

Theoretical Anharmonic Spectra of hot PAHs: the AnharmoniCaOS code

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Polycyclic Aromatic Hydrocarbons (PAHs) lock up between 10 and 20% of C in the interstellar medium (ISM), dominate the extinction curve in the UV via strong electronic transitions, convert most of the absorbed energy to vibrational excitation in the ground electronic state and then re-emit it via a cascade of vibrational transitions [1,2]. Most of these IR photons are emitted in hot bands, shifted around the fundamental 1-0 transitions due to anharmonicity. The resulting bands are thus broadened and shifted, and produced by an unknown mixture of species in several ionisation states, making their interpretation complex. Most astronomical PAH models are based on calculations under the so-called double harmonic approximation, with empirical scaling factors to account for anharmonic band shifts, and band widths assumed ad-hoc to match those observed in astronomical sources. The only models that attempt to deal with anharmonicity either restrict to transitions at 0K or neglect the effect of resonances to simplify the calculations at high temperatures [3].

We developed a tool to model full anharmonic PAH spectra and tested it on a medium-small PAH, namely pyrene, C₁₆H₁₀, fully accounting for both mechanical and electric anharmonicity. We sampled transitions from states vibrationally excited up to 12000 cm⁻¹ and obtained temperature-dependent spectra via a Laplace transform. As the temperature increases from 0K to ~600K we observe fundamental bands broaden and additional bands appear all over the spectrum. We report on the evolution of some of the most important bands with increasing temperature, comparing theoretical predictions with previously obtained experimental spectra [4]. We analyse the performance, computational cost, and caveats of our tool, in view of its systematic application.

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References:

- [1] Allamandola, L. J.; Tielens, A. G. G. M.; and Barker J. R. *Astrophys. J.* 1985, 290, L25–L28.
- [2] Léger, A.; d’Hendecourt, L.; Défourneau, D. *Astron. Astrophys.* 1989, 216, 148-164.
- [3] Mackie, C. J.; Candian, A.; Huang, X. et al. *J. Chem. Phys.* 2015, 143 (22), .224314.
- [4] Joblin, C.; Boissel, P.; Léger, A.; d’Hendecourt, L.; Défourneau, D. *Astron. Astrophys.* 1995, 299, 835-846