Spontaneous decay of small copper-cluster anions Cuₙ⁻ (n = 3–6), on long time scales

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We have measured the spontaneous neutral particle emission from copper-cluster anions (Cuₙ⁻, n = 3–6) stored at cryogenic temperatures in one of the electrostatic ion storage rings of the Double ElectroStatic Ion Ring ExpEriment facility at Stockholm University. The measured rate of emission from the stored Cuₙ⁻ ions follows a single power-law decay for about 1 ms but then decreases much more rapidly with time. The latter behavior may be due to a decrease in the density of available final states in Cuₙ⁻ as the excitation energies of the decaying ions approach the electron detachment threshold. The emissions from Cu₄⁻, Cu₅⁻, and Cu₆⁻ are well described by sums of two power laws that are quenched by radiative cooling of the stored ions with characteristic times between a few and hundreds of milliseconds. We relate these two-component behaviors to populations of stored ions with higher and lower angular momenta. In a separate experiment, we studied the laser-induced decay of Cu₆⁻ ions that were excited by 1.13- or 1.45-eV photons after 46 ms of storage.

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I. INTRODUCTION

The advent of a new generation of cryogenic electrostatic ion storage devices has greatly widened the feasible time range for studies of ion decay, opening the possibility to measure decay channels that are active on very long time scales [1–7]. At the Double ElectroStatic Ion Ring ExpEriment (DESIREE) facility at Stockholm University [4,7], the 13-K operating temperature yields a residual gas pressure of roughly 10⁻¹⁴ mbar, allowing for the observation of processes with characteristic decay times on the order of thousands of seconds. This development puts special emphasis on radiative cooling processes, which are expected to be the dominant decay channels for molecules and clusters at long times. Fast radiative cooling of molecular ions stored in electrostatic rings was first observed in experiments on C₆₀⁻ at the room-temperature ring ELISA in Aarhus [8]. These fullerene ions were then found to cool with a rate exceeding those expected for vibrational cooling by two orders of magnitude and with characteristic cooling times of several milliseconds [8]. Similarly, fast radiative cooling has been observed for anthracene cations (C₁₄H₁₀⁺⁺) [9] stored in MINIringer, a compact ion storage ring in Lyon [10]. Even faster radiative cooling rates, with corresponding time scales in the sub-millisecond range, have been measured for small carbon-cluster anions (Cₙ⁻, n = 4, 6) at the Tokyo Metropolitan University (TMU) E-Ring [11]. Also at TMU, slower cooling of C₄H⁻ ions [11] and of C₅⁻ and C₇⁻ clusters [12–14] on millisecond time scales was again observed.

These previous experiments have revealed several unexpected features of the radiative cooling process. Of particular note is that it can proceed very effectively via electronic transitions, even for clusters as small as C₄⁻ [8,9,14]. It is the availability of low-lying electronic excitations in C₄⁻ and C₅⁻ and the lack of such excitations in C₇⁻, C₉⁻, and C₁₀H⁻ that makes the cooling much more efficient in the former than in the latter cases. Recently, direct evidence for the emission of photons due to transitions from the lowest electronically excited optically active state in C₅⁻ to the electronic ground state was reported [15]. Cooling of metal clusters is of special interest because, in addition to evaporative cooling through emission of electrons, atoms, or molecules, metal clusters can radiate and thus cool via any of the following radiative mechanisms: decay from a single particle-hole electronic excitation; excitation of a short-lived surface plasmon resonance; or by vibrational and rotational cooling. The first two are unique to clusters of metals and other systems with delocalized electrons, including carbon and carbon-based molecules. Studies of metal clusters are thus key to understanding the importance of these types of radiative cooling processes.

Only a few radiative cooling experiments have so far been carried out using cryogenic electrostatic ion storage devices. These are experiments on Alₙ⁻, n = 4–5 clusters [16] and on SF₆⁻ [17] at the Cryogenic Trap for Fast Ion beams (CTF), in Heidelberg, and a recent study of Cuₙ⁻, n = 4–7, also in the CTF [18]. In the present paper we report measurements of the spontaneous emission rate of neutral particles from the small copper-cluster anions Cuₖ⁻, n = 3–6, stored in one of the DESIREE ion-storage rings at Stockholm University [4,7]. These measurements carry information on the rates of radiative cooling processes on different time scales.

