

Observation of very slow de-excitation dynamics of hot carbon cluster anions

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Synopsis The radiative cooling rates of small carbon cluster anions over a wide energy range from below to above the electronic excited states were measured in an electrostatic ion storage ring. The energy window concept and discrimination of one- and two-photon absorption are critical in understanding the obtained results. The experimentally obtained electronic and vibrational cooling rates were consistent with a simulation based on detailed-balance theory.

De-excitation (or cooling) process of isolated hot molecules, which have high internal energy, is itself important as a basic process of energy dispersion, and the evaluation of the cooling rates is highly needed for the modeling of molecular evolution in the interstellar medium. In general, slow radiative cooling by which vibrational transitions with emission of infrared (IR) photons after the internal conversion (IC) has been considered as a typical cooling process of such molecules. For molecules in solution, or in gas cell, IC is practically irreversible because of the fast collisional cooling. However, in the highly isolated environment, an inverse internal conversion (IIC) process will occur and the energies distributed into various vibrational modes may revert to the electronic energy with a certain probability. Some molecular ions cooled significantly faster than vibrational cooling by the electronic radiative cooling with emission of visible or near IR photon via the electronic excited states regenerated through IIC, called recurrent fluorescence (RF) or Poincaré fluorescence [1, 2, 3, 4].

In the present study, the electronic and vibrational radiative coolings from below to above the electronic excited states of C_4^- and C_6^- were measured in the electrostatic ion storage ring TMU E-ring (fig.1). The yields of laser induced delayed detachment were measured as a function of time after ion generation t_{las} at a fixed laser wavelength. The observed yield is proportional to the population of ions at a certain internal energy E_0 , corresponding to a specific electron detachment rate, because of the restrictions imposed by the time window of the delayed detachment measure-

ment. Therefore, the yield is proportional to the population at the sampled energy $E_0 - nh\nu$ just prior to n -photon absorption. The procedure providing information on the time evolution of the energy distribution from the t_{las} dependence works well for small anions since the rate of delayed detachment is a rapidly increasing function of internal energy. The present results show a significant reordering of the vibrational cooling rates as a function of size, relative to the theoretically predicted vibrational A coefficients [5].

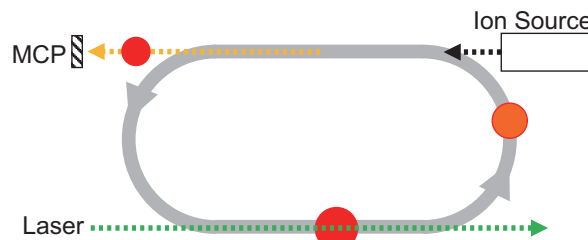


Figure 1. Experimental scheme of TMU E-ring. Ions were generated in a laser ablation source and then stored in the ring. Neutral particles from stored ions due to laser induced electron detachment were detected by a set of micro-channel plates (MCP) at a half-turn after the laser merging section.

References

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