Radiative cooling of Al$_4^-$ and Al$_5^-$ in a cryogenic environment

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**Abstract.** We have investigated the radiative cooling of initially hot Al$_4^-$ and Al$_5^-$ cluster anions during storage in a cryogenic ion beam trap at an ambient temperature of <15 K. By applying a statistical rate model to the ions’ measured delayed detachment rate following excitation with a laser, we have obtained their vibrational temperature as a function of cooling time. The temperature curves for Al$_4^-$ suggest that the vibrational cooling slows down considerably once the ion reaches approximately room temperature. This suggests the participation of transitions from recently found low-lying electronic states of the anion in the cooling process, prior to reaching approximately room temperature. The experimental results for Al$_5^-$ suggest slightly slower radiative cooling than for Al$_4^-$.

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1. Introduction

The cooling of physical bodies by exchange of photons with a surrounding radiation field is a process of fundamental importance to thermodynamics, and its theoretical interpretation has been a major contribution towards the development of quantum mechanics. For macroscopic bodies the large number of particles involved often allows a description of radiative cooling that is independent of the size of the system in question. The situation is different for systems on the molecular scale, where the optical emission and absorption properties depend on the geometric and electronic structure of the particle in question. For example, metal clusters and their ions have been found to exhibit radiative cooling on timescales as short as a few ms [1–3], whereas other species of similar size (e.g. CF$_3$O$^-$ and SF$_6^-$) only cool over much longer times [4]. Even for atomic clusters made up of identical constituents these properties change with the number of atoms and bonds as well as the geometrical structure of the cluster. Moreover, the straightforward application of statistical concepts developed for macroscopic bodies to the case of molecules and clusters is often prevented by the limited number of particles involved.

In addition to its fundamental interest, radiative heating and cooling of small particles also has many applications in science and technology. For example, the emission of radiation from vibrationally excited molecules is one of the key mechanisms for the cooling of interstellar clouds, which facilitates their contraction to a density sufficient for star formation [5]. As the degree of vibrational excitation generally influences the reactivity of molecules, radiative cooling or heating may also indirectly determine the chemical composition of dilute gases and plasmas. Conversely, the vibrational energy distribution of (ionized) molecules and clusters limits the precision with which e.g. reaction rates or threshold energies can be measured. This has over the last few decades led to the growing importance of heavy-ion storage rings and traps in these fields of physics, as they facilitate the reduction of vibrational excitation by storing particles over times much longer than their radiative lifetime, prior to a measurement [6].

Many aspects of the radiative cooling of small particles remain, however, uninvestigated. This is partly due to the experimental difficulty in directly observing or creating photons in the far infrared. A variety of indirect measurement procedures have therefore been established [4], which instead measure a readily accessible property of the system under investigation, which is sensitive to its degree of vibrational excitation. One such property is the rate of delayed electron detachment from a negative ion following the absorption of a photon: while the detachment rate is sensitive to the internal energy of the cluster anions, the photon provides the energy...
necessary to overcome the electron affinity, which is usually well above the total energy stored in small particles near room temperature. Together with a statistical model for the detachment rate as a function of vibrational energy this technique has been used to determine the vibrational temperature of $\text{Al}_4^-$ cluster anions during their storage in a room-temperature ion trap in [7]. It was found in the experiment that the ions cooled from a vibrational temperature of $\approx 1400$ K, measured 15 ms after their creation in a sputter ion source, to almost room temperature after 500 ms of storage. To probe radiative cooling at lower ambient temperatures, we have repeated the experiment using a liquid helium-cooled ion trap that affords a greatly reduced intensity of the black-body radiation field. After introducing the statistical model used to interpret the measured detachment rates in the next section, the experimental setup and the measured data will be presented, before turning to the discussion of the obtained temperature values.

2. Electron emission from excited Al cluster anions

In our experiment, the negative cluster ions were sputtered from the surface of an Al sample. It is well known from other investigations [8–10] that this process imparts a total energy of the order of 1 eV to both the vibrational and rotational degrees of freedom of the ion. While a fraction of the produced ions carry a total energy in excess of their electron affinity or dissociation energy, it is partitioned over many normal modes within a very short time, so that no single mode contains sufficient energy for a decay and the ion is stabilized. Over time the energy of several individual modes may be transferred to a single degree of freedom, resulting in delayed electron detachment or delayed fragmentation

