Cooling Dynamics of Photoexcited C_6^- and C_6H^-

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We report conclusive evidence of an efficient cooling mechanism *via* the electronic radiative transitions of hot small molecular anions isolated in vacuum. We stored C_6^- and C_6H^- in an ion storage ring and observed laser-induced electron detachment with delays up to several milliseconds. The terminal hydrogen atom caused a drastic change in the decay profiles. The decay of photoexcited C_6H^- is slow and nonexponential, which can be explained by depletion cooling, whereas that for C_6^- occurs extremely fast, on a time scale below 0.1 ms and can only be explained by electronic radiative cooling *via* low-lying electronic excited states.

In polyatomic molecules, internal conversion (IC) is a common phenomenon, by which electronic excitation energy is dissipated into the vibrational modes in a statistical way. For C_6^-, femtosecond laser photoelectron spectroscopy has revealed a scenario in which the $C\,^2\Pi_g^+$ state prepared by the pump laser decays into the vibrationally excited ground electronic states on picosecond time scales, through intermediate lower-lying excited electronic states [1,2].

The fate of the molecules after the IC process has been largely ignored, despite its potential importance in the excitation–relaxation cycle of highly isolated molecules. Vibrational radiative cooling by infrared (IR) photon emission commonly works for isolated polyatomic molecules, whereby the cooling rate can be estimated from the transition probabilities of the IR active modes. In general, this is a slow process (typically, active on a millisecond time scale) because of the relatively small transition probabilities and low energy release for a single transition. It is, therefore, natural to consider the reverse of the IC process, namely, the conversion of energy in vibrationally excited state to an electronically excited state (inverse internal conversion or IIC). This process is usually suppressed due to the small statistical weight of the excited state, but in an ergodic system, the IIC process will nevertheless be observed if the molecule is isolated for a long period [3]. The IIC process is critical to understand the molecular evolution in space, where two-body collisions produce highly excited products and radiative cooling determines whether they survive intact. The smaller the molecules, the more important the IIC processes because the competing decomposition rates are faster for them.

The observation of this phenomenon has been hampered by experimental difficulties that are today overcome by the development of ion storage techniques [4–7]. In ion storage experiments, IIC processes have been observed as anomalous fast radiative cooling mediated by electronic radiation following the IIC (recurrent fluorescence). So far, the IIC of molecular ions have been confirmed only for large ones; fullerene anions [8] and anthracene cations ($C_{14}H_{10}^+$) [9,10]. From an astrochemical point of view, the magnitude and general characteristics are in urgent need for clarification.

Here, we present conclusive evidence for the IIC for a small molecular anion and demonstrate how the contribution of the recurrent fluorescence is very sensitive to the electronic structure. An excited anion with internal energy above the detachment threshold energy, equal to the electron affinity (E_a), exhibits delayed electron detachment with rates that increase rapidly with energy [11,12]. This electron detachment process provides a very efficient tool for monitoring the cooling process of the hot anion. Conditions favorable for the recurrent fluorescence of the hot anion are expected to be a high detachment threshold and the presence of low-lying electronic excited states, for which the contribution of the thermally populated electronic excited states becomes non-negligible. Thus, we expect that the radiative cooling mechanism of photoexcited C_6H^-, for which the ground electronic state is a closed shell structure, is vibrational via emission of IR photons. That of C_6^-, for which the ground electronic state is an open shell structure, is expected to be significantly accelerated by recurrent fluorescence. These two will be ideal sample (C_6^-) and reference (C_6H^-) materials for the IIC study.

In the present Letter, the IIC was studied by observation of laser-induced delayed electron detachment of C_6^- and C_6H^- on the microsecond to millisecond time scale. Experiments were performed using an electrostatic ion storage ring at Tokyo Metropolitan University (TMU E-ring), with the procedure essentially the same as that described in our previous paper [13]. Hot anions of C_6^- and C_6H^- generated in a cesium sputter ion source were stored in the TMU E-ring with an energy of 20 keV. After a specific storage time, during which the ions cooled radiatively, they were irradiated in a merging configuration by the third harmonics (355 nm) of a nanosecond Nd:YAG laser (typically 1 mJ/pulse with a repetition rate of 10 Hz). The photoexcitation occurred only after the autodetachment component of the hot anions formed in the ion source had disappeared. The background due to collisions with the residual gas was practically flat within the time scale of the present study. Because the photon energy (3.49 eV) of the excitation laser was below the detachment threshold of C_6^- and C_6H^- (with E_a's 4.18 eV [14] and 3.81 eV [15], respectively), one-photon detachment could occur only for hot anions with sufficiently large internal energies.

