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Time evolution of internal energy distribution of Anthracene studied in an electrostatic storage ring, the Mini-Ring

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Abstract. Fast radiative cooling of polycyclic aromatic hydrocarbon (PAH) was studied by probing the time evolution of the internal energy distribution of hot molecular ensembles in the ms range. Anthracene cations $(C_{14}H_{10})^+$ prepared in an electron cyclotron resonance ion source were stored in an electrostatic storage ring, the Mini-Ring [1]. The experiment showed that in the first milliseconds, the time evolution of the stored ion population distribution was dominated by the unimolecular dissociation of the molecular ions with higher internal energy. Then, in the next milliseconds, the unimolecular dissociation was quenched by radiative cooling. In a larger time range, from 4 to 8 ms, the time evolution of the internal energy distribution was probed by reheating a part of the molecular ensemble by laser photon absorption at different storage times. We report here the measurement of a fast radiative cooling rate ($100s^{-1}$) that can't be explained by vibrational IR emission but rather by electronic fluorescence from thermally excited electronic states [2].

1. Introduction

Based on the early IR spectroscopy analyses, the presence of PAH molecules in the Interstellar Medium (ISM) has been proposed almost thirty years ago and since then, numerous laboratory investigations have been conducted in order to understand their origin and stability in astrophysical environments [3, 4]. Recently, PAHs as small as Anthracene, have been identified in a molecular cloud of the Perseus star-forming region [5]. Among other issues on laboratory studies, a fundamental one concerns the radiative cooling mechanism upon excitation, which is essential for estimating the photo-stability and therefore the size distribution of PAH in the ISM. Generally speaking, the radiative cooling of vibrationally excited hot molecules is explained by the Infrared (IR) emission of about 0.2 eV for aromatic molecules, with a typical cooling rate of several s^{-1}. However, in the 1980s, an alternative process, the Inverse Internal Conversion leading to a fluorescence emission has been proposed as another possible doorway to cool down the PAH molecules faster than the IR emissions.


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It was named in the letter [6] "Poincaré fluorescence" and it might explain some of the red-light luminescence observed from many interstellar regions. This process corresponds in fact to the radiation from thermally excited electrons observed in most recent years in the cooling of larger systems, the fullerene anions [7]. Similar process was also suggested in the measurement of cooling rates of small clusters, Al_4^- [8]. For the Anthracene, the emission of light due to this process is expected to be around 1.7 eV corresponding to the first electronic transition at 724 nm. In an earlier work, Boissel et al [9] have included the "Poincaré fluorescence" in their theoretical simulation to fit the trapped Anthracene cation photofragmentation efficiency curve induced by continuous visible light irradiation. However, due to its lifetime in the ms range, the predicted decay rate of 100 s^{-1} has been measured only very recently [2] using a small electrostatic storage ring, the Mini-Ring [1].

In this paper, we report on the measurement of the fast radiative decay rate of Anthracene stored in the Mini-Ring with more experimental and analytical details. Initially hot molecular $(C_{14}H_{10})^+$ ion ensembles stored in the Mini-Ring were "cooled" down first by the depletion of the high-energy part of the internal energy distribution via the dissociation process. After several milliseconds of storage, the unimolecular dissociation was progressively quenched by the radiative cooling and then this latter process became dominant. The further evolution of the high-energy edge of the internal energy distribution of the stored molecular ensembles was probed next by single photon excitation. From the time evolution of the distribution, the radiative cooling rate was determined and was compared with the expected theoretical value predicted by the "Poincaré Fluorescence".

