

Cooling dynamics of photo-excited C_6^- and C_6H^-

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Radiative cooling of an isolated single molecule is a ubiquitous phenomenon in collision-free environment. Particularly, recent identification of $C_{2n}H^-$ ($n=2-4$) in the interstellar medium [1] has stimulated a wide interest in their radiative cooling process. In the present study, we have measured the delayed electron detachment of photo-excited C_6^- and C_6H^- to investigate their cooling process in comparison.

The experiments were performed using an electrostatic ion storage ring at Tokyo Metropolitan University (TMU E-ring). Hot molecular anions of C_6^- and C_6H^- generated in a Cs-sputter ion source were accelerated to 20 keV and stored in the ring. After a specific storage time, the third harmonics of the Nd:YAG laser (355 nm) was introduced at the one of the straight section of the ring, and neutral products accompanied by electron detachment were detected by a micro-channel plate placed at the same side. We found a striking difference in the decay profiles of photo-excited C_6^- and C_6H^- . The decay lifetimes of C_6H^- were in the time range of 0.1-1 ms and showed the strong storage time dependence; the

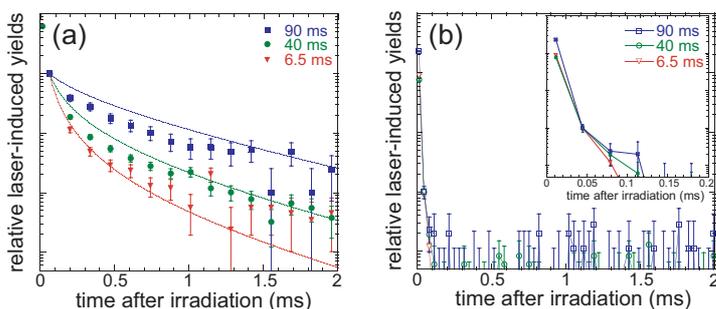


Fig. 1. Storage time dependence of the decay profiles for (a) C_6H^- and (b) C_6^- enhanced by 355nm laser irradiation. Simulated decay profiles of C_6H^- are given in (a) assuming that ions are cooled only by vibrational transitions.

longer storage leads to slower decay, which was well reproduced by a theoretical simulation based on the vibrational radiative cooling emitting IR photons. In contrast, the decays in the time range of 10 μ s were observed for C_6^- , and they were much shorter than C_6H^- and not sensitive to the storage time. This time range is also by far shorter compared with a theoretical prediction if only the vibrational radiative cooling is taken into account. We concluded that the different decay profiles between the species with similar heat capacities and detachment thresholds are most likely attributed to the contribution of the electronic radiative cooling (recurrent fluorescence) emitting visible photons, which has been recently confirmed experimentally in the cooling process of much larger anthracene molecules [2]. A crude estimate based on the statistical weights of the excited states and the electronic transition probabilities clearly indicates that the low-lying electronic excited states of C_6^- significantly enhance the cooling rate, being consistent with our observation. In contrast, the absence of such low lying excited states of C_6H^- , also well explains the results.

Thus, it was revealed that these molecular anions show a dramatic difference in their cooling process originating from the contribution of the electronic radiative cooling depending on the H atom addition or not.

References:

- [1] M. C. McCarthy et al., *Astrophys. J.* **652**, L141(2006).
- [2] S. Martin et al., *Phys. Rev. Lett.* **110**, 063003 (2013).