Radiative cooling of Al_4^- clusters

Y. Toker,[1] O. Aviv,[1] M. Eritt,[1] M. L. Rappaport,[1] O. Heber,[1] D. Schwalm,[1,2] and D. Zajfman[1]
[1]*Department of Particle Physics, Weizmann Institute of Science, Rehovot 76100, Israel*
[2]*Max-Planck-Institut für Kernphysik, D-69117 Heidelberg, Germany*

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The radiative cooling of isolated, negatively charged four-atom aluminum clusters has been measured using an electrostatic ion beam trap. Stored Al_4^- ions were irradiated by a short laser pulse at different times after their production in a hot ion source, and delayed electron emission was observed up to hundreds of microseconds after the laser pulse. The decay curves could be well reproduced using an Arrhenius decay law and allowed us to deduce the cluster temperatures at the time of the laser pulse. Using this sensitive molecular thermometer, the cluster temperature could be determined as a function of storage time. The radiation intensity is found to decrease from 40 eV/s at $T=1400$ K to 1 eV/s at 500 K with a temperature dependence as given by T^b with $b=3.5\pm0.2$—i.e., similar to what would be expected from a blackbody. This cooling behavior requires the presence of either electronic transitions or very collective infrared-active vibrations at transition energies around ~200 meV.

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INTRODUCTION

The radiative cooling process of polyatomic molecules and clusters is an interesting thermodynamical problem. It is especially interesting in the limit of molecular systems containing only a very small number of atoms, for which the application of thermodynamic principles is not *a priori* justified. Radiative cooling is also a key process in many physical systems and applications. In interstellar media, for example, molecules are the only cooling mediator that can convert the kinetic collision energy into radiation that can escape from the system enabling star formation [1]. On the more practical side, a major use of ion traps and storage rings is to confine molecules and clusters for times long enough to cool them down radiatively to ambient temperatures [2]. Radiative cooling has also been discussed as a source of decoherence for quantum technologies [3].

For small isolated systems radiative cooling is hard to measure directly due to the low photon flux. Such studies have therefore been conducted [4–6] only for medium-size clusters containing more than 60 atoms and at temperatures above 2000 K and with the exception of C_{60}, for which macroscopic amounts are available, without mass selection. With the advance of ion trapping and ion storage techniques [2], however, it has become possible to investigate radiative cooling indirectly and typical time scales for the cooling process have been determined for several systems. For metal clusters [7–9] fast radiative cooling rates have been reported, which are usually discussed in terms of a dielectric model based on a plasmon description of the response of the cluster to electromagnetic radiation. These experiments were typically performed at temperatures above 1000 K. On the other hand, for small polyatomic molecules much slower cooling rates have been measured [10] and attributed to cooling through infrared-active vibrational transitions.

For a more comprehensive understanding of the radiative cooling process, it is desirable to measure the time dependence of the temperature of the molecule. In the case of a close-to-constant heat capacity, the rate of change of the temperature is equivalent to the total energy radiated from the cluster; thus, such a measurement can be seen as a measurement of the Stefan-Boltzmann law. The experimental challenge in such a study is the assignment of a temperature scale to very small systems. It will be shown below that delayed electron emission can serve as a very sensitive temperature probe. Using this probe the cooling of stored isolated Al_4^- clusters has been studied. The clusters were irradiated by short laser pulses at different storage times—i.e., at different times after their production in the ion source—and the rate of delayed electron emission was measured. From the time dependence of the electron emission rate the temperature of the clusters was deduced. Thus the radiative cooling rate could be measured for Al_4^- clusters in a temperature range between ~1400 K and room temperature, where radiative cooling is the only available cooling channel. It will be shown that the temperature change with time is very similar to the Stefan-Boltzmann law describing the cooling of a blackbody, but requires the presence of electromagnetic transitions around ~200 meV.

