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The cooling of naphthalene cations studied within an electrostatic storage ring

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Abstract. Fast population decay of naphthalene cations ($C_{10}H_8{}^+$) has been observed in a compact electrostatic storage ring, the Mini-Ring, up to 5 ms. Laser induced dissociation due to single-photon absorption was used to probe the internal energy distribution (IED) of the stored molecular ions as a function of the storage time. To determine the energy distribution of naphthalene cations, the experimental neutral decay curve was analysed with a model including the competition between dissociation and radiative cooling. Fast cooling rates from about 70 s^{-1} at the internal energy 5.6 eV to 140 s^{-1} at 6.2 eV were measured and compared with the data in the literature. This fast cooling mechanism is attributed to the fluorescence from thermally excited electrons and may have important implications in astrophysics for the lifetime and the critical size of Polycyclic Aromatic Hydrocarbons (PAH) in the interstellar medium.

1. Introduction

The abundant presence of PAHs in the interstellar medium was proposed almost thirty years ago [1, 2] in order to explain the unidentified infrared (UIR) emission band. Since then, numerous laboratory studies have been initiated to understand their origin and stability in the astrophysical environments [3, 4]. The photophysics of isolated PAHs irradiated by UV photons has been studied taking into account the dissociation and IR cooling of the molecule [5]. However, an efficient and faster cooling process than IR emission was also proposed by Leger and Boissel with the name of Poincaré fluorescence [6]. This fast process involves inverse internal conversion (IIC) and relies on the fast electronic fluorescence from low lying electronic states. Recently, evidence of this fast electronic cooling mechanism was observed using electrostatic storage ring (ESR) in the case of anthracene cation ($C_{14}H_{10}{}^+$) [7] and hot small molecular anions C_6^- [8]. In earlier works, many other molecules and clusters have been studied within ESRs, like ELISA in Aarhus, which appeared to be very efficient to study the relaxation dynamics of complex systems in a long time range from microsecond to second [9]. In this paper, we study the cooling of naphthalene cations stored in our small electrostatic storage ring, the Mini-Ring. A numerical method is used to analyze the experimental data in order to determine the population decay rates of the stored ions for several excitation energies.

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2. Experimental set-up

The experiment consists in storing naphthalene cations ($C_{10}H_8{}^+$) in an electrostatic storage ring, the Mini-Ring, whose characteristics were described in details in papers [10, 11]. Naphthalene molecules were ionized and heated in an Electron Cyclotron Resonance (ECR) ion source with a broad initial internal energy distribution, and accelerated to 12 keV. The singly charged naphthalene molecular ions were selected using a 90° magnet and the ion beam was pulsed into bunches of 1 µs width every 5 ms. These ion bunches were injected into the Mini-Ring and stored with a 5.5 µs revolution period. The Mini-Ring vacuum chamber was pumped down to a pressure of 2.10^{-9} mbar to limit the probability of collision with the residual gas molecules. The stored naphthalene ions were expected to dissociate mainly via the emission of C_2H_2 and H. These neutral fragments due to unimolecular dissociation were detected at each turn by a position sensitive detector (PSD) facing one of the straight lines of the stored ion trajectory. After dissociation, the daughter ions could not remain on a stable trajectory because their kinetic energy did not fulfill the stable storage conditions and so, they were quickly ejected out of the ring. Nanosecond laser pulses with a photon energy of 2.33 eV (second harmonic of a 1 kHz Nd-YAG OPO laser) were sent at a different precisely controlled storage time t_{laser} = 0.5, 1.5, 2.5, 3.5, and 4.5 ms to excite a fraction of the stored ions in order to probe the internal energy distribution (IED) of the ion bunch. The intensity of the laser pulse was about 300 µJ per pulse, corresponding to a low enough photon flux to ensure the single-photon absorption condition.

3. Results

The number of emitted neutral particles (with laser pulses) is plotted in the Figure 1 as a function of the storage time, integrated over 3.10^6 injected bunches. Without laser excitation, after a storage time of 0.5 ms, the dissociation probability of the excited ions from the source was negligible and the detected neutrals were due to collisions with residual gas molecules. Therefore, for storage time longer than 0.5 ms, further evolution of the IED is assumed to be due to radiative cooling only.

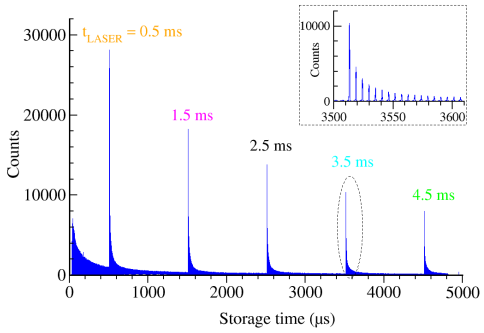

Figure 1. Evolution of the number of neutral particles emitted as a function of the storage time. Laser pulses were sent to excite the ions from 0.5 ms to 4.5 ms every 1 ms.

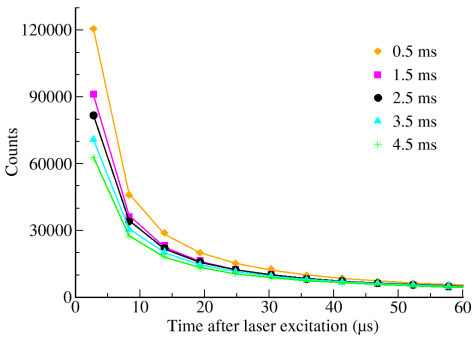

Figure 2. (colored online) Symbols : neutral yield integrated over each revolution period as a function of time after laser excitation, taking t_{laser} as the time reference. Full lines: simulated decay curves adjusted to the experimental data.

