Search for dimer emission from photoexcited Al_4^-

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Aluminum cluster anions were stored in an electrostatic ion storage ring and irradiated by a laser pulse. Neutral as well as charged decay products emitted 20 μs after the excitation were identified and recorded using the daughter ion mass spectrometry method. Besides delayed electron detachment, only monomer emission was observed for Al_4^-. The branching ratio for the monomer channel was determined to be $8 \pm 2\%$, while the dimer channel was found to be $<0.01\%$.

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I. INTRODUCTION

Size-selected hot-cluster anions are excellent candidates for exploring the microscopic analogs of macroscopic thermodynamic properties [1]. Similar to bulk material they can cool down by emitting photons (radiative cooling), atoms (evaporation), or electrons (thermionic emission). Radiative cooling, which is not limited by an energy threshold and is the only cooling mechanism that leaves the cluster intact, typically occurs on time scales of milliseconds. When energetically allowed, delayed electron emission and delayed fragmentation, connected with typical time scales of tens up to hundreds of microseconds, will dominate the cooling process and may well compete with each other if their reaction-barrier energies are comparable.

The smallest aluminum cluster anion found to still exhibit delayed electron emission after photoexcitation by 2.063 eV photons is Al_4^- [2], and despite its low number of degrees of freedom, the decay could reasonably be well described within a statistical model formulated in Refs. [3,4]. Based on this model and taking the calculated binding energies [5] for electron detachment (2.13 eV) and one-atom loss (2.67 eV) as the relevant threshold energies, delayed fragmentation was expected to be negligibly small as compared to the electron channel ($<0.1\%$). However, in a recent experiment performed in a bent electrostatic trap [6], which allows to measure simultaneously delayed one-atom loss and electron detachment, it was found that the branching fraction was actually $\sim 10\%$. Even more interesting, in a different experiment [7] performed at longer wavelengths, delayed fragmentation is not only observed down to photon energies as low as 1.37 eV, but also becomes the dominant decay channel at these wavelengths. One possible interpretation is that despite the fact that the Al_4^- clusters were stored for up to 400 ms prior to the photoexcitation to let them relax presumingly to temperatures close to room temperature [2]—a fraction of the Al_4^- clusters is trapped in an excited metastable conformation that has a considerable lower barrier toward fragmentation. But then also delayed dimer emission would be a conceivable decay channel after excitation by ~ 2 eV, as the calculated dimer binding energy is only 0.6 eV higher than for monomer emission. As for higher photon energies, prompt ionization takes over [7], the most promising energy region to search for delayed dimer emission is at ~ 2 eV.

The only experiment on negative photoexcited Al_n^- clusters sensitive also to dimer emission was performed more than 20 years ago by Saunders *et al.* [8] for a cluster with $n \leqslant 8$. Integrating over prompt and delayed products, monomer emission was observed for $n \geqslant 4$, while dimer decays were not reported. In one of our ongoing attempts to get more insight into the decay properties of hot Al_4^-, we performed a dedicated experiment to search for dimer emission from photoexcited Al_4^- clusters. As the acceptance of the bent electrostatic trap [6] only allows observation of monomer emission from Al_4^-, the experiment was carried out at the electrostatic ion storage in Aarhus (ELISA) [9] using the recently developed time-resolving daughter ion mass spectrometry technique [10]. This technique was already successfully used to identify the masses of fragmentation products and to determine the branching ratios between different fragmentation pathways of large photoexcited molecules [10,11].

II. EXPERIMENTAL PROCEDURE

A scheme of the electrostatic storage ring ELISA, which is described in more detail in Ref. [9], is shown in Fig. 1. Briefly, negatively charged Al_4^-clusters are produced in a cesium sputter source as in our previous investigations [2,6], accelerated to 22 keV, mass selected by a magnet, and chopped by an electrostatic chopper, which is synchronized with the injection-storage cycle. The ion bunch is then steered, focused, and injected into the storage ring, where the ions are held on a stadiumlike orbit by two groups of deflectors, each consisting of two 10° deflectors and a 160° deflector. The revolution time of the Al_4^- clusters amounts to 41 μs. A residual gas pressure of $\sim 10^{-11}$ mbar is maintained in the ring resulting in a lifetime of the ion beam of a few seconds. After being stored for 35 ms, the ions are overlapped in the straight section between deflectors D_1 and D_2 with a short (~ 4 ns) laser pulse, which is generated by a master optical parametric oscillator with tunable wavelength (420–700 nm). The laser power used in the experiment was limited to 0.2 mJ to allow only for one-photon processes [12]. The daughter ion mass spectrometry method