DELAYED ELECTRON EMISSION AND THE ARRHENIUS DECAY LAW

Delayed electron emission is a process in which clusters, after being irradiated by a short (ns) laser pulse, emit electrons even several hundreds of microseconds after the laser pulse occurred. This process has been studied in detail for metal clusters and biomolecules (see [11,12] and references therein). The generally accepted picture is that the photon excites an electron to a higher-energetic electronic state, which immediately couples to the vibrations of the cluster such that the subsequent emission of an electron is a statistical process equivalent to the thermionic emission from bulk material; i.e., the "hotter" the clusters are, the faster the electron emission will be.

The rate of delayed electron emission, $k(\epsilon)$, from an excited state of energy ϵ can be described by an Arrhenius decay law

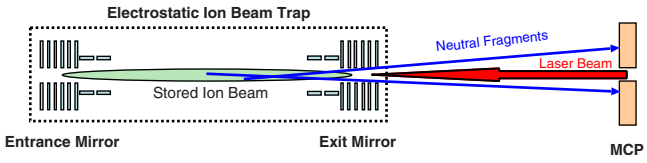

FIG. 1. (Color online) Schematic view of the experimental setup. A beam of Al_4^-, produced in a Cs sputter ion source and accelerated to 4.2 keV, is stored between the mirrors of an electrostatic ion beam trap [14]. At a time t_i from production in the ion source they are irradiated by a laser pulse injected parallel to the main axis of the trap. Neutral fragments are no longer confined by the mirrors and can be counted by a multichannel plate (MCP) detector located outside the trap.

$$k(\epsilon) = Ae^{-E_b/k_B T_e(\epsilon)}, \tag{1}$$

where A is the Arrhenius factor, E_b the barrier energy for electron emission, and k_B the Boltzmann constant. The effective temperature for electron emission, $T_e(\epsilon)$, is given by

$$T_e(\epsilon) = T_\mu(\epsilon) - \frac{E_b}{2C}, \tag{2}$$

where $T_\mu(\epsilon)$ denotes the microcanonical temperature related to ϵ by $d\epsilon/dT_\mu = C$ and C is the microcanonical heat capacity of the cluster. The factor $E_b/2C$ is called the finite heat bath correction [13].

The rate of electron emission can range from $k=A$ in the limit of $T_e \to \infty$ down to $k=0$ in the limit of $T_e \to 0$. By exciting a cluster with internal temperature $T_\mu(\epsilon)$ with a photon of a suitable energy ϵ_{photon} the rate of electron emission can be brought to a desired time scale range: a rate faster than other competing processes such as radiative cooling or ion loss due to collisions with the residual gas, but slow enough to be measurable. In the experiment described below the time scale is set by the oscillation time in the trap, which is 16 μs for Al_4^-.

EXPERIMENTAL SETUP

Hot Al_4^- clusters are produced in a cesium sputter ion source, accelerated to 4.2 keV, mass selected using a 90° magnet, and injected into an electrostatic ion beam trap [14] operated at a vacuum pressure of $\sim 10^{-11}$ mbar. The travel time from the source to the trap is 100 μs. The trap, shown schematically in Fig. 1, basically consists of two sets of electrodes which act as electrostatic mirrors, between which the trapped ions oscillate. For storage times >40 ms the number of ions in the trap decrease exponentially with lifetimes of the order of 1 s. Neutral fragments, which are generated inside the trap either by residual gas collisions or through the interaction with the laser beam, are no longer confined and can be recorded by a microchannel plate detector (MCP) located outside the trap. The MCP used in the present work has a 2.5-mm hole in its center through which the laser beam of $\sim$2 mm diameter is guided into the trap parallel to the main axis of the trap. The laser beam is from a master optical parametric oscillator (MOPO) tunable pulsed laser

