DECAY DYNAMICS IN MOLECULAR BEAMS

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The phenomenon of power law decays in molecular beams is reviewed. The transition from a canonical to a microcanonical description of the decay is analyzed, and the appearance of the power law decay derived. Deviations from a power law often contain information on parallel competing processes. This is illustrated with examples where thermal radiation or dark unimolecular channels are the competing processes. Also corrections to the power law due to finite heat capacities and from nonideal energy distributions are derived. Finally, the consequences for the interpretation of action spectroscopy data are reviewed. © 2020 The Authors. Mass Spectrometry Reviews published by Wiley Periodicals, Inc. Mass Spec Rev

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I. INTRODUCTION

Molecular beams represent the cleanest method to study the structure of molecules and clusters due to the absence of interactions with substrates, which will unavoidably modify the properties of deposited particles, often in less than perfectly understood ways. For clusters, molecular beam studies are of particular importance because these species are thermodynamically unstable and must be produced on the spot where they are investigated. Both reasons have rendered molecular beam studies extremely important for cluster science, in spite of the fact that a number of applications are aimed at the use of deposited clusters, with catalysis as a prime example (Ishida et al., 2020). The power of molecular beam studies has been demonstrated by the discoveries of shell structures, both of the geometric packing type (Echt, Sattler, & Recknagel, 1981), of electronic shell structure (Knight et al., 1984; Katakuse et al., 1985), and of the fullerenes (Kroto et al., 1985).

Molecular beams come with some special features when it concerns the thermal behavior of both clusters and molecules. The principal reason is that the components of molecular beams are decoupled from the thermalizing heat bath that is necessary to describe a system as canonical. Although the production of clusters can often be described in terms of canonical equilibrium or quasi-equilibrium processes, once the particles leave the region of production and move into the ultrahigh vacuum sector of a molecular beam device, contact to the environment is reduced to a very occasional, and usually destructive, collision with a residual gas molecule.

Systematic studies of these special molecular beam features have produced diagnostic tools for a range of thermal phenomena of clusters. The purpose of this review is to describe how the special beam features arise and how they find applications in thermally activated unimolecular decays, including emission of electrons and photons in thermal processes.

These aspects are by now well established experimentally, primarily by work at ion storage rings (Andersen et al., 1996, 2001; Hansen et al., 2001, 2018a, b), and here the focus will be on the theoretical aspects.

The remainder of the paper contains a detailed discussion of the exponential decay frequently considered a paradigm for thermal decays, and demonstrate that there are significant limits to its applicability. This is followed by a derivation of decay rates for hot systems (molecules, clusters and nanoparticles) in vacuum, which introduces the 1/t dependence. The following section analyzes cases where corrections to the leading order 1/t rate are needed and provides those. After this, a section describes the effect of dark competing channels, and the paper ends with a description of the consequences for the analysis of action spectroscopy data.

II. LIMITS OF EXPONENTIAL DECAY

The exponential decay is a standard representation of statistical decays of quantal and thermal nature in both physics and chemistry. In spite of its frequent use, it applies only to a very special class of situations. Exponential functions represent decay
rates when systems (molecules, nuclei, etc.) decay out of a single state or, more generally, out of a collection of states with the same decay constant. The situation is realized in the decay of nuclei that disintegrate by the weak nuclear interactions from some very long-lived state which is effectively an eigenstate of the Hamiltonian describing the system (Pais, 1988). This is perhaps the simplest manifestation of the decay of a single state.

Also thermally activated processes may proceed exponentially, although the setting is very different from that of nuclear disintegration. Chemical reactions that proceed over an energy barrier in thermal processes have rates that depend strongly on the internal energy present in the reacting systems. This very well-known fact is reflected in the theories of unimolecular reactions that have been developed during the last century, and it is the basis of the empirical relationship between reaction rate constants and the temperature that was proposed by Arrhenius more than a century ago (Arrhenius, 1889).

For thermally activated processes, an exponentially decaying state requires an ensemble of molecules with an internal energy distribution that is independent of time, apart from the exponentially decreasing overall amplitude. For gas phase systems such distributions may be maintained by intermolecular collisions. Radiative equilibration is possible and can be included on an equal footing with collisions in the description, although only a few examples of a dominating radiative equilibration mechanism that lead to complete equilibrium distributions have been reported so far for lab experiments (O’Connor et al., 2016; Schmidt et al., 2017). As an energy source for beams, absorption of ambient radiation provides an important mechanism for dissociation of loosely bound molecules and clusters on long time scales, see e.g. (Niedner-Schatteburg & Bondybye, 2000; Dunbar, 2004; Rahinov et al., 2016). The phenomenon is known as blackbody infrared radiative dissociation (BIRD).

