Clusters in Storage Rings

P. Hvelplund, J.U. Andersen and K. Hansen

Institute of Physics and Astronomy
University of Aarhus, DK – 8000 Aarhus, Denmark

Abstract. Anions of fullerenes and small metal clusters have been stored in the storage rings ASTRID and ELISA. Decays on a millisecond time scale have been interpreted as electron emission from metastable excited states. For the fullerenes the fast decay is caused by thermionic emission quenched by radiative cooling. The stored clusters were heated by a Nd:YAG laser resulting in increased emission rates. With an OPO laser this effect was used to study the wavelength dependence of the absorption of light in hot C_{60}^- ion molecules.

INTRODUCTION

The present paper describes studies of lifetimes of cold and hot clusters in ASTRID (the Aarhus STorage RIng Denmark). The first lifetime studies of clusters in the new electrostatic storage ring ELISA (ELectrostatic Ion Storage Ring Aarhus) are also included. ASTRID (1) has a perimeter of 40 m, two bending magnets in each of the four corners, 16 quadrupoles and 16 correction dipoles (cf. Fig. 1). The negative clusters were produced in a plasma source or in a sputter source and were accelerated and mass selected before injection into the ring at an energy around 50 keV. The rate of neutral particles detected behind one of the dipole magnets is then recorded as a function of time after injection and a so-called lifetime spectrum is obtained. The clusters are normally "born" in the ion source with a broad distribution in internal excitation ('temperature') and the decay of hot clusters by electron emission is derived. The injected clusters can also be heated in the ring in one of the straight sections with the beam from a Nd:YAG laser or an OPO pumped by this laser.

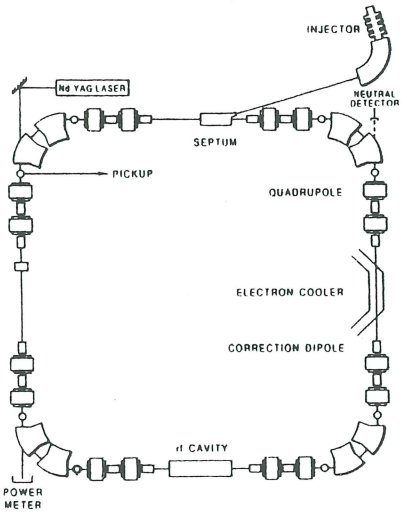

Figure 1. Layout of the ASTRID storage ring with injector and a laser for beam heating.

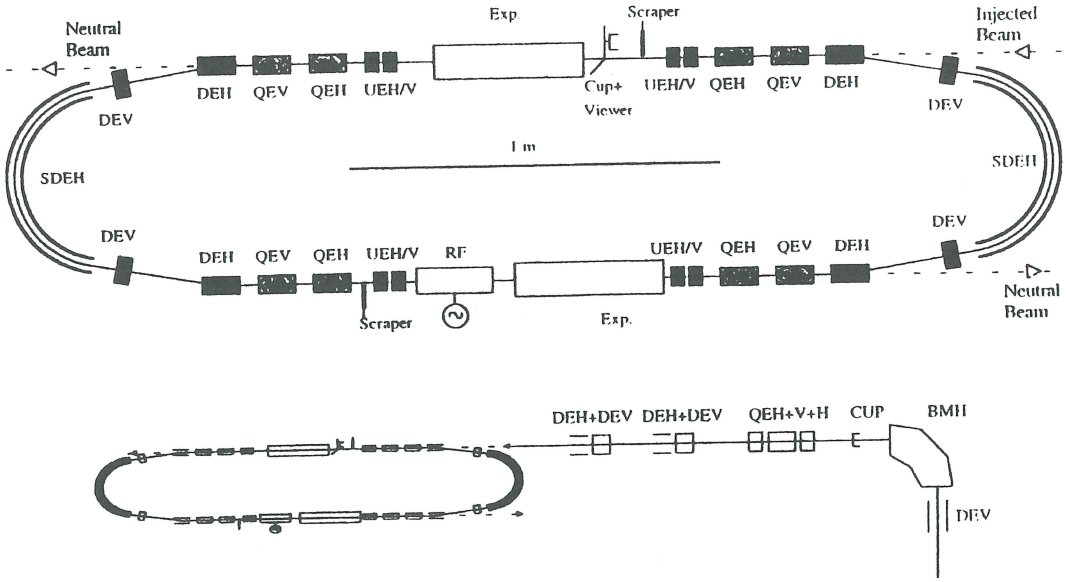

Figure 2. Layout of the ELISA storage ring (top) with injector (bottom). SDEH designates the spherical 160° horizontal deflectors, DEH and DEV horizontal and vertical electrostatic deflector, QEH and QEV horizontally and vertically focusing electrostatic quadrupoles, UEH and UEV horizontal and vertical pick-up electrodes, RF the drift-tube RF-system, and BMH the separator magnet in the injector