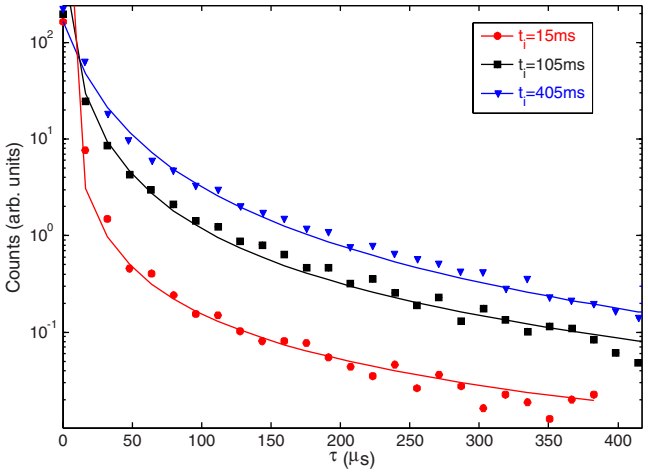

FIG. 2. (Color online) Delayed electron emission from Al_4^- clusters measured for three different storage times t_i between ion production and irradiation by a short laser pulse. The number of neutral fragments detected by the MCP is plotted as a function of the time τ since the laser pulse. The spectra are background subtracted and normalized to the number of ions in the trap at time t_i. The solid lines are fits to Eq. (5).

(440–690 nm and 730–1800 nm). As delayed electron emission can be observed when the energy of the photon lies between the barrier energy for electron emission (1.74 eV for Al_4^-) [15] and the vertical detachment energy (2.25 eV for Al_4^-) [15,16], a wavelength of $\lambda = 600$ nm corresponding to 2.063 eV has been chosen, thereby fulfilling the additional requirement that the wavelength has to coincide with an electronic absorption band. An intensity of $\sim$200 μJ per pulse has been used at a pulse length of $\sim$9 ns. At these intensities, only single-photon absorption occurs.

RESULTS

Figure 2 shows the number of additional neutral fragments—i.e., the number of fragments after subtraction of the background due to residual gas collisions—arriving at the detector as a function of time after irradiation by the laser at three different storage times $t_i = 15, 105, 405$ ms. The curves were normalized to the number of Al_4^- ions in the trap at time t_i. As can be seen, neutral fragments are produced by delayed electron emission even hundreds of microseconds after the irradiation. Delayed fragmentation is not expected to be able to compete with delayed electron emission in the temperature range studied in the present experiment. In fact, by using a bent electrostatic trap, it has been recently shown [17] that the ratio between delayed fragmentation and electron emission is only of the order of a few percent. Moreover, by measuring the delayed event rates at a different rest gas pressure in the trap it was excluded that these events are caused by an increased cross section of the hot Al_4^- clusters with the residual gas.

As displayed in Fig. 2, for short storage times (small t_i), when the clusters are still highly excited ("hot") due to their production in the ion source, electron emission is very fast,

but the longer the clusters are stored prior to the laser irradiation—that is, the "colder" they become—the slower the electron emission. Thus the Al_4^- clusters can be clearly seen to cool down during storage and the cooling rate to decrease with time: The difference between the delayed emission curves from $t_i=15$ ms to 105 ms is much more pronounced than the difference between $t_i=105$ ms and 405 ms.

Delayed electron emission has been measured in this way in steps of 5 ms for storage times between $t_i=5$ ms and 400 ms. For every measured time step, t_i, $\sim 10^3$ individual injection cycles have been summed. After 400 ms the shape of the delayed emission curves becomes almost constant, indicating that the ions have reached values close to room temperature.