$$\text{Al}_n^- \rightarrow \text{Al}_n^- + e,$$

$$\text{Al}_n^- \rightarrow \text{Al}_{n-1}^- + \text{Al}.$$ 

Both processes have been found to exhibit a decay rate that decreases with time by a power function for anion species as diverse as $\text{SF}_6^-$ [11], $\text{Ag}_n^-$ [2], Fullerene anions [2] and biomolecular ions [12, 13]. For sputtered $\text{Al}_4^-$ and $\text{Al}_5^-$, the delayed detachment rate was observed to also follow a power law [3, 14]. A qualitatively similar behaviour was found for photo-excited $\text{Al}_4^-$ ions, where both the detachment rate and the rate of fragmentation into $\text{Al}_3^- + \text{Al}$ pairs were observed to follow power laws with distinctive amplitudes and exponents, with a branching ratio strongly in favour of detachment [15].

Restricting this discussion, therefore, to decay by electron detachment while neglecting fragmentation, it is generally accepted that the overall decay rate after excitation of an ensemble of polyatomic anions arises by the superposition of the decay rates from many rovibrational states. After the initial excitation, the ions are considered isolated both from each other and from any external heat bath so that the total energy $E$ of each ion is conserved and its vibrational excitation is described by a microcanonical temperature $T_m(E)$. The kinetic energy transferred to the ejected electron was measured in [16] to be of the order of 100 meV. Together with the size of the ion it originates from, one can estimate that the electron will only carry away a few, if any, quanta of angular momentum. In addition, the bond lengths in the negative and the neutral clusters are quite similar for both $\text{Al}_4^-$ and $\text{Al}_5^-$ [17, 18], so that their rotational constants should be nearly identical. The rotational energy is therefore approximately conserved during electron detachment, so that mainly vibrational (and possibly electronic) energy is transferred to the electron. Rotation is therefore ignored from now on, so that the ions are characterized by the energy $E$ of their individual vibrational states before the decay. These states are populated
in the ensemble according to a (time-dependent) distribution function $N(E, t)$. Each of these levels decays individually with a rate constant $k(E)$, leading to an exponential decrease of its initial population:

$$\frac{dN(E, t)}{dt} = -N(E, t = 0) k(E) e^{-k(E)t}. \quad (1)$$

The total decay rate $R$ is thus given as a function of time $t$ after excitation by integrating over energy:

$$R(t) = \int - \frac{dN(E, t)}{dt} \, dE = \int N_0(E) k(E) e^{-k(E)t} \, dE, \quad (2)$$

where $N_0(E) = N(E, t = 0)$. Following the argumentation in [19], the decay rate $k(E)$ can be obtained by the principle of detailed balance, from the cross-section $\sigma_c(\epsilon)$ for the reverse process of capturing an electron with kinetic energy $\epsilon$:

$$k(E) = \int \frac{2m_e}{\pi^2 \hbar^3} \sigma_c(\epsilon) \frac{\rho^0(E - E_a - \epsilon)}{\rho^-(E)} \, d\epsilon, \quad (3)$$

where $m_e$ is the electron mass and $\rho^0$ and $\rho^-$ are the respective level densities of the neutral and the negative cluster.

Since the expression $k(E) t e^{-k(E)t}$ is sharply peaked at an energy $E_m(t)$ where $k(E_m) = 1/t$, the integral in equation (2) can be approximated by

$$R(t) \approx \text{const} \frac{N_0(E_m)}{t}. \quad (4)$$

In the ideal case of a constant distribution function $N_0(E)$ and a monotonically increasing decay rate constant, the total decay rate is inversely proportional to time [19]. Including the energy dependence of $k(E)$ and a slight skewness in $N_0(E)$ with respect to $E$ can also result in a power law $R(t) \propto t^{-\alpha}$ with an exponent $\alpha \neq -1$ [20], as has been experimentally confirmed in [3, 11]. If the energy distribution function cannot be considered flat, such as for an ensemble of cooled ions (see below), the overall detachment rate must be calculated numerically.

