

# Vibrational radiative cooling of isolated $C_4^-$ and $C_6^-$

Ryuta Suzuki<sup>\*1</sup>, Naoko Kono<sup>\*</sup>, Reito Andou<sup>§</sup>, Takeshi Furukawa<sup>\*</sup>, Jun Matsumoto<sup>§</sup>,  
Toshiyuki Azuma<sup>†\*</sup>, Hajime Tanuma<sup>\*</sup>, Klavs Hansen<sup>‡¶</sup>, Haruo Shiromaru<sup>§</sup>,

<sup>\*</sup> Department of Physics, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan,

<sup>§</sup> Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan,

<sup>†</sup> AMO Physics Laboratory, RIKEN, Wako, Saitama 351-0198, Japan,

<sup>‡</sup> Department of Physics, University of Gothenburg, 41296 Gothenburg, Sweden,

<sup>¶</sup> Tianjin International Center of Nanoparticles and Nanosystems, Tianjin University, Tianjin 300072, P.R.China.

**Synopsis** We have observed the storage-time dependence of the laser-induced electron detachment yields for the linear carbon cluster anions  $C_4^-$  and  $C_6^-$  stored in an electrostatic ion storage ring (TMU E-ring) with several laser wavelengths. The electron detachment yield reflects the decrease of the internal energy of the stored ions. We succeeded in obtaining the time evolution of the excitation energy distribution below the first dipole-allowed electronic excited energy  $E_{ex}$  for  $C_4^-$  and  $C_6^-$ , which was well consistent to the behavior explained by vibrational IR-radiative cooling.

Radiative cooling of isolated molecular ions has recently been recognized as an important factor in the creation and stabilization of interstellar molecular anions. The radiative cooling process occurs both by IR photon emission with vibrational transition and/or visible-photon emission, referred to as recurrent fluorescence (RF) [1]. The RF was experimentally measured for the molecular ions,  $C_4^-$  and  $C_6^-$ , equipped with the low-lying electronic excited state through the observation of the characteristic fast cooling [1–3]. The RF mechanism is valid only when the internal energy is larger than that of the electronic excited state  $E_{ex}$ . Once the stored ions are cooled down below this energy, further cooling should proceed slowly by the normal vibrational cooling. In this study, we focused on this slow process, which is observable only by storing the ions for the longer time than the typical vibrational cooling time scale of approximately tens ms in an electrostatic ion storage ring (the TMU E-ring).

We irradiated the stored ions with a tunable visible optical parametric oscillator (OPO) laser to induce the statistical thermally-driven delayed detachment. The neutralized products were detected by a microchannel plate (MCP) detector. The observed laser induced neutral yields reflects the population in a particular internal energy region  $E_0$  after laser absorption of the energy of  $nh\nu$  where  $n$  is the number of photon absorbed, and thus  $E_0 - nh\nu (= E_{obs})$  before photo-excitation. This energy window  $E_0$  is

defined by the decay times determined by the experimental configuration ( $E_0 = 3.88$  eV for  $C_4^-$ , 4.49 eV for  $C_6^-$ ), as demonstrated for these anions with internal energies above  $E_{ex}$  [1, 2].

Measuring the laser induced neutral yields as a function of laser firing time after storage at each sampling energy  $E_{obs} = 0.43 - 1.06$  eV, we observed the time evolution of the excitation energy distribution during the cooling processes via the vibrational transitions at internal energies below  $E_{ex}$  (1.34 eV for  $C_4^-$ , 1.16 eV for  $C_6^-$ ). The neutral yields increased and then decreased with time in the tens ms range as the result of the decrease in the excitation energy distribution. Every sampling energy  $E_{obs}$  was smaller than  $E_{ex}$ , and the neutral yields varied with much longer time than the RF cooling time scale of approximately 0.1 ms. This result is consistent with the behavior explained by vibrational cooling. At higher sampling energy  $E_{obs}$ , the peak of the neutral yields appeared earlier. From time difference of these peaks, we estimated the vibrational cooling rate. These were reasonably reproduced by simulation.

## References

- [1] G. Ito *et al.* 2014 *Phys. Rev. Lett.* **112** 183001
- [2] N. Kono *et al.* 2015 *Phys. Chem. Chem. Phys.* **17** 24732
- [3] Y. Ebara *et al.* 2016 *Phys. Rev. Lett.* **117** 133004

---

<sup>1</sup>E-mail: [suzuki-ryuta@ed.tmu.ac.jp](mailto:suzuki-ryuta@ed.tmu.ac.jp)