DATA ANALYSIS

As mentioned earlier, the rate of decay $k(\epsilon)$ of a cluster with internal energy ϵ is given by the Arrhenius decay law, Eq. (1). We follow the procedure which has been used in [18] to analyze the shape of delayed electron emission from biomolecules. It is assumed that the probability $g(\epsilon,\epsilon_i)$ to find the cluster at an internal energy ϵ can be described by a canonical ensemble with a temperature T_i and that this distribution can be approximated [13] by a Gaussian, i.e.,

$$g(\epsilon,\epsilon_i)=\rho(\epsilon)e^{-\epsilon/k_BT_i}\simeq\frac{1}{\sqrt{2\pi\sigma^2}}e^{(\epsilon-\epsilon_i)^2/2\sigma^2}, \tag{3}$$

with

$$\sigma=(k_BC)^{1/2}T_i, \tag{4}$$

where $\rho(\epsilon)$ is the density of states and ϵ_i is the energy for which $T_\mu(\epsilon_i)=T_i$. After the absorption of a photon the energy distribution is shifted by the energy $h\nu$ of the photon. The delayed emission curve is thus given by

$$n_i(\tau)=\int d\epsilon\, N(t_i)P_{ph}g(\epsilon,\epsilon_i+h\nu)k(\epsilon)e^{-k(\epsilon)\tau}, \tag{5}$$

where $N(t_i)$ is the number of cluster ions in the trap at time t_i, τ is the time after the laser pulse, and P_{ph} denotes the probability that the cluster absorbs a photon.

For the barrier energy, $E_b=1.74$ eV has been used in the analysis of the emission curves, which is the threshold binding energy measured by [15] using ultraviolet photoelectron spectroscopy. The effect of the choice of E_b on the measured results will be discussed below. Moreover, for the heat capacity C the values calculated by [19] for neutral aluminum clusters Al_4 have been used; we would like to point out, however, that the deduced temperatures T_i change only marginally when a constant heat capacity of $C=(3N-3)k_B=9k_B$ is assumed.

The analysis of the emission curves with Eq. (5) starts with the data obtained for $t_i=480$ ms, assuming an initial temperature T_{480} and adjusting two free parameters, which are the Arrhenius factor A and a normalization factor N_0, which is proportional to P_{ph}. Next the emission curves observed for shorter storage times t_i are fitted using the derived value of A and N_0 to extract the temperatures T_i of the ions prior to the irradiation by the laser. In Fig. 2 the solid lines are the fits obtained for the three delayed emission curves shown. The fits are generally found to result in a very satisfactory description of the data, giving confidence in the assumptions made. The derived temperatures T_i are shown as a function of the delay time t_i in Fig. 3. The absolute temperature scale is set by the choice of T_{480}. Its value was finally chosen such that the experimental temperatures extrapolated to very long storage times are approaching 300 K.

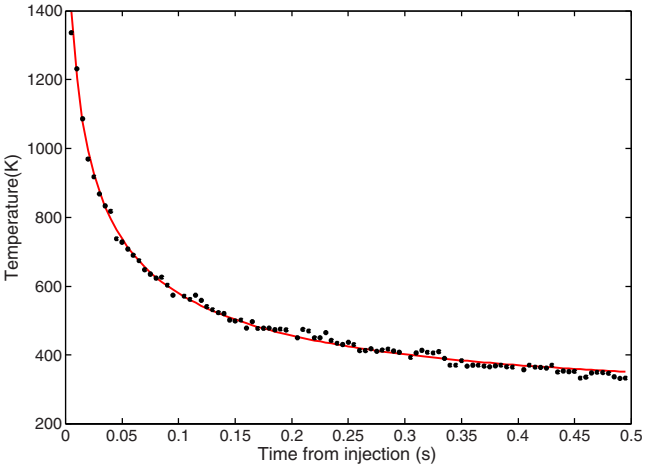

FIG. 3. (Color online) Derived temperatures of the Al_4^- clusters as a function of storage time. The solid line is the result of a fit to the data points, which is based on Eq. (10), assuming a generalized Stefan-Boltzmann law with $I(T)\propto T^{3.5}$.