The electrostatic storage ring ELISA (2) has a race-track shape as shown in Fig. 2. The injection system with a separator is also shown. ELISA has a perimeter of 7.62 m with two 160° spherical electrostatic deflectors, four 10° parallel plate deflectors and four pairs of electrostatic quadrupoles in two straight sections. The revolution time of 25 keV C_{60} is about 100 μs as compared with about 500 μs for C_{60} ions at the same energy in ASTRID. At present, the first test experiments have been performed on ELISA with C_{60}^- and improved short time (~ 1 ms) information has been obtained as compared to similar measurements at ASTRID. We are currently testing an electro-spray ion source (3) for production of multiply charged biomolecules and plan in the near future to install this ion source on ELISA in order to study free protein molecules. Both the spontaneous decay of hot, metastable molecules and decay induced by laser excitation can be measured, in analogy to the cluster studies.

LIFETIME STUDIES OF FULLERENE ANIONS

A typical lifetime spectrum for C_{60}^- is shown in Fig. 3. The storage lifetime is limited by collisional destruction in rest gas interactions and the decay has been observed to follow an exponential law. The lifetime is ~ 10 s at a rest gas pressure of ~ $2 \cdot 10^{-11}$ mbarr. The high point at $t \approx 0$ shows that a major part of the C_{60}^- ions decay at very short times, presumably by auto-detachment

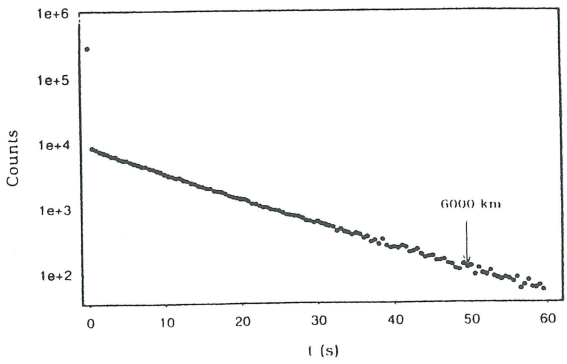

Figure 3. The yield of neutral particles at the detector as a function of time after injection of 50 keV C_{60}^-. The average pressure in the ring was 2×10^{-11} mbar, and the collision-induced lifetime is found to be ~7 s. The arrow points to the time where the fullerene ions have traversed a distance of 6000 km.

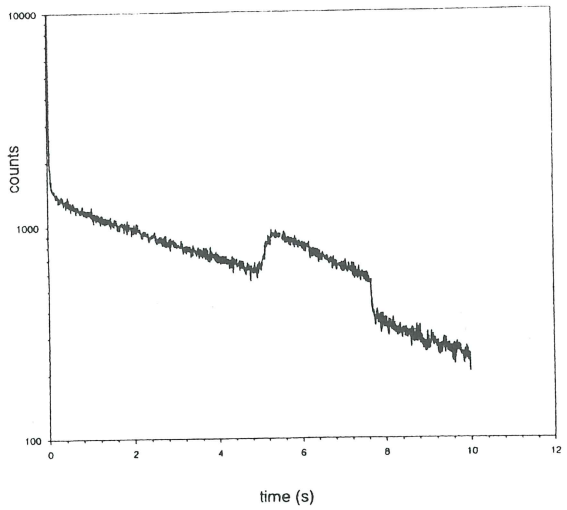

Figure 4. A spectrum like the one shown in Fig. 3 but with a 4.5 W Nd:YAG laser beam merged with the ion beam in a 2.6 s time interval starting 5 s after ion injection in the ring.

from hot molecules (4, 5, 6). We will return to this point later. In Fig. 4 is shown the effect of laser heating of the beam. A 4.5 W Nd:YAG laser is turned on 5 sec after ring injection and turned off 2.6 s later. In this time interval the detachment rate is increased by almost a factor of 2 due to heating and autodetachment of the circulating C_{60} anions.

