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Fluorescence decay of naphthalene studied in an electrostatic storage ring, the Mini-Ring

S. Martin [a,*], J. Matsumoto [d], N. Kono [d], M.-C. Ji [a,c], R. Brédy [a], J. Bernard [a], A. Cassimi [b], L. Chen [a]

[a] Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon, 69622 Villeurbanne cedex, France
[b] CIMAP, GANIL Université de CAEN, Bd. H. Becquerel, Caen, France
[c] Université de Toulouse, UPS-OMP, IRAP, Toulouse, France
[d] Department of Physics, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hchioji, Tokyo 192-0397, Japan

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ABSTRACT

The cooling of naphthalene cations $(C_{10}H_8)^+$ has been studied in a compact electrostatic ion storage ring, the Mini-Ring. A nano second laser pulse of 532 nm (2.33 eV) was used to probe the internal energy distribution every millisecond during the storage time up to 5 ms. The evolution of the internal energy distribution of the stored ions was simulated with a model taking into account the dissociation and the radiative decay processes. Calculated decay curves were fitted to the corresponding laser induced neutral decays. For a laser power of 200 μJ/pulse, a good agreement between experiment and modeling was found using an initial Gaussian energy distribution centered to 5.9 eV and a fluorescence decay rate varying from 200 to 300 s^{-1} in the energy range from 6 to 7 eV. This fast decay was attributed to the delayed Poincaré fluorescence process.

1. Introduction

Studies of evolution of internal energy distribution (IED) of highly isolated polycyclic aromatic hydrocarbon (PAH) molecules are of great interests for estimating the minimum stable size of molecules irradiated under UV in the interstellar medium (ISM) [1]. Up to now, only the cooling via infrared emission was taken into account in the astrophysical model on the population of vibrationnally excited hot PAH in ISM. Recently, we have shown that the delayed fluorescence called also Poincaré fluorescence process for Anthracene and Naphthalene cations [2,3] was a very efficient cooling process and should be taken into account in the modeling of the size distribution of PAH in ISM. This mechanism, referred also as the "recurrent fluorescence", results from the coupling between highly excited vibrational states and a low energy electronic excited state, which could jump back to the ground electronic state via fast electronic transition. In laboratory, cooling processes of molecules are not easy to measure precisely because they occur in large time range (ms). In recent years, many laboratories have developed new electrostatic storage devices for molecules, which are well adapted to study the cooling processes in good conditions (very low collision rates, long storage time up to hours, high ion density, slow kinetic energy dispersion, well defined ion beam in order to perform merged beam experiment...).

In our laboratory, we have developed a table-top electrostatic storage ring the Mini-Ring [4] which can store molecular ions up to second. A nanogan ECR ion source initially developed for multicharged ions has been used with a 10 GHz HF power supply operated at a few Watt to produce molecular ion beams. The main advantage of this kind of source is to provide ion beams with low kinetic energy dispersion, high intensity and the possibility to change the internal energy distribution of molecules by adjusting the pressure and the HF power of the source. Another advantage is that the heating of molecules occurs mainly by electronic excitation via collisions with hot electrons in the plasma of the ECR source. This process is close to the heating by UV photon absorption in the ISM regions. The energy range of the heating is very large and we can adjust parameters to obtain a distribution with a maximum of hot molecules staying stable versus the dissociation process. For molecules just situated at the high energy edge of the distribution, the absorption of a single photon (here 2.33 eV) is enough to bring the molecules to an internal energy region around 8–9 eV for which the delayed dissociation process occurs typically with a lifetime from 1 to 200 μs.

In this work, we study the cooling mechanism of hot Naphthalene cations stored in the Mini-Ring. We have probed the IED

* Corresponding author.
E-mail address: smartin@univ-lyon1.fr (S. Martin).

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of stored ions using irradiation with a laser pulse from 0.5 ms to 4.5 ms storage time by 1 ms step with merged beam technique. In our previous works, the measured laser induced neutral decay curves were fitted by simulating separately the energy distributions at each laser excitation time. In the present work, we have performed simulations on the global time evolution of the energy distribution including the dissociation and the radiative decay processes. By adjusting the initial IED and the fluorescence decay rate, the experimental neutral decay curves were fitted. This modified simulation method allowed us to estimate the fluorescence decay rate of the naphthalene molecules and to get more insight on the evolution of the low energy part the IED.

2. Experimental setup

The experiments were performed on the Mini-Ring setup, which consisted of four deflectors and two electrostatic off axis mirrors (see Fig. 1). Detailed information about the setup can be found in previous papers [4]. Briefly, the naphthalene molecules were ionized in an ECR ion source and accelerated to 12 keV. Singly charged intact naphthalene cations were selected by a 90° magnet and chopped into bunches in width of 6 μs every 40 ms. A bunch of naphthalene ions was stored in the ring up to 40 ms with a revolution period of 5.5 μs. The ring was completely filled excepting a very small part due to the short time necessary for the closing of D_1 (see Fig. 1). Due to the energy dispersion of the beam, the ion density can be considered uniform after a few ms of storage time. The storage cycle of 40 ms was much shorter than the storage lifetime of 300 ms limited by collisions with residual gas under high vacuum conditions in the ring chamber (2×10^{-9} mbar). Neutral particles, mainly C_2H_2 [5], emitted from stored naphthalene cations through D_3 and D_4 were collected at each turn by a 2D-multi channel plate detector. Emission of neutral H occurred also. However the detection efficiency of hydrogen atom is very poor due to its much lower kinetic energy (12 keV/128 = 0.1 keV) than C_2H_2, the contribution of H to the neutral decay is negligible. In the present configuration, the laser beam can be tilted more precisely than in previous experiments to ensure a better overlap between ion and laser beams. We have also reduced the Betatron oscillations in order to reduce the error for the overlapping with laser for different storage time. The detection time of a neutral was converted through a time to digital convertor TDC V4 developed by the Institute of Nuclear Physics of Orsay. The time range of this TDC was up to second with a resolution of 120 ps.