The neutral particles produced in the laser induced electron detachment were detected at the side where ion and laser beams were merged. The yield of neutral particles was recorded as integrated counts of the microchannel plates during each revolution of the ions in the ring. Because of the merging beam configuration, all neutral particles produced within the interval 0–3 μs were counted as the yield of the zeroth revolution, $I(0)$. The yields in later revolutions [$I(1)$, $I(2)$, …] resulted from delayed decay only. In the following analysis, $I(0)$ were excluded from the discussion, since the laser-fluence dependence manifested a considerable contribution of the two-photon processes. On the other hand, a two-photon contribution is negligible for the first and subsequent revolutions. For C_6^-, the known detachment rate enabled us to exclude the two-photon contribution. According to the photoelectron study in [16], the delayed detachment rate for two-photon energy of the 355 nm laser was much faster than 10^8 s^{-1}, even for a cold target, whereas delayed processes were observed in the ring at least 30 μs after excitation. For C_6H^-, the calculated detachment rate constant is similar to C_6^-, and the one-photon nature of the process is confirmed by the simulation to be shown later.

The decay profiles of C_6H^- and C_6^- excited after different storage times are shown in Figs. 1(a) and 1(b), respectively. The laser firing times were 6.5–115 ms for C_6H^- and 6.5–90 ms for C_6^-. The two ions show strikingly different pictures. The decay time of photoexcited C_6H^- was in the range of 1 ms, and a longer storage led to slower decay. The decays of the photoexcited C_6^- were much faster (below 0.1 ms) and displayed no discernible variation of this time scale with storage time. Generally, the origins of these decays were attributable to depletion
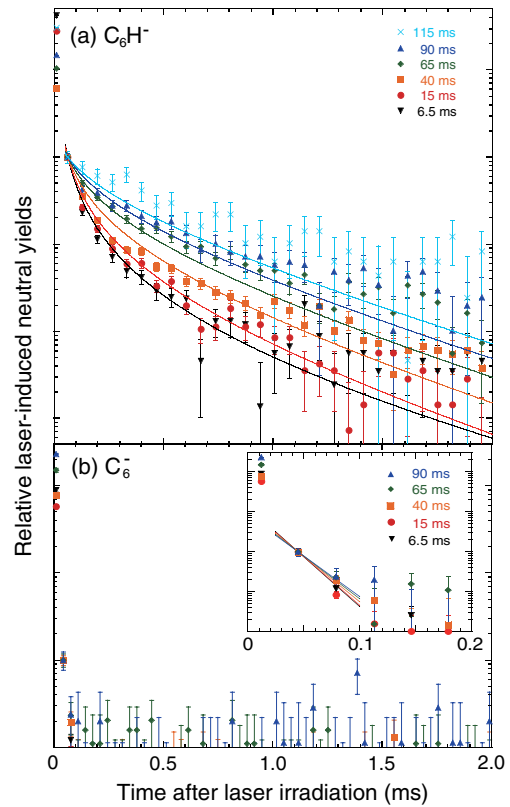

FIG. 1 (color online).   Storage time dependence of the decay profiles for (a) C_6H^- and (b) C_6^- enhanced by 355 nm laser irradiation. The corresponding revolution periods are 33.78 and 33.55 μs, respectively. The $I(0)$ data points are shown merely for reference. In (a), the average yields of two consecutive revolutions are plotted for clarity, except for $I(0)$. The decay is normalized at the average of $I(1)$ and $I(2)$, to compare with the simulated decay shown as the lines. In (b), the yields of individual revolutions normalized at $I(1)$ are plotted. Simulated decay profiles are shown as solid lines. Refer to the main text for more details.

and/or radiative cooling. The former is the process where the delayed detachment preferentially eliminates the hotter anions, resulting in cooling of the ensemble, while the reaction yields neutral particles to be detected. The rate of decay of depletion cooling depends on the amount of energy above the detachment threshold. In contrast, radiative cooling quenches the decay of the hot (active) anions without giving rise to neutral particles. It reduces the number of active anions, and thus causes the neutralization rate to decrease faster. The cooling rate depends on the internal energy but is independent of the detachment threshold. Smaller heat capacity and higher detachment thresholds enhance the relative importance of the radiative cooling of the photoexcited anions and vice versa.

