

## 学位論文要約 (博士 (理学))

論文著者名 河野 直子

論文題名 : Radiative cooling processes of isolated molecular ions in electrostatic ion storage rings (静電型イオン蓄積リングにおける孤立分子イオンの輻射冷却過程) (英文)

本文

Radiative cooling of hot molecules has a great importance when they are isolated in vacuum. It is a fundamental process in the excitation and relaxation cycle, and plays a critical role in competing reactions, for example those of the interstellar molecules. At relatively low energies, vibrational radiative cooling, namely vibrational transitions with emission of infrared (IR) photons with a time constant of a few hundred ms, has been considered the dominant cooling process of such molecules. At higher energies, dissociation and ionization become dominant. For molecular anions, electron detachment is instead the main pathway to dissipate an excess energy at above the electron detachment threshold  $E_{th}$  (electron affinity of the neutral molecule). In addition to these processes, electronic radiative cooling with emission of visible/near IR fluorescent photon via inverse internal conversion (IIC), called recurrent fluorescence (RF) or Poincaré fluorescence, was theoretically predicted about 30 years ago [1]. The occurrence of RF was suggested by the observation of IR multiphoton-induced fluorescence in 1979 [2], but the observation was disputed two years later [3]. Clear evidences were obtained only recently, by using storage rings and electrostatic ion beam traps [4-12]. Up to now, a series of works reveals that the RF cooling is not a very rare phenomenon.

In the present study, the electronic and vibrational radiative cooling of isolated carbon cluster anions and the naphthalene cation were measured in electrostatic ion storage rings. The works were carried out at three different facilities, as described in the following parts; (I)  $C_n^-$ ,  $n=4-7$  (Works at TMU), (II)  $C_{10}^-$  (Works at Stockholm), and (III)  $[C_{10}H_8]^+$  (Works at Lyon).

In part I, the electronic and vibrational radiative cooling process of small carbon cluster anions  $C_n^-$  ( $n=4-7$ ) in an electrostatic ion storage ring at Tokyo Metropolitan University (TMU E-ring) [13, 14] is discussed. The radiative cooling processes were

observed by two complementary approaches. The analysis of the fast decay time profile after photo-excitation was valid for the internal energy  $E > E_{\text{th}}$ , whereas the total yield analysis at various photon energies and the laser firing times (i.e. delays after ion generation) was valid for  $E < E_{\text{th}}$ . Hot carbon cluster anions produced in a laser ablation ion source were stored in the ring at a kinetic energy of 15 keV. At a certain laser firing time the ions were reheated by photons from a pulsed laser. Delayed electron detachment yields of  $\text{C}_4^-$  and  $\text{C}_6^-$  induced by photo excitation were measured as functions of time after photo-excitation, excitation energy, and laser firing time, up to 95 ms. It allows for a mapping of their radiative cooling in a wide energy range from far below to above the electron detachment threshold. The experimentally obtained electronic and vibrational cooling rates were consistent with simulations based on detailed-balance theory. From an astrochemical point of view, prevented by the difficulty in detection by the rotational transitions, chain-form carbon cluster anions  $\text{C}_n^-$ , have not been identified in space. However, they must be abundant in the interstellar clouds. These ions are expected to be produced in collisions of the neutral molecule and an electron, and their stability is determined by the competition between radiative cooling and electron detachment. The observation of the fast radiative cooling suggests that  $\text{C}_4^-$  and  $\text{C}_6^-$  have a chance to survive the electron detachment.

In part II, the spectroscopy of the cold carbon cluster anion  $\text{C}_{10}^-$  in the double electrostatic ion-ring experiment (DESIREE) in Stockholm, Sweden, is described. The small carbon clusters  $\text{C}_n^-$  ( $n < 10$ ) are primarily found in chain-form, whereas the large clusters  $\text{C}_n^-$  ( $n > 10$ ) are typically ring-formed [15].  $\text{C}_{10}^-$  is the smallest negative carbon cluster which can be stable in both chain and mono-cyclic forms, and thereby a key component in the composition process leading to large molecules, such as fullerene  $\text{C}_{60}^-$ , from small chain molecule. In this study,  $\text{C}_{10}^-$  was generated in a Cs sputter ion source, injected into DESIREE at a kinetic energy of 10 keV. A laser-induced electron detachment spectrum in vacuum at temperature of 12.5 K were measured in laser wavelength range from 500 nm to 620 nm. Compared to an electronic absorption spectrum of  $\text{C}_{10}^-$  chain in 5 K neon matrix, reported by J. P. Maier and coworkers in 1997 [16], remarkable new peaks at 520 nm and 560 nm were found in the spectrum from DESIREE. This may be due to presence of the mono-cyclic isomer of  $\text{C}_{10}^-$ , as isomers are not separated by neither the storage ring itself nor the magnet mass selector is the setup. To get more information, a spectroscopy with same wavelength range using TMU E-ring was also measured. A peak which is slightly shifted to shorter wavelength

side by that from DESIREE was observed. This difference may be due to the higher temperature in TMU E-ring than in DESIREE.

In part III, the cooling process of naphthalene cations  $[C_{10}H_8]^+$  in a table-top ion storage ring (Mini-Ring) in Lyon, France [10] is described. The evolution of the internal energy distribution in 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 environment [17]. In the experiment, a laser pulse was used to probe the internal energy distribution every millisecond during the storage time. The evolution of the internal energy distribution of the stored ions was simulated with a model by 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  $\mu\text{J}/\text{pulse}$ , 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  $\text{s}^{-1}$  in the energy range from 6 to 7 eV. This fast decay was attributed to the RF process.

In conclusion, electronic and vibrational radiative cooling (relaxation) process of isolated cluster and molecular ions isolated in vacuum were investigated taking full advantage of electrostatic ion storage rings. Characteristic dynamics and underlying fundamental mechanism in the time range of from tens of  $\mu\text{s}$  to hundreds of ms were clearly elucidated. The methodology developed in these studies and the acquired knowledge on radiative cooling will help further understanding of the behavior of isolated molecular ions.

## References

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