Kinetic Monte Carlo Modelling of Recurrent Fluorescence in PAH Cations for the Delhi Penning Trap

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Synopsis Recurrent fluorescence (RF) can stabilise highly excited polycyclic aromatic hydrocarbon (PAH) cations against fragmentation. We present a kinetic Monte Carlo (KMC) model of RF, infrared (IR) cooling and dissociation, benchmark it against tetracene storage-ring data, and predict that RF from PAH cations in the Delhi Penning Trap (DPT) is observable under detuned MeV electron excitation.

Polycyclic aromatic hydrocarbons (PAHs) are widespread in interstellar environments, where they are identified through their infrared (IR) emission bands. UV photons and cosmic rays, including relativistic electrons, can deposit enough energy in PAHs to raise them above their dissociation thresholds. Although IR emission provides a cooling pathway, the dissociation rate increases rapidly with internal energy, raising the question of how highly excited PAHs survive. Recurrent fluorescence (RF), in which optical photons are emitted from electronically excited states thermally repopulated through inverse internal conversion, provides an additional cooling mechanism. By removing energy in eV-scale quanta, RF can stabilise PAH cations above their dissociation thresholds, as shown in storage rings [1].

Model: To describe this competition, we developed a kinetic Monte Carlo (KMC) framework with three parts. An energy-distribution module provides the initial internal-energy distribution $P(E_0)$. A rate module provides $k_{\mathrm{RF}}(E)$, $k_{\mathrm{IR}}(E)$ and $k_{\mathrm{diss}}(E)$. A propagator follows each ion using the Gillespie algorithm: waiting times are sampled as $\Delta t = -\ln U/k_{\mathrm{tot}}(E)$, with $k_{\mathrm{tot}} = k_{\mathrm{RF}} + k_{\mathrm{IR}} + k_{\mathrm{diss}}$ and U a uniform random number, and each event is chosen with probability k_i/k_{tot}. RF and IR events reduce E by the corresponding photon energy, whereas dissociation terminates the trajectory. Averaging over many trajectories gives survival probabilities and RF photon statistics.

Benchmark: The framework was tested with the tetracene ($C_{18}H_{12}^{+}$) rates of Bernard *et al.* [1] (measured RF, theoretical IR and literature dissociation rates). For $E_0 = 7.0$–9.4 eV, the simulated dissociation fractions follow the branching ratio $k_{\mathrm{diss}}/k_{\mathrm{tot}}$ (Fig. 1) and exceed it slightly at the highest energies, where ions can dissociate after emitting IR photons.

DPT predictions: The Delhi Penning Trap (DPT) [1, 2] combines a 1.1 T Penning trap with radial optical access and the 1–8 MeV electron beam of the Delhi Light Source (DLS) at IUAC [2]. With full beam–ion overlap, fragmentation dominates. When the beam is detuned, the ions are excited by its electromagnetic field and recurrent fluorescence competes with dissociation; 83 % of the ions survive and each emits on average 0.2 RF photons per 10 ms, corresponding to $\sim 2 \times 10^5$ photons s^{-1} for 10^4 stored ions.

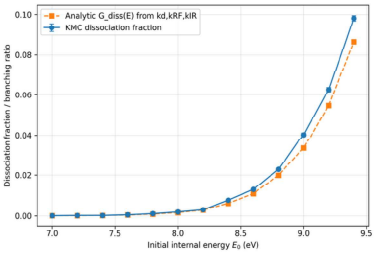

Figure 1. KMC and analytic dissociation fractions for tetracene.

References

[1] Bernard J *et al.* 2023 *Phys. Chem. Chem. Phys.* **25** 10726
[2] Kumar S *et al.* 2026 *Mon. Not. R. Astron. Soc.* **548** stag684
[3] Kumar S *et al.* 2025 *J. Instrum.* **20** C05016
[4] Ghosh S *et al.* 2017 *Nucl. Instrum. Meth. B* **402** 358

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