Electronic and vibrational radiative cooling of the small carbon clusters $C_4^-$ and $C_6^-$

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Delayed electron detachment yields of $C_4^-$ and $C_6^-$ induced by photoexcitation in an electrostatic ion storage ring were measured as functions of excitation energies and laser firing times, allowing for a mapping of their radiative cooling in a wide energy range. 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. The even-odd alternation of vibrational cooling rates, predicted from IR intensities, was also examined. We found that the larger anion cools faster, with no indication of an even-odd alternation.

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I. INTRODUCTION

The understanding of radiative cooling of hot molecules has been drastically improved by the recent development of ion storage devices such as storage rings and ion traps [1]. In the highly isolated environment realized in such devices, the internal conversion (IC) process by which the electronic energy is distributed to various vibrational modes is no longer irreversible. That is, an inverse internal conversion (IIC) process will occur, and the energies distributed into various vibrational modes may revert to electronic energy with a certain probability.

In general, radiative cooling has been considered purely vibrational. For example, the cooling of hot $C_5^-$ and $C_7^-$ stored in a ring can be explained solely by the vibrational radiative cooling [2,3].

However, sometimes IIC is not negligible. For example, cooling rates of fullerene anions [4], polycyclic aromatic hydrocarbons (PAHs) ($C_{14}H_{10}^+$ [5] and $C_{10}H_8^+$ [6]), semiconductors ($B_8^+ - B_{18}^+$ [7] and $Si_{15}^+ - Si_{13}^+$ [8]), metal clusters ($Al_4^− - Al_{13}^− [9]$), and small carbon clusters ($C_6^− [10,11]$ and $C_4^− [12]$) are found to be much higher than expected for vibrational radiative cooling alone. The electronic radiative cooling process referred to as recurrent fluorescence (RF) cooling, with its visible or near infrared (NIR) photon emission via the electronic excited states regenerated through IIC, is invoked to explain this discrepancy. For very large molecules and particulate matter, the emission of visible photons from hot species is not surprising; it is a well-known consequence of black-body radiation. However, fullerenes are definitely not described as particulate matter, and the other clusters examined are even smaller. For instance, RF photons were directly detected from $C_6^−$ [13] and $C_4^− [14]$.

The fact that RF cooling is found only for the even-numbered carbon cluster anions is a manifestation of the even-odd alternation generally found for chain-forming carbon clusters. That is, these anions show an even-odd alternation in the electronic structures; only even-numbered cluster anions possess low-lying electronic excited states, which is required for the RF process. In summary, the cooling scheme of the carbon cluster anions is as follows:

(1) ($n$: odd)

\[ C_n^{-\varepsilon(e)} \rightarrow C_n^{-\varepsilon(v)} \rightarrow C_n^{-\varepsilon} + \text{IR photons} \]

(2) ($n$: even)

\[ C_n^{-\varepsilon(e)} \rightarrow C_n^{-\varepsilon(v)} \rightarrow C_n^{-\varepsilon} + \text{IR photons} \]

\[ C_n^{-\varepsilon(e)} \rightarrow C_n^{-\varepsilon(v)} \rightarrow C_n^{-\varepsilon} \rightarrow C_n^{-\varepsilon} + \text{vis or NIR photons} \]

where $C_n^{-\varepsilon(e)}$ and $C_n^{-\varepsilon(v)}$ are anions in their electronic and vibrational excited states, respectively, above the electron detachment threshold.

The electronic excited states of $C_4^-$ and $C_6^-$ are shown in Table I. Low-lying, optically active electronic excited states are present in each anion. The C-X transitions are favored by their very large cross-sections [16]. The B-X ($C_4^-$) and A-X ($C_6^-$) transitions are instead favored by high populations of the B ($C_4^-$) and A ($C_6^-$) states due to their lower energies, which allows the RF to happen also at lower excitation energies for these anions. The energy regions surveyed so far, as shown in Table I, are mostly above the lowest electronic excited states, with RF processes having been observed from these states.

