

Modeling the emission spectra of polycyclic aromatic hydrocarbons by recurrent fluorescence

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The presence of polycyclic aromatic hydrocarbons (PAH) in the interstellar medium (ISM) was first proposed over 40 years ago, following the observation of the aromatic infrared bands (AIB) [1]. This hypothesis was later confirmed by the detection of Buckminsterfullerene C₆₀ [2] and several nitrogen-bearing PAH species [3] in the ISM. The AIBs results from a transient heating mechanism: isolated molecules absorb a UV or visible photon, reaching an excited electronic state. Non-adiabatic processes then rapidly convert this electronic energy into vibrational energy within the ground electronic state [4], allowing the molecule to relax via spontaneous emission.

Despite this general understanding, many interrogations remain about the transient heating mechanism and the structure, dynamics and stability of PAHs that play a crucial role in the ISM chemistry.

Recent experiments on the relaxation kinetics of PAH cations trapped in storage rings [5,6,7] reveal a competition between several processes: spontaneous vibrational infrared emission, dissociation, isomerization and recurrent fluorescence (RF). The latter occurs when vibrational energy is converted back into electronic energy, through a process called inverse internal conversion (IIC), putting the molecule in a low lying electronic state, from which it can relax by fluorescence. RF is a key mechanism for stabilizing PAHs in highly ionized environments such as those found in many regions of the ISM.

In this contribution, we will present a new vibronic model of PAH relaxation by recurrent fluorescence [8] and discuss its application to various cationic PAHs. This model takes explicitly into account the vibrational levels and includes Duschinsky rotations and Herzberg-Teller effects. We will focus on our results regarding the Stokes shift and the vibrational activation of forbidden transitions, their contribution to the total RF emission in relation with experimental measurements [6], and what the consequences are for the stability of small PAH species in the environments of the ISM.

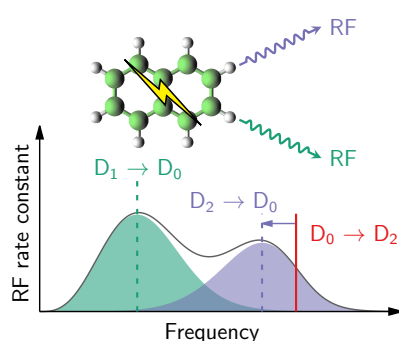


Figure 1 : Typical state-resolved differential RF rate constant for the D_1 and D_2 electronic state of naphthalene cation. The Stokes shift of the D_2 state is highlighted.

[1] A. Léger and J. L. Puget. *Astron. Astrophys.* **137**, L5 (1984).

[2] J. Cami, J. Bernard-Salas, E. Peeters, and S. E. Malek. *Science* **329**, 1180 (2010).

[3] B. McGuire, et al., *Science* **371**, 1265 (2021).

[4] K. Sellgren, M. W. Werner, and H. L. Dinerstein. *Astrophys. J.* **271**, L13 (1983).

[5] M. H. Stockett, J. N. Bull, H. Cederquist, S. Indrajith, M. Ji, J. Navarro Navarrete, H. T. Schmidt, H. Zettergren, and B. Zhu. *Nature Com.* **14**, 395 (2023).

[6] M. Saito, H. Kubota, K. Yamasa, K. Suzuki, T. Majima, and H. Tsuchida. *Phys. Rev. A* **102**, 012820 (2020).

[7] J. Bernard, M. Ji, S. Indrajith, M. H. Stockett, J. E. Navarro Navarrete, N. Kono, H. Cederquist, S. Martin, H. T. Schmidt, and H. Zettergren. *Phys. Chem. Chem. Phys.* **25**, 10726 (2023).

[8] D. Borja, et al., JCP submitted, arXiv:2601.02173v1

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