II. EXPERIMENT

The cluster anions were produced in a cesium-sputter ion source using a solid copper cathode and accelerated to 10 keV. A bending magnet was used to select the desired

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mass before injection into the ring. For the smallest cluster sizes, the smallest mass isotopologs were used. No sign of hydrogenation was found and for the larger clusters the most intense peak in the isotope distribution was used. Ions were injected, stored, and dumped every 0.1–10 s depending on the time scale of interest. The intrinsic ion storage lifetime in DESIREE is much longer than this, as demonstrated by measurements of metastable excited states in atomic anions where a storage lifetime of 30 min was measured for a 10-keV kinetic-energy Te− beam [19]. For the Cu6−, n = 3–6 cluster anions studied here, the signal due to spontaneous decays of excited ions always becomes negligibly small within a few seconds after injection and time windows of the order of 10 s are thus sufficient in these particular cases.

In the experiment, we detected the neutral particles that were produced through electron detachment and/or unimolecular dissociation in spontaneous decay processes or, in separate experiments, from decays induced by absorption of a photon from a laser pulse. In both types of experiments, neutral particle counts were recorded as functions of time, t, with the detector placed along the line of sight of one of the straight sections of the ion-beam storage ring as shown in Fig. 1. Since the detector only registers neutral particles, it is not possible to assign the decay channel from the signal. Identification of specific decay channels is, however, not necessary for the determination of cooling times. The decay curve for Cu5− was recorded using time windows of 200 ms and 10 s. After normalization, the decay curves agree with each other in the region where they overlap. The spectra for Cu4,5,6− were recorded with time windows of a few seconds.

In addition to these measurements, crossed-beam laser excitation experiments were performed on Cu6− with the wavelengths 850 nm (1.45 eV) and 1100 nm (1.13 eV), as shown in Fig. 1. The delayed photoinduced signals for the smaller clusters were found to be significantly weaker than the ones for Cu6− and are not reported here. For both wavelengths the laser was fired 46 ms after injection of the Cu6− beam. At this time the spontaneous decay from hot clusters produced in the source has almost disappeared and the measurement is close to background free.

Decay curves of the stored ions are shown in Figs. 2–5, in double logarithmic plots of the measured neutral emission rate for the stored ions versus the time t after production in the source. The data (recorded number of events) are binned in time intervals that increase linearly in width with t. These binned data are then divided by the width of the time bin to obtain the rate. This gives an even distribution of rate values along the horizontal axes in Figs. 2–5. The background is due to detector dark counts and collisions with residual gas. The largest component of this background is due to the detector dark counts, which has been measured separately, and which is subtracted prior to the binning of the data.

### B. Cu5−

The Cu5− spectrum shown in Fig. 2 is well described by a power law at short times. At longer times the curve has a much steeper slope. This apparent two-component power-law decay could in principle be accounted for by the small number of vibrational degrees of freedom, as indicated by a direct numerical calculation. The general expression for the radiation-free spontaneous particle emission rate, R(t), is

\[ R(t) \propto \int_{0}^{\infty} g(E)k(E)e^{-k(E)t}dE, \]  

in which k(E) is here taken to be the electron emission rate constant for ions with internal excitation energy E, and g(E) is the distribution of excitation energies. When this distribution is sufficiently broad, i.e., varies much slower with E than k(E),
Eq. (1) can be approximated by a power-law decay rate [20]:

$$R(t) \propto t^p,$$

(2)

with $p \approx -1$. In general, this approximate result holds irrespective of whether the process is the statistical emission of an electron, an atom, or a molecular fragment. It may fail, however, for clusters with small heat capacities, such as Cu$_3^-$ (see the discussion in Sec. IV C below). A quantitative estimate of the deviation from the power law in Eq. (2) requires the calculation of an explicit expression for the rate constant, $k(E)$, that enters into Eq. (1). Here, the calculation was done with the detailed balance rate constant for electron emission [21,22]:

$$k(E,\epsilon)d\epsilon = \frac{2m_e}{\pi \hbar^2} \epsilon \sigma_c \rho^{(0)}(E - E_a - \epsilon)/\rho^{(-1)}(E) d\epsilon,$$