2. Preparation and storage of monocharged Anthracene

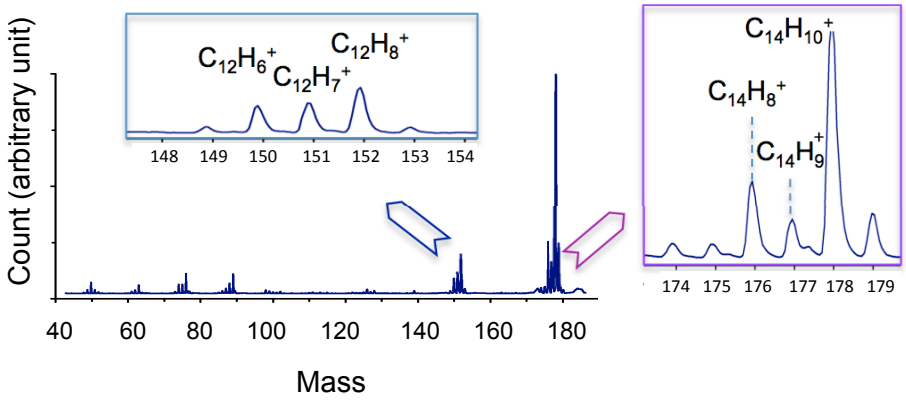


Fig.1 Mass spectrum of molecular ions from the ECR source

Anthracene molecules were ionized and heated in the plasma of an electron cyclotron resonance (ECR) ion source with a rather broad initial vibrational energy distribution. A mass spectrum of ions extracted from the ECR source and accelerated to 10 keV per charge is presented in fig.1. One can notice a dominant peak corresponding to the monocharged intact $(C_{14}H_{10})^+$ and also small peaks corresponding to charged fragments from the main dissociation channels via the successive loss of neutrals H, H_2 or C_2H_2. The small peak at the nominal mass 179 is due to the isotope contribution of ^{13}C. In our experiment, intact $(C_{14}H_{10})^+$ ions of mass 178 were selected with the magnet (fig.2). Very low HF power (about 0.2 W) was required to optimize the beam intensity. Molecular ion bunches of about 1μs passing through the ion beam chopper were sent to the Mini-Ring chamber every 10 ms (fig.2). The Mini-Ring is composed of 2 mirrors of a conical shape and 4 deflectors made of parallel plates. It is about 40 cm in length and is installed in a high vacuum chamber (2 10^{-9} mbar). With six straight sections, it offers multiple opening axes for the ion injection, ion excitation and neutral detections. Ion bunches were injected into the ring via the first straight section through D_1 and D_2 (fig.

2b) and stored with a revolution period measured to be 7.23 μs. The mass resolution of the ring is about 1/300. The pulse applied to the chopper was defined as the time reference of the following dissociation events for each storage cycle.

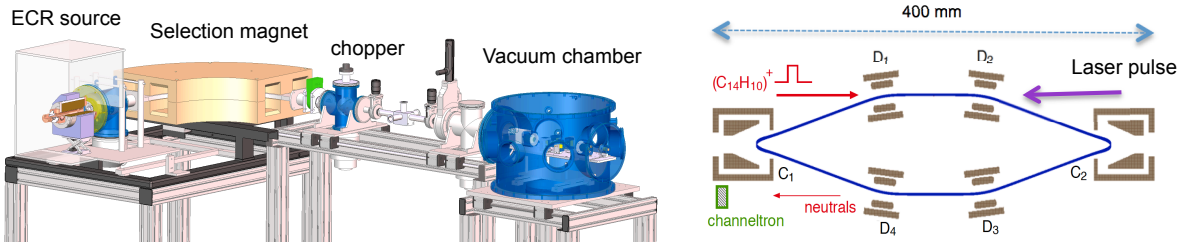


Fig.2 Experimental setup and the drawing of the Mini-Ring.