This mechanism and collisional (re-)equilibration both have the potential to ensure that decays will not completely deplete the high energy tail of the distribution, which is the part of the distribution from which the decays occur. Re-equilibration will cause the balance between depletion and repopulation to reach a steady state, which will make the decay exponential. The single quantum state of the nuclear decay is then replaced by the entire thermal, time invariant excitation energy distribution, which acts as, and indeed is, a single decaying state in thermal decays.

An obvious question for the quantitative description of unimolecular decays in a nominally canonical thermal equilibrium is what requirements must be fulfilled by the re-equilibration process to ensure that a decay can be represented by the rate constants pertaining to an actual canonical equilibrium. Specifically, what values must a re-equilibration rate constant take to make the canonical energy distribution relevant for calculating rate constants? As this question is closely related to the question of the decay rates in the limit of no equilibration, this will first be examined.

The gas phase unimolecular reactions that will be considered here can be described as

\[ A \rightarrow B + C, \]  

with a rate constant which depends on the excitation energy, \( E \), of \( A \):

\[ k = k(E). \]  

Rotational degrees of freedom can be disregarded for the present purpose. The species \( B, C \) can be molecules, atoms or electrons. Their precise nature is irrelevant for the considerations that follow here, as long as the reaction is thermally activated, i.e., that it requires that some subset of the internal degrees of freedom are elevated above a threshold, \( E_{\text{th}} \), for the reaction to proceed.

In canonical thermal equilibrium at temperature \( T \), the distribution of excitation energies in the reactant species \( A \) is given by its vibrational level density (density of states) \( \rho(E) \), as

\[ P(E)\,dE = \frac{\rho(E)e^{-E/T}}{Z}\,dE, \]  

where \( Z \) is the canonical partition function:

\[ Z = \int_{0}^{\infty} \rho(E)e^{-E/T}\,dE. \]  

Boltzmann's constant is set to unity, which is simply a choice of unit system. Energies and temperatures are measured in identical units, and heat capacities and entropies are dimensionless.

For any process that occurs with a rate constant significantly below the collision frequency in the gas, the reaction will be of activated nature and will occur predominantly from the high energy tail of the distribution of Equation (3) due to the strong energy dependence of the \( k \) in Equation (2) in this type of reactions. The Arrhenius formula pertains to such energy distributions. To see how the formula appears, represent the involved rate constant in terms of the level densities of the reactant, \( \rho(E) \), and the product, \( \rho_p(E) \), as

\[ k(E) \approx \frac{\omega \rho_p(E - E_0)}{\rho(E)}. \]  

with \( \omega \) a frequency factor, and \( E_0 \) the activation energy of the process. The appearance of the ratio of level densities in this rate constant follows from detailed balance. See e.g., Weisskopf, 1937; Brink & Stringari, 1990; Hansen, 2018b, where also examples of the detailed balance expression for \( \omega \) can be found. Here it will set to a constant. These matters are discussed at length in chapter 5 of Hansen (2018b) to which the interested reader is referred for more details. The salient point here is that a number of details provided by more accurate theories of unimolecular decay rates will not appear in the ensemble averages that are the core of the material presented here, and it would be misleading to elaborate on such details. A number of different, relevant corrections to the expression are discussed below, though (see Eq. (35) and the text following that), and will be included after the theoretical baseline has been established.

