Journal of Physics: Conference Series

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To cite this article: L. Chen *et al* 2017 *J. Phys.: Conf. Ser.* **875** 012005

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IOP Conf. Series: Journal of Physics: Conf. Series **875** (2017) 012005 doi:10.1088/1742-6596/875/2/012005

Excitation, fragmentation and radiative decay of molecules studied with fast ion beams

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Abstract: Dissociation of doubly charged Anthracene was studied in collisions with a fast 3 keV F^+ ion beam. From fragmentation mass spectrum measured in coincidence with the energy deposited in the molecule, we have determined the dissociation rate for the loss of C_2H_2 and H as a function of energy. The cooling of singly charged Anthracene was studied using a small electrostatic storage ring. The fluorescence emission rate has been determined and compared with a theoretical model.

1. Introduction

Charged atomic and molecular ions A^{q+} accelerated to about q keV to 10q keV provide a powerful tool for studying the fragmentation and relaxation of isolated molecules. In this report, we recall two types of experiments developed in our group in the last years: a collision chamber to study the collision induced dissociation of molecules under energy control [1] and a small electrostatic storage ring (Mini-ring) [2][3] to study the cooling of charged molecules prepared in an electron cyclotron resonance (ECR) ion source. We present especially studies on Anthracene $C_{14}H_{10}$, which is a Polycyclic Aromatic Hydrocarbons (PAH). PAH is a family of Hydrocarbon molecules composed of multiple aromatic rings. Based on early IR spectroscopy analyses, the presence of PAH molecules in the Interstellar Medium (ISM) has been proposed almost thirty years ago and this proposal has initiated numerous laboratory studies [4]. One of the interesting issues concerns the decay mechanism upon excitation, because it is essential for estimating the photo-stability and the size distribution of PAH possibly in the space.

It is known that hot molecules with high vibrational energy may release their internal energy by dissociation or radiative decay. At higher energy, the dissociation is dominant; the molecule breaks and emits small fragments. At lower energy, the vibrational transition is dominant; the molecule is cooled down by infrared emission. For singly charged Anthracene, the energy dependent dissociation rate [5] and the mean IR emission rate have been studied in previous works [6]. In the intermediate energy range, another mechanism, the fluorescence emission by electronic transition was predicted to be dominant. However, this mechanism is not really well known. In fact, people are more familiar with the heating mechanism of molecules. To heat a molecule already in highly excited vibrational states, one can excite an electron by photon absorption. Then through the internal conversion, the electronic energy is transferred to vibrational energy. The molecule is prepared at higher vibrational state. About thirty years ago, a French group in Orsay proposed to consider the inverse process in the cooling of molecules [7]. For Anthracene, this process starts with the so-called inverse internal conversion, where a fraction of the vibrational energy of the ground electronic state D_0 is converted to electronic excitation energy of the state D_2, with very low probability, 10^{-5} at about 7 eV [6]. Therefore, this process has been neglected during longtime. Nevertheless, once the electron is raised to the excited state D_2, it may jump back to the ground state D_0 with high spontaneous transition rate. The product of these two values is defined as the fluorescence emission rate. It was estimated to be about one hundred per second for singly charged Anthracene. Its contribution in the cooling of the molecule was predicted to be larger than the IR emission in this energy region [6]. In spite of the important role this mechanism might play in the cooling of PAH molecules, its laboratory demonstration is actually a challenging work due to the long lifetime of the process.


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In this paper, we address two topics concerning the decay of Anthracene: the measurement of the dissociation rate of doubly charged Anthracene and the fluorescence emission due to electronic transition for singly charged Anthracene.

