Fast Radiative Cooling of Anthracene Observed in a Compact Electrostatic Storage Ring

S. Martin,[1] J. Bernard,[1] R. Brédy,[1] B. Concina,[1] C. Joblin,[2,3] M. Ji,[1] C. Ortega,[1] and L. Chen[1,*]
[1]*Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex, France*
[2]*Université de Toulouse, UPS-OMP, IRAP, 31028 Toulouse, France*
[3]*CNRS, IRAP, 9 Avenue colonel Roche, BP 44346, 31028 Toulouse cedex 4, France*

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Fast radiative cooling of anthracene was observed in a compact electrostatic storage ring by probing the evolution of the internal energy distribution of a stored $(C_{14}H_{10})^+$ molecular ensemble via laser excitation. We have measured the mean radiative decay rate to be about 120 to 250 s^{-1} for internal energies in the range from 6.6 to 6.8 eV. Such a high decay rate is 2 orders of magnitude larger than the infrared emission cooling rate expected for vibrational transitions. It is attributed to fluorescence from thermally excited electrons. This fast cooling mechanism may have important implications in astrophysics concerning the lifetime and the critical size of polycyclic aromatic hydrocarbons in interstellar conditions.

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The ubiquitous presence of polycyclic aromatic hydrocarbon (PAH) molecules in the Interstellar Medium (ISM) was proposed almost thirty years ago [1,2] and this proposal has initiated numerous laboratory studies to identify individual species and to understand their origin in astrophysical environments (see the recent state of the art on this subject in Ref. [3]). The photophysics of an isolated PAH irradiated by UV photons has been described in Ref. [4] with emphasis on the statistical relaxation mechanisms such as photo-thermo dissociation and IR cooling. Measurements of radiative cooling rates of PAHs in nonequilibrium conditions are essential in estimating the photostability and therefore the size distribution of PAHs in the ISM. Following fast internal conversion from the excited electronic state to the electronic ground state, the radiative cooling process is assumed to be governed by the IR emission leading to a lifetime in the range of tens of seconds. An additional cooling process was, however, proposed in which inverse internal conversion can lead to efficient cooling by electronic fluorescence with emission of visible or near-IR photons [5]. Boissel *et al.* [6] included this process in their theoretical simulation of the measured photofragmentation efficiency curve of trapped anthracene cations under continuous visible light irradiation. Andersen *et al.* [7] have studied the radiative cooling of fullerene anions at high temperature in a storage ring and demonstrated that radiation from thermally excited electrons was the dominating mechanism. However, to our knowledge, there is no direct experimental evidence for this radiative cooling mechanism in small PAH molecules.

Recent experiments using electrostatic storage rings (ESR) with a circumference of a few meters have demonstrated their large potential in the studies of the relaxation dynamics of complex systems in a time range from sub-millisecond to second. Delayed electron emission from anions, delayed dissociation, radiative cooling of fullerenes and other large molecules or clusters have been extensively studied with such ESRs [7–9]. In parallel, several issues relative to the long term stability of clusters or molecules have been addressed successfully using smaller linear or bend electrostatic ion beam traps of a half meter long, analogous to an optical oscillator [10,11]. More recently, we have developed a small ESR [12], called Miniring which combines the advantages of the large ESRs and the small electrostatic ion beam traps. Similarly to the larger ESRs, the stored ions, having kinetic energies in the keV range, can be excited along one of the straight sections (9.2 cm long) by a laser beam. Neutral fragments resulting from dissociation processes occurring at the opposite straight section can be easily detected due to their high kinetic energy. Owing to the compactness of this ring, we are able to measure the laser-induced dissociation in a typical time ranging from the very first microseconds to the order of a millisecond after a laser excitation. This provides the opportunity to get access to the internal excitation energy distribution of the stored molecular ion ensemble and as a consequence to the radiative decay rate.

In this Letter, we report on the observation of fast radiative cooling of anthracene ions and the first experimental determination of its decay rate. This rate is compared with previous theoretical estimations and is attributed to electronic fluorescence from hot PAH species.