For the schematic level densities

\[ \rho(E) \propto E^s, \]  

corresponding to \( s + 1 \) classical harmonic oscillators, the rate constant becomes

\[ k(E) = \omega \left( \frac{E - E_0}{E} \right)^s. \]  

This is close to a realistic description of thermionic emission rate constants where the number of vibrational degrees does not change during the process, and this very simple expression allows to focus on the essential points, although it should be stressed again that Equation (7) does not apply as a universally valid description of all aspects of unimolecular decays.
The rate constant for an equilibrium energy distribution is given by

$$k(T) = \int_0^\infty k(E)P(E)\,dE.$$  \hspace{1cm} (8)

(The same symbol is used for both the rate constant as a function of temperature and of energy, but this abuse of notation should not cause any confusion.) With Equation (5) and the expression for the population, the rate constant is calculated to

$$k(T) = \int_0^\infty \omega \rho_p(E - E_0) \frac{\rho(E)e^{-E/T}}{Z} \,dE$$

$$= \int_0^\infty \omega \rho_p(E - E_0) \frac{e^{-E/T}}{Z} \,dE$$

$$= \frac{Z_p}{Z} e^{-E_0/T},$$  \hspace{1cm} (9)

where $Z_p$ is the product partition function. Both partition functions in the expression refer to the internal degrees of freedom. For systems where the thermal excitations are carried predominantly by vibrations and where the geometric averages of the vibrational frequencies of precursor and product are the same, $\omega$, their ratio is equal to

$$\frac{Z_p}{Z} = \left( \frac{\hbar \omega}{2T} \right)^3$$  \hspace{1cm} (10)

in the classical (high temperature) limit. At lower temperatures the ratio is closer to unity. In either case, the variation with energy is relatively slow, and whether or not one wants to include this into $\omega$ or not is partly a matter of taste. Apart from these qualifications, Equation (9) is the Arrhenius formula.

In the absence of a re-equilibration mechanism, the decay will proceed in time by slowly eroding the high energy end of the distribution in Equation (3). The energy distributions at some measurement time, $t$, defined as the time elapsed after the ensemble has been created, will then be given by

$$P(E; t)\,dE = \frac{\rho(E)e^{-E/T}}{Z} e^{-k(E)t} \,dE.$$  \hspace{1cm} (11)

Figure 1 shows the energy distributions, initially generated with a temperature of 1500 K, that remain after $t = 1 \mu$s, 1 ms, and 1 s for a molecule decaying with the schematic rate constant given by

$$k(E) = 10^{15}s^{-1} \left( \frac{E - 3 \text{eV}}{E} \right)^{20},$$  \hspace{1cm} (12)

corresponding to the expressions in Equations (5) and (6) for 21 harmonic oscillators. The depletion shown in Figure 1 leads to an approximate power law decay with a power of $-0.89$ in this model case, as illustrated in Figure 2. The precise value of the power is influenced by the initial energy distribution, a question that will be discussed in detail below, but the nonexponential decay is a robust feature of this and similar situations.

Adding a re-equilibration mechanism to the energy distributions in Figure 1 provides a continuous repopulation of the high energy, decaying parts of the distribution. With a simple description of the (re-)equilibration it can be modeled as a reshuffling of the energy distribution with a rate constant denoted $k_e$. A realistic description is considerably more involved and is the topic of active research (King & Barker, 2019; Lendvay & Schatz, 2019; Robertson, 2019), but the simple description used here will make the point. Including

$$\frac{dP(E; t)}{dt} = -k(E)P(E; t) - k_e(P(E; t) - P_e(E; t)),$$  \hspace{1cm} (13)

where the time dependence of the equilibrium distribution $P_e$ amounts to a time dependent normalization constant. Normalization of $P_e$ to the same value as $P_e$ ensures conservation of mass in the re-equilibration process.

Figure 3 shows the numerically calculated temporal development of the ensemble average rate constant of the model system for three values of the equilibration constant, $k_e$, and identical values of all other parameters. Note that the quantity plotted is the average rate constant in the remaining population versus time, and not the population nor the decay rate. The horizontal sections of the curves thus represent exponential decays. As the ensembles generated at different times by Equation (13) are not those of

![Figure 1](image1.png)

**FIGURE 1.** The canonical energy distribution at time zero (black, full line), and as depleted at $t = 1 \mu$s (red, dashed line), 1 ms (blue, dash-dotted line), and 1 s (magenta, full line). The decayed fractions are 0.4%, 3%, and 7% at the three times mentioned. The inset shows the same data on a linear scale. [Color figure can be viewed at wileyonlinelibrary.com].

![Figure 2](image2.png)

**FIGURE 2.** The decay rates calculated with Equation (11) at 1 $\mu$s, 1 ms, and 1 s, corresponding to the distributions shown in Figure 1. The strongly bending, red curve is the exponential decay fitted from the first two points (note the double-logarithmic scale). The straight line is a fit of a power law with the exponent $-0.89$. [Color figure can be viewed at wileyonlinelibrary.com].
thorough, the average rate constant is also not the thermal average, i.e., \( \langle k \rangle \neq k(T) \).