2. Dissociation rate of doubly charged Anthracene studied using the CIDEC method [8]

In collision between a singly charged projectile ion A^+ and a molecular target M, two-electron capture process may lead to the formation of scattered anion, $A^+ + M \rightarrow A^- + M^{2+}$. By analyzing the kinetic energy loss of the anion and measuring in coincidence the target fragments, we are able to study the fragmentation dynamics of doubly charged molecules as a function of the excitation energy deposited in the target during the collision. With this method, called CIDEC (Collision Induced Dissociation under Energy Control) [1], we have studied the dissociation of a large number of doubly charged molecules, such as C_{60}, C_{70}, 2-Deoxy-D-Ribose, Adenine, Anthracene, HDO, $W(CO)_6$ and Porphyrine.

To study the dissociation of doubly charged Anthracene, we send a fast 3 keV F^+ ion beam to collide on nearly motionless Anthracene molecules. During the very short interaction time, in the order of fs, the electron transfer from the molecule to the projectile is the dominant process. Especially in close collisions, two-electron transfer may occur leading to the formation of ground state F^- and the energy deposition in the molecule. When we apply the total energy conservation law before and after the collision, the deposited energy E* can be expressed with the kinetic energy loss of the projectile during the collision ΔE and the energy defect of the interaction δ. δ known to be -1.6 eV is estimated using several characteristic constants of the fluorine atom and Anthracene molecule [8]. So, the excitation energy deposited in the molecule can be determined by measuring the kinetic energy loss ΔE of the scattered anion.

The experimental set-up is presented in fig.1. A F^+ projectile beam from an ECR ion source accelerated to 3keV crossed an effusive molecular jet evaporated from an oven. The scattered F^- formed in a single collision was selected and analyzed in kinetic energy by an electrostatic analyzer. The charged molecule or its fragments are analysed in mass over charge by a TOF spectrometer. The experimental data were recorded in a two-dimensional spectrum event by event in multi-coincidence mode. In this spectrum, each point keeps the correlated information of a collision event: the excitation energy of the parent doubly charged molecular ion and the decay product of the molecule.

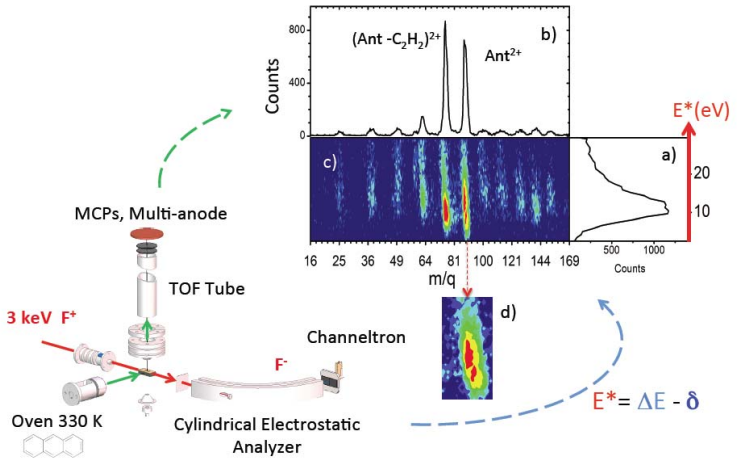


Fig.1 Experimental setup and the spectra:

a) Kinetic energy loss ΔE of F^- converted to the deposited excitation energy E*
b) Mass spectrum (m/q) of recoil molecules or fragments. "Ant" stands for Anthracene here after.
c) Coincidence spectrum between m/q (horizontal axis) and E* (vertical axis).
d) Spots corresponding to Ant^{2+} and $(Ant\text{-}2H)^{2+}$

The main peaks of the mass spectrum fig.1 b) are assigned to the doubly charged Anthracene (Ant^{2+}) and the successive loss of C_2H_2 fragments. The decay channel with the loss of 2H is resolved in the two-dimensional spectrum fig.1 d). The energy distribution of doubly charged Anthracene parents followed by different dissociation channels was then obtained by the projection of each spot to the energy axis. Using a statistical unimolecular dissociation model [8], we have reproduced the measured energy distributions by adjusting the dissociation rates for the loss of C_2H_2 and the loss of H. The obtained dissociation rates (fig.2 a) show similar energy-dependent variation tendency as the singly charged Anthracene obtained according to the ref. [5] (fig.2 b). However, at a given energy, the dissociation rate was found much larger for the doubly charged molecule than the singly charged one, showing a strong charge effect in the stability of the molecule.

