

Observation of a $1/t$ Decay Law for Hot Clusters and Molecules in a Storage Ring

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The exponential law is valid both for decay from a single quantum state into a continuum and for an ensemble maintained in thermal equilibrium. For statistical decay of an ensemble of isolated systems with a broad energy distribution, the exponential decay is replaced by a $1/t$ distribution. We present confirmation of this decay law by experiments with cluster anions in a small electrostatic storage ring. Deviations from the $1/t$ law for such an ensemble give important information on the dynamics of the systems. As examples, we present measurements revealing strong radiative cooling of anions of both metal clusters and fullerenes.

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Ion storage rings have, in the past decade, become an important tool in the study of atomic physics and this has, for example, led to significant progress in our understanding of the properties of negative ions [1]. We describe here the application of a recently constructed small electrostatic storage ring, ELISA, to study the time dependence of the decay of highly excited anions of molecules and clusters. The excitation by irradiation with electrons or with a laser beam, or by collisions in a gas, and subsequent detection of decay products is a general method for studying clusters and molecules, including structural analysis of large biomolecules. It is important for the interpretation to understand the dynamics of the decay processes and their time scale.

A storage ring is very well suited for such studies because an absolute time scale is established by the ion injection, and the decay can easily be recorded turn by turn over several orders of magnitude in time. As illustrated in Fig. 1, ELISA consists of two ~ 2 m long straight sections connected by electrostatic deflection plates [2]. A bunch of ions is injected into the ring at 22 keV, and the decay is followed in time by detection of neutral clusters or fragments at the end of one of the straight sections. Results for Ag_5^- clusters are shown in Fig. 2. The ions were produced with large excitation energy in a sputter source, and the yield of neutrals is at short times dominated by emission of electrons or of monomers and dimers [3]. The decay is clearly not exponential but instead close to a $1/t$ distribution. We have observed the decay to be close to this form for anions of a number of molecules and clusters, and this result has a simple interpretation as we discuss in the following.

The exponential decay law is a paradigm for microscopic systems like an excited atom or molecule. It is justified, for example, when the decay occurs from a single state into a continuum but has a much broader applicability. For a highly excited cluster with many degrees of freedom, the level density is so high that it becomes impossible to prepare the system in a single state or even distributed over a few states. If the decay is statistical, i.e.,

if energy is exchanged so rapidly between the internal degrees of freedom that an equilibrium distribution over the available states is established, the rate k of particle emission is a function of energy only. (The value of the other conserved quantity, angular momentum, is usually not important.) The rate is then proportional to the ratio of the level densities in the microcanonical ensembles of final and initial states, that is,

$$k(E) = \nu \rho_f(E - E_b) / \rho_i(E), \quad (1)$$

where E_b is the binding energy of the particle [4]. The frequency factor ν is of order 10^{11} – 10^{14} s^{-1} for electron emission.

If the clusters are isolated and their energy is conserved, the initial distribution, $g(E)$, is at time t depleted by a factor $\exp[-k(E)t]$ and the emission rate is given by

$$I(t) = t^{-1} \int dE k(E)t g(E) e^{-k(E)t}, \quad (2)$$

where we have extracted the factor t^{-1} to make the integral dimensionless. With a narrow energy distribution, $g(E) \propto \delta(E - E_0)$, we obtain the familiar exponential decay with rate constant $k(E_0)$. Also for a system in thermal equilibrium with a heat bath, the decay is exponential, since the canonical energy distribution is maintained by rapid energy exchanges and the distribution therefore is depleted by a common factor at all energies.