(3)

in which $m_e$ is the electron mass, $\rho^{(0)}$ and $\rho^{(-)}$ are the level densities of the neutral and the anion, $E$ is the Cu$_3^-$ excitation energy, $E_a$ is the electron affinity of Cu$_3$, $\sigma_c$ is the Cu$_3$ electron capture cross section, and $\epsilon$ is the kinetic energy of the decay channel—effectively the kinetic energy of the electron. The factor of 2 in Eq. (3) accounts for the spin degeneracy of the emitted electron. The level densities were calculated with the Beyer-Swinehart algorithm [23] using the following four vibrational frequencies determined by density functional theory [Becke three-parameter Lee-Yang-Parr and Los Alamos National Laboratory two-double-$\zeta$ (B3LYP/LANL2DZ)]: 230, 142, and 52 cm$^{-1}$ (doubly degenerate). The same frequencies were used for both Cu$_3$ and Cu$_3^-$. For the electron affinity, which acted as the activation energy, the experimental value 2.45 eV [24] was used. The electron attachment cross section, $\sigma_c$, was set to the constant value of $5 \times 10^{-21}$ m$^2$. This small cross section is strongly reduced from the Langevin value as an assumed effect of a small electron-cluster sticking coefficient. This assumption is made here as the density of states in Cu$_3^-$ may well be very low due to a very narrow range of electron energies. In the calculation of the total rate constant, $\epsilon$ is integrated out by a numerical summation over
the states,

\[ k(E) = \sum_i k(E, \epsilon_i) \delta \epsilon, \]

in which the sum runs over the discretized values of \( \epsilon \) and \( \delta \epsilon \) is the energy resolution of the level density defined by the Beyer-Swinehart calculation. In addition to the rate calculated by numerical integration of Eq. (1) with the rate constant from Eqs. (3) and (4), the calculated function, \( R(t) \), is multiplied by the time to the power 0.67 in Fig. 2. This power is a fit factor which could possibly be related to the shape of the excitation energy and angular momentum distributions of the clusters produced in the source.

We assign the deviation from a single power-law decay behavior of \( \text{Cu}_{3}^- \) to the low density of vibrational states in neutral \( \text{Cu}_3 \) close to the vibrational ground state. The crossover from one slope to the other could be a result of the freezing out of a single vibrational degree of freedom. However, both slopes will be too steep without the fit factor \( t^{-0.67} \). Furthermore, the second part of the curve requires the electrons to be captured in the inverse process with the reduced Langevin cross section mentioned above. The effect of the reduction is to postpone the freezing out of the last vibrational degree of freedom and instead make the next-to-last freezing out observable in the experimental time window. Apart from this last shift, the mechanism proposed is similar to the one made in connection with the CTF study of \( \text{SF}_6^- \) in Heidelberg [17]. The main difference to those data is that not all final-state vibrations freeze-out at the same excitation energy in the copper trimer. Therefore the decay may continue to follow a power law but with a different slope than at earlier times.

Finally, we note a very slight change in the slope for the experimental data at times longer than 0.1 s in Fig. 2. A weak component from a second distribution of internal energies of \( \text{Cu}_3^- \) that could be due to trimer ions with different conformations and/or angular momentum distributions cannot be ruled out.

### C. \( \text{Cu}_{4,5,6}^- \)

The measured neutral particle emission signals for \( \text{Cu}_4^- \), \( \text{Cu}_5^- \), and \( \text{Cu}_6^- \) are more complex than that of \( \text{Cu}_3^- \). For \( \text{Cu}_4^- \), the measurements span more than four orders of magnitude in time (see Fig. 3), and for \( \text{Cu}_5^- \) and \( \text{Cu}_6^- \) the range is nearly four orders of magnitude in time (see Figs. 4 and 5).