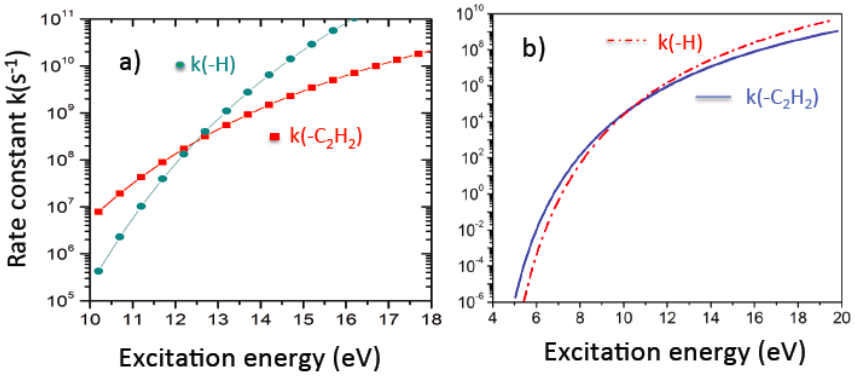


Fig.2 Dissociation rate k for the loss of C_2H_2 and H from a) Ant^{2+} and b) Ant^{+} (calculated following the ref.[5])

3. Fluorescence emission rate of Anthracene studied using a small electrostatic storage ring [9]

According to the theoretical prediction [6], to study the fluorescence emission, we need to prepare hot molecular ions at a relatively high energy around 7 eV. The phenomenon is expected in a time range larger than ms. In our experiment, Anthracene cations were prepared in an Nanogan ECR ion source. The internal energy of the molecular ions depends sensitively on the high frequency (HF) power injected in the source. At very low HF power, we got a majority of intact singly charged Anthracene. At higher HF power, above 300 mW, almost all molecules broke into small pieces as shown in the mass spectrum (fig.3). By fine-tuning of the HF power, we could control the plasma ionic temperature in the ECR source and prepare intact molecular ions with a broad energy distribution.

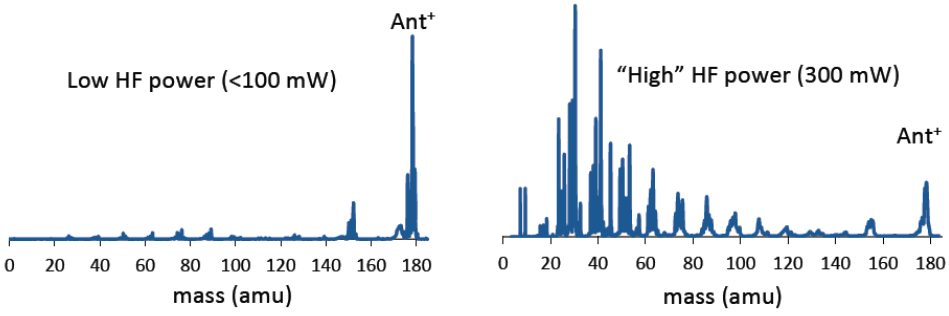


Fig.3 Mass spectra of ions from the ECR source obtained at different HF power.

Molecular ions were then extracted from the ion source, accelerated to 12 keV, selected with the magnet. They were bunched into a 1 μs pulse and injected to the Mini-Ring. The Mini-Ring is composed of 2 mirrors of conical shaped electrodes and 4 deflectors made of parallel plates [9]. Thanks to the high kinetic energy, the stored molecular ions turned around in the ring with high velocity, at more than 100 km/s. The circumference of the ion trajectory is about 73 cm. The revolution period is only 6.5 μs. The ions can be stored up to 100 ms. It is long enough for studying the fluorescence emission process.