3. Population depletion of high internal energy ions due to unimolecular dissociation

With the Mini-Ring, we could experimentally follow the time evolution of the energy distribution of an initially hot stored molecular ensemble. During the first 36 μs corresponding to the flight time from the ECR source to the Mini-Ring, most of the hottest molecular ions were lost from the beam due to the unimolecular dissociation. For dissociation occurring before or inside the mass selection magnet, the charged fragments were deviated from the beam by the magnetic field; for dissociation during the flight time between the magnet and the ring, charged fragments such as $(C_{14}H_9)^+$ entered first in the Mini-Ring and then escaped from the stable storage trajectory within one or two revolution turns. For Anthracene ions surviving until entering in the ring, the high-energy side of the population distribution continued to be depleted by unimolecular dissociation. Dissociation events in the ring were observed at each revolution turn by detecting fast neutral fragments (mostly C_2H_2, partly H) going out of the ring through the straight section between deflectors D_3 and D_4 with a channeltron. The dissociation time of each event was determined using a digital convertor (TDC) connected to the channeltron (fig.2). The measured neutral count versus the storage time (fig.3 (a)) shows that unimolecular dissociation occurs within 4 ms. At longer time range (t>4ms), the neutral yield follows an exponential decay law with a time constant of about 300 ms which corresponds to the storage lifetime limited due to collisions with the residual gas. Therefore, after 4 ms, the unimolecular dissociation can no longer induce significant population depletion to the stored molecular ensemble.

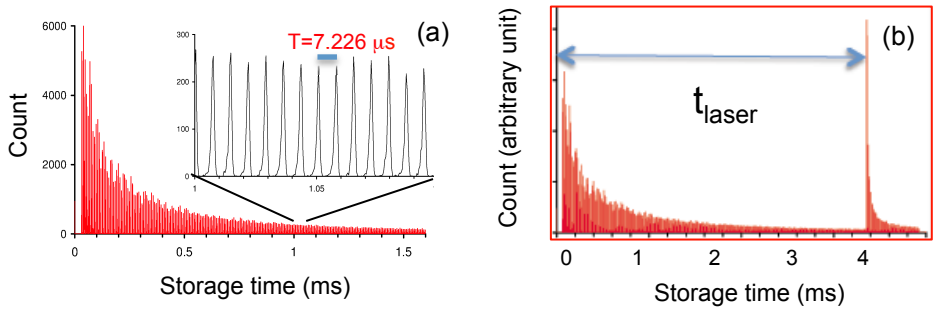


Fig.3 Neutral count number as a function of the storage time (a) without laser (b) with laser excitation at t_{laser}. The zoom in (a) shows the revolution period of stored ions.

4. Laser induced dissociation

In order to probe the evolution of the energy distribution in the time range, t>4ms, a nanosecond UV laser pulse (hν=3.55 eV, the third harmonics of a 100Hz Nd:YLF laser) was sent between D_1 and D_2 to merge the stored ion bunch (fig.2) at a controlled storage time t_{laser}. The intensity of the laser pulse was controlled to ensure single photon absorption condition. A small part of the ions absorbed one photon leading to the formation of a "new" molecular ensemble. Its internal energy distribution was suddenly shifted towards higher values by the quantity hν at the storage time t_{laser}. The reheated high-energy molecules dissociated leading to a sharp neutral yield during the first 100 μs after the laser excitation (fig.3 (b)). Taking t_{laser} as the time reference, the neutral yield integrated over each revolution period was plotted in fig.4(a) as a function of time after laser excitation for t_{laser}=4, 5, 6, 8 ms.