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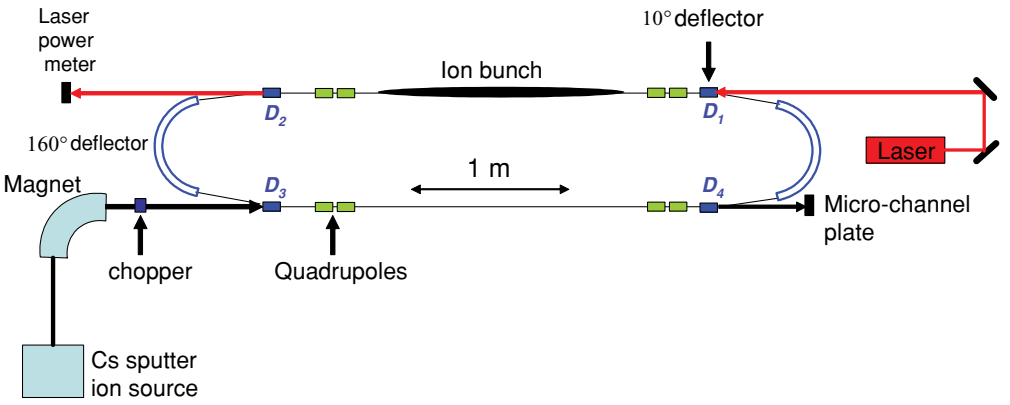

FIG. 1. (Color online) Schematic of the electrostatic storage ELISA.

[10] is then employed to identify and detect product clusters resulting from delayed decays in the straight section between D_3 and D_4: While neutral products can be directly detected by a microchannel plate (MCP) viewing the straight section between D_3 and D_4, a system of fast high voltage switches allows to swiftly adjust the setting of the storage ring such that one can select and store a particular ion species and dump it after one revolution on the *same* MCP.

For a more detailed discussion of the measurement procedure, we refer to Fig. 2, which illustrates the position of the stored Al_4^- clusters and their decay products at several time instances relative to the timing of the laser pulse. The time steps are given in units of $T/4$ with T being the revolution time of the ions in the ring: (I) While being stored, Al_4^- clusters colliding with the residual gas constituents can neutralize or dissociate. Charged fragments will be deflected out of the ring, neutral products (Al_m with $m = 1,2,3,4$) are unaffected by the ring potentials and will hit the MCP. (II) After 35 ms of storage, a laser pulse is overlapped with the Al_4^- clusters located in the linear section. (III) While photoexcited Al_4^- clusters staying intact remain stored, charged and neutral fragments

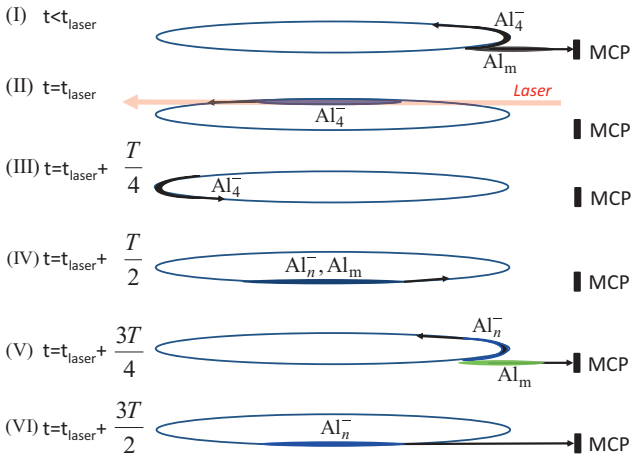

FIG. 2. (Color online) Position of the Al_4^- bunch and their decay products at various times relative to the time the laser was fired (t_{laser}). The time steps are multiples of $T/4$ with T being the revolution time of the ions in the ring. See main text for more details.

from decays occurring before the deflector D_3 (see Fig. 1) have improper energy-to-charge ratios and will thus hit the ring walls. (IV) When the excited ion bunch is located in the linear section between deflectors D_3 and D_4, the ring voltages are quickly scaled to allow a specific daughter ion (Al_m^- with $m = 1,2,3$) to be stored for an additional revolution (V), while neutral products produced between D_3 and D_4 are unaffected and hit the MCP. (VI) The Al_m^- daughters formed between D_3 and D_4 complete an additional revolution before the D_4 deflector is grounded to allow the Al_m^- to exit the ring and to hit the same MCP. Thus, *delayed* neutral and *delayed* charged aluminum fragments produced at times $T/2 \sim 20\ \mu$s after the laser excitation are detected at different times and are thereby well distinguished from each other. As the kinetic energies of the different ions are sufficiently high, their detection efficiencies are essentially equal. For technical reasons, the relative decay probabilities are determined in two steps: First, the relative abundances between the different delayed fragmentation channels are measured, and second, the delayed electron-detachment yield is determined relative to the main fragmentation channel. By scaling the ring voltages right after the laser pulse (i.e., while the excited ions are still in the straight section between D_1 and D_2), also charged daughter products from prompt decays (decays occurring within times $<20\ \mu$s) can be collected and transported to the MCP detector. In this case, however, the corresponding prompt neutrals resulting from electron detachment could not be measured, and thus, only relative rates between the charged daughter products were accessible.

