

Cooling dynamics of PAHs cations probed by laser photo-dissociation in a compact electrostatic storage ring, the Mini-Ring

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Synopsis Small hot polycyclic aromatic hydrocarbons (PAHs) cations have been stored in a compact electrostatic ion storage ring, so-called Mini-Ring, in order to study the competition between the radiative cooling and the dissociation processes in the millisecond time range. We have demonstrated that the main radiative cooling could be attributed to the now called recurrent fluorescence (RF) process, predicted theoretically in the 1980s by Leger et al.[1] Two methods of measurement of the radiative cooling rate will be discussed.

Since the 1980, when PAHs have been suggested as good candidates for being responsible of mid-infrared absorption bands in the interstellar medium (ISM), there are debates about the size, the formation/destruction mechanisms, etc. Measurements of radiative cooling rates of isolated PAHs in non-equilibrium conditions are crucial for estimating of the photostability and therefore the size distribution of PAHs in the ISM.

Using our compact electrostatic ion storage ring, so-called Mini-Ring[2], we have experimentally demonstrated the importance of a fast radiative cooling mechanism for PAH cations, the recurrent fluorescence (RF), that quenches the dissociation process in the millisecond or sub-millisecond time ranges[3]. Figure 1 shows a simplified scheme of the energy levels of a typical small PAH cation and displays the RF process after photon absorption: Internal conversion (IC) populates the vibrationally excited ground state D_0 . The inverse internal conversion (IIC) with a rather low probability may populate the electronic excited state D_2 that can in turn fluoresce by emission of a visible photon ($h\nu_{el}$) to lower vibrational states of D_0 . The molecule is then cooled down at once by an energy corresponding to the energy of the emitted photon (about 1.7 eV for anthracene cations).

In order to quantify the evolution of the internal energy distribution (IED), the PAH cations were reheated after different storage times using laser absorption. The shape of the laser-induced fragmentation decay reveals the shape of the IED. It shows that the IED presents a high energy edge (HEE) that shifts with storage time down to

lower energy due to dissociation and radiative cooling. The time evolution of this HEE helps us to determine the radiative cooling rate of the stored PAH cations as a function of the internal energy. However, this method relies on the knowledge of the dissociation rates of the PAH cation, which has been measured or calculated for few of them. We have developed another model independent method by using photons of slightly different energies, $\Delta E=0.2$ eV (with an OPO laser). Assuming that identical decays corresponds to identical IEDs, the radiative cooling rate is measured by determining the storage time difference Δt leading to the same decay for the both photon energies. Results obtained for several PAH cations and di-cations as well will be discussed.

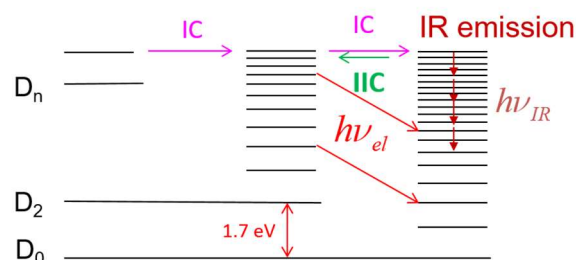


Figure 1. Scheme of the energy levels of a typical small PAH cation (anthracene) displaying the RF process after photon absorption.

References

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