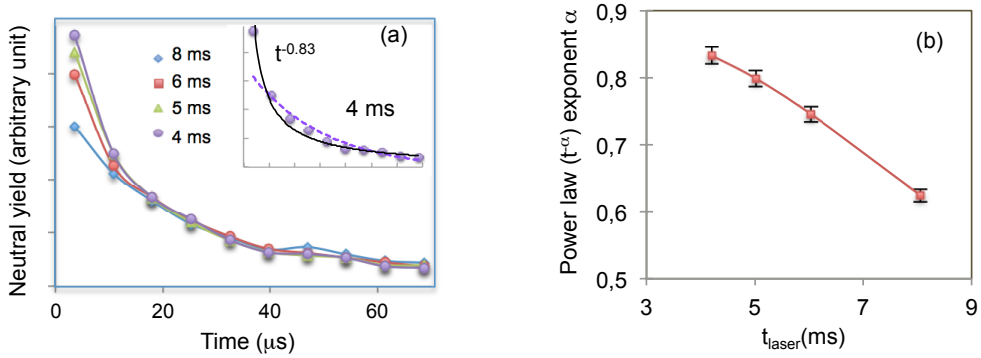


Fig.4 (a) Neutral yield as a function of time for the first 10 turns taking t_{laser} as time reference.
Inset : Data for t_{laser} = 4ms;
Broken line: fit with an exponential function; solid line: fit with $t^{-0.83}$.
(b) Power law exponent α as a function of t_{laser}.

Comparing the neutral yield curves in fig.4 (a), a decrease of the first value (at 3.6 μs) with increasing t_{laser} can be noticed and the curve for 8 ms was found to decay slower than that for 4 ms. Contrary to expectations, the measured decay curves could not be well reproduced by exponential functions, while power functions, $t^{-\alpha}$, were found to be more appropriate for fitting (inset fig.4 (a)). The power law exponent α (fig.4(b)) provides in fact a good indicator for the dissociation dynamics. Smaller α value is related to slower dissociation process from molecules with lower internal excitation energies. The simple α variation tendency with t_{laser} indicates that, on average, the internal excitation energy of molecules that dissociated after laser irradiation was smaller for t_{laser} = 8 ms than for t_{laser} = 4 ms. The energy shift due to the photon absorption being constant (hν), we deduce that the stored molecular population distribution before laser excitation was shifting towards lower internal energies with time. As the contribution from the unimolecular dissociation is negligible in such long-time range (t > 4 ms), this shift has to be attributed to the radiative cooling.

Based on the knowledge of the energy dependency of the statistical dissociation rate of Anthracene molecules [10], we have extracted the energy distribution of the stored ion bunches after laser excitation [2]. From fig.4 of ref. [2], by subtracting the energy of the photon, the energy distributions at 4, 5, 6 and 8 ms of storage time of the stored ions before laser excitation were obtained (fig. 5). Fig.5 shows clearly the time evolution of the energy distribution. Typically, the high-energy edge of the energy distribution shifts to lower values with the time at a rate of about 50 eV per second. Meanwhile, a vertical line drawn at a given energy E crosses all energy distribution curves

corresponding to different storage time. These crossing points describe actually the population decay of molecules at this energy. For example, population decay obtained from the crossing points at E=6.6 eV has been fitted with an exponential law. The estimated decay rate, 120 s^{-1}, is interpreted as the radiative cooling rate of molecules at this energy, denoted thereafter as k_{rad}.

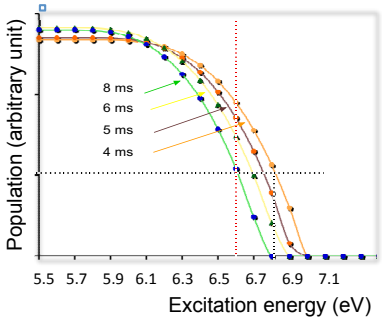


Fig.5 Energy distribution of stored ion bunches at 4, 5, 6 and 8 ms of storage time

5. Comparison with the theoretical model

In an early work, Boissel et al [9] have included contributions of the infrared vibrational emission and electronic fluorescence emission in a theoretical model. A "mean cooling rate" on the basis of an ensemble of ions was defined in order to account for both slow, multistep, vibrational transitions and faster, single-step electronic transitions,