Two features are immediately noted from the curves. The first is that there is a long transient before the exponential decay is established, and that the duration of this depends strongly on the value of \( k_e \). The second is that the measured rate constants, given by the plateaus at long times, also depend strongly on the value of \( k_e \). The two observations are clearly related; the smaller the re-equilibration rate, the later in time the steady state will appear and the smaller therefore also the observed exponential decay constant. At very short time, the curves coincide with the Arrhenius value \( k(T) = \omega \exp(-E_\text{act}/T) \), as expected, because no decay has taken place and the energy distributions are still canonical.

To describe the long time horizontal parts of the curve where decays are observed to be exponential, a stationary energy distribution state with an overall exponential decay can be used as an Ansatz for the energy distribution \( p_\text{E} (E; t) \). Both this and the normalized equilibrium distribution are decaying exponentially. It is therefore possible to extract the exponential time dependence from both and write the two distributions as

\[
p_\text{E} (E; t) = a p_\text{E} (E) e^{-k' t}, \quad p_\text{E} (E; t) = a p_\text{E} (E) e^{-k t},
\]

where the factor \( a \) incorporates the accumulated effect over time of the transient behavior, and hence is not necessarily equal to unity, and \( p_\text{E} \), \( p_\text{E} \) are both normalized to unity (this makes \( p_\text{E} \) equal to \( p_\text{E}(E) \) in Eq. (3)). The parameter \( k' \), unknown at this point, is the decay constant one measures. Inserting these two populations into Eq. (13) and canceling factors gives

\[
-k' p_\text{E} (E) = -k (E) p_\text{E} (E) - k_e p_\text{E} (E) + k_e p_\text{E} (E).
\]

Integrating over the energy immediately gives

\[
k' = \int_0^\infty k (E) p_\text{E} (E) dE.
\]

Rearranging Equation (15) gives the energy distribution that is required to calculate this integral:

\[
p_{\text{E}} (E) = k_e \frac{p_{\text{E}} (E)}{k (E) + k_e - k'}.
\]

Combining Equations (16) and (17) provides an equation for the determination of \( k' \):

\[
k' = k_e \int_0^\infty \frac{k (E)}{k (E) + k_e - k'} p_{\text{E}} (E) dE.
\]

A somewhat similar expression is given in (Malpathak & Hase, 2019). The differences from this work are that their \( k_e \) is identified with a gas collision frequency, which seems an unnecessary assumption, and that \( k' \) is absent from the denominator in the integrand.

Equation (18) is the key equation that describes the value of the observed rate constant \( k' \) in the steady state exponential decay. The equation generally does not lend itself to easily determined closed form solutions, but some properties can be extracted. The value \( k' = k_e \) is a solution to the equation. However, this value leads to both mathematical inconsistent and unphysical distributions. This is seen by introducing this solution into Equation (17) and noting that \( k (E) \) is identically zero below the threshold given by the activatio energy. For these energies, \( p_\text{E} (E) \) becomes infinite over a finite interval.

Another solution exists, as inspection of the left vs. the right hand side of Equation (18) shows, because the curves representing the two sides will in general cross at a value of \( k' \) below \( k_e \). We will not go into details of the behavior here, but just point out that considerations of the behavior of these solutions will show that we have the Arrhenius limit \( k' \approx k(T) \) for low temperatures and the high temperature limit \( k' \approx k_e \). These are also the expected limits, because at high temperatures the bottlenecks for decays is not the intrinsic rate constants \( k (E) \), but the rate of reheating of the high energy part of the distribution. In other words, in the heating sequence of a molecule \( M \) leading to decay, \( M (E < E_0) \to M (E > E_0) \to M \) (fragmented), where the energy \( E_0 \) is defined as \( k (E_0) = k' \), the speed of the first reaction is the rate defining. Conversely, at low temperatures the last rate is the defining. The high and low temperature limits are then those for which most of the energy distributions are respectively above or below the energy \( E_0 \). In terms of thermally average rate constants \( k \), the two limits are \( k \gg k' \) and \( k \ll k' \).