The energy distribution of the stored bunch evolved with the time. During the first 3 ms, molecules with high internal energy dissociated. Neutral fragments C_2H_2 and H lost by the molecules escaped from the ring and were detected one by one using a particle detector. The residual charged fragments were also lost, because their kinetic energy would no longer fulfill the storage condition. This led to the depletion of the high-energy part of the distribution. After 3 ms, no more neutrals due to dissociation were detected. From this moment, a bunch of ions, which was still hot but free from dissociation, turned in the ring. We were now ready to study the fluorescence emission process, which was expected to induce photon emissions and population transfer from high energy to lower energy.

Normally, to study fluorescence emission, the straight way is to collect photons. Unfortunately, up to now no one has been able to detect these photons from PAH cations. The radiative decay is actually a kind of "invisible" channel in our experiment. So the challenge is to get fluorescence information by following the evolution of the internal energy distribution due to the radiative cooling. 3 ms after the ion injection, at any controlled time t_{laser}, a UV laser pulse was sent to merge the ion bunch along one of the straight sections of the Mini-ring [9]. Under laser irradiation, a small fraction of the population could be excited leading to the formation of a "new" molecular ensemble. The reheated high-energy molecules dissociated very fast. Sharp neutral yield decay was detected during the first 100 μs after the laser excitation (fig.4 a)). The measurement was performed for t_{laser} from 3 to 7 ms.

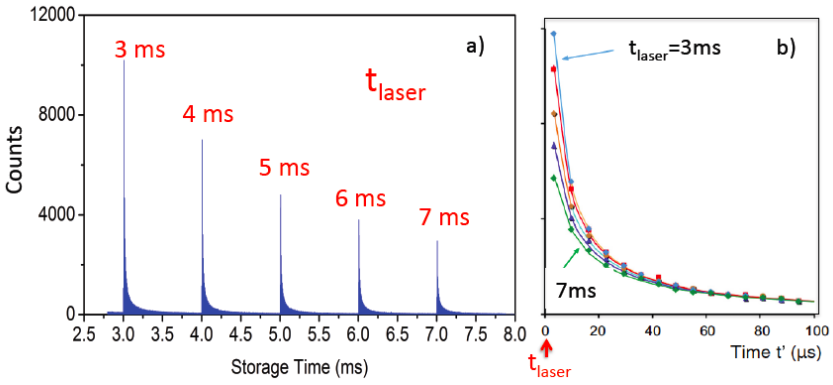


Fig.4 a) Neutral counts following laser pulse fired at t_{laser} from 3 to 7 ms.
b) Neutral decay curves taking t_{laser} as time reference.

From fig.4 b) one can see that the neutral decay curves become less and less steep with the storage time t_{laser}. For each t_{laser} time, we have simulated the corresponding excited energy distribution using a statistical dissociation model to reproduce the measured decay curve [9]. By subtracting the energy of the photon, we have determined the energy distribution before excitation from 3 to 7 ms.

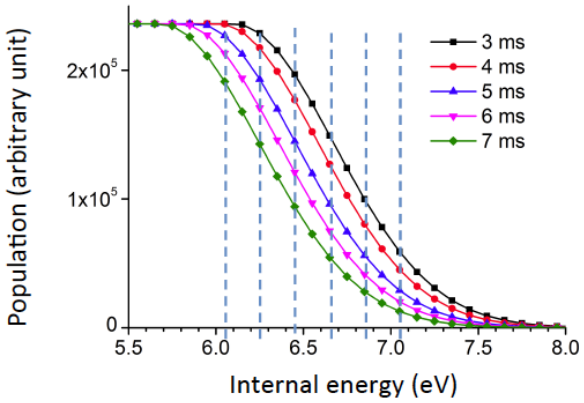


Fig.5 Population distributions simulated for t_{laser} from 3 to 7 ms. Crossing points with a vertical broken line give the population decay for each energy value.