A calculation similar to the one for \( \text{Cu}_3^- \) shows a qualitatively similar effect for \( \text{Cu}_4^- \), albeit so strongly reduced that the decay rate is very close to a single power law (see the dotted line in Fig. 3), and therefore it cannot explain the experimental data. For \( \text{Cu}_5^- \), \( \text{Cu}_5^- \), and \( \text{Cu}_6^- \), the data are instead well represented by a sum of two curves:

\[ R(t) = a_1 t^{-1+\delta_1} e^{-t/\tau_1} + a_2 t^{-1+\delta_2} e^{-t/\tau_2}. \]

As mentioned above, the power-law decay at short times is an effect of the broad internal energy distribution of the cluster ions from the source [20], and the exponential decay is the consequence of radiative cooling.

### IV. DISCUSSION

#### A. Role of angular momentum

The existence of two components of the decay curves for \( \text{Cu}_{4,5,6}^- \) will be discussed in terms of two distinct populations of ions, characterized by different angular momenta. The observation of two beam components with very different lifetimes will then be linked to a conserved quantity that effectively preserves the integrity of the two populations, and endows them with distinct and conserved properties.

Of primary importance for the following reasoning are the different lowest-energy geometries of species with different angular momenta. The sputter source that we use is of a type known to produce dimer and larger anions in high rotational states [16,17,25–27], and this is most likely the case also in the present experiment. We therefore tentatively assign the two characteristic times for each of the three cluster sizes \( n = 4, 5, 6 \) to species with higher and lower angular momentum.

The suggested mechanisms are discussed with the aid of Fig. 6. In this figure we show relative excitation energies for \( \text{Cu}_3^- \) and \( \text{Cu}_4^- \) ions in different conformations and as functions of their rotational angular momenta, \( J \), with cluster structures from density-functional theory calculations (B3LYP/LANL2DZ). These energies are given relative to the energies of the most stable nonrotating isomers of \( \text{Cu}_3^- \) and \( \text{Cu}_4^- \) in their vibrational ground states. For each anion conformation there are progressions of vibrational states from the yrast line and upward. Conformers can convert into each other as long as energy and angular momentum are conserved, but the higher-energy conformer populations are suppressed by their small level densities relative to those of the ground states.

Copper trimer anions in states with total excitation energies and \( J \) values above the lowest gray line in the upper panel of Fig. 6 may decay through electron detachment or through fragmentation. The latter process is, however, most likely slowed down as it leaves the product with only a single vibrational degree of freedom while electron emission gives products with four vibrational degrees of freedom. Electron detachment will thus be entropically favored in this upper region of energies and \( J \) values. Trimer anions with total energies below the same gray line, but above the dot-dashed lines, may only decay through dissociation channels.

For the \( \text{Cu}_4^- \) ions, the situation is more complicated. There are three conformer detachment limits that are close in energy and mostly lie above the fragmentation limits as indicated in the lower panel in Fig. 6. The three conformers have linear, rhombic, and Y-shaped forms with the detachment limit for the linear one being highest in energy for all values of \( J \) below 500. The detachment limits for the rhombic and Y-shaped forms cross near \( J = 400 \); the latter has the lowest energy for \( J > 400 \) while the rhombic form is lower in energy for \( J < 400 \). There is a region of total and rotational energies where \( J < 300 \) and where the detachment limit for the rhombic form lies below the lowest fragmentation limit. Only electron detachment processes are possible in this \( (J < 300) \) region.

These relations between conformer detachment limits for \( \text{Cu}_3^- \) and \( \text{Cu}_4^- \) indicate that the decay behaviors can be different for \( \text{Cu}_4^- \) ions in low and high rotational states while
summarizing the suggested explanation, we have seen that
the trimer decay can be explained without invoking two popula-
tions, consistent with the linear ground-state structure seen in
quantum chemical calculations including the present ones. the
larger clusters with theoretically more compact ground states,
on the other hand, display double decay curves, consistent with
anionic clusters belonging to two populations with different
angular momenta and conformations—linear (or Y-shaped)
species at high J and more compact (rhombic) species at low
J. At the high angular momenta the neutral Cu3− clusters may
be rhombic or Y shaped, depending on the precise value of J.
These trends for Cu4− are likely to apply to the two larger clus-
ters, also, as these are not expected to be linear for low J values.

