Radiative cooling processes of vibrationally hot C₄⁻ and C₆⁻ stored in an electrostatic ion storage ring

N. Kono¹, T. Furukawa¹, J. Matsumoto², H. Tanuma¹, T. Azuma¹,³, K. Hansen⁴, H. Shiromaru²

¹ Department of Physics, ² Department of Chemistry, Tokyo Metropolitan University, Japan
³ Atomic, Molecular and Optical Physics Lab., RIKEN, Japan
⁴ Department of Physics, Gothenburg University, Sweden

kouno-naoko@ed.tmu.ac.jp

Chain-form carbon cluster anions (Cₙ⁻) have been recognized as prominent interstellar species since the discovery of hydrogen-capped polyyne anions (C₂₅H⁻: n=2-4) in space. These anions are considered to be formed by electron capture collision of neutral polyynes, in which radiative cooling of hot transient anions plays a critical role, especially for small molecules. Recently, in addition to the vibrational IR photon emission, the existence of the electronic radiative cooling process referred to as recurrent fluorescence (RF), manifested as visible/NIR photon emission, were experimentally clarified for C₄⁻ and C₆⁻ [1-3]. This fast cooling mechanism requires two conditions; 1) the presence of low-lying electronic excited states, and 2) the total internal energy of the molecule should be higher than those of the electronic excited states.

The observation of the RF process has been so far limited to the case where the internal energy is above their electron detachment threshold E_{th} or relatively high even below E_{th}. In the present study, we focused our attention to the case of relatively cold ions at an internal energy much below E_{th}.

In the experiments, hot C₄⁻ and C₆⁻ ions were stored in an electrostatic ion storage ring, the TMU E-ring. The neutralization yield of the ions after photo-excitation was measured as a function of the ion storage time between ion generation and absorption of photons of different energies. The laser-induced neutrals were detected in a time window delayed relative to the laser irradiation, leading to the condition where the decay of ions with a specific internal energy E_w is monitored. Thus, the observed yield is proportional to the population of the ions at the internal energy E_w-hν prior to photon absorption.

Depending on the photon energy, the sampled internal energy is below or above the lowest-lying electronic excited state, E_{ex}. For energies above E_{ex} (between E_{ex} and E_{th}), the yield decreases with decay time up to 6 ms, reflecting the contribution of the electronic cooling. On the other hand, when the sampled internal energy is below E_{ex}, the neutral yield decreases with time scales in the 100 ms range, ascribed exclusively to the slow vibrational cooling. These time scales should be compared to the ones measured at E_{th}, which is 10 μs.

In conclusion, we have succeeded in observing a critical contribution of RF in the cooling dynamics of the relatively cold ions with the internal energy close to the energy level of the lowest-lying electronic excited state E_{ex}.