As vibrational frequencies for small aluminium clusters and anions in their ground state are available from theory (see, e.g., [17, 21]), level densities could in principle be calculated. However, Al$_4$ and Al$_5^-$ have several electronic states at very low excitation energies, to which radiationless transitions from the respective ground states are possible [17] and for which no such data are available. It is, therefore, not currently possible to obtain a good representation of the level densities of the neutral and anionic clusters from ab-initio data for the excitation energies considered here. As pointed out in [19], however, the level densities of the parent and daughter particles are often very similar for electron detachment because the number of vibrational modes is conserved in the reaction. As in the room-temperature experiment, we therefore adopt an Arrhenius rate equation

$$k(E) = \nu e^{-E_a/k_B T(E)}, \quad (5)$$

which is expected to yield a good representation of the decay constant under these circumstances. Here $E_a$ is the adiabatic electron affinity (1.74 and 1.82 eV for Al$_4^-$ and Al$_5^-$, respectively [22]) and $k_B$ is the Boltzmann constant, while $\nu$ is the so-called Arrhenius constant, which is determined empirically. In our analysis we are using the value of $\nu = 3.3 \times 10^{10} \text{ s}^{-1}$ found for Al$_4^-$ in the room-temperature experiment described in [7]. While that publication accidentally states a different value, we are using the correct number that was obtained in the
analysis of the room-temperature experiment [23]. From a similar measurement on Al$^{-5}$ a value of $\nu = 1.3 \times 10^{12}$ s$^{-1}$ was found [23].

$T_e(E)$ in equation (5) denotes an effective temperature that describes the distribution of energy over the continuum states of the electron. This temperature is related to the microcanonical temperature $T_m(E)$ of the ion prior to detachment by taking into account that the energy required for the detachment of an electron constitutes a large fraction of the total energy stored in the vibrational heat bath [19, 24] so that both temperatures differ by the so-called finite heat-bath correction:

$$T_e(E) = T_m(E) - \frac{E_a}{2C}, \quad (6)$$

where $C$ is the microcanonical heat capacity of the parent. While the heat capacities of Al$^{-4}$ and Al$^{-5}$ are not known, the previous assumption of nearly identical level densities for the anionic and the neutral particles means that the heat capacity should show a similar behaviour. As in [7], we therefore use the calculated heat capacities of neutral Al$^4$ and Al$^5$ from [25] as approximations for the anionic quantities.

After the creation of an excited ion ensemble an evaporative cooling process continues as long as ions with a total energy in excess of the adiabatic electron affinity remain. As the detachment rate diminishes strongly over time and the fraction of ions with small excitations increases, cooling by the emission of photons takes over as the dominant cooling mechanism. It has been found for Al$^{-4}$ in [7] that the energy distribution of the ions approached a steady state over time. An absolute calibration of the temperature scale was introduced in that experiment by identifying the asymptotic vibrational temperature of the ions with the temperature of the vacuum system ($\approx 300$ K). During the radiative cooling process, the ion ensemble is therefore considered to be in contact with the heat bath represented by the surrounding radiation field and approaches a canonical energy distribution with a (time-dependent) temperature $T$:

$$N(E, t) = N_i \rho^{-}(E) e^{-E/k_B T(t)}, \quad (7)$$

where $N_i$ is the number of ions considered. As the temperature of the initially hot ensemble decreases, the distribution becomes increasingly peaked so that it can be approximated by a Gaussian as discussed in [24]:

$$N(E, t) \approx \frac{N_i}{\sqrt{2\pi} \sigma^2} e^{(E-E_0)^2/2\sigma^2}, \quad (8)$$

where $\sigma = \sqrt{k_B C T}$. While $E$ is not conserved over timescales of hundreds of milliseconds, for the purpose of treating the comparatively fast electron detachment the individual ions are still considered to be in a state with a well-defined energy and microcanonical temperature related by $dE/dT_m = C$. The median energy $E_0$ of the distribution in equation (8) is therefore determined by equating the corresponding microcanonical temperature to the canonical temperature of the ensemble, $T_m(E_0) = T$.

In order to probe the (canonical) vibrational temperature of the ion ensemble during this radiative cooling phase, the ions were re-excited by absorption of photons with an energy of $E_\gamma = 2.06$ eV, which is above the electron affinities of Al$^{-4}$ and Al$^{-5}$ (1.74 and 1.82 eV, respectively [22]), but below the dissociation thresholds (2.67 and 2.22 eV, respectively [18]), so that only the delayed electron detachment was re-activated. While a variety of values have been reported in the literature for both the adiabatic and vertical electron affinities of Al$^{-}$.
Figure 1. Schematic overview of the CTF experiment (not to scale). The ion beam is created in the Cs sputter ion source (left), chopped into short pulses in the beam chopper and injected into the ion trap. The stored beam is crossed at a right angle with the expanded beam from a pulsed dye laser. Neutral particles emerging from the trap are detected by an MCP on the right. The shaded area indicates the cryogenic vacuum chamber of the trap, which is 2.7 m long; all other vacuum chambers are at room temperature. The trap electrodes are indicated at the centre. The liquid-helium cooling system is not shown.