LIFETIME STUDIES OF SMALL NEGATIVE METAL CLUSTERS

An example of lifetime measurements involving small metal clusters is shown in Fig. 5 (see next page). The decay curve for anions Al_n^- ($2 \leq n \leq 7$), which are "hot" when they leave the sputter source, are observed to be similar to the one observed for fullerene anions (7). The rate is seen to drop two orders of magnitude within the first few milliseconds. For these metal clusters the electron affinity and the binding energy per atom are similar (1-2 eV) (8) and the hot anions may decay either via electron emission or unimolecular fragmentation. Radiative cooling of the hot metal cluster is also believed to be active but has not yet been modelled. The stored ions were heated by a CW YAG laser with a power of ~ 25 W from 10 ms to 140 ms after injection. Note that the intensity of the detected neutrals drops for Al_2^- when the laser is on whereas it increases for the larger clusters. This observation indicates that destruction of Al_2^- is a "prompt" process whereas destruction of the larger clusters is delayed by at least half the revolution time in the ring, ~ 0.1 ms. This is consistent with the fact that the electron binding for Al_2^- is smaller than the photon energy, 1.17 eV. It should also be noted that the decay rate within the first few ms changes dramatically as a function of cluster size. The variation is probably related to differences in the rate of radiative cooling of the cluster anions.

STATISTICAL DESCRIPTION OF THE DECAY AND COOLING OF STORED IONS

Only if the injected cluster ions are stable against all forms of spontaneous particle decay will the evolution of the number of stores particles be described by a simple exponential time dependence due to destruction in collisions with the rest gas. If clusters possess internal energy, decay channels such as unimolecular fragmentation and thermionic emission open up (5). Figure 6 shows the decay of stored C_{60}^- ions in the millisecond range after subtraction of the nearly constant contribution from rest-gas collisions, illustrated in Fig. 3. The rapid decay on the millisecond time scale is caused by electron emission, since the electron affinity of C_{60} (2.7 eV) is much smaller (9, 10) than the activation energy for unimolecular fragmentation ~ 10 eV (11).

The functional form of the decay rate at short times carries information about the internal state of the clusters and the development of that state over time. In the atomic case, when all or a fraction of the ions are in a well-defined metastable state, the decay is described by a single exponential. If several metastable states are populated, the decay function will be more complicated, containing exponentials with different lifetimes. However, in the limit, where many states are populated, with a broad distribution of lifetimes, the decay function again becomes simple and the decay is described approximately by a t^{-1} law (5, 12).

This description may be expected to apply to negative fullerene ions stored in ASTRID or ELISA. In the ion source, the clusters are bombarded with electrons, and the extracted negative ions have a broad distribution in excitation energy. Furthermore, even at moderate excitation energies, the vibrational level density is enormous. With the new storage ring ELISA we have