Previously, the RF rates in the vicinity of the electron detachment thresholds $E_{dB}$ of $C_4^-$ and $C_6^-$ (electron affinity
TABLE I. Excitation energies of the electronic states of $C_4^-$ and $C_6^-$ [15–19] and the internal energies of anions where electronic or vibrational cooling rates were measured previously [10–12,20]. The rightmost column shows the energies studied in this work. The $A$ state of $C_4^-$ and the $B$ state of $C_6^-$ are dipole-forbidden with respect to their corresponding $X$ state. All energies are given in eV.

<table>
<thead>
<tr>
<th>Ion</th>
<th>State Reported</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4^-$</td>
<td>$X^3\Sigma_u^-$ 3.88</td>
<td>3.88</td>
</tr>
<tr>
<td></td>
<td>$C^2\Pi_u$ 2.71</td>
<td></td>
</tr>
<tr>
<td>$C_5^-$</td>
<td>$X^3\Sigma_u^-$ 4.18</td>
<td>4.18</td>
</tr>
<tr>
<td></td>
<td>$D^2\Pi_u$ 2.49</td>
<td></td>
</tr>
<tr>
<td>$C_6^-$</td>
<td>$X^3\Sigma_u^-$ 4.18</td>
<td>4.18</td>
</tr>
<tr>
<td></td>
<td>$D^2\Pi_u$ 2.04</td>
<td></td>
</tr>
<tr>
<td>$C_7^-$</td>
<td>$X^3\Pi_u$ 0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

TABLE II. Vibrational quantum energies (cm$^{-1}$) and IR intensities (km mol$^{-1}$) of the relevant modes for $C_n^-$ ($n = 4 – 7$) [2,21].

<table>
<thead>
<tr>
<th>Ion</th>
<th>Vibrational quantum energy</th>
<th>IR intensity</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4^-$</td>
<td>1785</td>
<td>87</td>
<td>$\nu_1 (\sigma_g)$</td>
</tr>
<tr>
<td>$C_5^-$</td>
<td>1807</td>
<td>855</td>
<td>$\nu_1 (\sigma_g)$</td>
</tr>
<tr>
<td>$C_6^-$</td>
<td>2037</td>
<td>726</td>
<td>$\nu_1 (\sigma_g)$</td>
</tr>
<tr>
<td>$C_7^-$</td>
<td>1836</td>
<td>2331</td>
<td>$\nu_5 (\sigma_g)$</td>
</tr>
</tbody>
</table>

The radiative cooling of small anions with internal energies below the detachment threshold was mainly studied by employing the energy window concept. Here the yields of delayed detachment induced by laser irradiation were measured as a function of $t_{\text{ls}}$ at a fixed laser wavelength. The procedure providing information on the time evolution of the energy distribution from the $t_{\text{ls}}$ dependence is shown schematically in Fig. 1, illustrating the window concept. This works because, for small anions, the rate of delayed detachment is a rapidly increasing function of internal energy. Thus, the laser-induced neutrals detected in a specific delay after the laser pulse will come from anions with a specific internal energy, called the “energy window ($E_0$)”, as indicated by the purple area in Fig. 1. The observed yield is proportional to the population of ions at $E_0$ and therefore to the population at the sampled energy $E_s = E_0 - nh\nu$ just prior to photon absorption. For the observation of the decay yield at a specific time after laser excitation, the internal energy of the decaying species is fixed. When the photon energy is constant, the cross sections of the absorbing species are also constant, and in particular, independent of the ion storage time preceding the laser pulse. The neutral yield is therefore rigorously proportional to the prelaser population of the ion at the specific excitation energy probed. Based on this concept, multiphoton processes lead to the sampling of populations at lower internal energy.

Utilizing this window concept, RF cooling of $C_4^-$ [12] as well as the vibrational cooling of $C_5^-$ [2], $C_7^-$ [3], and $C_6H^-$ [10] were studied. Very recently, precise values of the RF and vibrational cooling rates of $C_6^-$ were obtained by an electrostatic ion beam trap study [20].