(see, e.g., [18, 21, 22]), the value of 1.74 eV from [22] was best compatible with the data in [7]. We therefore adopt the values for both Al$_{-4}$ and Al$_{-5}$ from this same reference for our analysis.

For those ions that have absorbed a photon from the laser at time $t$, in a transition from one of the densely lying vibrational levels to another, higher one, the distribution is almost instantly projected towards higher energies. Hence, in analogy to equation (2) the ion decay rate due to the re-activated detachment process becomes

$$R(t, t') = \int p_\gamma N(E - E_\gamma, t) k(E) e^{-k(E) t'} dE,$$

where $p_\gamma$ is the probability for an ion absorbing a photon, which is approximated as independent of the ion state, and $t'$ is the time between the absorption of the photon and the emission of the electron.

3. Experiment

We have measured the rate of delayed electron emission from Al$_{-4}$ and Al$_{-5}$ ions stored in an ion trap, as a function of time after excitation by a laser. In contrast to the earlier measurement in a room-temperature trap [7], this experiment was performed using the Cryogenic Trap for Fast ion beams (CTF) at the Max-Planck-Institute for Nuclear Physics. An overview of the experimental setup, which is described in more detail in [26], is shown in figure 1. A beam of negatively charged aluminium clusters of various sizes was produced in a standard cesium
sputter ion source and accelerated to a kinetic energy of 6 keV. An ion bunch of several \(\mu s\) length was created from the coasting beam with a set of pulsed electrostatic deflectors in a beam chopper unit. The bunches were injected into an electrostatic ion beam trap (EIBT; [27]), where the ions are constantly reflected back and forth between two electrostatic mirrors. For confinement of the stored ion beam in the radial direction an electrostatic einzel lens is attached to each mirror. While the distance between the turning points of the ion beam is approximately 700 mm, a 316 mm long section between the mirror/lens units is a field-free drift region that houses an electrostatic pick-up electrode, on which the stored ion bunch induces a voltage twice during every oscillation in the trap. The entire trap, plus an additional 1 m long section of beam pipe on either side, is enclosed by radiation shields and insulation and is mounted inside an outer cryostat vacuum chamber. By bringing liquid helium at 1.8 K into direct contact with the beam pipe in two locations, the trap itself is cooled to \(<15\) K. The adjoining beam pipe sections, which are connected to room-temperature vacuum chambers by edge-welded bellows, reach a temperature of 35 K. By cryo-condensation of hydrogen at the locations where the beam pipe is in contact with the liquid helium, an extremely low residual gas density of 2000 cm\(^{-3}\) (corresponding to a pressure of \(8 \times 10^{-14}\) mbar in a room-temperature device) is obtained [26].

Injection into the trap is accomplished by temporarily lowering the voltages of the mirror on its entry side and then switching them on again before the ions have had time to exit the trap after their first reflection in the other mirror. Following each injection, the ions were stored in the trap for up to 5.5 s, depending on whether the early or the later phase of vibrational cooling was to be investigated, and were then ejected by lowering the mirror voltages. By setting both the duration over which the beam chopper transmitted ions and the delay before the trap was closed, lower and upper limits were imposed during injection on the drift time and hence the mass of ions admitted to the trap. The desired cluster size was thus enriched to \(\approx 70\%\) of the stored ions, as is confirmed by the amplitudes of the pick-up voltage at the second harmonic of the respective ions’ trap oscillation frequencies. A more precise mass selection was not needed prior to injection, as the measured detachment events were assigned to their proper parent ion species by time-of-flight discrimination during data analysis (see below). This allowed us to measure the delayed detachment rate simultaneously for Al\(_{4}\) and Al\(_{5}\).

The stored ion beam is crossed with the beam of a pulsed dye laser in the middle of the trap. The laser beam is guided through the vacuum system from above by means of two sapphire windows in the cryogenic beam pipe. The dye laser is pumped by the frequency-doubled beam from an Nd:YAG laser and delivers pulses of \(\approx 10\) ns duration and an average energy of 3.5 mJ at the beam crossing, at a wavelength of 600 nm (2.06 eV photon energy) and a repetition rate of 10 Hz. The diameter of the beam coming from the dye laser was widened to 12 mm, resulting in a peak power density of \(\approx 0.4\) MW cm\(^{-2}\) to prevent the occurrence of two-photon processes, which was verified by observing that the detachment signal (see below) depended linearly on the laser pulse energy.