III. RESULTS

Photoexcited Al_4^- anions can decay via the following processes:

$$Al_4^- + h\nu \rightarrow (Al_4^-)^* \rightarrow \begin{cases} Al_4 + e^- & (2.13\ \text{eV}) & \text{(a)} \\ Al_3^- + Al_1 & (2.67\ \text{eV}) & \text{(b)} \\ Al_2^- + Al_2 & (3.28\ \text{eV}) & \text{(c)} \\ Al_1^- + Al_3 & (4.09\ \text{eV}) & \text{(d)} \\ Al_4^- + h\nu' & & \text{(e)} \end{cases}$$

provided the internal energy of the hot cluster $(Al_4^-)^*$, determined by the sum of the internal energy of Al_4^- before the excitation and the photon energy, is sufficient to overcome the

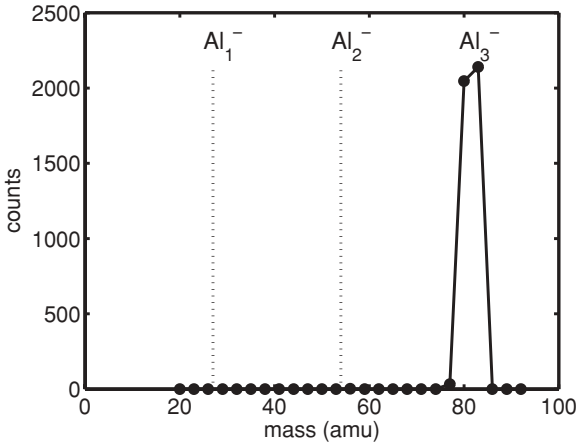

FIG. 3. A fragment spectrum obtained with Al_4^- clusters about 20 μs after absorption of a laser photon of 2.063 eV. The expected positions for Al_2^- and Al_1^- fragments are indicated by the dotted lines.

respective barrier energy. Lower limits for the barrier energies are set by the binding energies given in parentheses (calculated values from Ref. [5]). As the radiative decay times at the relevant excitation energies can be estimated from the results obtained in Ref. [2] to exceed 1 ms, radiative cooling (e) can hardly compete with the other delayed decay channels at the times they are measured ($\sim$20 μs).

Figure 3 shows the daughter mass spectra of the delayed charged fragments when exciting the Al_4^- cluster 35 ms after injection into the ring with photons of 2.063 eV. Each point corresponds to a specific ring voltage setting that was scanned between 5.4 and 16 kV. The data were accumulated for 12 500 injections with 500 injections per setting. During the measurement, the Al_4^- current as well as the laser power were kept constant. As the main beam has been removed from the ring before the daughter ions are dumped, and the MCP is gated to accept only hits during this dumping period of 30 μs, the mass spectrum is free of background hits. Only delayed Al_3^- fragments are detected; no counts are observed where the dimer and trimer channels leading to Al_2^- and Al_1^-, respectively, are expected, which limits the emission probabilities for these channels to be lower than 10^{-3} with respect to Al_3^-.

The competition between delayed electron emission and delayed one-atom loss was then measured using again the scheme outlined in Fig. 2, but the ring voltages were only stepped to three different settings, which ensure optimal storage of Al_4^- (V_p), optimal transport of the daughter Al_3^- (V_d), and which will finally dump the Al_3^- onto the MCP (V_0). These settings are shown as a function of time (measured relative to the laser pulse) in the upper panel of Fig. 4. The laser was again tuned to 2.063 eV and fired 35 ms after the injection of the Al_4^- cluster into the ring. The lower panel of Fig. 4 displays the number of counts collected as a function of time. Three time windows with respect to the time of the laser pulse are to be distinguished during which aluminum fragments resulting from different decay processes are detected: (i) $t < 0$: Neutral fragments induced by collisions of the stored Al_4^- clusters with the residual gas (background). The periodicity reflects the revolution period of Al_4^- in ELISA, and the aspect