In this paper, the RF and vibrational radiative cooling of $C_4^-$ and $C_6^-$ in a wide internal energy range, 0.43–2.24 eV for $C_4^-$ and 0.34–2.28 eV for $C_6^-$, will be presented. For $C_4^-$, only vibrational cooling was studied; the RF rate of $C_4^-$ has been reported in our previous study [12]. For $C_6^-$, the RF and vibrational cooling rates were obtained and compared to the previously reported values [20]. The even-odd alternation in vibrational cooling will also be discussed in light of the results of $C_5^-$ and $C_7^-$ reported previously [2,3].
II. EXPERIMENTS AND SIMULATION

The experiments were performed at the electrostatic ion storage ring "TMU E-ring" [23] with a laser-ion beam merging configuration shown schematically in Fig. 2.

Hot carbon cluster anions produced in a laser ablation ion source were stored in the ring at a kinetic energy of 15 keV. At a certain laser firing time, up to 90 ms after ion generation, the ions were re heated by photons from an optical parametric oscillator (OPO) (Spectra-Physics MOPO-SL) pumped by a pulsed Nd: YAG laser (Spectra-Physics Quanta-Ray Pro-230-10) at the straight section on the side opposite to that of neutral detection. The neutral particles, which appeared due to delayed electron detachment, were detected by a set of microchannel plates (MCPs) half turn after the photon absorption. The detection of neutrals occurred more than 10 μs after laser excitation due to the circulation periods of C6− and C6− (about 32 and 39 μs, respectively). The laser pulse energy was kept below 3 mJ/μs with a pulse duration below 10 ns. Under these irradiation conditions multiphoton absorption may still occur; thus, the neutrals induced by one- or two-photon absorption were detected.

The procedure used in the simulation of RF and vibrational radiative cooling was basically the same as that reported previously [12,24]. In brief, a detailed-balance theory was used to calculate the energy-dependent detachment rate, which was then used to determine the detectable portion of generated neutrals and hence the energy window. Rotational cooling was ignored because it is much less effective than other decay channels [25]. The level densities were calculated assuming that all the vibrations are harmonic. The theoretical value of the neutrals and hence the energy window. Rotational cooling was basically the same as that reported previously by fitting the tobs dependence without the need of simulations. On the other hand, the vibrational cooling rates Pj(E) were obtained by comparing the experimental and simulated tobs dependence curves. For this purpose, neutral yields were calculated for the simulated energy distribution as a function of tobs, and the scaling factor matched to reproduce the experimental yield curves. The time variation of the population at the sampled energy Eν was calculated as follows: the initial internal energy distribution was assumed to be of Boltzmann type with an effective temperatures of 5000 K at the time of ion generation, i.e., the Boltzmann factor multiplied by the vibrational level density. Then the time evolution of the distribution was calculated, considering the depletion by electron detachment (loss of ions) and energy loss due to electronic and vibrational cooling.

III. RESULTS AND DISCUSSION

A. Radiative cooling of C6−

The energy window E0 is located at 4.49 eV for C6−, slightly above Eeh (4.18 eV), and has a width of 0.16 eV. Typical tobs dependence plots of the neutral yields for C6−, obtained with 550 and 480 nm laser irradiation, are shown in Figs. 3(a) and 3(b), respectively. The plots show the evolution of the population p(Eν) at the sampled energy Eν. The yield curves are observed to behave differently in earlier (I) and later (II) time regions. At the earlier time region I, the yields quickly decrease, both in Fig. 3(a) and 3(b). This is a typical feature of RF cooling, which removes so much energy that the upper-energy component of the energy distribution jumps into E ≪ Eν. Since Eν must be above the RF-active electronic states, the yields in this region are consequently due to one-photon (Eν = E0 − hν) processes. As for region II, an increase in the yield is seen in Fig. 3(a), indicating that the sampled energy is initially below the peak of the distribution. That is, the main contribution switches from a one-photon to two-photon (Eν = E0 − 2hν) process at around 10 ms when the high energy population p(Eν = E0 − hν) is exhausted by the RF radiation. On the other hand, the yields do not increase in region II of Fig. 3(b). This is simply due to the negative value of Eν = E0 − 2hν for 480 nm photons. In other words, two-photon excitation raises the energy of C6− to considerably above E0 irrespective of its initial internal energy, and the resulting rate of detachment is too fast to be observed in the present experimental configuration. It should be noted that E0 − 3hν is negative for all laser wavelengths employed in this work.