There is some uncertainty connected with the barrier energy E_b which is used in the analysis. In general, E_b should lie between the vertical electron affinity and the adiabatic electron affinity, probably closer to the latter. An upper limit for E_b is provided by the threshold energy observed in ultraviolet photoelectron spectroscopy experiments, which was determined in Ref. [15] to be 1.74 eV, while in a more recent experiment [20] a value of about 2.01 eV was deduced. Repeating the analysis of the emission curves for different values of E_b we were able to determine the barrier energy to be $E_b=1.74\pm0.05$ eV, which is in good agreement with the threshold energy measured in [15]. The corresponding Arrhenius factor A is found to be about $A\sim 1.4\times 10^{10}$ s^{-1}. As can be seen from Eq. (1), the deduced Arrhenius factor depends exponentially on the choice of E_b and A is therefore changing by several orders of magnitude for different values of E_b; the deduced temperatures T_i, on the other hand, depend only linearly on the choice of E_b and are therefore comparatively insensitive to the exact barrier energy.

The observed dependence of the temperature of the Al_4^- clusters on their storage time in the trap (Fig. 3) shows the typical behavior expected for radiative cooling of initially hot systems embedded in a colder radiation environment. Adjusting the asymptotic temperature to 300 K, the temperature at the start of the measurement (5 ms after production and injection) is thus determined to be $\sim$1350 K. This temperature corresponds to an average excitation energy of the

cluster of ~1.1 eV, which is well below the electron barrier energy of 1.74 eV, leaving radiative cooling to be the only cooling process.

DISCUSSION: RADIATIVE COOLING

The energy radiated per unit time from a system at temperature T (or absorbed from a radiation field of temperature T) can be written as [21]

$$I(\omega,T)d\omega = \sigma(\omega,T)p(\omega,T)d\omega, \tag{6}$$

where $\sigma(\omega,T)$ is the cross section for absorption or emission of a photon of energy $\hbar\omega$ and $p(\omega)$ is the Planck function given by

$$p(\omega,T) = \frac{\hbar\omega^3}{\pi^2c^2}\frac{1}{\exp(\hbar\omega/k_BT)-1}, \tag{7}$$

with c denoting the speed of light. Equation (7) assumes that the emitting system is in equilibrium with its own radiation field. As pointed out in Ref. [22], for small hot clusters in a cold surrounding this will not be fulfilled. In these cases no induced emission will occur and Eq. (7) reduces to

$$p(\omega,T) = \frac{\hbar\omega^3}{\pi^2c^2}\exp(-\hbar\omega/k_BT). \tag{8}$$

Since in the present experiment the cooling down of hot Al_4^- clusters is observed until they reach equilibrium with the 300-K background radiation, where the Planck distribution will become valid, we expect the $p(\omega,T)$ function relevant in our temperature range to lie between these two limiting distributions.

The total amount of radiation emitted from the cluster is obtained by integrating Eq. (6) over all frequencies and is usually expressed in terms of the Stefan-Boltzmann law

$$I(T) = \sigma_{sb}S\varepsilon(T)T^4, \tag{9}$$

where σ_{sb} is the Stefan-Boltzmann constant, S is the surface of the system, and $\varepsilon(T)$ denotes the emissivity (or absorptivity) of the system. For a blackbody, for which $\sigma(\omega,T)$ is constant, the emissivity is independent of the temperature and the radiation power $I(T)$ is thus proportional to the fourth power of the temperature. This proportionality is found for the Planck [Eq. (7)] as well as for the modified Planck [Eq. (8)] distribution, with emissivities agreeing within 10%. In general, the emissivities can be calculated if the frequency dependence of the electromagnetic absorption cross section $\sigma(\omega,T)$ of the system at temperature T is known.

