



Cooling dynamics of photo-excited negative carbon cluster ions stored in an ion storage ring



T. Furukawa^a, G. Ito^a, M. Goto^b, T. Majima^a, H. Tanuma^a, J. Matsumoto^c, H. Shiromaru^c, K. Hansen^d, T. Azuma^{b,a,*}

^a Department of Physics, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

^b Atomic, Molecular and Optical Physics Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

^c Department of Chemistry, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

^d Department of Physics, University of Gothenburg, 41296 Gothenburg, Sweden

ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form 3 December 2014

Accepted 3 December 2014

Available online 23 December 2014

Keywords:

Carbon cluster anion

Radiative cooling

Depletion cooling

Inverse internal conversion

Recurrent fluorescence

ABSTRACT

A newly found fast radiative cooling process of C_6^- is studied by simulation based on statistical sharing of the internal energy by the vibrational modes both in the electronic ground and excited states. For comparison, a contrasting slow cooling of C_6H^- is simulated by the same procedure. The simulation demonstrates a distinct difference in the time evolution of energy distributions between C_6^- and C_6H^- , and well reproduces the observed fast cooling of C_6^- by recurrent electronic transitions and the slow cooling of C_6H^- by vibrational de-excitation.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Radiative cooling processes of molecules are a fundamental process, nevertheless they have been attracting continuous attention to these days since they will fill a missing piece of information of the electronic excitation – internal conversion (IC) – de-excitation (radiative cooling) cycle of molecules isolated in vacuum. In many cases, the IC processes take place very fast in the time scale of ps and the internal energy is readily distributed to all the vibrational modes according to the statistical weight. Subsequent radiative cooling is usually slow since vibrational transition probabilities are much smaller than dipole allowed electronic ones and single vibrational transition carries only small portion of the energies away.

Recently, an inverse process of the IC, namely the process of vibrational energies returning back to the electronic energy [1], has been revealed by an ion storage experiment as a fast electronic radiative cooling of anthracene cation [2]. This process, called “inverse internal conversion” or “IIC” followed by “recurrent fluorescence,” was evidenced by our group also for much smaller molecule, C_6^- , which cools significantly faster than polyynes anions

(C_6H^-) [3]. The fast cooling originates in the presence of low-lying electronically excited states. It is considered to be a common feature of the small even-numbered carbon cluster anions, whereas the cooling of odd-numbered clusters (C_5^- and C_7^-) is as slow as polyynes anions [4,5].

In this paper we present a simulation of the cooling processes of hot C_6^- and C_6H^- , and those of reheated ones, where the electronic transitions from thermally populated excited states are invoked for C_6^- .

2. Experimental procedure to derive the internal energy

To study the cooling dynamics of anions stored in the ring, it is required to measure the internal energy distribution of the micro-canonical ensemble of hot anions at a specific ion storage time. We employ “the rate constant of delayed electron detachment processes (k_d)” as an index of the internal energy since the ion storage device allows us to perform a highly sensitive measurement of this process in the timescale of up to milliseconds or beyond. In general, the delayed detachment is considered to be a statistical process, in which the electron is emitted after the IC process. The lifetime, or k_d , will be simply a function of the total internal energy (E) [6]. Conversely, if the population of the anions with a specific rate constant is determined, the energy distribution is obtained

* Corresponding author at: Atomic, Molecular and Optical Physics Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan.

from the function of $k_d(E)$. On the basis of this assumption, we have measured the radiative cooling rates of C_5^- and C_7^- [4,5].

Relevant experiments were conducted using an electrostatic ion storage ring at Tokyo Metropolitan University (TMU E-ring). A scheme of the experiments is shown in Fig. 1. Hot anions produced in a Cesium sputter ion source were stored in the ring as a pulsed beam with an energy of 20 keV. After a specific storage time, during which the ions cooled down below the detachment threshold, they were reheated by a pulsed laser in a merging configuration. Then, the delayed detachment of reheated anions gives a sequence of peaks of neutral particles in the time spectrum detected by a micro channel plate (MCP) as shown in Fig. 1. While a very fast detachment component due to multi-photon absorption mingles with slower single-photon components in I_0 , the subsequent components I_n ($n \geq 1$) are due to single photon exclusively. Under such a condition, we introduce an energy window concept for anions to be detected at a specific time.

The $k_d(E)$ is a rapidly-changing function of E , and the width of the energy window converted from the time window for I_n : $n \geq 1$ are quite narrow represented by a peak value E_0 , which is slightly above the detachment threshold reflecting small heat capacities of C_6^- and C_6H^- . Thus, the observation of the delayed detachment induced by a photon with the energy of $h\nu$ is considered to be a sampling of the population of the anions with the internal energy at $E_0 - h\nu$.

The decline of the intensities of the peaks I_0, I_1, \dots is governed by two competing cooling processes. One is the “depletion cooling” standing for the process in which higher energy components are preferentially removed from the ensemble by detachment resulting in cooling of the stored anions. For hot anions with fairly broad energy distribution, depletion cooling generally leads to a decay of the peaks represented by the power law. The other is “radiative cooling.” Vibrational and electronic coolings push the distribution toward the lower-energy side to reduce the number of active anions above the detachment threshold keeping the ions themselves in the ring. The inactive anions further cool down only by the radiative processes.