As illustrated in Fig. 1, the Miniring consists of two off-axis electrostatic reflectors (C_1, C_2) and four deflection plates (D_1 to D_4). Details of this ESR can be found in Ref. [12]. Anthracene molecules ionized in the plasma of an electron cyclotron resonance ECR nanogan ion source were extracted at 10 kV. The $(C_{14}H_{10})^+$ molecular ions were produced with a rather broad initial vibrational energy distribution. After a time of flight of 32 μs through the beam line, bunches of ions of about 1 μs were injected into the ring every 10 ms via the first straight section through D_1-D_2 and stored with a revolution period

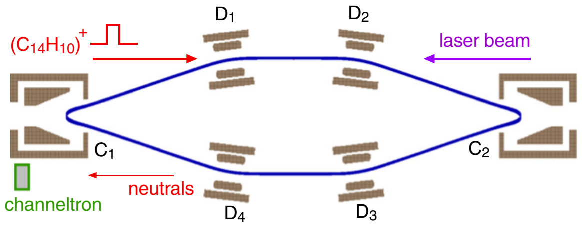

FIG. 1 (color online). Experimental setup: the stored ion trajectory was simulated with SIMION software.

measured to be 7.23 μs. Neutral fragments, mostly C_2H_2 or H, emitted by the dissociation of $(C_{14}H_{10})^+$ along the second section through D_3-D_4 were detected at each turn by a channeltron. The storage lifetime limitation due to collisions with the residual gas (2×10^{-9} mbar) was measured to be about 300 ms, much larger than the storage cycle (10 ms) of this experiment. A few ms after the injection, the ions could be irradiated by a nanosecond pulse of the third harmonic (3.55 eV) of a 100 Hz Nd:YLF laser that merged with the ion bunch through D_1 and D_2. The intensity of the laser pulse was about 100 μJ/pulse to ensure the single photon absorption condition.

To get a typical decay curve, the count of neutrals integrated over each revolution period was plotted as a function of the storage time. Figure 2(a) displays, with a log-log scale, the decay curve obtained without laser irradiation and accumulated over about 3×10^5 bunch-injection cycles. Considering the time of flight from the source to the ring and the first half period in the ring, the first neutrals were detected about 36 μs after the formation of the molecular ensemble in the ECR source. For $t > 36$ μs, the dissociation decay curve presents three distinct regions and can be fitted using a multi-parameter function according to Eq. (1) in Ref. [13],

$$N(t) = \frac{N_0}{e^{t/\tau} - 1}\left(\frac{t}{\tau}\right)^{\delta} + N_{BG} \qquad (1)$$

where τ is a time constant, δ a dimensionless parameter, N_{BG} the contribution of background gas collision and N_0 a normalization constant. From the obtained fitting parameters ($\delta = 0.2$ and $\tau = 1$ ms), we find that the decay at short time range ($t < \tau$) follows approximately a time dependent power law, $t^{-(1-\delta)} = t^{-0.8}$. It is attributed to the delayed dissociation of hot $(C_{14}H_{10})^+$ produced in the ion source. At intermediate time range, from $t = 1$ to 4 ms, a faster decrease of the measured neutral yield deviates significantly from the $t^{-0.8}$ power law. This suggests the appearance of other competing nondissociative decay mechanisms. Similar behaviors have been observed for amino acids and interpreted as a quenching of the dissociation by radiative cooling [13]. Following this previous work, our fitted characteristic time τ (1 ms) is interpreted as the quenching time after which the radiative cooling becomes competitive. At longer times ($t > 4$ ms), the curve follows an exponential decay with a time constant of about 300 ms corresponding to the storage lifetime, which is limited due to collisions with the residual gas. This suggests that at a time scale larger than 4 ms, the neutrals are produced mainly by collision-induced dissociation. Therefore, from the analysis of $(C_{14}H_{10})^+$ spontaneous decay curve, we deduce that, after the extraction from the ECR source, the molecular ensemble is first "cooled" down by the depletion of its high energy population mainly via the dissociation process ($t < 1$ ms). Then, from 1 to 4 ms, the high energy population is partly depleted via the dissociation and partly transferred to a lower energy region via radiative decay. After 4 ms, the dissociation can no longer induce significant population depletion to the surviving "cooled" molecular ensemble. Any further evolution of the energy distribution is essentially governed by the radiative cooling.

