Inverse internal conversion of laser-heated C₄⁻ and C₆⁻


Polyyne anions C₂nH⁻ (n=2-4) existing in space [1] have been considered to be formed by two-body collisions of a neutral radical and an electron (M + e⁻ → M⁻*), where M⁻* is a hot anion above the detachment threshold, heated by gaining the exothermicity of the electron attachment and collision energy. Since the reactions occur in a highly isolated environment, competition between auto-detachment (M⁻* → M + e⁻) and stabilization by radiative cooling (M⁻* → M + hν) governs the abundance of anions. In the present study, we find that the radiative cooling of C₄⁻ and C₆⁻ isolated in vacuum is much faster than that expected for vibrational radiative cooling [2]. This peculiar behavior is explained only by the inverse internal conversion (IIC) followed by the electronic transition (recurrent fluorescence). On the other hand, the radiative decay of hot C₆H⁻ is found to be vibrational, as observed for various other molecular anions.

A schematic drawing of the internal conversion (IC) and IIC is shown in Fig.1. The IIC works when the internal energy is large enough and contribution of the thermally populated electronic excited states becomes non-negligible. It is considered to be a rare case, since such hot molecules tend to decompose quickly. On the other hand, vibrational radiative cooling by emitting IR photons is a common case for polyatomic molecules. The importance of the recurrent fluorescence for highly isolated molecules has been pointed out [3] and experimentally confirmed for PAH cations [4]. Although the finding of the IIC process can fill the “missing link” in the excitation-relaxation cycle of highly isolated molecules, from an astrochemical point of view, IIC in a small molecule is more important. Since the heat capacity plays a critical role in the hot anions formed by the two-body collision, auto-detachment will be faster for small molecules and cooling will be faster for large ones. According to theoretical calculations, the crossover occurs between C₄⁻ and C₆⁻, where the ratio of the detachment rate to the cooling rates were calculated to be 11 and 3.6×10⁻⁵, respectively [5]. For such small anions, experimental determination of the radiative cooling rate at an energy slightly above the detachment threshold will strongly encourage the re-estimation of the anion abundance in space.

The experiments were performed using an electrostatic ion storage ring at Tokyo Metropolitan University (TMU E-ring). Hot anions produced with a Cs sputter source (C₆⁻) or a laser ablation source (C₄⁻) were stored in the ring, and were reheated by a pulsed laser resulting in electron emission. To observe delayed detachment exclusively, the neutral particles generated one revolution (20 keV C₆⁻, lifetime > 34 μs) or a half revolution (15 keV C₄⁻, lifetime >16 μs) after laser irradiation was detected. With this experimental configuration, the anions within a specific range of lifetimes, or internal

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![Fig.1. Schematic drawing of IC and IIC. In the present case, IIC to the lower electronic excited states is considered.](image-url)
energies (energy window), were selectively detected, allowing us to survey the energy distribution. For small anions, the energy window is located just above the detachment threshold (4.18 eV for C$_6^-$, 3.88 eV for C$_4^-$, 3.81 eV for C$_6$H$^-$).

The neutral yields for 3.49 eV laser irradiation of C$_6$H$^-$, and those for C$_6^-$, are shown in Figs.2a and 2b, respectively. The decay for C$_6$H$^-$ follows a power law indicating that it is due to preferential depletion of hotter anions by auto-detachment (depletion cooling). The decay curves for various storage times are well reproduced by simulation using theoretical detachment rate and the vibrational pre-cooling rate (cooling before reheating). On the other hand, the fast decay for C$_6^-$ cannot be explained by depletion cooling without making unreasonable assumption that the C$_6^-$ is not pre-cooled during the storage. It follows that the decay is due to fast radiative cooling of the reheated anion, which is possible if the electronic transition participates. Since the photoelectron study shows that the internal conversion (IC) of electronic excited states of C$_6^-$ is much faster than the timescale of the ion storage experiment [6], the cooling by electronic transition should not be due to direct fluorescence from the photo-excited state.

That is, the IIC followed by the recurrent fluorescence is the only answer. The semi-empirical calculation shows that the cooling rate for the recurrent fluorescence from low-lying electronic excited states (A $^2\Sigma_g^+$ and C $^2\Pi_g^-$) well reproduces the experiments. Although the thermally populated C states is 0.1 % of all ions at the energy window, a large transition probability from the C state makes the IIC the dominant cooling pathway. The reheated C$_4^-$ behaves in a similar way to C$_6^-$, allowing us to extend the size limit of recurrent fluorescence to 4-atomic molecular anions.

In conclusion, we have confirmed that C$_4^-$ and C$_6^-$ are cooled by recurrent fluorescence, which guarantees a considerable amount of these anions in space. So far, the theoretical calculation of the cooling rate employs the harmonic oscillator approximation and the transition moment at low temperature, since the molecular constants at high temperature are not available. Although it gives reasonable results as a rough estimation, the cooling rate is a quantity to be determined experimentally. For this purpose, C$_4^-$ storage/reheating experiments are now under way.

References