schemes and energy-grid refinement.

The charge-balance solver was subsequently extended to four charge states (PAH−, PAH0, PAH+ and PAH2+), incorporating electron attachment and anion photodetachment. The implementation was validated through

[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.

analytical scaling and non-regression tests, while uncertain molecular parameters were explicitly explored through sensitivity analyses.

The modelling was further extended towards molecular survival. A sequential H-loss fragmentation model for the coronene dication was implemented and validated against a published fragmentation benchmark, reproducing the characteristic ordering and even–odd alternation of successive dehydrogenation states.

These developments extended the initial working plan by establishing a direct pathway from anharmonic molecular spectroscopy to an astrophysical charge-and-survival model. Using the same ωB97X-D/6-311+G(d,p) framework, charge-dependent calculations for coronene were initiated to provide a homogeneous set of molecular properties that can progressively refine the charge model and subsequently incorporate molecular fragmentation and survival.

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

The STSM achieved its principal objectives and established a concrete computational and collaborative framework for connecting PAH molecular spectroscopy with astrophysical modelling. In particular, the visit initiated a systematic anharmonic study extending from benzene to coronene and established a common ωB97X-D/6-311+G(d,p) computational protocol for the investigation of PAH structures, vibrational properties and charge-dependent energetics. A specific motivation for the anharmonic calculations is the interpretation of the astronomical 5.2 μm emission feature, whose origin cannot be adequately addressed through standard harmonic vibrational calculations alone. The calculations initiated during the STSM will therefore be analysed to assess whether anharmonic vibrational contributions in PAHs of increasing size can account for, or contribute to, this spectral feature and its observed characteristics.

A major outcome of the STSM was the development and numerical validation of a coronene charge-balance model linking molecular properties to astrophysical conditions. The model provides charge fractions as a function of the physical environment and was extended to include anionic, neutral, cationic and dicationic states. Numerical tests demonstrated the robustness of the photoionisation-rate calculations and of the charge-balance solver. In addition, the implementation and validation of a sequential H-loss fragmentation model established the basis for extending the approach from a charge-balance model to a combined charge-and-survival model.

The follow-up work will first focus on completing and analysing the anharmonic calculations initiated during the STSM, with particular emphasis on the 5.2 μm region, and on assessing how the predicted anharmonic spectral contributions evolve with PAH molecular size. In parallel, the charge-dependent calculations for coronene will be completed to obtain a consistent set of electron affinities, successive ionisation energies and zero-point-energy corrections. Selected fragmentation pathways and their energetics will subsequently be calculated and incorporated into the astrophysical model to determine not only which PAH charge states are favoured under given conditions, but also whether these molecular species can survive.

The resulting predictions will be confronted with the observational picture of PAH populations in different astrophysical environments, particularly predominantly neutral PAHs in AGN/outflow regions compared with more strongly ionised populations in star-forming regions.

These activities directly contribute to the NanoSpace objectives by improving molecular data for nanoscale carbonaceous species and strengthening the interface between quantum chemistry, molecular spectroscopy and observational astrophysics. The STSM has established a concrete basis for continued collaboration with the Oxford astrophysics group and for the preparation of joint scientific publications based on the spectroscopy and charge-survival modelling developed through this work.

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