From the obtained time evolution of the energy distribution, one can notice an energy shift of the high energy edge of about 0.4 eV to lower energy from 3 to 7 ms, leading to a shift rate of about 100 eV per second. Actually, this value is much larger than the predicted energy shift rate due to pure IR emission. So, this measured fast energy shift rate is mainly attributed to the fluorescence emission process. The second parameter we extract from these curves is the population decay rate. For a given energy value, a vertical line crosses the energy distributions curves obtained at different t_{laser}. These crossing points describe, in fact, the population decay of the sub-group of stored molecular ions with this particular internal energy. By fitting with an exponential law, we got a population decay time constant. We repeated this procedure for different energy values. The measured population decay rate was obtained as a function of energy and attributed mainly to the fluorescence emission by electronic transition.

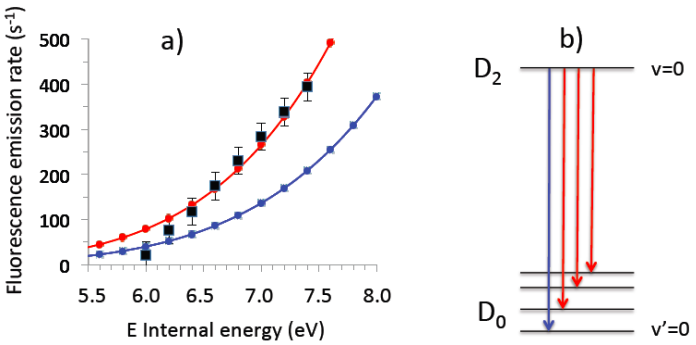


Fig.6 a) Squares: fluorescence emission rate estimated in this work; line (bleu) with small squares: fluorescence emission rate calculated according to the previous work of Boissel et al.; line (red) with circles: fluorescence emission rate calculated with the modified model.
b) Illustration for the spontaneous transition routes from D_2 to D_0.

The fluorescence emission rates estimated using our experimental data were compared with the theoretical model following the early work of Boissel [6]. The theoretical values were found to be about half of the measured ones, fig.6 a). This discrepancy is due to the fact that the spontaneous transition rate A_0 from D_2 to D_0 in the model was underestimated. In fact, A_0 in the early work of Boissel et al. ($7\ 10^6\ s^{-1}$) [6] corresponds to the spontaneous emission rate for the v=0 to v'=0 transition (fig.6 b)). It was obtained from the main 0-0 line of the absorption spectrum of Anthracene cation trapped in an Ar matrix at 12 K. However, when we study the spontaneous emission from D_2 to D_0, we

should consider not only the 0-0 transition line but also other lines in the low energy band. By summing over the contributions from all possible transition routes, we have found a total spontaneous emission rate of 1.5 10^7 s^{-1} [9], which is about twice the rate of 0-0 transition. This factor of 2 is just what we need in the theoretical model in order to reproduce the experimental data.

So, by following the evolution of internal energy distribution of the stored ions in a long time range (3-7 ms), we have estimated the fluorescence emission rate as a function of internal excitation energy. We have modified the early model of Boissel et al. and confirmed their original idea. The present work provides therefore evidence for the fluorescence emission process in the cooling of singly charged Anthracene. It should be noted that the agreement between the modified model and the estimated values is not satisfactory in the low energy region around 6 eV. More experimental investigation is planned to improve the precision of the simulated population distribution in this energy region in order to get a better estimation of the fluorescence decay rate.

4. Conclusion

In the CIDEC experiment, fast atomic ions from an ECR source were used to ionize and excite molecular targets and induce the fragmentation. In the experiment using Mini-Ring, the studied molecules were ionized and excited directly in an ECR source and accelerated to several keV. The decay dynamics of the fast molecular ions were studied in a long time range. From these two experiments, we obtained complementary information concerning the same molecule: the dissociation rate of doubly charged molecule and the fluorescence emission rate of singly charged one. These methods could be applied to other molecules. Notably, it would be interesting to investigate if the fluorescence emission process is valid also for large molecules of biological interests.

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