$$k_{cool}(E) = \frac{1}{E}\frac{dE}{dt} \quad . \qquad (1)$$

A nearly energy-independent $k_{cool,IR}$ (2 s^{-1}) due to vibrational IR emission was found in a large energy region from 2 eV to 10 eV. Faster radiative cooling rate due to electronic fluorescence emission was estimated considering the so-called "Poincaré fluorescence". In fact, for hot molecules, the ground electronic state with high vibrational excitation is populated predominantly, while other degenerated electronic excited states with lower vibrational excitation are occupied with much lower probability due to their relatively lower density of states. However, these states should not be neglected in the radiative cooling process, because the Einstein coefficient of the electronic transition (in the order of 10^6-10^7 s^{-1}) is much larger than that of the infrared vibrational transition and the energy carried out by a single photon is much higher. A rate of emission k_{el} of photon ($h\nu_{el}$) was calculated in ref. [9] by the product of the Einstein coefficient with the probability of presence in the electronic excited state. The mean cooling rate k_{cool} was obtained by summing over the contributions of all possible excited states and including $k_{cool,IR}$,

$$k_{cool} = \frac{1}{E}\sum_{el} k_{el} h\nu_{el} + k_{cool,IR} \qquad (2)$$

In this equation, the contribution of the first electronic transition of Anthracene (at 724 nm, $h\nu_{el}$ =1.7 eV) is dominant. By neglecting transitions from higher electronic states in eq. (2), we have estimated approximately the transition rate k_{el} via the first electronic excited state from the data of $k_{cool}(E)$ presented in fig.2 of ref.[9], using $k_{el} \approx (k_{cool} - k_{cool,IR})\, E/(h\nu_{el})$. For the energy range studied in this work, the predicted rate k_{el} of electronic transition was found to be about 100 s^{-1}. Based on this analysis, one can notice that our measured decay rate k_{rad} matches quite well with the theoretical electronic transition rate of Boissel et al, k_{rad}(this work) $\approx k_{el}$. Therefore, we attribute the fast radiative cooling of the stored Anthracene molecules in the time range from 4 to 8 ms mostly to the electronic fluorescence.

6. The choice of the photon's energy

The compactness of the Mini-Ring proved to be critical for the observation of the fast laser-induced dissociation of Anthracene ions. Indeed, the delay between the laser excitation and the detection of the first neutrals was 3.6 μs. The main contribution to the neutral fragment yields shown in fig.4(a) arose from molecular ions excited in an energy window around 10 (±0.5) eV. In order to obtain decay curves sensitive enough to the time evolution of the energy distribution, the high-energy edge (E_{edge}) of the laser-excited population should vary inside this energy window for the different laser probing time ($4<t_{laser}<8$ ms). In the case where E_{edge} is below the energy window, molecules with internal energy close to E_{edge} should be mostly stable during the first turns. In the case of E_{edge} above the window, molecules with internal energy close to E_{edge} dissociate mainly during the first half period at $t<3.6$ μs. In both cases, fragments from molecules at the high-energy part of the distribution would not be efficiently detected. The determination of the energy distribution from the neutral decay curves would become very difficult.

In the present experiment, the choice of the UV photon was not arbitrary. Laser pulses with other wavelengths have been also used, for example, the green 2nd harmonics of the Nd:YLF laser at hν=2.37 eV. Comparing to the UV photons, the energy of a green light photon is about 1.2 eV smaller. So, with single photon absorption, the high-energy edge of the excited molecule population distribution remained below the sensitive energy window, while with two-photon absorption, the high-energy edge was pushed above the window. As a consequence, the measured neutral decay curves did not show significant evolution with the storage time and the analysis method presented in this work is not applicable to Anthracene using green light photons. In the contrary, the UV photon carries the right amount of energy needed to bring E_{edge} in the sensitive window. For future experiment with other PAH molecules, special care will be needed to the choice of the laser wavelength in order to be able to measure the radiative cooling rate with the Mini-Ring.

7. Summary

Using an ECR ion source and a small electrostatic storage device, the Mini-Ring, we have measured the radiative cooling rate of Anthracene molecular ensembles by following the time evolution of the energy distribution. The measured decay rate was compared with the electronic fluorescence rate predicted in a theoretical model. We plan to apply this method to other molecules in the PAH family. Enhanced or absence of this fast electronic cooling rate may have important consequences for the presence of particular PAHs in the ISM. Preliminary experiments have been performed with some other small PAH molecules and more results will be reported in forthcoming papers.

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