The C_6H^- decay profiles are readily understood as depletion cooling after photoexcitation. Their variation with storage time is explained in terms of the radiative

cooling during the storage (hereafter referred to as "precooling" to avoid confusion with the cooling of photo-excited anions). The lowering of the internal energy before photoexcitation naturally lowers the excess energy of the reheated anions, giving rise to slower decay.

The decay profiles of photoexcited C_6^- are surprising at first glance, even though the fast decay is consistent with the fact that even-numbered carbon cluster anions formed in a hot ion source do not show millisecond-order auto-detachment just after injection into a storage ring [17,18]. If the rate of this fast decay were governed by depletion cooling, the C_6^- would be very hot even after 90 ms storage; however, it is not the case. As already described, an attached H atom reduces the detachment threshold of the anion from 4.18 to 3.81 eV and increases the heat capacity slightly. Due to the highly symmetric structure of C_6^- ($D_{\infty h}$), radiative precooling is dipole forbidden for several vibrational modes, whereas all the modes are dipole allowed for C_6H^- ($C_{\infty v}$). This would naturally lead to slower IR radiative cooling of C_6^-.

We estimated the contribution of vibrational radiative precooling rate from the reported vibrational transition probabilities, assuming that all the vibrations are harmonic and the radiation processes are statistical [19,20]. As shown in Fig. 2(a), the calculated vibrational cooling rate of C_6^- is about half of that of C_6H^-. Thus, the difference in vibrational radiative precooling does not explain the observation at all.

The alternative explanation is that recurrent fluorescence effectively cools the photoexcited C_6^-. Then, the peculiar behavior of C_6^- is ascribed to fast radiative cooling, rather than depletion cooling. To assess the validity of this interpretation, we estimated the population of the electronic excited states as a function of the internal energy, based on the statistical weights given by the level densities. The possible contributors for C_6H^- and C_6^- are listed in Table I. First, C_6H^- has no chance of recurrent fluorescence because the population of the excited state of $A^1\Pi$ at an

internal energy corresponding to the detachment threshold, i.e., $E_a = 3.81$ eV, is negligibly small. Next, C_6^- has several electronically excited states. The calculated de-excitation rates of C_6^- by recurrent fluorescence are shown in Fig. 2(b), as a function of the internal energy. For relatively low energy, the main decay channel is recurrent fluorescence from the $A^2\Sigma_g^+$ state, whereas at energies around 3 eV, the transition from $C^2\Pi_g^+$ becomes the main source of recurrent fluorescence. This is because of the strong electric dipole coupling to the ground $X^2\Pi_u$ state, whereby a large transition probability for optically allowed transitions compensates the low population [21].

At the detachment threshold of 4.18 eV, the photon emission rate constant is on the order of 10^4 s^{-1} (i.e., a lifetime of 0.1 ms). Because the energy dissipated in a single transition is large enough to stabilize the anion against electron detachment, delayed electron detachment on a millisecond time scale should be highly suppressed. The decay is determined dominantly by this recurrent fluorescence rate, which is consistent with the observed absence of a detectable ion storage time dependence in the decay profile. Therefore, our calculation rationalizes the assumption that the decay profile for C_6^- is governed by fast electronic radiative cooling and not by depletion cooling. One must expect that low-lying optically allowed electronic excited states, which can be a consequence of open-shell electronic structure in the ground state, will greatly facilitate radiative cooling via recurrent fluorescence. This effect will be enhanced for higher detachment thresholds.