The model system’s numerically calculated distribution \( p_\text{E} \) distribution for \( T = 1500 \text{ K} \) is shown in Figure 4, together with the equilibrium distribution, \( p_\text{E} \).

Figure 5 shows the numerical solution of Equation (18) for \( k_e = 10^3 \text{ s}^{-1}, 10^4 \text{ s}^{-1}, \) for a range of temperatures. It is abundantly clear that the rate constants are strongly influenced by the finite value of the re-equilibration constant already for \( k_e = 10^6 \text{ s}^{-1}, \) and even more so for the lower value of \( k_e \), where the measured rate constants can be wrong by an order of magnitude or more, even at temperatures where it is orders of magnitude smaller than the re-equilibration constant.

A note on the value of the re-equilibration constants used here is in place. In a gas with a thermal speed of \( v \), a collision cross section \( \sigma \), and a density of \( N/V \), the collision frequency is

\[
f = \sigma v \frac{N}{V}.
\]
and \( \leq I \): The estimate of the value of \( I \) with Equation (20) gives the decay rates \( I_1 \) in the source and the time of measurement. Using \( g = f_1 \) for the collision frequency \( 10 \text{ s}^{-1} \), and \( g \) can be assumed depends on energy and that for statistical decays, it can be.

\[ \text{FIGURE 4.} \text{ The equilibrium energy distribution for the model system of Equation (12) (dashed line), and the modified long time energy distribution} \ p_i \text{ (full line) for } k_6 = 10^6 \text{ s}^{-1}, \text{ shown in the energy range where the latter is depleted by decay. The difference between the two is responsible for the difference of more than a factor 20 between the Arrhenius value and the asymptotic curve for the same } k_6 \text{ value used in Figure 3. The inset shows the product of the rate constants and the two distributions for the same abscissa values, for an illustration of the reason for the large effect that occur out of the small difference between the two distributions.} \]

With a numerical example using a temperature 1500 K, a pressure of one atmosphere, the mass 100 u, the cross section 100 Å², and the ideal gas law to calculate the molecular density, the collision frequency \( f \) is on the order of \( f \sim 2 \times 10^9 \text{ s}^{-1} \). But for an activated process, this is not the re-equilibration time constant, which is far smaller. The bulk part of the energy distribution is located around the equilibrium mean thermal energy. To move such an energy into the decaying part of the distribution requires a minimum number of collisions, \( n_{\text{min}} \) equal to the relevant energy difference divided by the average energy transfer per collision.

For the example with an activation energy of 3 eV, the absolute minimum amount needed to fragment is this threshold energy. Subtracting the thermal energy at the assumed temperature of 1500 K means 2.3 eV needs to be transferred to the molecule by collisions. With an energy transfer of 1500 K, equal to 0.13 eV, per collision, we get an order of magnitude estimate equal to \( n_{\text{min}} \sim \frac{2.3 \text{ eV}}{0.13 \text{ eV}} = 17 \), where the denominator is the thermal kinetic energy.

\[ \text{FIGURE 5.} \text{ The rate constants calculated self-consistently with Equation (18) for the re-equilibration rates } k_6 = 10^3, 10^6, \text{ and } 10^9 \text{ s}^{-1} \text{ (circles, bottom to top). The full, curved line is the Arrhenius rate constant, and the horizontal lines are the associated values of } k_6. \]

As the energy transfer process is statistical, effectively a random walk, a better estimate of the average number of collisions required to induce decay is given by the square of this number; \( n = n_{\text{min}}^2 \). The estimate of the value of \( k_6 \) for the collision frequency considered is therefore closer to \( k_6 \sim 6 \times 10^6 \text{ s}^{-1} \) than to the more than two orders of magnitude larger collision frequency.

The approximate nature of this estimate should be stressed. A more precise estimate than this would require a more detailed study (see e.g., Smith, 1997; Houston, Conte, & Bowman, 2014; Matsugi, 2018, 2019 for numerical studies).

The conclusions of this simple model is that the re-equilibration constant plays an important role in determining observed decay rates, even in the exponential regime, and that in the absence of any significant re-equilibration mechanism, the exponential decay fails completely and must be replaced by another description.

III. DERIVATION OF THE 1/T DECAY RATE

It is clear from the preceding section that thermal decays will in general not be exponential even if energy distributions are sampled from distributions that are initially canonical. It is also clear that even if a state with exponential decay is eventually reached, the latency time increases with the decrease of the re-equilibration rate. In the limit of no re-equilibration, the transient part of the curve is the only part observed.