To probe the variation of the energy distribution in a time range larger than 4 ms, a laser pulse can be fired at a controlled storage time. Assuming that the electronic excitation is fully converted into vibrational energy, the ions that have absorbed a photon experience an increase of their internal energy by 3.55 eV. This leads to the formation of a "new" molecular ensemble whose internal energy distribution was shifted by 3.55 eV towards higher energy. Neutral decay curves due to laser induced dissociation of the excited molecules were recorded and analyzed to get the energy distribution before photon excitation. A similar method was previously used to study the cooling of C_{60}^- [9]. In the latter work, the probed energy variations were attributed to the combined action of depletion via electron emission and radiative cooling, while in the present case, the depletion via dissociation was effectively observed to be quenched in the studied time range.

Figure 2(b) displays both the spontaneous decay curve ($t < t_{laser}$) and the decay curve induced by a laser pulse fired at $t_{laser} = 5$ ms. Apparently, the laser induced decay curve looks sharper with a surprisingly high relative maximum yield, although the total number of detected laser-induced neutrals is estimated to correspond to only 1% of

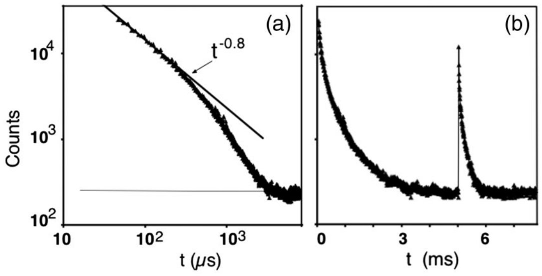

FIG. 2. Neutral yield decay curves: (a) without laser irradiation (gray horizontal line shows the contribution of collisions with the residual gas), and (b) with one photon excitation at $t_{laser} = 5$ ms.

the stored molecules. The high contrast of the laser-induced decay curve is due to the very short time interval between the formation of the excited molecular ensemble and the detection of the first neutrals. This curve was indeed recorded half of a revolving period, i.e., about 3.6 μs, following the laser excitation, whereas the spontaneous decay curve was recorded 36 μs after the extraction of molecules from the ECR source.

The decay curves induced by laser pulses fired at $t_{\text{laser}} =$ 4, 5, 6, and 8 ms, corrected from the collision-induced dissociation background, are plotted as a function of time over 50 μs (Fig. 3). The time reference is defined by t_{laser} for each decay curve. It can be noticed in Fig. 3 that the measured yield decays faster for $t_{\text{laser}} = 4$ ms than for 8 ms and the maximum yield decreases with increasing t_{laser}. This suggests that the mean internal excitation energy of molecules that dissociate after laser irradiation has decreased from 4 to 8 ms. Considering that the change of internal energy associated to photon absorption is independent of t_{laser}, we deduce qualitatively that the stored molecular population distribution before laser excitation shifts to lower energy with time.

In order to estimate more quantitatively the evolution of the energy distribution $N(E)$ of the stored molecular ensemble, we have fitted the laser induced decay curves with a simple unimolecular statistical dissociation model. The energy dependent dissociation rate $k_d(E)$ for $(C_{14}H_{10})^+$ established in an earlier time-resolved photoionization experiment by Ling *et al.* [14] was employed. The energy distribution $N(E)$ was approximated using a broad multi-parameter function:

$$
\begin{aligned}
N(E) &= N_a \quad \text{if } E < E_0 \\
N(E) &= N_a - Y(E - E_0)^3 \quad \text{if } E > E_0 \qquad (2)
\end{aligned}
$$

A simulated neutral decay curve was then built by summing over the contributions from all excited molecules. By adjusting the parameters, N_a, Y, and E_0, the experimental dissociation decay curves were reproduced nicely (Fig. 3).

