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 C_{60} [2] and several nitrogen-bearing PAH species [3]. 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 issues 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 emission, dissociation, isomerization and recurrent fluorescence (RF). The latter in particular, is key to stabilizing PAHs in highly ionized environments found in many regions of the ISM.

In this contribution, we will present a new vibronic model of PAH relaxation by RF mechanism [8]. This model takes into account explicitly the vibrational levels and includes Duschinsky rotations and Herzberg-Teller effects. We will discuss its application to various cations, focusing on the Stokes shift, as well as the vibrational activation of forbidden transitions and their contribution to the total RF emission, in relation with experimental measurements [6].

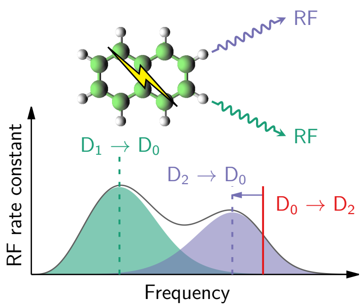

Figure 1 : Typical state-resolved differential RF rate constant for the D_1 and D_2 electronic state of naphthalene cation. The Stokes shift of the D_2 state is highlighted.

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