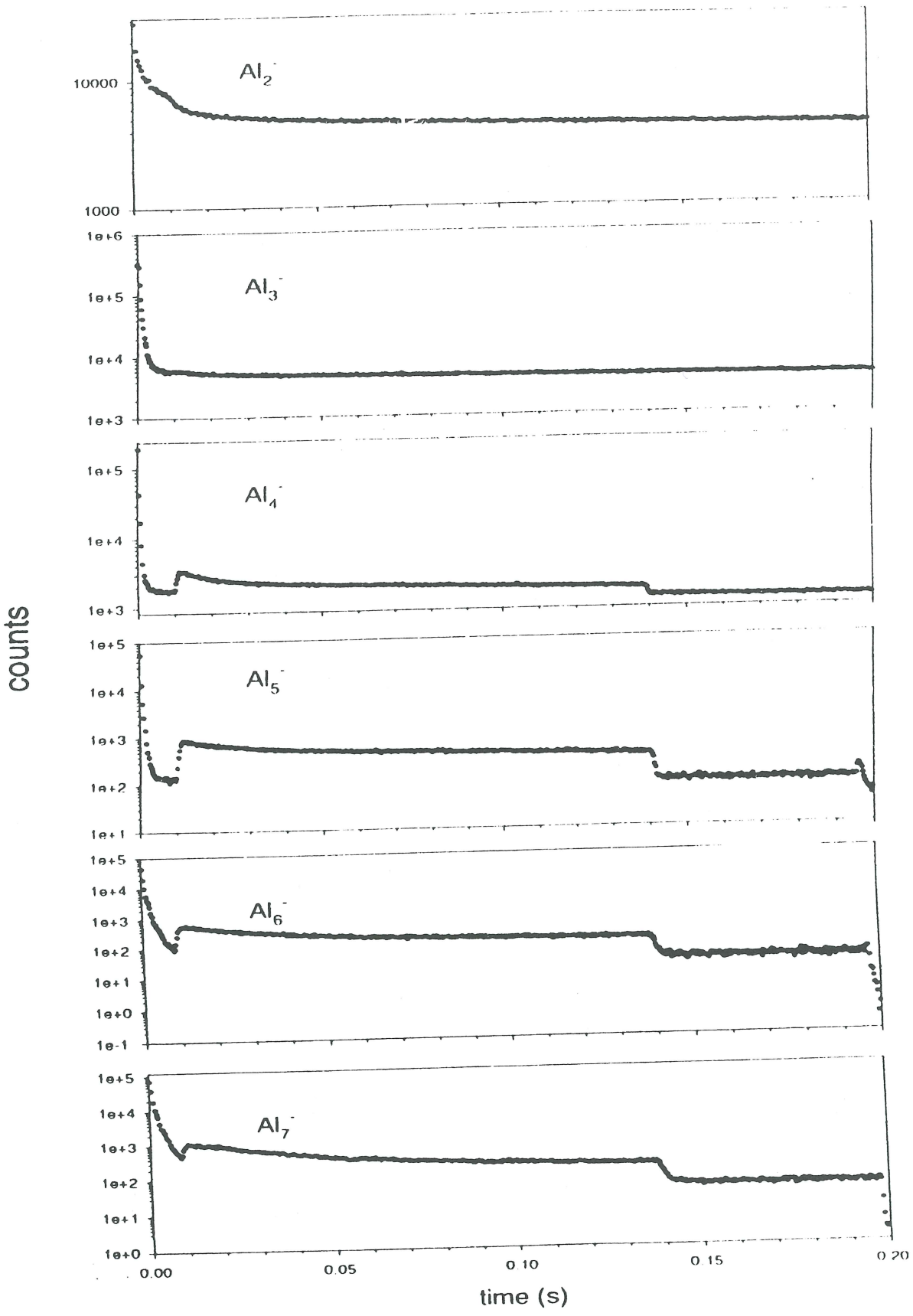

Figure 5. Lifetime spectra of Al_n^- ($2 \leq n \leq 7$) where a 25 W Nd:YAG laser has been merged with the ion beam in the time interval from 10 to 140 ms.

extended our earlier measurements at ASRID to shorter times, as seen in Fig. 6a. In the range 0.2 – 1 ms, the expected t^{-1} law is seen to describe the decay quite well, while the signal decreaeses faster at longer times. The results from ASTRID in Fig. 6b illustrate the nearly exponential decrease in the millisecond range. We have interpreted this as evidence for radiative cooling of the hot clusters (5). Just as for the negative atomic ions with very small binding energy, the interaction with the radiation field can have a strong influence on the decay rate (13), but here it is a quenching of the decay due to *emission* of radiation.

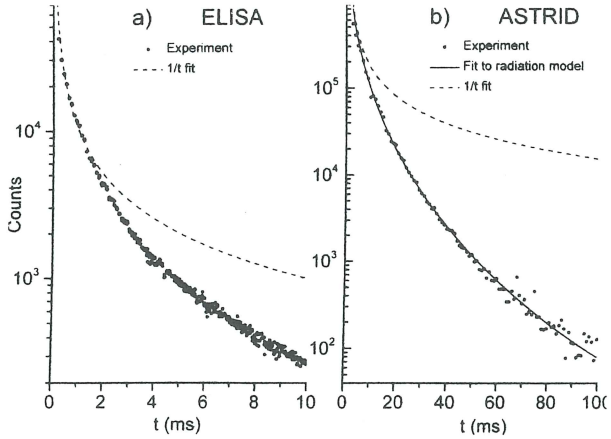

Figure 6. Rate of decay by thermionic emission of a stored C_{60}^- beam. A contribution from collisions with the rest gas has been subtracted.