During a storage cycle of 40 ms, laser pulses of photons (532 nm, 2.33 eV) were sent to excite the stored ions at well-controlled storage time every millisecond. The laser pulse repetition frequency was about 1 kHz with energy controlled to 200 μJ pulse^{-1}. The laser repetition frequency was adjusted precisely in order to irradiate different part of the bunch by different laser pulses in order to reduce the reheating effect. Indeed, the reheating of ions due to the absorption of two photons from two laser pulses was negligible, because neutral decays obtained at a given storage time using multi-pulse or a single pulse laser were observed with no notable difference. In the following typical spectra were accumulated over about 10^5 storage cycles.

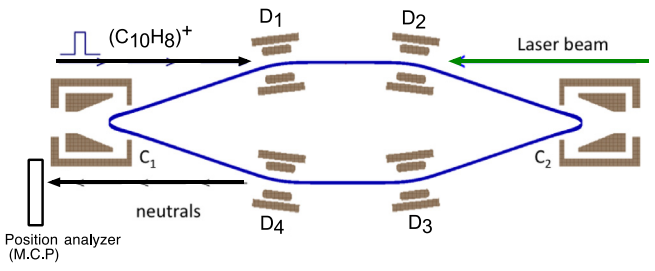

Fig. 1. Experimental set up.

3. Data analysis and discussion

In Fig. 2, a typical spectrum is shown from 30 μs to 4.8 ms. Neutral decay due to the spontaneous dissociation of hot molecules produced in the ECR source is observed from 30 μs to 0.5 ms storage time. This spontaneous or naturel decay corresponds to the contribution of about 1% of the total population of the stored ions. Neutral yields recorded right after each laser pulse at t_{laser} = 0.5, 1.5, 2.5, 3.5 and 4.5 ms are first enhanced strongly and then decrease rapidly from turn to turn. The peaks associated to each turn cannot be distinguished in Fig. 2, but they are well separated with a time interval corresponding to the revolution period of the ions in the ring. In order to describe the laser induced neutral decay tendency versus time, the total neutral count of each turn was integrated and plotted in Fig. 3 as a function of t, the storage time with respect to t_{laser}. Corrections have been made taking into account the background and the beam intensity normalization (see paper [3] for details). As already observed, slower neutral decays correlate to longer storage times, i.e. larger t_{laser}, due to the evolution of the IED.

To simulate the evolution of the IED of the stored ions, in our previous works, we adjusted independently the IED after each laser excitation time t_{laser} by fitting the calculated neutral decay curve to the corresponding measured one. The IED of the stored ions at t_{laser} before excitation was deduced by an energy shift to lower values with the energy of the photon. In the simulation, the population decay of parent ions at a given energy was characterized by the total rate corresponding to the sum of the H and C_2H_2 emission rates. According to West et al. [5], the emission rate ratio between C_2H_2 and H is nearly constant in the present internal energy range. Then the simulated parent population decay is proportional to that of one of the lost neutrals. It means that the evolution of the parent molecular population could be obtained by the measurement of either all neutral products or only one of them, C_2H_2 in this case. From the evolution of the IED obtained separately at different storage time t_{laser}, the fluorescence decay rate was determined. Similar data analysis procedure has been employed in the studies of Anthracene and Naphthalene molecules [3,6]. The disadvantage

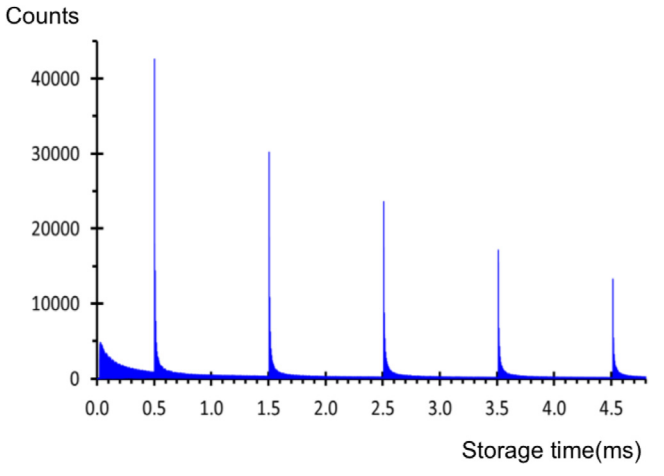

Fig. 2. Neutral yields due to the dissociation of naphthalene cations with laser irradiation (532 nm) pulses at t_{laser} from 0.5 ms to 4.5 ms (step one ms).

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