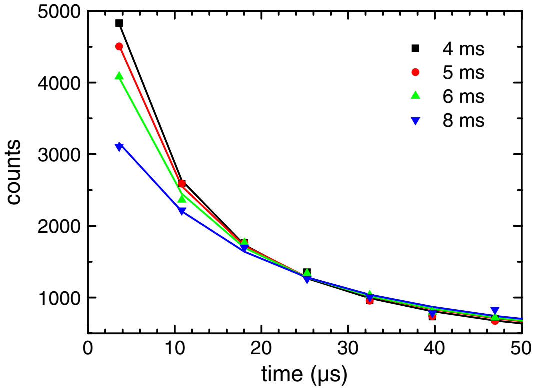

FIG. 3 (color online). Experimental (symbols) and modeled (plain line) decay curves for a laser pulse fired at $t_{\text{laser}} = 4$, 5, 6, and 8 ms.

The adjusted energy distributions $N(E)$ are displayed in Fig. 4. Although the decay curve fitting procedure was found suitable for modeling the high-energy region of the distributions, it was not sensitive to the exact shape of the low energy part of $N(E)$, typically for $E < 9$ eV. In fact, molecules at lower energy dissociate mainly in a time range larger than 120 μs after laser excitation, and their contribution to the measured fast decay curve is negligible. Analyzing the high-energy part of $N(E)$ (Fig. 4), we have defined a characteristic high-energy edge E_{edge} with $N(E_{\text{edge}}) = N_a e^{-1}$ represented by the horizontal broken line in Fig. 4. For $t_{\text{laser}} = 4$ and 8 ms, E_{edge} was found at about 10.3 and 10.1 eV, respectively, corresponding to 6.8 and 6.6 eV (E_{edge}-$h\nu = E_{\text{edge}} - 3.55$ eV) before laser excitation. Therefore, in this energy region, the high-energy edge was estimated to shift at a rate of $\Delta E_{\text{edge}}/\Delta t = -50$ eV/s. As the contribution from unimolecular dissociation is negligible in such a long-time range ($t > 4$ ms), the measured decrease of the high-energy edge is attributed without ambiguity to the radiative cooling of the stored molecular ions.

The time evolution of the number of molecules at internal excitation energy (E-$h\nu$) before laser excitation can also be studied from Fig. 4 by drawing a vertical line at a given energy E that crosses all $N(E)$ curves for different t_{laser}. The extracted populations at the crossing points for $E = 10.1$ eV are plotted in the inset of Fig. 4 and fitted with an exponential function. The population at $t = 0$ extrapolated from the exponential decay is quite comparable to the low-energy horizontal part of the distribution, showing that the population distribution at $t = 0$ is roughly independent of the energy. This feature is expected because the considered energy range is a narrow part of the broad

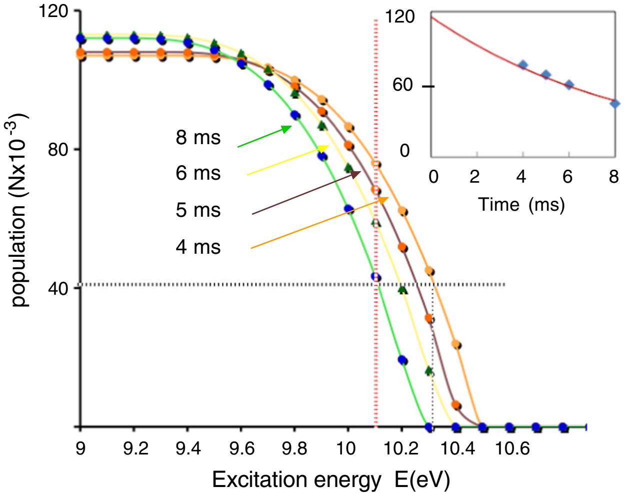

FIG. 4 (color online). Adjusted excitation energy distributions $N(E)$ of the anthracene ions after the absorption of a single photon at $t_{\text{laser}} = 4$, 5, 6, and 8 ms. Inset: time evolution of the population at internal energy 6.6 eV obtained from $N(E)$ at 10.1 eV. Solid line: exponential fit.