For a more quantitative analysis, we simulated the observed electron detachment behavior. We took into account the internal energy region from which the anions emit electrons in the experimentally observed time window, referred to as the energy window (E_0) [24]. The procedure of evaluating E_0 was the same with that employed for C_5^- [25] and C_7^- [26]. The energy window extends from 3.8 to
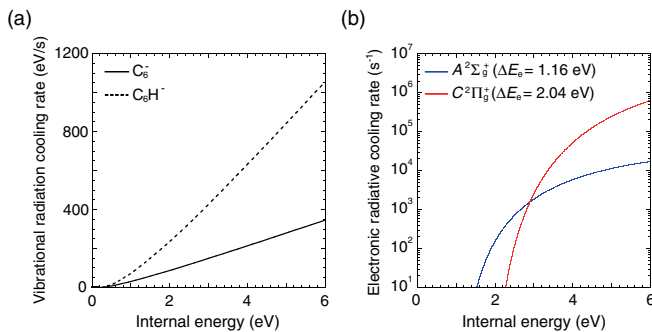

FIG. 2 (color online).   (a) Simulated vibrational radiative cooling rates of C_6^- (solid line) and C_6H^- (dashed line) as a function of the internal energy. (b) Simulated electronic radiation rates of C_6^- from statistically populated electronic excited states $A^2\Sigma_g^+$ (blue), $C^2\Pi_g^+$ (red).

TABLE I.   Energy levels above the ground state, ΔE_e (a) and Einstein's A coefficients, and estimated population of the excited states at the detachment threshold, $E_a = 3.81$ eV for C_6H^- and $E_a = 4.18$ eV for C_6^-.

anion	state	ΔE_e (eV)	A^e (s^{-1})	population
C_6H^-	$X^1\sum^+$	—	—	≈ 1.0
C_6H^-	$A^1\Pi$	3.77[a]	—	$< 10^{-12}$
C_6^-	$X^2\Pi_u$	—	—	0.94
C_6^-	$A^2\sum_g^+$	1.16[b]	1.86×10^5	0.035
C_6^-	$B^2\sum_u^+$	1.32[c]	0.0	0.020
C_6^-	$C^2\Pi_g^+$	2.04[d]	5.64×10^7	0.0013
C_6^-	$D^2\Pi_g^+$	2.79[b]	3.2×10^6	2.8×10^{-5}

[a]ΔE_e was taken from [22].
[b]ΔE_e was taken from [23].
[c]ΔE_e was taken from [21].
[d]ΔE_e was taken from [16].
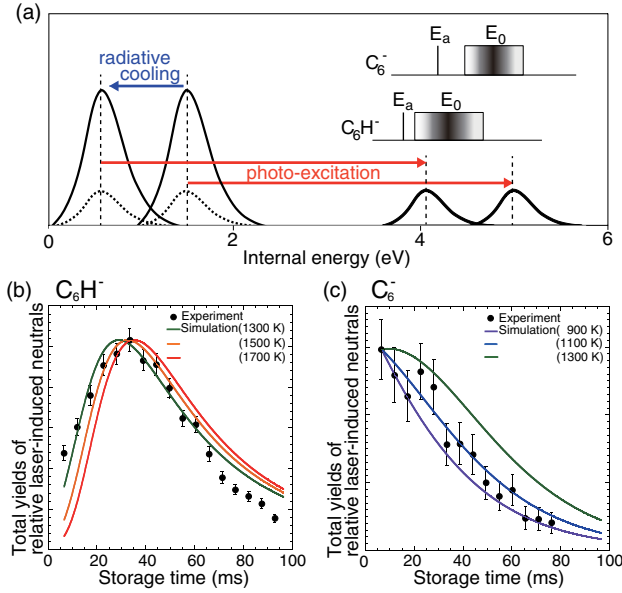[e]A was taken from [21].

FIG. 3 (color online). (a) Schematic of the energy distributions before and after one-photon excitation of the 355 nm laser, together with radiative cooling. The detachment threshold and calculated energy windows for C_6^- and C_6H^- are indicated. For simplicity, the initial distributions for C_6^- and C_6H^- were assumed to be the same. (b) Plot of the laser-enhanced neutral yields for C_6H^- evaluated by summing up $I(1)$ to $I(11)$. (c) Plot of $I(1) + I(2)$ for C_6^-. The curves both in (b) and (c) are simulated yields for various internal temperatures after 6.5 ms storage. Refer to the main text for more details.