Semilog plots of the fast decay components are shown in Fig. 4, obtained by (a) 480, (b) 500, (c) 530, (d) 550, and (e)
560 nm photons. The $E_s$ values are shown in the figures. The yields decrease exponentially as expected and similar to the case of $C_4^-$ in our previous study [12]. The slopes of the fast components, which give the RF rate constants at $E_s = E_0 − h\nu$, are steeper for longer wavelengths. As mentioned before, the RF cooling rates are directly obtained from these slopes. In Fig. 4(d), and more prominently in Fig. 4(e), slowly varying components due to two-photon processes appear. Thus, the $E_s$ at $\lambda = 560$ nm consists of $E_0 − h\nu = 2.28$ eV and $E_0 − 2h\nu = 0.06$ eV. In Figs. 4(a) to 4(c), such components are also expected to be present but are hidden by the dominant one-photon process.

The experimental RF cooling rates for $C_6^-$ are shown in Fig. 5 as a function of internal energy, together with those at higher energies reported previously [10,11]. The theoretical curve with the scaling factor $f_{RF} = 1.0$ (red line in Fig. 5) agrees well with the experimental plots except for a small vertical shift, as also seen for $C_4^-$ in our previous study [12]. The curve reproduces the experiments even better in the wide range of the internal energies when the scaling factor $f_{RF}$ is $1.8 \pm 0.4$, which agrees with the previous report [20] (black line in Fig. 5). The obtained RF cooling rates are adopted for the subsequent analysis of vibrational cooling behavior. Although the fast RF cooling is completed in the time range of vibrational cooling analysis, it should be taken into account because it determines the “initial” distribution that undergoes vibrational cooling.

The plots of neutral yields against $t_{\text{las}}$ on a longer time scale up to 90 ms are shown in Fig. 6 for the longer wavelengths from 610 to 640 nm. The sampled energies $E_s = E_0 − 2h\nu$ are 0.34 eV (610 nm), 0.40 eV (620 nm), and 0.53 eV (640 nm). As shown in each plot, the yield initially increases (except the point at $t_{\text{las}} \approx 0$) and at a specific laser firing time it starts decreasing due to cooling-induced depletion of the population in the upper energy region. The peaking time depends on $E_s$, with later times for lower values of $E_s$; i.e., higher photon energy, as expected. Such a peaking profile was also observed for the one-photon studies of $C_5^-$ and $C_7^-$ [2,3], and is consistent with the window concept.

From these simulated energy distributions, the time evolution of the population at $E_s$ was obtained. When the scaling factor of the theoretical vibrational cooling rate ($f_i$) is 1.0, the theoretical neutral yield curves (red lines) do not reproduce
FIG. 6. \( t_{\text{las}} \) dependence of the relative neutral yields for \( \text{C}_6^-\) up to 90 ms at the wavelengths (a) 610, (b) 620, and (c) 640 nm. The yields are normalized to the peak value. The red lines are the simulated yield from the theoretical rates and black lines are those scaled by the factors of 1.8 for electronic and of 2.7 for vibrational cooling rates. The error bars are statistical. The points at \( t_{\text{las}} \approx 0 \) in each plot are due to one-photon processes and are not included in the fitting.

The \( t_{\text{las}} \) dependencies of the neutral yields up to 90 ms, induced by irradiation of 440 nm (\( h\nu = 2.82 \text{ eV} \)), 760 nm (1.63 eV), and 840 nm (1.48 eV) photons are shown in Fig. 7. On this timescale, the decrease of the neutral yields induced by one-photon absorption of 760 and 840 nm light is too fast to be seen (faster than 5 ms) since it measures the population of highly excited states. In addition, two-photon absorption of 440-nm light, and three-photon absorption of 760- and 840-nm light elevates anions from the ground state to too far above \( E_0 \) to be detected in the present experiments. Thus the plots show the population changes at \( E_s = 0.62 \text{ eV} \) (760 nm two-photon), 0.92 eV (840 nm two-photon), and 1.06 eV (440 nm one-photon) exclusively.