energy distribution from the ECR source. The characteristic decay constant 120 s^{-1} is defined hereafter as the mean radiative decay rate k_{rad} for molecules with the corresponding internal energy 6.6 eV before laser excitation. Similarly, for molecules at 6.7 and 6.8 eV, the mean radiative decay rate k_{rad} has been estimated to be about 200 and 250 s^{-1}.

The radiative cooling of anthracene molecular ions has been investigated theoretically [6] including contributions from both the IR vibrational emission and fluorescence electronic emission. In a wide energy range from 2 to 10 eV, the IR cooling rate was found to be about 2 s^{-1} and nearly energy independent. Such a slow IR rate can certainly not explain our observed radiative decay, k_{rad}, which is 2 orders of magnitude higher. A faster radiative cooling rate due to electronic emission was indeed predicted in Ref. [6]. In such a process, the coupling between the vibrationally hot molecules in the ground electronic state and other electronic excited states may lead to the conversion of a fraction of the vibrational energy into electronic excitation [5]. In the work of Boissel *et al.* [6], the rate k_{el} of photon emission was defined as the product of the known Einstein coefficient of the electronic transition (in the order of 10^6–10^7 s^{-1}) by the probability of presence in the corresponding electronic excited state. Because of a lower probability of presence in higher excited electronic states, it can be considered that the thermal excitation process involves mainly the first electronic excited state of anthracene and the energy of the emitted photons falls therefore around $h\nu_{el} = 1.7$ eV (724 nm), which corresponds to the transition energy from the first electronic excited state to the ground state. Using the data of Ref. [6], the predicted electronic emission rate k_{el} was found to be about 100 s^{-1} for the energy range studied in this work, which is in agreement with our measured decay rate k_{rad}. Furthermore, the theoretical model predicted an increase of k_{el} with energy due to the increasing probability of presence in electronic excited states. This is in qualitative agreement with the trend of our measured k_{rad}. Therefore, we can attribute the fast radiative cooling that we have measured for stored anthracene molecules to electronic fluorescence from hot species. Although the emitted photons were not analyzed, the measured cooling rate is consistent with emission arising mainly from the first electronic excited state. In larger systems such as carbon fullerene anions, thermally excited electrons can occupy large energy bands where the quantum structure is washed out [7,15].

In summary, fast radiative decay, of the order of 10^2 s^{-1}, was observed by following the evolution of the internal energy distribution of a stored $(C_{14}H_{10})^+$ ensemble in a long time range (4–8 ms). The mean radiative decay rate, measured to be typically 120 s^{-1} at 6.6 eV and 250 s^{-1} at 6.8 eV, is attributed to fluorescence from thermally excited electrons, a process which occurs in the cooling of hot fullerenes and involves energy transfer from vibrational to electronic excitation. The possibility that this fluorescence leads to an emission band at about 1.7 eV, as previously suggested, still awaits for a direct experimental evidence. This fast cooling mechanism might have important implications, in particular concerning the stability of PAHs in UV-irradiated regions of space. This experiment also demonstrates the potential of the new generation of small ESR, such as the Miniring, in measuring the radiative cooling rate of a molecule. The compactness of the Miniring is indeed essential for the observation of the fast and sharp laser-induced neutral decay, which is very sensitive to the time evolution of the energy distribution of a molecular ensemble. This ring provides therefore an excellent tool for probing the relaxation dynamics of complex systems.

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*chen@univ-lyon1.fr

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