However, for an isolated system with a broad distribution in energy, the decay is not exponential. As we shall show, the analysis becomes simple in the limit where the energy distribution $g(E)$ varies much more slowly than the decay rate. Since $k(E)$ is rapidly varying, the weight function in Eq. (2), $kt \exp(-kt)$, is strongly peaked at the energy $E_m(t)$ where $kt = 1$, and $g(E)$ can be pulled out of the integral as a factor $g(E_m)$. Also, the ratio $k'/k = d(\ln k)/dE$ varies slowly compared to k , and the integral is therefore approximately given by

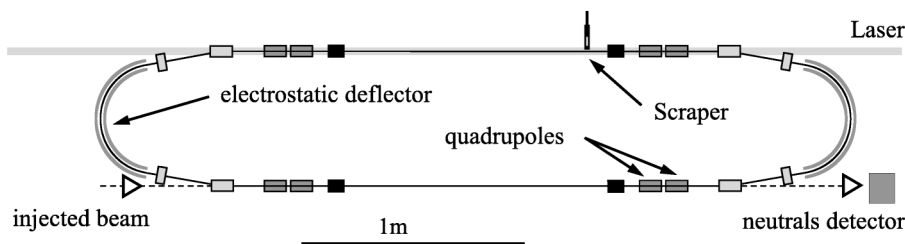


FIG. 1. Schematic illustration of the electrostatic ion storage ring ELISA.

$$\int dE k(E) t e^{-k(E)t} = \int d(kt) k/k' e^{-kt} \approx k(E_m)/k'(E_m). \quad (3)$$

This leads to the decay law,

$$I(t) \approx g(E_m) \left(\frac{k(E_m)}{k'(E_m)} \right) t^{-1}. \quad (4)$$

According to our assumption, the variation of the first two factors is much slower than t^{-1} , and the time dependence of the emission rate is therefore close to a $1/t$ distribution.

This is a remarkably simple decay law. In contrast to the exponential, it does not contain a characteristic time; i.e., it is scale invariant. The law is also independent of the type of particle emitted, whether an electron or a massive fragment. On the other hand, the function t^{-1} is not invariant under time displacements like the exponential but refers to an absolute zero, the point in time when the ensemble was created. An integrated form of this decay law has been derived by Klots [5] and used on several occasions to account for metastable decay in mass spectrometric studies of clusters (see, for example, [6–9]).

The crucial feature which distinguishes the expression in Eq. (2) from decay in a thermal equilibrium is that the depletion is energy dependent. The depletion of an ensemble of isolated clusters is illustrated in Fig. 3. The main contribution to $I(t)$ comes from a region around

the energy E_m , which decreases slowly with time, and the number of decays within a small time interval dt is given by the hatched area of width $-dE_m$. This illustration suggests an alternative simple derivation of the decay law. The emission intensity is given approximately by $I(t) \approx g(E_m)(-dE_m/dt)$, and, when the time differentiation is carried out with the help of the relation $k(E_m)t = 1$, one retrieves the formula in Eq. (4).

The derivation of the approximate $1/t$ decay law requires $k(E)$ to be rapidly varying but does not depend on the mathematical form of the function. However, to estimate the additional weaker time dependence of the integral in Eq. (3), we need an explicit expression for $k(E)$. For a cluster with N atoms, the level density is at moderate excitation dominated by the $3N - 6$ degrees of freedom of the atomic vibrations, and the system may then be represented by a collection of classical harmonic oscillators with level density $\rho(E) \propto (E + E_0)^{s-1}$, where s is an effective number of degrees of freedom, and E_0 is the zero point energy of the oscillators. It may be shown that for small clusters, $s \lesssim 20$, the power of t in Eq. (4) is then modified to $-[1 + 1/(s - 1)]$. This is in accord with the data in Fig. 2, which are best reproduced with a power $n \approx -1.1$.