The shape of this part of the curve is already suggested in Figure 2. For a general derivation of the shape of the infinitely long transient part of the curve, consider the expression for the decay rate, i.e. the negative derivative of the abundances, \( I \), with respect to time,

\[ R = -\frac{dI}{dt}, \quad (20) \]

where \( I \) is the integrated form of the energy-specified density of internal excitation energy, \( g(E; t) \):

\[ I \equiv \int_0^\infty g(E; t) dE. \quad (21) \]

The rate defined in Equation (20) is the one measured in e.g. storage rings. The time-integrated form is measured as the so-called metastable decay fraction in single pass devices such as mass spectrometers. In the absence of re-equilibration the energy-specified abundance can be factorized into an initial distribution, \( g(E) \), and a time dependent survival probability, \( P_{\text{sur}} \leq 1 \) as

\[ g(E; t) = g(E) P_{\text{sur}}(E; t). \quad (22) \]

The salient point of this separation is that the survival fraction \( P_{\text{sur}} \) depends on energy and that for statistical decays, it can be written as the energy-specified exponential decay:

\[ P_{\text{sur}}(E) = \exp(-k(E)t). \quad (23) \]

As before, \( t \) is the time between the creation of the distribution \( g(E) \) in the source and the time of measurement. Using \( P_{\text{sur}}, g(E; t) \) and \( I \) with Equation (20) gives the decay rates

\[ R(t) \propto \int_0^\infty g(E)k(E)\exp(-k(E)t) dE. \quad (24) \]

In the first, simplest description, \( g(E) \) can be assumed constant. The integrand of Equation (24) has a maximum emission rate as a function of energy given by
where $\alpha$ is a positive but so far unspecified constant. This form is chosen to represent any rate constant that varies sufficiently rapidly with energy. Although a number of different expressions for unimolecular rate constants have been proposed, they all share this rapid variation with energy, and it must be considered a safe parametrization. The relevant energies here are the ones for which $k(E) \sim 1/t$. This translates into a fairly low energy per degree of freedom and a rather steep curve of $k$ versus $E$. Even for experiments on long time scales will the difference in energy at the start and the experiment therefore be fairly small.

The energy for which the decay rate $k(E) \exp(-k(E)t)$ peaks, $E_m$, is found by equating Equation (27) to $1/t$ and solving for $E$:

$$E_m = E_0 - \alpha^{-1} \ln(k_0) t. \quad (28)$$

Crucially, this is also the energy that divides between the systems with energies too low to have decayed and those with too high energy to have survived at time $t$. The energy is time dependent, and for broad and flat energy distributions the decay rate is therefore proportional to the negative of the rate of decrease of this energy:

$$R(t) \propto -\frac{dE_m(t)}{dt} = \alpha^{-1} \frac{1}{t}, \quad (29)$$

where the constant of proportionality left out from the first equality is the density of excitation energies, $\omega$. The mutually dependent choices of $k_0$ and $E_0$ cancel, and the result depends only on $\alpha$.

Specifying the rate constant to find the value of $\alpha$, Equation (7) is applied here.

$$k(E) = \omega \left( 1 - \frac{E}{E_0} \right)^{9/7}. \quad (30)$$

To connect to the value of $\alpha$, the logarithm of Equation (30) is expanded in $E$. Using the energy given by $k(E) = 1/t$ as the expansion point results in the coefficient

$$\alpha^{-1} = \frac{E_0}{s(1 - (\omega t)^{1/7})^2}. \quad (31)$$

This makes the decay rate in Equation (29) proportional to $E_0$, which has a straightforward dimensional interpretation; The decay rate is proportional to the density of excitation energy, $g(E)$, which has dimension of $1/\text{energy}$. The only other parameter of dimension that appears in the problem is $E_0$, and consequently the rate must be proportional to $E_0 g(E)$.