B. Radiative Cooling

We now turn to the quasiexponential decrease of the
Cu4−, Cu5−, and Cu6− decay curves after a few milliseconds,
ascribed to radiative cooling. Radiative cooling, i.e., photon
emission from excited vibrational [28], electronic [9], or
plasmonic [8] states, depletes the population of hot ions
without producing neutral particles and effectively quenches
the power-law decay rate. Depending on the magnitude of
the energies of the emitted photons, the resulting spontaneous
decay rate may vary either as [20]

\[ R(t) \propto \frac{t^p}{e^{\delta t} - 1}, \]

which is valid for small photon energies, or as [14]

\[ R(t) \propto t^{-1+p} e^{-\delta t}, \]

for larger photon energies. Here, “large” photon energies are
those for which the emission of a single photon suppresses
any further unimolecular decay. For short times, t < \tau, both
expressions reduce to the power law, \( R \propto t^p \), with \( p = -1 + \delta \),
and for long times to a quasiexponential decay.

The photon energy required to quench the decay can be
compared with the vibrational energy. The (room-
temperature) Debye temperature of bulk copper is 310 K [29],
corresponding to a quantum energy of 0.027 eV. Even for
emission of such a comparatively low-energy photon, the
effect for the present clusters will be a quenching of further
unimolecular decay, corresponding to a decay rate following
Eq. (7) [13]. For electronic transitions, the quenching effect
is even stronger because of the much larger energies of the
emitted photons. In either case, we can use Eq. (7) for the
fits of the data reported here. The fitted effective quenching
times, \( \tau \), then directly give the photon emission rate constants
without any further analysis.

The fitted radiative time constants in Table I are mean
values of the thermally populated, vibrationally excited states.
The detailed balance expression for the photon emission rate
constant, \( k_p \), can be represented as [22,30]

\[ k_p(E) = \int \frac{8\pi \nu^2}{c^2} \sigma_{abs}(\nu) \frac{\rho(E-h\nu)}{\rho(E)} \left( 1 - e^{(E-2h\nu)/(k_B T)} \right) d\nu, \]

in which \( \nu \) is the cyclic frequency of the emitted photon and
\( c \) is the speed of light. We have assumed an excitation energy
independent absorption cross section, \( \sigma_{abs}(\nu) \). Finally, \( \rho \) is the
The power-law exponent \( p \) is equal to \(-1 + \delta \). The magnitudes of the time constants indicate that they are due to vibrational transitions. Uncertainties from the fits are \( \pm 0.05 \) for the \( \delta \)'s and between 10 and 20\% for the lifetimes. Vertical detachment energies, VDEs, from Ref. [24] are given in the right column.

<table>
<thead>
<tr>
<th>( N )</th>
<th>Short</th>
<th>Long</th>
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<tr>
<td>( \delta )</td>
<td>( \tau ) (ms)</td>
<td>( \delta )</td>
</tr>
<tr>
<td>4</td>
<td>-0.1</td>
<td>2.6</td>
</tr>
<tr>
<td>5</td>
<td>-0.2</td>
<td>7.5</td>
</tr>
<tr>
<td>6</td>
<td>-0.28</td>
<td>5.9</td>
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level density, calculated with all modes except the emitting states. From the expression it is clear that thermal photon emission is an activated process. The broad energy distribution and resulting spread in the radiative rate constant may therefore potentially render the radiative decay nonexponential, in analogy to the nonradiative electron emission. The effect will, however, not appear here because the radiative rate constant, \( k_p \), is much less energy dependent than the unimolecular decay constant, and a description in terms of an energy independent photon emission rate constant is a very good approximation. For an illustration of this point, see Fig. 3 of [14].