For large clusters, it is more convenient to express the decay rate in Arrhenius form,

$$k(E) = \nu \exp\left(-\frac{E_b}{k_B T_e}\right), \quad (5)$$

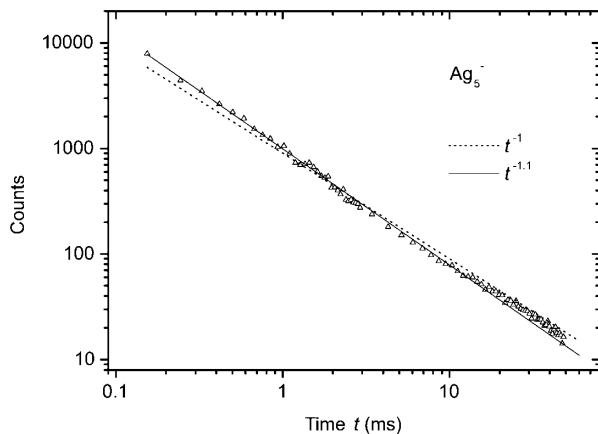


FIG. 2. Yield of neutrals detected turn by turn after injection of Ag_5^- clusters into ELISA from a sputter source. The decay is close to a $1/t$ distribution but is fitted better with a power ~ -1.1 . For $t > 3$ ms, the counts are averaged over ten revolutions.

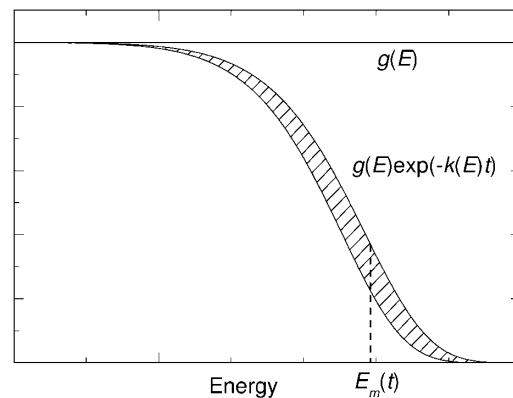


FIG. 3. Illustration of the depletion at time t of an energy distribution which was initially constant. At the energy $E_m(t)$, the distribution is reduced by a factor e^{-1} . The hatched area indicates the additional depletion during a small time interval dt .

where k_B is Boltzmann's constant and T_e is an emission temperature. We shall in the following apply the concept of a microcanonical temperature T , defined by $1/k_B T = d \ln \rho(E)/dE$. For the decay of cluster anions by electron emission, which we shall consider below, the vibrational level densities in Eq. (1) are nearly the same in the initial and final states. If the electron binding E_b is small compared to E , the function $\ln \rho(E)$ may then be expanded to first order around the average of the energies in the initial and final states. This leads to Eq. (5) with an emission temperature equal to the microcanonical temperature at this energy [10],

$$1/(k_B T_e) \approx \frac{d}{dE} \ln \rho(E - E_b/2). \quad (6)$$

With k given by Eq. (5), the expression in Eq. (3) is proportional to the square of the emission temperature T_m corresponding to E_m , multiplied by the slowly varying heat capacity. The functional dependence on t is $T_m(t)^2 \propto [\ln(\nu t)]^{-2}$ and the effective power of t in Eq. (4) is then corrected to $[1 + 2/\ln(\nu t)]$. Typically, the corrections to the power of t are of order 0.1 or less.

We now turn to strong modifications of the $1/t$ law, which can give important information on the cluster dynamics. As a first example, we mention the study in Ref. [11] of the competition between emission of electrons and of C_2 fragments from an ensemble of hot C_{60} molecules. The rate of decay in the weak channel (electron emission) was shown to follow a power law, with a power determined by the relative magnitude of the two activation energies. From the known ionization energy, an estimate of the C_2 dissociation energy could therefore be derived.

Photon emission is often a competing process. If the hot clusters radiate on the time scale of the decay, their energy decreases and particle emission is quenched nondestructively. For small clusters, emission of a single photon is usually sufficient to quench particle emission. Normally, the rate of photon emission varies more slowly with excitation energy than the decay rate, and it may be included approximately in Eq. (2) as an additional energy independent term in the exponent, $-k(E)t \rightarrow -[k(E) + 1/\tau]t$. This leads to a factor $\exp(-t/\tau)$ in Eq. (4).