Instead of observing the low-energy electrons ejected from the stored anions, we have measured the rate of neutral particles created, which are no longer confined by the trap and emerge on either end in a narrow cone along its axis. Those particles leaving the trap towards the right in figure 1 were detected by a chevron-stack of two 40 mm diameter multi-channel plate (MCP) detectors, located in a room temperature vacuum chamber (10\(^{-10}\) mbar) at a distance of 2.2 m from the trap centre. The MCPs were operated in single-particle counting mode, and the time elapsed between an injection cycle and each MCP signal was measured in a multi-hit time-to-digital converter (TDC) with a precision of 100 ns. The number of counts from the MCP was
Figure 2. Sample TDC spectrum showing the counts of the MCP detector as a function of time $t$ after injection into the trap. Ions were stored for 3 s, after which only the dark counts of the MCP were measured. At early times the count rate from electron detachment of ions excited in the sputter source is visible. The spikes at later times indicate the times when the laser triggered the production of neutral particles by photodetachment.

thus measured as a function of time, while ions were stored in the trap and during the subsequent background window when the ions had been ejected. The 10 MHz reference clock defining the time base of the TDC was also divided down to 10 Hz and used to trigger the laser pulses. In addition, after the end of each injection/measurement cycle the next laser trigger to arrive was used to start the next injection into the trap. This ensured a constant phase relation between the injection cycle, the pulses of the laser system and the time base of the TDC throughout the entire experiment, so that laser pulses always occurred at the same position in the TDC spectrum as shown in figure 2. Here, the MCP counts have been plotted versus the time $t$ after injection. For short times the signal rate due to electron detachment by the initially hot ions from the ion source is visible. Starting at 50 ms, when the initial decay has subsided, the detachment rate due to excitation by the laser pulses can be seen as narrow spikes every 100 ms. Background from residual-gas collisions is visible between the laser-induced events. Due to the low pressure and very long beam lifetime in the CTF, this rate is extremely small and essentially constant. After 3 s the ions were finally ejected from the trap for a measurement of the MCP dark count rate.

Figure 3 shows a magnification of the previous plot after the first laser pulse, under conditions where the trap injection had been optimized for preferred storage of Al$_n^-$. This signal is to a large extent caused by the immediate (non-delayed) detachment of cluster ions illuminated by the laser. The excitation takes place only along a small region of $\approx 1$ cm diameter in the middle of the trap and the neutral detachment products retain the velocity of their parent ions. The size $n$ of the parent is therefore readily inferred by the characteristic drift time $\delta_n$ towards the MCP detector. The small peak near 17 $\mu$s in figure 3 is thus identified as belonging to the detachment of Al$_4^-$, while those at later times originate from Al$_n^-$ ions with $n = 4, \ldots, 8$. It can be seen that despite Al$_4^-$ being the most abundant ion in the beam, the
Figure 3. MCP counts following shortly after the laser pulses at $t = 50$ ms (averaged over several hours of measurement), as a function of the delay time $t'$. The contributions from different cluster sizes have been identified by their respective time of flight towards the MCP detector. Despite $\text{Al}_4^-$ being the most abundant ion in the beam, detachment of $\text{Al}_5^-$ can be seen to be the dominant contribution to the signal at 70%, with the remaining 30% shared among clusters of other sizes.

The majority of laser-induced counts registered is attributed to $\text{Al}_5^-$, while detachment of smaller and larger cluster ions accounts for 30% of the total number. These observed signal intensities arise from a convolution of the relative abundance of a respective ion species in the stored beam, its internal excitation energy before the laser pulse, its cross-section for non-delayed and delayed detachment (and possibly fragmentation) and the detection efficiency of the MCP for the particle type in question. Separation of the signal contribution from a particular cluster species is achieved by applying time-of-flight discrimination to the delayed detachment events as well, which arrive at the MCP at time intervals determined by the characteristic oscillation periods $\tau_n$ of ions of size $n$ between the trap mirrors. Counts from the laser-induced detachment of cluster ions with $n$ Al atoms are expected in narrow ($\pm 700$ ns) windows around the median times

$$t'_{n,k} = \Delta_n + k \frac{\tau_n}{2}; \quad k \in \mathbb{N}$$

after each pulse of the laser, with $k = 0$ referring to the immediate detachment signal. The factor of 1/2 originates from the fact that those ions moving away from the MCP at the time of the laser pulse will, after half an oscillation, also move towards it and cause counts to be registered.