3. Simulation of the radiative cooling process

The simulation of the radiative cooling process was performed with the following procedure.

- 1: To determine the energy window, the detachment rate constant $k_d(E)$ was calculated based on the detailed balance theory. From the $k_d(E)$ and the time window for detection, the energy window E_0 was derived.
- 2: From the vibrational transition probabilities and statistical weights of the IR active vibrational modes at a given internal energy, the vibrational cooling rate k_v was calculated.
- 3: If there is non-negligible contribution of the thermally (statistically) populated electronic excited states, they were taken into account by statistical sharing of the internal

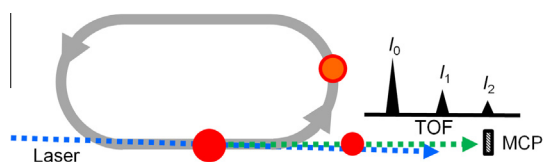


Fig. 1. Schematic view of the ion storage experiments at TMU E-ring. The neutral particles produced by the laser-induced detachment in the straight section were detected by a MCP located at the extension of this straight section giving rise to the peak I_0 . Then, the anions surviving subsequent revolutions followed by the delayed detachment in this section give a train of the peaks (I_1, I_2, \dots) in this manner reflecting their revolution time.

energy by the vibrational modes both in the electronic ground and excited states. This is a key concept in the present simulation. And the previously reported electronic transition probabilities k_e were used.

- 4: At a given temperature as the initial condition of stored anions, the initial energy distribution was derived assuming the Boltzman type distribution, and time evolution of the distribution was calculated using the cooling rates.
- 5: The energy distribution before photoexcitation is shifted by $h\nu$ to generate the energy distribution after photoexcitation. Then, considering the k_d, k_v and k_e , the neutral yield against the time after laser excitation, to be referred to as the “decay profile”, was simulated. By summing up the detectable yield at $E_0 - h\nu$, the neutral yield against the storage time was simulated. The simulated decay profiles and total yields were finally compared with the experimental results.

These procedures are described more in detail in the subsequent sections.

3.1. Electron detachment rate

The rate constant of electron detachment $k_d(E)$ is given by the detailed balance expression [7],

$$k_d(E) = \int_0^{E-E_{th}} \frac{2m}{\pi^2 \hbar^3} \sigma_c(\epsilon) \epsilon \frac{\rho_d(E-E_{th}-\epsilon)}{\rho_p(E)} d\epsilon. \quad (1)$$

where m is the mass of an electron, ϵ the kinetic energy of the emitted electron, σ_c the kinetic energy dependent capture cross section as the reverse process, the ρ 's the level densities of the species given by the subscripts p and d as that of parent and daughter, respectively. E_{th} is the detachment threshold which is the electron affinity, as 4.18 eV [8] for C_6^- and 3.81 eV [9] for C_6H^- . The numerical factor two in the formula is the spin degeneracy for the emitted electron while the electronic degeneracies of the parent and daughter are included in their level densities.

The Langevin cross section in atomic unit is adopted for the capture cross section of the electron,

$$\sigma = \left(\frac{2\alpha}{\epsilon} \right)^{1/2}, \quad (2)$$

where α is the polarizability of neutral molecules, and ϵ is the electron energy. For C_6 , the geometry-averaged value of 100.0 atomic units is available in literature [10]. If ϵ is given in the eV unit,

$$\sigma = \sigma_0 \epsilon^{-1/2}, \quad (3)$$

Table 1

Vibrational frequencies of carbon clusters. Degenerate modes are indicated by the asterisk (*). The A-coefficients of the IR emissions for the anions are given in parentheses.

| Species | Frequencies [cm^{-1}] (for anions: A-coefficients [s^{-1}]) |
|---------------|---|
| C_6^- [12] | 127 (0.1394), 133 (0.1223), 285 (0), 293 (0), 517 (0.924), 553 (0.2643), 658 (0), 775 (0), 811 (0), 1222 (0.430), 1865 (0), 2037 (867.85), 2193 (0) |
| C_6H^- [13] | 111* (0.0251 \times 2), 264* (0.2763 \times 2), 483* (6.6484 \times 2), 494* (2.648 \times 2), 550* (0.0502 \times 2), 641 (2.10), 1207 (11.8), 1979 (375), 2142 (0.297), 2222 (2579), 3480 (541) |
| C_6 [14] | 108, 108, 234, 234, 434, 434, 653, 665, 665, 1233, 1697, 2037, 2142 |
| C_6H [15] | 93, 93, 210, 210, 397, 397, 567, 567, 570, 570, 650, 1224, 1895, 2105, 2137, 3457 |

Download English Version:

<https://daneshyari.com/en/article/8040899>

Download Persian Version:

<https://daneshyari.com/article/8040899>

[Daneshyari.com](https://daneshyari.com)