Using the dielectric model different approximations lead to different power law dependences of the emissivity (see [11]). It has been conjectured [7], for example, that the radiative cooling of C_{60}^- ions of ~1500 K temperature is caused by electronic transitions and that the absorption cross section is dominated by the low-frequency tail of the plasmon resonance occurring around $\hbar\omega \approx 6-10$ eV. Describing the resonance by a simple dielectric function (Mie theory) pertaining to a free electron gas, the absorption cross section is found to be proportional to ω^2, which leads to $\varepsilon(T) \propto T^2$ and therefore to $I(T) \propto T^6$. Again the power law is not affected by the presence [Eq. (7)] or absence [Eq. (8)] of stimulated emission; however, the emissivity obtained with Eq. (7) is a factor of 10 larger than in case Eq. (8) is valid. Using the ω^2 approximation together with the Planck distribution [Eq. (7)], optical emission studies of C_{60} [4] and of Nb clusters (of sizes 260 atoms) [6] have shown that the emitted radiation (at temperatures of 2000–3000 K) can be fitted to Eq. (6). On the other hand, the total rate of cooling measured through analysis of the thermionic emission of C_{60} has been found to follow $I(T) \propto T^7$ at temperatures of 1500 K [7].

The plasmon description, which in the present case would result in a less steep temperature dependence of $I(T)$ because of the transition from Eq. (7) at 300 K to Eq. (8) valid at high temperatures, does not seem to be applicable *a priori* to clusters comprising only a few atoms like Al_4^-: Similar to neutral aluminum [23] and other few-atom metallic clusters, the electronic absorption cross section is expected to be highly fragmented into a series of discrete atomiclike lines, rendering a description by a smooth tail of a plasmon resonance to be unrealistic. At the temperatures studied in this work (T=300–1400 K), the $p(\omega,T)$ distributions [Eqs. (7) and (8)] are concentrated at such small energies (at about 0.07–0.34 eV) that only a few (if at all) electronic absorption lines are expected to overlap. In particular, for all electronic transitions we have $\hbar\omega \gg kT$ and the difference between the Planck [Eq. (7)] and the modified Planck [Eq. (8)] distribution will be negligible. Vibrational transitions in Al_4^-, on the other hand, have been calculated by [24] and found to be in the 6–40 meV range. These transitions are below the maximum of the $p(\omega,T)$ distributions of $\approx 3k_BT$, where the two distributions do differ. In fact, assuming $\hbar\omega \ll kT$, then the total radiated intensity is expected to be proportional to T in case of the Planck function [Eq. (7)], while with Eq. (8) we obtain the surprising result that $I(T)$ would be even independent of the cluster temperature.

For the time being we shall assume a power law dependence for the emissivity, $\varepsilon(T) \propto T^\alpha$. Then the radiation intensity $I(T)$ will follow a generalized power law $I(T) \propto T^b$. Taking into account also the absorption of room temperature radiation by the cluster, the rate of change of the cluster temperature should then be given by

$$C\frac{dT}{dt} = \frac{dE}{dt} = -I(T) + I(T_R). \tag{10}$$

Using the generalized power law one can integrate Eq. (10), and by fitting the result to the data displayed in Fig. 3, a remarkably good description of the temperature change of the Al_4^- clusters with time is achieved (solid line in Fig. 3). The value for the exponent b derived from the best fit is $b = 3.5 \pm 0.2$, which is surprisingly close to what is expected for a blackbody radiator. This indicates that the temperature dependence of the emissivity of the Al_4^- clusters is weak and can be approximated, at least in the observed temperature range, by $\varepsilon(T) \propto T^{-1/2}$.

The magnitude and temperature dependence of $I(T)$, which results from this fit, is shown in Fig. 4. The radiation