The result can be seen in figure 4, where the MCP signal is shown over a time comprising several oscillations after a laser pulse. The series of bars in the upper part of the figure indicates the time windows over which counts were integrated and assigned to a particular parent cluster anion. Obviously, there are occasions when detachment products from two different ion masses arrive at the MCP at the same time, for example near $t' = 82 \mu$s where events from both $\text{Al}_4^-$ with $k = 7$ and $\text{Al}_5^-$ with $k = 6$ are detected simultaneously. Counts from windows coincident...
Assignment of delayed emission events after the laser pulses to different ion sizes, by means of their trap oscillation periods (averaged over all laser pulses during several hours of measurement). The bars indicate the position and width of the time intervals where events from cluster anions of size \( n = 4 - 7 \) are expected. Vertical lines have been drawn from the centre of the time intervals to the peaks in the time spectrum corresponding to \( \text{Al}^-_4 \) to demonstrate the quality of agreement.

with contaminant ions were excluded from further analysis, leaving only events which could be clearly assigned to a specific cluster anion. A procedure identical to the one described here for \( \text{Al}^-_4 \) was used to obtain the delayed detachment rate for \( \text{Al}^-_5 \), by analysing those measurements where the trap injection was optimized for preferred storage of that particular ion and then applying the appropriate drift times and trap oscillation periods.

4. Results

From the measurements on \( \text{Al}^-_4 \) described above, decay curves (delayed detachment rate versus the times \( t'_{4,k} \)) were retrieved for every time \( t \) a laser pulse had been applied; the same was done with the signals at \( t'_{5,k} \) in the \( \text{Al}^-_5 \) measurements. Some of the decay curves measured for \( \text{Al}^-_4 \) are shown by the symbols in figure 5(a), for laser pulses at \( t = 50, 750 \) and 2750 ms after the injection; the corresponding curves for \( \text{Al}^-_5 \) are shown in figure 5(b). As discussed in more detail below, a small systematic difference is found between decay curves compiled exclusively from detachment events at even and those at odd values of \( k \) in equation (10), corresponding to detachment of ions moving towards and away from the detector at the time of the laser pulse. The figures therefore show only decay curves obtained for even \( k \). The small background of counts from residual gas collisions and the dark count rate of the detector have already been subtracted in the plots, and the time axis has been corrected for the drift times \( \delta_n \) in equation (10) from the trap centre to the MCP, to retrieve the times when the actual detachment events occurred. Although the statistical scatter of the data points is considerable, it can be clearly seen that the decay curves become increasingly shallow for longer storage time \( t \).

New Journal of Physics 14 (2012) 065007 (http://www.njp.org/)
Figure 5. Sample delayed detachment curves obtained for (a) Al$^-$ and (b) Al$_2^-$ at different times $t$ after injection, averaged over all measurements made at even values of $k$ (see text). The symbols denote the experimental data (circles, 0.05 s; squares, 0.75 s; diamonds, 2.75 s) after correction for background rate and the drift time of ions from the trap centre to the detector. For comparison, the triangles in (a) show data from [7] taken after 0.5 s at 300 K ambient temperature. Symbols are connected by lines to guide the eyes. The thicker lines show the fits with the rate model described in the text; the obtained temperatures are given in the legend.

This is expected from the emission model presented in section 2, as the decrease in the mean excitation energy during storage and cooling corresponds to a larger population of states with low detachment rates. The heavy lines show the results of a quantitative analysis performed by fitting equation (9) to the experimental decay curves. The only free parameters in these fits are the canonical temperature $T$ of the ion as listed in figure 5(a), and a normalization constant representing the product of the photon absorption probability and the total number of ions present in the interaction volume. In addition, the electron affinities and Arrhenius constants detailed for both ions in section 2 entered into the Arrhenius rate in equation (5) but were kept constant in all fits. With these fits, the delayed detachment curves from the statistical rate model are generally found to be in good agreement with the measurement for a large range of $t$. For the Al$^-$ measurement, a sample decay curve from the earlier experiment [7] is also shown for comparison. Data from our measurement on Al$_2^-$ are shown in figure 5(b).