4.3 eV for C_6H^- and 4.2 to 4.6 eV for C_6^-. Figure 3(a) shows a schematic of the energy distributions of the hot anions before and just after photoexcitation, and those undergoing radiative precooling, together with E_a and E_0. As shown in the figure, what we observe as delayed detachment is the number of anions with energy $(E_0 - h\nu)$ before photoexcitation, where $h\nu$ is the one-photon energy of the laser. Thus, the decay profile is a reflection of the distribution function inside the energy window, and the yield is proportional to the population there. The variation of the total yield with the storage time gives information on the radiative precooling on this time scale (up to 100 milliseconds). If the stored anions are initially hot and photoexcitation shifts the distribution above the window, detachment events occur on time scales too fast to be detectable. Then, radiative precooling during the longer storage period cools the anions, gradually pushing the distribution down to the lower energy side. Photoexcitation of cooled anions gives better overlap with the energy window, resulting in an increase of the yield until further precooling lowers the distribution. Such a behavior was recently reported for C_5^-, in which the experimentally obtained cooling rate was a factor of 2.5 slower than that expected for harmonic oscillators [25]. The plots of the total yields against the storage times are shown in Figs. 3(b) and 3(c) for C_6H^- and C_6^-, respectively. The

yield for C_6H^- shows a peak, while that for C_6^- decreases monotonically. This indicates that the peak of the energy distribution of C_6H^- is initially located on the higher energy side of $E_0 - h\nu$ and the cooling increases the population at $E_0 - h\nu$, while that of C_6^- is initially located on the lower energy side. For various initial (at 6.5 ms) temperatures, the total yield curves were simulated by summing up the detectable yield at given energy shifted by $h\nu$. The initial energy distribution at 6.5 ms was parameterized with the Boltzmann distribution, and scaled vibrational transition probabilities were employed to trace the vibrational precooling, where the scaling factor was used as another fitting parameter [27]. The results are shown as the solid curves in Figs. 3(b) and 3(c).

For C_6H^-, the simulation reproduces the observation well when the temperature at 6.5 ms storage is 1500 K. In the simulation, the vibrational cooling rate of C_6H^- and C_6^- are a factor of 1.5 and 2.3 lower than those shown in Fig. 2(a), respectively. Although the outcome of the fitting procedure is rather uncertain for C_6^-, the "peakless" condition allows us to deduce the initial temperature to be lower than 1500 K.

These fitted temperatures are consistent with the observed fast radiative cooling of C_6^-, compared to C_6H^-, and contradicts the naive expectation that the C_6^- might be hotter in the ring, based on consideration of both the initial temperature and the cooling rate. That is, 1) the higher detachment threshold of C_6^- may lead to production of hotter anions in the source, and 2) at the given internal energy, the vibrational radiative cooling of C_6^- is always slower than that of C_6H^-, as shown in Fig. 2(a).

We return to the discussion of Figs. 1(a) and 1(b), with the simulated decay curves for a given temperature at 6.5 ms. For C_6H^-, adopting 1500 K as the 6.5 ms temperature and using detachment rates inside the energy window, we obtained the solid curves corresponding to the decay curves for C_6H^- in Fig. 1(a). The simulated decays agree well with observation, supporting our conclusion that the decay curves for C_6H^- reflect the electron detachment rates during depletion cooling at each temperature, and that the dependence on the storage time is due to radiative precooling through vibrational cooling. It also shows that the relevant processes are induced by one-photon absorption.

The decay for C_6^- was simulated adopting 1300 K as the 6.5 ms temperature, where use of the average rate constants over the energy distributions at the first revolution leads to near single exponential decay curves as shown in Fig. 1(b). The simulated decay time depends on the storage time, reflecting the lowering of the excited electronic state population, whereas the experimental time resolution is not enough to identify this dependence. The time scale is on the order of 0.1 ms, which is consistent with our observation. It strongly supports the aforementioned scheme that the decay was determined by the radiative cooling rate through recurrent fluorescence.

In summary, we have observed that the neutralization signal of photoexcited C_6^- showed a remarkably fast decay compared with C_6H^- when the delayed electron emission process of the anions was observed on a time scale up to a few millisecond. This difference is caused by the presence of a low-lying electronic excited state in C_6^- that leads to electronic radiative cooling through recurrent fluorescence after an inverse internal conversion process. The presence of the IIC will have a significant influence on the abundance of small carbon cluster anions and related species in the interstellar medium [28].

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