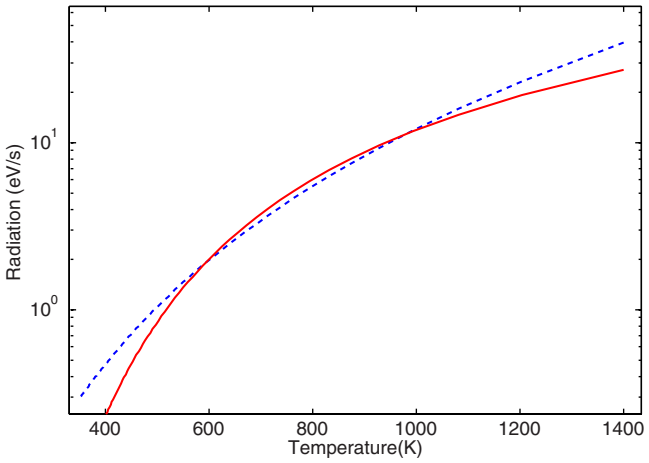

FIG. 4. (Color online) The derived intensity radiated by the Al_4^- clusters as a function of the temperature (solid line). The dashed line represents the approximation using Eq. (11).

intensities reach values of up to 40 eV/s at the highest temperatures covered and approach ~0.2 eV/s at 300 K. Note that by neglecting $I(T_R)$ in Eq. (10), which seems justified for temperatures $T>500$ K, $I(T)$ is just proportional to the time derivative of the measure $T(t)$ curve. Thus by interpreting the solid line in Fig. 3 as a reasonable interpolation between the data points, the size and temperature dependence of $I(T)$ presented by the solid line in Fig. 4 can be regarded (at least for $T>500$ K) as an experimental result independent of any model assumptions.

In an attempt to shed some light on the magnitude of the observed radiation intensities we will assume in the following that the effective absorption cross section in the relevant frequency region can be described by a group of resonances centered at ω_0 and of integrated strength $\langle\sigma\rangle$ and width $\ll\omega_0$. Then the radiated power $I(T)$ will be approximately given by

$$I(T) = \langle\sigma\rangle p(\omega_0, T). \tag{11}$$

Using Eq. (11) together with Eq. (7) or (8), the observed cooling curve shown in Fig. 4 can be reasonably well described assuming $\hbar\omega_0 \sim 0.22$ eV and $\langle\sigma\rangle \sim 5\times10^{-5}$ cm^2/s (see dashed curve in Fig. 4).

If the resonances are due to electronic transitions, $\langle\sigma\rangle$ can be expressed by the summed oscillator strength f using $\langle\sigma\rangle = (2\pi^2e^2)/(m_ec)f$ with m_e being the electron mass, which results in $f=3\times10^{-4}$. In view of the 13 valence electrons of the Al_4^- cluster such a summed transition strength is not inconceivable, but transition energies of ~220 meV are considerably below typical electronic scales and candidates for such transitions are presently not known. If the resonances are attributed to infrared-active vibrational transitions, $\langle\sigma\rangle$ can be connected to the corresponding dipole derivatives by [25] $\langle\sigma\rangle = (2\pi^2e^2)(Mc)q^2$, where M denotes the mass of the Al atom and $q^2 = 1/(3e^2)\Sigma|d\mu_e/d\xi|^2$. In this case the resonance strength needed to explain the data requires $q\sim4$, which has to be compared to $q=1$ expected for a three-dimensional harmonic oscillator of mass M and charge e. Thus very collective infrared-active vibrations have to be assumed if the radiative cooling is to be explained by vibrations only. While different conformations expected to be excited in hot Al_4^- clusters (see, e.g., [26]) are energetically separated by a few 100 meV, it remains to be seen if transitions between them are collective enough to account for the required transition strengths.

In conclusion, delayed electron emission from hot Al_4^- clusters irradiated by short laser pulses with photon energies of 2.063 eV has been measured. The rate of electron emission was found to be sensitive to the internal excitation of the cluster prior to its laser excitation, thus rendering this process to be a suitable probe for the canonical temperature of clusters as a function of storage time in an electrostatic trap. The radiative cooling rate thus measured for Al_4^- could be well described by a generalized Stefan-Boltzmann law, similar to the cooling of a blackbody. Thus radiative cooling of a system which contains only four atoms seems to be well accounted for within a thermodynamic framework, although the magnitude of the observed cooling rate still remains to be explained.

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