The temperatures extracted from these fits are shown in figure 6(a) for Al$^-$, together with the results from [7] taken at room temperature, while those for Al$_2^-$ are shown in figure 6(b). Because of the limitations of the employed TDC, the maximum observation time of 5.5 s was achieved by combining measurements made over the time interval 0–3 s with the ones where data acquisition was delayed so that the region of $t = 2.5–5.5$ s was probed. The data in the overlap region of these measurement windows are consistent with each other. At short times after injection into the trap, the temperature of the ions exhibits a steep decline, with the temperatures of the earliest data points being 1400 K for Al$^-$ and under 400 K for Al$_2^-$. The vibrational temperature of the ions directly after their production in the sputter source is expected to be higher. The differences between the observed values and the expected initial temperatures are most likely a result of the respective intensities of thermionic emission of...
Figure 6. Temperatures retrieved from the delayed detachment curves of Al$^-_{4}$ (a) and Al$^-_{5}$ (b), as a function of storage time. Circles: data from this experiment, at even $k$; squares: odd $k$ (see text); thin line: temperatures measured in [7]; thick solid line: the cooling model from equation (12) for an ambient temperature of 15 K; thick dashed line: model for an ambient temperature of 300 K.

electrons, which dominates the cooling process on timescales of up to a few ms. As this time interval is not probed by the experiment, the corresponding initial decline in temperature is not observed. At later times the rate of temperature change becomes smaller until the temperatures appear almost constant for both ions, with the final temperatures being around 220 K for Al$^-_{4}$ and 240 K for Al$^-_{5}$. Above the scatter of data points from the present experiment, which is mostly due to the statistical error of the delayed detachment rate, it can be seen that the temperature retrieved from the detachment signal of those ions moving towards the MCP at the time of the laser pulse (even $k$ in equation (10); green circles in figure 6) is systematically higher by $\approx 20$ K than that determined from the ions initially moving away from the MCP at the time of the laser pulse (odd $k$; blue squares). The most likely explanation is a slight underestimation of the detachment rate by the model at early times, resulting in the obtained temperature always being slightly higher for the series containing the earliest data. As we had to reject the data point at $k = 1$ because of a likely contamination by fragmentation events [15], the earliest data point now belongs to the series with even $k$. We therefore interpret this behaviour as an indicator of the systematic accuracy of the temperature measurement, which is nonetheless very high. From here onwards, only the average between the odd-$k$ and even-$k$ temperatures is considered.

5. Discussion

It is interesting to compare the Al$^-_{4}$ cooling curves for both the 300 and 15 K environments (see the inset in figure 6(a)). Over the entire range of times investigated, we find the ion temperature to be somewhat lower in the 15 K measurement. At very short times, i.e. for the first one or two data points, this can be explained by the ion temperature still being strongly influenced by the ion production process. With different sputter ion sources used under different operating conditions in the room temperature and the 15 K experiments, it is not surprising that the initial temperatures of the ions should also be different. For longer cooling times, a certain difference
between both measurements is expected due to the lack of radiation transferred back to the ions from the vacuum chamber walls in the 15 K trap. In the analysis of the temperature curve measured on Al\(^{−4}\) at 300 K ambient temperature, the observed cooling rate \(dT/dt\) could be well described by assuming that the radiation power \(I\) emitted from the cluster anions depended on their temperature approximately as

\[
I(T) \propto T^{3.5}.
\]

With this relation and the radiation power balance

\[
\frac{dT}{dt} = \frac{I(T) - I_{\text{rad}}}{C(T)},
\]

the time dependence of the Al\(^{−4}\) temperature is obtained. Here \(I_{\text{rad}}\) is the power absorbed from the ambient radiation present in the ion trap. The dashed red line in the main graph of figure 6(a) shows the result from [7] for \(T(t)\) at an ambient temperature of 300 K, which has been extrapolated to the longer observation times achieved in the present experiment. Our data lie systematically below this curve, indicating that the ions cool slightly faster and to a lower vibrational temperature in the cryogenic environment. For comparison, the solid red curve in the figure shows the behaviour expected for an ambient temperature of 15 K, where \(I_{\text{rad}} \approx 0\). Considering the scatter of the data points, this is in good agreement with the present measurement before 1.5 s. However, the fact that in the present experiment the ion temperature changes only very slowly after 1.5 s requires further investigation. While the solid cooling curve shows that equilibration with the trap temperature should require much longer storage times than applied here, starting at times \(> 2\) s the experimental data lie systematically above the curve. At the latest storage times investigated, the ion temperature exceeds the value of 112 K calculated from equation (12) by \(\approx 110\) K.