This modified decay law is illustrated in Fig. 4 by a measurement for Al_7^- clusters. We have concluded from earlier observations that the decay of small negatively charged aluminum clusters occurs mainly by electron emission [12]. The reciprocal count rate is plotted against time and, hence, the $1/t$ law corresponds to a straight line through the origin. The positive curvature indicates that the clusters are cooled by radiation, and the data are instead fitted by a constant times the function $t \exp(t/\tau)$ with $\tau = 2.4$ ms.

Radiative cooling quenches the electron emission from Al_7^- molecules, which has virtually disappeared after 20 ms, but the signal can be regenerated by heating: About 20 ms after injection, the beam was irradiated by a laser pulse (640 nm, 6 mJ) in one side of the ring. This resulted

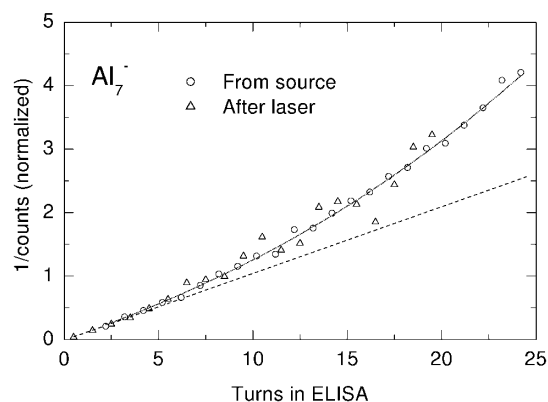


FIG. 4. The reciprocal counts of neutrals recorded turn by turn after injection of Al_7^- clusters into ELISA. The ions exit from a sputter source at $t = 0$. The triangles indicate the reciprocal counts after excitation of the stored clusters with a laser pulse. One turn corresponds to about 50 μ s.

in an increase by 3 orders of magnitude in the count rate of neutrals collected from the other side. The decay of this signal with time is also shown in Fig. 4, normalized to the initial count rate. The time variable is in this case the delay between the laser pulse and the arrival of the irradiated clusters at the middle of the straight section from which neutralized molecules are collected. There is good agreement with the initial decay of the injected beam, and this demonstrates that the means of excitation is not important, i.e., that the decay is statistical.

Measurements on stored Al_8^- and Al_9^- clusters show a very similar influence of photon emission, with characteristic lifetimes of 3 and 4 ms for photon emission. The temperature corresponding to a decay time of a few ms is of order 2000 K for $E_b \approx 2$ eV and $\nu \approx 10^{12}$ s $^{-1}$, and these lifetimes are in good agreement with a simple estimate based on a dielectric description with a bulk plasmon line at 17 eV [see Ref. [13], Eqs. (29) and (39)]. For the small silver clusters, Ag_n^- , a strong odd-even effect is observed: For $n = 5$ and 9, there is no indication of photon emission, and for $n = 7$ the characteristic time for photon emission is very long, $\tau \approx 100$ ms. This time is much shorter for the even clusters (with an odd number of valence electrons), $\tau \approx 5$ ms for $n = 4$ and 6, and $\tau \approx 20$ ms for $n = 8$. This difference cannot be explained by cluster temperature, since the even clusters have a lower excitation energy for fixed decay rate, as shown in Ref. [3].

For large clusters, we may include cooling in the argument leading to Eq. (4) by introducing a time dependence of the decay rate, $k(E, t)$, where E refers to the initial excitation energy of a cluster as it leaves the source. If the relative changes in excitation energy are small, we obtain, from Eq. (5),

$$k(E, t) \approx k(E, 0)e^{-t/\tau}, \quad (7)$$

where τ^{-1} is proportional to the radiation intensity, I_{rad} , divided by the heat capacity, C ,