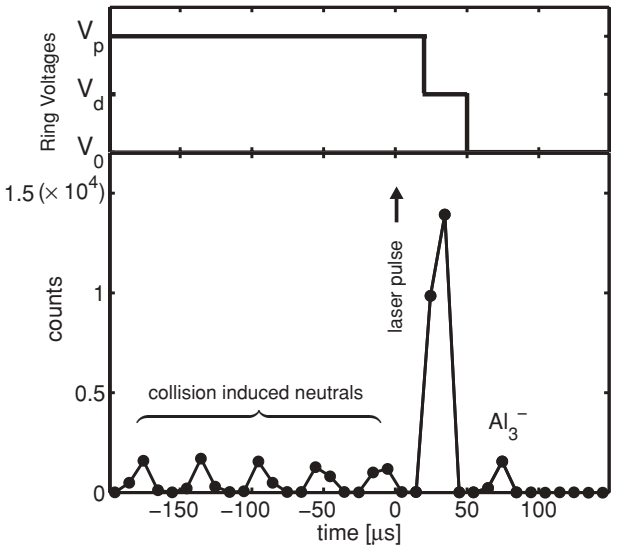

FIG. 4. Measurement of the relative probability for delayed electron detachment and one-atom loss for laser excited (E_λ = 2.063 eV) Al_4^-. (Upper panel) Voltage setting of the storage ring as a function of time relative to the laser pulse. (Lower panel) Number of counts detected with the MCP as a function of time (see main text for more details).

ratio shows that the bunch is still well preserved after 35 ms of storage. (ii) 20 μs $< t <$ 40 μs: Mainly delayed neutral Al_4 clusters reflecting the electron detachment channel (a), delayed Al_1 atoms from the fragmentation channel (b), as well as neutrals originating from residual gas scattering of the still present Al_4^- beam. (iii) 60 μs $< t <$ 80 μs: Al_3^- fragments from delayed decays, which occurred in time window (ii). From the number of counts N_2 and N_3 observed in time windows (ii) and (iii), respectively, the relative yields of the two channels can be deduced. While the measurement of Al_3^- is background free as discussed earlier, N_2 has to be corrected for contributions from residual gas events [determined by averaging over the event detected in time window (i) several revolutions before the laser was fired] and for the Al_1 contribution from the $Al_3^- + Al_1$ channel, which is measured by N_3. As the geometrical acceptances of the MCP detector for detecting the various fragments are expected to be similar and the transport efficiencies of the charged fragments around the ring are estimated to be larger than 90%, the results of this and the previous fragment mass measurement can be readily combined to determine the branching ratios. Denoting the relative yields for the four channels by n_i ($i = a,b,c,d$), the branching ratios are given by $B_i = n_i / \sum_{i=a}^{d} n_i$. The resulting values are compiled in Table I. The errors given take care of the uncertainties of the relative transport and the known

TABLE I. Experimental branching ratios B_i for delayed decays of photoexcited (E_λ = 2.063 eV) Al_4^- clusters, measured 20 μs after the laser pulse.

(a)	(b)	(c)	(d)
$Al_4 + e^-$	$Al_3^- + Al_1$	$Al_2^- + Al_2$	$Al_1^- + Al_3$
$92 \pm 2\%$	$8 \pm 2\%$	$<0.01\%$	$<0.01\%$

acceptance efficiencies. To verify that the absence of dimer emission in the observation window around $\sim$20 μs is not due to exceptionally short decay times, fragment mass spectra were also taken using the fast switching scheme, where products produced within the first 20 μs after the laser pulse are collected; again no Al_2^- ions signaling dimer emission were observed ($<10^{-2}$ as compared to Al_3^-). Furthermore, prompt dimer emission was not observed even up to photon energies of 2.91 eV. However, in a separate experiment, prompt dimer emission was found to occur from Al_5^- and Al_6^- for photon energies above 2.0 and 2.3 eV, respectively, although the corresponding calculated threshold energies for such processes are 3.46 and 3.28 eV [5], respectively (i.e., similar to that of Al_4^-). For both Al_5^- and Al_6^-, the dimer emission amounts to a few percent relative to monomer emission.

IV. DISCUSSION AND CONCLUSION

The branching ratios measured in this investigation confirm the findings of Ref. [6] that delayed one-atom loss of hot Al_4^- clusters is successfully competing with the delayed electron-detachment channel on time scales of tens of microseconds. Dimer (and trimer) emissions are not observed in Al_4^- within the sensitivity reached in this study, which translates into a branching ratio limit of $<0.01\%$. In larger clusters Al_5^- and Al_6^-, dimer emission was observed indicating improved sensitivity compared to earlier studies [8]. The suppression of dimer emission in Al_4^- is unexpected: According to Ref. [2], the temperature of the Al_4^- clusters after 35 ms of storage is still $\gtrsim$800 K. Thus, even in the absence of any excited metastable conformations, the addition of a photon of $\gtrsim$2 eV should be sufficient to lift some of the clusters above the dimer binding energy of 3.28 eV [5]. As several effects leading to a suppression of dimer emission are conceivable, it remains to be seen if the absence of the dimer branch rules out the presence of excited metastable conformations in Al_4^-, which is one of the scenarios presently discussed to explain the increasing dominance of delayed one-atom loss over the electron-detachment channel observed when decreasing the energy of the absorbed photon [7].

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