Improving potential energy surface expansions for *in silico* spectroscopic studies of PAHs of astrophysical interest

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Abstract: Polycyclic Aromatic Hydrocarbons (PAHs) are a family of organic compounds composed of aromatic rings of carbon atoms, whose peripheral valencies are saturated by hydrogen atoms. PAHs (or closely related species) are thought to be the carriers of the so-called Aromatic Infrared Bands (AIBs) at ∼3.3, 6.7, 7.7, 8.6, 11.3 μm. These features are among the strongest emission features observed in the interstellar medium in the infrared (IR), and present some interesting variability from one observed source to another. Therefore, the IR spectroscopy of PAHs is of paramount importance in astrophysics and astrochemistry: A better understanding of it, is essential to infer from IR observations, informations about PAHs composition and physical parameters of their environment [1].

In our laboratory, we have developed a computer code, CONVIV, which solves the Schrödinger equation for molecular vibrational degrees of freedom with state-of-the-art accuracy [2, 3]. It can be used to perform calculations of the infrared spectrum of molecules of arbitrary sizes. The internship will consist in using the CONVIV code to compute and interpret theoretically, the IR spectra of selected members of the PAH family.

A particular attention will be devoted to the improvement of ab inito Quartic Force Field (QFF) which are actually not accurate enough for the interpretation of astrophysical observations, in particular those from the James Webb Space Telescope (JWST) and from MATISSE operating at the Very Large Telescope Interferometer (VLTI) of the European Southern Observatory (ESO). The QFF is a tractable means by which one can describe the near equilibrium anharmonicity of potential energy surface (PESs) for a medium-size molecular system. However, the accuracy of the IR frequencies one can obtain by truncating the force field at fourth order, is not sufficient with respect to the resolution of JWST spectra, whatever the electronic structure level, used for its ab initio quantum chemistry calculation, might be. Moreover, such truncated QFF can produce PESs diving artefactually to $-\infty$ when negative force constants are present. A possible workaround to this issue investigated in this internship will be to replace the quartic Taylor expansion along the vibrational modes by more adapted functional forms (Kratzer potential for vibrational modes carrying the totally symmetric representation and trigonometric Pöschl-Teller for other modes).

Prérequis: Basis of quantum mechanics and spectroscopy, computational skills (Fortran and Python).

References

[1] G. Mulas, C. Falvo, P. Cassam-Chenaï, C. Joblin, J. Chem. Phys. **149**, 144102 (2018).

[2] P. Cassam-Chenaï, J. Liévin, Journal of Computational Chemistry **27**, 627-640 (2006).

[3] P. Cassam-Chenaï, Y. Scribano and J. Liévin, Chemical Physics Letters **466**, 16-20 (2008).