The shorter of the characteristic cooling times for \( \text{Cu}_4^- \) (2.6 ms), for \( \text{Cu}_5^- \) (7.5 ms), and for \( \text{Cu}_6^- \) (5.9 ms) are all rather close to each other. These lifetimes, as well as their associated power-law exponents \( p = -1 + \delta \) discussed below, are very similar to those measured for \( \text{Al}_4^- \) and \( \text{Al}_5^- \) [16]. These ions were also produced with a sputter source and stored in a cryogenic ion-beam trap. Time constants of several milliseconds are expected for vibrational transitions, which suggests emission of infrared photons as the source of this cooling. The assignment of the two different time constants requires a more detailed analysis which is outside the scope of this paper.

### C. Power-law exponents

Turning finally to the question of the initial power-law decay, we address the deviations of \( p \) from minus unity. The fitted values for the spontaneous decay of the three largest clusters are summarized in Table I. We see that the size dependence of the rate constants does not seem to be influenced in any significant way by the well-known shell structure and odd-even effects observed in abundances of copper-cluster anions [31], and also does not seem to reflect the vertical detachment energies [24] (last column in Table I). The power is expected to be less than \(-1 \) for small clusters. In the simplest case, when \( g(E) \) in Eq. (1) is constant and the heat capacity is not too small, the exponent \( p \) is close to \(-1 \). Including the effect of the finite heat capacity gives [20,22,28]

\[
 p \equiv -1 + \delta \approx -1 - \frac{1}{C} - \frac{2}{C} \times \frac{e^{-\ln(\omega)/C}}{1 - e^{-\ln(\omega)/C}} \tag{9}
\]

in which \( C \) is the effective microcanonical heat capacity in units of \( k_B \) and \( \omega \) is the frequency factor in the rate constant of this channel.

Although the short-time \( \delta \)'s are negative as expected, the quantitative agreement with Eq. (9) is poor. This is even more pronounced for the slow component, where the value is large and positive for \( \text{Cu}_6^- \). This suggests that the values may be influenced by the excitation energy distributions produced in the source. The idea can be further investigated by comparing the value of \( \delta \) measured in photoexcitation experiments as the absorption of a photon and the resulting enhanced decay probes the cluster’s energy distribution at an excitation energy which is smaller than the energy at which the spontaneous decay occurs.

The rates of decay of the signal induced by absorption of photons at the wavelengths 850 and 1100 nm in \( \text{Cu}_6^- \) are shown in Fig. 7. These two measurements show power-law decays with exponents that are very similar: \(-1.29 \pm 0.08 \) for the 850-nm measurement and \(-1.28 \pm 0.07 \) for the 1100-nm measurement yielding a weighted average of \(-1.28 \pm 0.05 \). This is identical to the value of \( \delta \) in Table I from the spontaneous decay at short times. If the energy of the clusters that decay spontaneously is denoted by \( E_0 \), the distributions are thus probed at the three energies \( E_0 \), \( E_0 - 1.13 \) eV, and \( E_0 - 1.45 \) eV, yielding similar \( \delta \) values. Given that \( E_0 \) is close to the threshold, these three points span a significant part of the distribution. We thus conclude that a value of \( \delta \) of \(-0.28 \) reflects a property of the clusters themselves and not a property of the production process, i.e., not of the distribution \( g(E) \).

It should be noted that laser excitation experiments, also on \( \text{Cu}_6^- \), with photon energies of 1.165 eV (1064 nm) gave a time-dependent exponent starting at \(-1.2 \) at short times and reaching \(-0.8 \) at 2 s [18]. The change is ascribed to radiative cooling and the related change of the excitation energy distribution. The energy distribution was found to agree with a canonical distribution with an initial temperature of 1100 K.
V. SUMMARY

In summary, we have measured the spontaneous decay of small copper-cluster anions Cu$_n^-$ with $n = 3$–6. We observe a complex decay behavior with two power-law decays each with their characteristic radiative lifetimes for Cu$_4^-$, Cu$_5^-$, and Cu$_6^-$, but no observe radiative cooling for Cu$_3^-$, Cu$_7^-$, and Cu$_8^-$, analogous to Cu$_6^-$, which gives values between $0.10$ and $0.11$ for electron detachment and atomic evaporation, respectively. We conclude that the measured value of $\delta$ is influenced by (as yet undetermined) factors intrinsic to the cluster, beyond the properties of the model used here. It is not clear to what degree this conclusion holds for the other cluster sizes.

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