The \( t_{\text{las}} \) dependencies of the neutral yields up to 80 ms, induced by irradiation of 440 nm (\( h\nu = 2.82 \text{ eV} \)), 760 nm (1.63 eV), and 840 nm (1.48 eV) photons are shown in Fig. 7. On this timescale, the decrease of the neutral yields induced by one-photon absorption of 760 and 840 nm light is too fast to be seen (faster than 5 ms) since it measures the population of highly excited states. In addition, two-photon absorption of 440-nm light, and three-photon absorption of 760- and 840-nm light elevates anions from the ground state to too far above \( E_0 \) to be detected in the present experiments. Thus the plots show the population changes at \( E_s = 0.62 \text{ eV} \) (760 nm two-photon), 0.92 eV (840 nm two-photon), and 1.06 eV (440 nm one-photon) exclusively.

B. Radiative cooling of \( \text{C}_4^-\)

As mentioned before, the RF cooling rates of \( \text{C}_4^-\) were measured previously using the energy window \( E_0 = 3.88 \text{ eV} \), which is approximately equal to the electron detachment threshold (3.88 eV) with a width of less than 1 meV [12]. The small width is due to the small heat capacity of \( \text{C}_4^-\). The fitting of the experimental and theoretical values gives the scaling factor \( f_{\text{RF}} = 2.7 \pm 0.3 \) (see Fig. 7 in Ref. [12]). It should be noted that the RF rate constants at these energies are much larger than for \( \text{C}_6^-\).

The vibrational cooling rates, or the scaling factors for the theoretical rate, are derived with the same procedure as employed for \( \text{C}_6^-\). As in the case of \( \text{C}_6^-\), simulations with \( f_{\text{RF}} = 2.7 \pm 0.3 \) (black lines) gives a reasonable fit except at the very beginning of the storage. As for the short storage time region,
the simulations show much faster rise, and the lowering of the RF scaling factors does not improve the situation. Such disagreement is not observed for C6− (Fig. 6), probably due to the relatively small RF cooling rate. For C4−, the much faster RF rate strongly enhances incoming components from the region just below $E_\text{th}$, leading to a sudden increase of the population at $E_s = E_0 - 2h\nu$. It should be noted that the rise becomes slower if the broad feature of the emitted RF energies is taken into account. In fact, a recent RF photon detection study indicates that the RF emission is very broad [14]. The broad spectrum of the RF photon energy does not affect the RF cooling rate obtained from the rapid decrease of the population at the upper levels. It only has an influence on the increase of the population at the lower levels, the destination of the RF processes. Although further analysis must wait until the spectral features are determined in more detail, we conclude that the precise details do not affect the observed vibrational cooling rate.

**C. Size dependence of vibrational cooling of C$^-$**

To investigate the expected even-odd alternation in vibrational cooling rates, the theoretical cooling rates without scaling factors are shown in Fig. 8(a) for C$^-$ ($n = 4$–$7$). Because of the aforementioned even-odd nature of the IR intensities of the main active vibrational mode, odd-numbered cluster anions are predicted to cool faster. The experimentally scaled vibrational cooling rates of C4− and C6− obtained in the present study are shown in Fig. 8(b). Those of C5− and C7− are also shown with the factors obtained previously [2,3,26]. As can be seen in Fig. 8(b), it is obvious that the even-odd alternation is absent. Simply stated, the larger the anion, the faster it cools. That is, the even-odd alternation in vibrational frequencies and IR intensities is not large enough to make a difference in the overall cooling rate of the hot anions.

**IV. CONCLUSION**

We measure the electronic and vibrational radiative cooling rate over a wide energy range from below to above the electronic excited states of C4− and C6−. Under both one- and two-photon absorption, the approach based on the energy window concept is a powerful tool to measure radiative cooling, especially for small ions, in which the window is fairly narrow. 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. The method used is generally applicable and provides access to the complex process of vibrational radiative cooling, for which detailed theoretical predictions, to the best of our knowledge, do not exist.

**ACKNOWLEDGMENTS**

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[26] In Refs. [2], [3], and [24], the erroneous term of ln(10) is included, which is corrected in the present study.