The strong increase of neutral numbers at t_{laser} is characteristic of the laser shots. After each laser pulse, about 1% of the ions in the bunch absorbed a photon. With their increased internal energies, these molecules had a higher probability to dissociate. An enlargement inserted in the Figure 1 shows the emission period of neutral particles, which corresponds to the naphthalene cation revolution period. The integral of the neutral yield over each revolution period is plotted in the Figure 2 as a function of the storage time, taking t_{laser} as the time reference.

For each t_{laser}, a neutral decay curve was simulated using a code written in C language. The simulations started with an initial IED of the stored ions at t_{laser} after the photon absorption. The number of emitted neutrals was calculated as a function of time considering the energy dependency of the dissociation rate [12] as well as the probability for the electronic fluorescence emission, which was considered to be negligible for the energies larger than 7.5 eV [13]. Each experimental decay curve was then fitted independently with the modeled decay curve by varying the parameters of the initial IED. The best fit provided the IED after laser excitation. The IED of the stored ions at different t_{laser} prior to laser absorption was then obtained by subtracting the energy of the photon $h\nu = 2.33$ eV (Figure 3). It is noteworthy that due to the sensitive energy window of the experiment (see [11] for more details) the choice of the modeled initial IED is not unique for the low energy part. However the decay curve is very sensitive to the position of the high energy edge of the IED, and not to the low energy shape. For this work a Gaussian shape has been chosen to model the high energy part of the IED, but other shapes with similar high energy edges [7] would provide similar results.

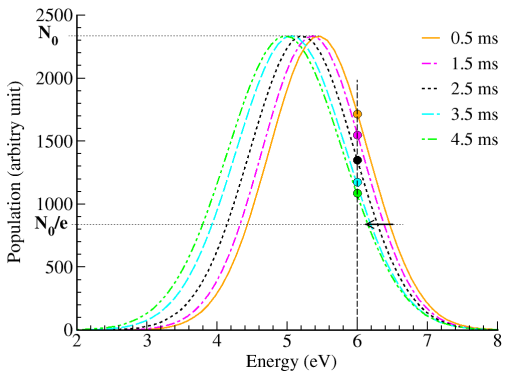

Figure 3. (colored on line) IED of the stored ions before laser excitation. The vertical line shows the population decay from 0.5 ms to 4.5 ms at a given energy.

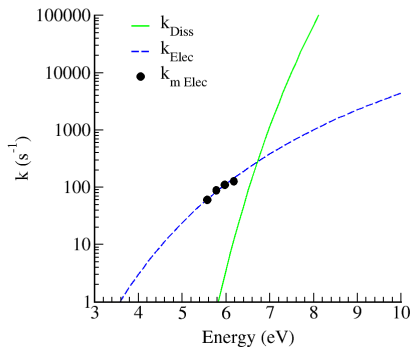

Figure 4. The measured electronic rates k_m compared to the evolution of the theoretical dissociation rate k_{Diss} [12] and fluorescence emission rate k_{Elec} [13].

The time evolution of the energy distribution is distinctly visible in Figure 3. An average shift $(\frac{\Delta E}{\Delta t})_m = 100\,\text{eV} \cdot \text{s}^{-1}$ of the high energy edge at N_0/e to lower energy values was measured at about 6.5 eV. This shift is faster than the value $(\frac{\Delta E}{\Delta t})_{IR} = 13\,\text{eV} \cdot \text{s}^{-1}$ for infrared emission at about 6.5 eV deduced from Figure 2 of reference [13]. From Figure 3 a measured population decay rate k_m can be determined by fitting with an exponential law the evolution of the population as a function of time for a given energy (not shown). A k_m of 120 s^{-1} was deduced from the fit of the five crossing points at E = 6.0 eV (vertical line in Figure 3). The same method was used to measure the population decay rate at 5.6, 5.8

and 6.2 eV. To extract the measured electronic transition rate k_{mElec} from k_m, it is needed to take account of the contribution from IR emissions. As k_m is proportional to $(\frac{\Delta E}{\Delta t})_m$, k_{mElec} was deduced by subtracting 10% from k_m. The deduced k_{mElec} values are plotted in Figure 4 in comparison with the evolution of the theoretical dissociation rate k_{Diss} and fluorescence emission rate k_{Elec}, as a function of the naphthalene cation internal energy.

Our measured electronic transition rates are in good agreement with the theoretical values calculated with an electronic transition energy of 2.1 eV [14] and an oscillator strength of 0.052 [15]. In the sensitive energy window, k_{Diss} is negligible comparing to k_{Elec}. This demonstrates that the cooling of the hot naphthalene cations stored in the Mini-Ring in the time range from 0.5 to 4.5 ms is mainly due to the electronic radiative transition, as already observed with the anthracene cations [7].

4. Conclusion

Fast population decay rates of naphthalene cations were found to be ranging from about 70 s^{-1} at 5.6 eV to 140 s^{-1} at 6.2 eV. The measurements were performed using a small electrostatic storage ring and laser induced dissociation to probe the evolution of the internal energy distribution (IED) of the stored molecular ions from 0.5 to 4.5 ms storage time. The IED were obtained by fitting the measured decay curves of the emitted neutrals due to unimolecular dissociation. The measured population decay rates were obtained at different internal energies from the evolution of these IED and the measured electronic transition rates were deduced by subtracting the contribution of the IR emission. The fluorescence emission from low lying electronic states is found to be the most efficient radiative cooling channel. This process is strongly dependent on the energy gap from the first electronic state to the electronic ground state of the cation. Further studies with different PAH are planned in order to study the evolution of the fast electronic emission with the molecule properties, which may have an important role in the lifetime and critical size of PAH in interstellar clouds.

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