Anharmonic vibrational spectroscopy of PAHs

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Polycyclic aromatic hydrocarbons (PAHs) are widely believed to be an important component of the interstellar medium (ISM), and to be the carriers of the ubiquitous aromatic infrared bands (AIBs). Since the emission mechanism assumes that emission of the AIBs takes place from molecules transiently heated to high temperatures by the absorption of UV/visible photons, it must occur from highly excited vibrational states. Anharmonicity is crucial in such conditions, since it affects substantially band positions and profiles, and must be taken into account to model astronomical observations.

The AnharmoniCaOs [1,2] software is being developed to compute anharmonic vibrational spectra of large, semirigid species such as polycyclic aromatic hydrocarbons (PAHs), both at 0K and finite temperatures (or excitation energies) of the molecules. We here illustrate the potentialities of AnharmoniCaOs, in terms of its accuracy with respect to available experimental data, also in comparison with other similar codes and/or with different theoretical approaches.

AnharmoniCaOs applies the van Vleck formalism to implement a 2nd order generalised perturbation theory approach to obtain anharmonic vibrational states and permitted dipole transitions. The potential energy surface is approximated by its Taylor expansion, cut to the 4th order, around the stable geometry of the molecule, and the electric dipole moment operator by its Taylor expansion up to the 2nd order. Terms of the potential expansion that cause resonances are excluded from the perturbative treatment and instead used to set up variational calculations, which become very large at high enough excitation. AnharmoniCaOs can be coupled with a Monte Carlo approach to sample the behaviour of bands as a function of excitation energy, from which the temperature dependence can be obtained via a Laplace transform.

We will discuss the approximations which are needed to make feasible calculations suitable for use with astronomical models, computational costs and caveats.

References
[1] G. Mulas, C. Falvo, P. Cassam-Chenaï, and C. Joblin, *The Journal of Chemical Physics* 2018, 149, 144102.
[2] https://sourceforge.net/projects/anharmonica/