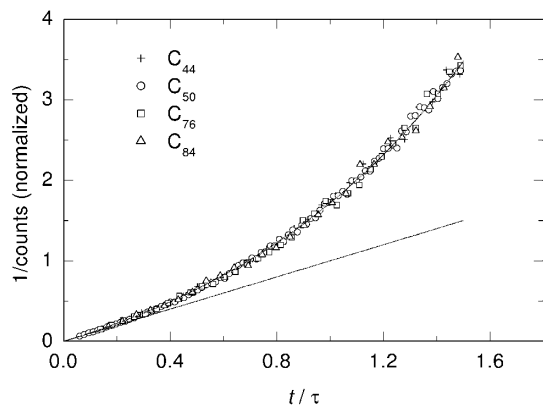


FIG. 5. The reciprocal counts of neutrals for fullerene anions stored in ELISA. The measurements were for each fullerene fitted with a function proportional to $[\exp(t/\tau) - 1]$, with $\tau \sim 1-5$ ms, and are shown in a scaled plot.

$$\tau^{-1} = \frac{E_b}{k_B T_e^2} \frac{I_{\text{rad}}}{C}. \quad (8)$$

Over a small energy range, we may treat τ as a constant. The depletion factor in Eq. (2) then becomes $\exp[-\int_0^t k(E, t') dt'] = \exp\{-k(E, t)\tau[\exp(t/\tau) - 1]\}$, and the integral in Eq. (2) may be estimated as before, if instead of t^{-1} we extract a factor $\tau^{-1}[\exp(t/\tau) - 1]^{-1}$ from the integrand. This leads to

$$I(t) \approx g(E_m) \left(\frac{k(E_m)}{k'(E_m)} \right) \tau^{-1} (e^{t/\tau} - 1)^{-1}, \quad (9)$$

where the energy E_m is now determined by $\tau[\exp(t/\tau) - 1]k(E_m, t) = 1$. From Eqs. (5) and (7), the corresponding initial emission temperature T_m is obtained as

$$k_B T_m = E_b \{ \ln[\nu\tau(1 - e^{-t/\tau})] \}^{-1}. \quad (10)$$

Note that this time dependence of T_m implies that, with increasing time, clusters with lower initial temperatures dominate the decay. According to Eq. (10), cooling is not important at short times, $t/\tau < 1$, and the characteristic emission temperature decreases slowly due to depletion of the hottest clusters by decay, $k_B T_m \approx E_b / \ln(\nu t)$. In the opposite limit, $t/\tau > 1$, depletion becomes unimportant and T_m approaches a constant value, $k_B T_m \approx E_b / \ln(\nu\tau)$. However, due to the cooling, the intensity in Eq. (9) decreases nearly exponentially, with a lifetime τ given by Eq. (8) with T_e equal to the limiting value of T_m .

An example is the decay of hot fullerenes. We have stored fullerene anions, C_N^- , in ELISA for all even values of N from 36 to 94. The ions were produced in a plasma source from fullerene powder heated in an oven. Their decay is completely dominated by electron emission since the electron binding (~ 3 eV) is much smaller than the activation energy for the competing process of C_2 emission (~ 8 eV or larger). As illustrated in Fig. 5 by a few ex-

amples, the decay curves can all be fitted by the function in Eq. (9) with cooling times τ of a few ms. We have previously observed the cooling of fullerene anions in the storage ring ASTRID [14] but, owing to the longer revolution time, the transition from a $1/t$ law to nearly exponential decay could not be studied. A detailed analysis of the measurements on fullerene anions in ELISA will be published separately [15].

In conclusion, we have observed a $1/t$ decay law for anions stored in a new electrostatic ring, and we have argued that this decay law is characteristic for ensembles of clusters or large molecules with a broad distribution in excitation energy. When emission of photons is significant on the time scale of the decay, it leads to a transition to a nearly exponential decay, with a characteristic time determined by the rate of photon emission. This has been demonstrated both for anions of small metal clusters and for anions of the large fullerene molecules. Thus, a paradigm for the decay of ensembles of clusters or molecules with a broad distribution in excitation energy has been established, and deviations from this paradigm have been shown to give information about the dynamics of the highly excited systems.

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