As discussed in Ref. 5, there are strong theoretical arguments and experimental evidence for the description of electron detachment from excited C_{60}^- ions as a thermally activated process analogous to thermionic emission from a hot filament. Without cooling, the distribution is depleted from the high-energy side by electron emission. Cooling by radiation will quench the electron emission when the increase of the lifetime becomes significant on the time scale given by the decay rate.

The curve through the date points in Fig.6b is a fit calculated from a statistical model of the competition between electron emission and cooling. The radiation intensity is about 190 eV/s at an internal temperature of 1500 K and is approximately proportional to T^7. The major contribution to the radiative cooling comes from a thermally stimulated transition at 1.16 eV of the electron attached to C_{60} to form the anion (14, 15). In the following, we describe a spectroscopic study of absorption of radiation by this transition in hot C_{60}^- molecules.

THERMIONIC EMISSION LASER SPECTROSCOPY OF C_{60}^-

Thermionic emission of electrons from clusters is, as we have seen, enhanced by absorption of photons. The process can

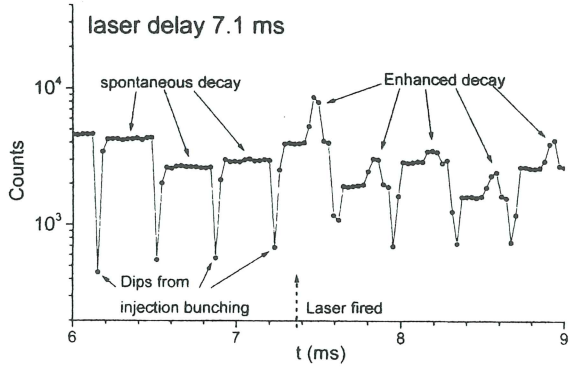

Figure 7. "Enhancement" spectrum for a laser firing time of 7.1 ms.

therefore be used to monitor the wavelength dependence of the photo-absorption cross sections of hot molecules and clusters. A stored C_{60}^- beam can at a preselected time be irradiated with a pulse from a tunable, Nd:YAG pumped OPO laser. In Fig. 7 is

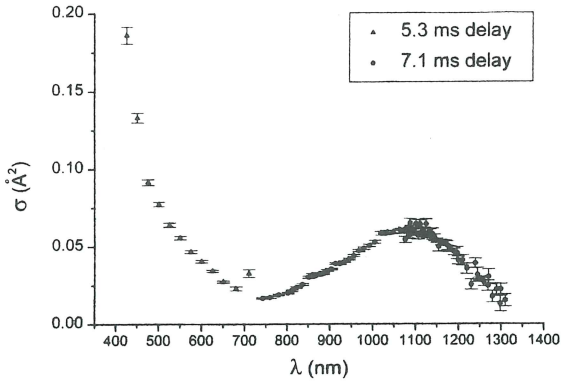

Figure 8. Photon absorption cross section as a function of laser light wavelength at a laser firing time around 5–7 ms.

shown a neutrals spectrum, where the laser was fired 7.1 ms after C_{60}^- injection in the ring. The resulting enhanced electron emission, measured with a ~ 200 μs delay, reflects the photon absorption cross section. The absorption strength decreases with photon wavelength up to 700 nm, followed by a broad absorption peak around 1070 nm (Fig. 8). This absorption peak has been studied extensively for C_{60}^- ions at lower temperature, for example for C_{60}^- in solution (14, 15). The peak is ascribed to the lowest transition ($t_{1u} \rightarrow t_{1g}$) of the additional electron in the anion. Strong sidebands at shorter wavelengths have been observed, corresponding to vibrational excitation. At the high temperatures of the stored ions (~ 1400 K according to the analysis illustrated in Fig. 6b), such excitations should be stronger because dipole matrix elements increase with excitation of an oscillator, $|\langle n+1|x|n\rangle|^2 \propto n+1$, and also hot bands with vibrational deexcitation should be observed. These expectations are consistent with the observed, bery broad absorption peak. We had hoped to be able to deduce a temperature from the asymmetry between the sidebands corresponding to vibrational excitation and deexcitation, respectively, but since the sidebands are not resolved there is a large uncertainty in the analysis from the broadening and a possible shift of the central electronic transition.

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