We have investigated several possible reasons for this result. From a worst-case consideration of the radiation from room-temperature parts of the apparatus illuminating the trap volume, we estimate a radiation power density inside the trap of 0.2 W cm\(^{-2}\). This power density is equivalent to that of a black-body radiator at a temperature around 40 K. From equation (11) one obtains that even at the lowest predicted temperature of 112 K reached after 5.5 s of cooling, the ions would emit more than 25 times \((I(112\) K)\)/\((I(40\) K)\)) as much power as absorbed at the above increased ambient temperature. The possibility of heating the ions by the repeated illumination with the laser was also considered, but through the high photon energy the majority of excited ions will subsequently detach, so that the population in the beam will not be affected. As a result, apparatus effects are ruled out as a reason for the observed slower cooling. It is in principle possible that the approximations made in the detachment model lead to a systematic overestimation of the ion temperature. In particular, the adiabatic electron affinity of the ions is not known with good accuracy; a deviation from the values selected in the analysis could thus affect the fidelity of the temperatures obtained with the statistical rate model. But as the model was originally calibrated to yield a good reproduction of the data at 300 K (the Arrhenius constant \(\nu\) was actually determined from fits to the experimental data in [7]), it seems very surprising that a deviation as large as the one observed should arise over such a small temperature range. Moreover, the shape of the detachment curves measured at long storage times, e.g. that at \(t = 2.75\) s in figure 5(a), is clearly not compatible with the single exponential function expected for ions in a single state. This is strong evidence that the ions have not yet cooled to the ground state but retain a certain amount of vibrational energy.
On the other hand, the slow cooling observed in the experiment may also be real and have its origin in the properties of the anion itself: in [7] it was argued that the cooling most likely proceeded via infrared-active transitions between vibrational states. These had to be assumed to be strongly collective in order to explain the high oscillator strength needed to drive the observed cooling rates, as electronic transitions were considered to be not available in the necessary energy region around 220 meV. Evidence has, however, recently been found in [17] that Al$_5^-$ and also Al$_4^-$ actually possess several excited electronic states near this energy, which also exhibit strong vibronic mixing. These states would well boost the available oscillator strength at energies where the mixing is efficient. Hence, as the ion temperature decreases into the region around several hundreds of K, the excited electronic states may no longer be energetically available for energy transfer from the vibrational heat bath, effectively cutting off the vibronic pathway and leaving only vibrational transitions to promote the cooling.

In modelling such processes it should be considered that not only the anion but also the neutral cluster was found to possess electronic states accessible at comparatively low temperatures. Thus, the assumption of an Arrhenius decay rate may no longer be justified as it relies on both level densities being smooth and rather similar functions of energy. A calculation of the level densities is likewise complicated by the fact that the vibrational level spacing would most likely change at the energy threshold of every electronic state with significant vibronic coupling. It would therefore be highly desirable in the experiment to gain independent information about the temperature or excitation energy of the anions. This could be achieved, e.g., by preparing the clusters at a well-known temperature before their injection into the trap, but requires the use of different ion sources than those used so far, or of additional preparation techniques such as buffer gas cooling.

Turning to the temperature curve of Al$_5^-$ in figure 6(b), it can be seen that while this ion starts to cool at a much lower temperature, it reaches a very similar temperature as Al$_4^-$ towards the end of the measurement. Unfortunately a detailed interpretation of this finding is prevented by the much more pronounced lack of information, compared to Al$_4^-$, on the electronic structure of this ion. Because of the limited number of data points available at short times it is also not possible to deduce the exponent by which the radiated intensity depends on the temperature from our data. Nevertheless, it can be seen that Al$_5^-$ also exhibits a very slow decrease of temperature at long times. While this can partly be attributed to the larger heat capacity compared with Al$_4^-$, it may again hint at a mechanism affecting the cooling speed of this ion.

6. Summary

We have measured the time dependence of the delayed detachment rate following laser excitation of both Al$_5^-$ and Al$_4^-$ cluster anions to investigate the vibrational cooling of the initially hot ions. By storing the ions in a cryogenic ion beam trap we were able to extend both the time and temperature range of our investigation. We have determined the vibrational temperature of the ions over a time of 5.5 s by fitting a statistical rate model to the measured detachment curves. The temperature curves for Al$_5^-$ suggest that the vibrational cooling slows down considerably once the ion reaches approximately room temperature. While shortcomings of the employed rate model cannot be entirely ruled out, our experimental findings may also be explained by the recently found existence [17] of low-lying electronic states in the anion. The experimental results obtained for Al$_5^-$ suggest that the radiative cooling is even slower for these
ions, but that cooling by electron emission must be comparatively faster than for Al$^{-4}$ in order to explain the low temperature observed for the earliest laser pulses. Our measurements show that the radiative cooling of even small polyatomic particles is far from understood, and constitutes a formidable challenge to both experiment and theory because of the detailed knowledge needed about the interaction of electronic and vibrational excitation.

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