The dependence on $s$ is less easy to understand in the form it appears in Equation (31). The following expansion will shed some light on the question:

$$1 - (\omega t)^{-1/7} = 1 - e^{-\ln(\omega t)/s} = 1 - (1 - \ln(\omega t)/s + (\ln(\omega t)/s)^2/2 - \cdots ) = \ln(\omega t)/s - (\ln(\omega t)/s)^2/2 + \cdots \quad (32)$$

As the dependence on frequency and time in this expression is logarithmic, there is fairly little variation in the values of $\ln(\omega t)$, and the range is typically limited to between 20 and 30. This range holds for emission of both electrons (Andersen, Bondurup, & Hansen, 2002) and atoms (Gspann, 1986; Hansen & Campbell, 2004), although the values for electron emission and for systems that are both small and very cold, such as small helium droplets (Brink & Stringari, 1990), tend to be a little
lower. For loss of small fragments with rotational degrees of freedom, the $\omega$ increases due to the larger phase space of the products and the logarithm can have values between 35 and 40 (Hansen, Campbell, & Echt, 2006).

For not too small values of $s$, second term and higher order terms in the expansion can be ignored and the rate therefore expressed as

$$R(t) \propto \frac{sE_0}{\ln(\omega t)^2} t. \quad (33)$$

This is identical to the exact result one obtains for a rate constant of the form $k(E) = \omega \exp(-E_0 s/E)$, i.e. equivalent to an Arrhenius expression with the emission temperature identified with $E/s$.

The expression in Equation (33) is derived for a specific and somewhat idealized situation, and it is of interest to have a more general expression. The generalization that will be applied here consists in parametrizing the level densities of both reactant and product as

$$\rho_i(E) = a_i(E + E_i)^\gamma \quad (34)$$

where subscript $i = r, p$ can denote either reactant ($r$) or product ($p$). For the special case of harmonic oscillators, for example, the value of $E_i$ is the zero point energy of the oscillators in the high energy limit. As such it gives the energy offset in the canonical caloric curve $E(T) = (s_i + 1)T - E_i$ for either of the two systems at the relevant temperature range. Similarly, $s_i + 1$ is the canonical heat capacity, and $a_i$ related to the entropy, although the connection is not as simple as that for the two other parameters.

The expression covers a lot more ground than just harmonic oscillator systems, although it is still an approximate relation.

The more general expression for a rate constant in Equation (5) then reads

$$k(E) \equiv \frac{\omega a_p(E + E_p - E_0)^\gamma}{a_r(E + E_r)^\gamma}. \quad (35)$$

Relating this to the exponential form

$$k(E) \approx \omega e^{-E/kT}, \quad (36)$$

requires the calculation of the primed parameters that enter the expression. As pointed out in (Hansen, 2018b) the definition of the temperature and the assignment of a value to the frequency factor are related and they cannot be determined without the application of another criterion. The criterion that was applied in (Hansen, 2018b) was that the caloric curve should be linear;

$$E = C_i T' - E_0. \quad (37)$$

This choice was motivated by the desire to have the simplest possible relation between excitation energy and measurement time. This facilitates the description of decays and it provides directly the interpretation of measurements of metastable decays, for example. It does mean that also $C_i$ and $E_0$ need to be determined. The somewhat lengthy calculation was reported in (Hansen, 2015) and only the results will be given here. The (re-)defined quantities were found to be the following:

$$\Delta s \equiv (s_r + s_p)/2, \quad (38)$$

$$E' \equiv E_r + E_p - E_0, \quad (39)$$

$$C_i \equiv \frac{G^2}{s} e^{-G/\gamma} \left(1 - e^{-G/\gamma}\right)^{-2}. \quad (40)$$

$$k(E) \equiv \omega \frac{dE}{dt} \left(\frac{E + E_i - E_0}{E_0 - E_r}\right)^{-\Delta s/2}, \quad (40)$$

$$\tilde{\tau} \equiv \frac{1}{2}(s_r + s_p), \quad (41)$$

$$G \equiv \ln(\omega t), \quad (42)$$

$$E_0 \equiv \frac{G}{s} \left(1 - e^{-G/\gamma}\right)^{-2} - \frac{G}{s} \left(1 - e^{-G/\gamma}\right)^{-1} + E_r \approx -\frac{G}{s} \left(\frac{1}{2} + \frac{G}{6\tilde{\tau}}\right) + E_r, \quad (43)$$

In summary, the decay rate is then given by

$$R(t) \propto \frac{C_i E'_r}{\ln(\omega t)^2} t, \quad (45)$$

where the parameters are given in Equations (39), (44), and (40). This expression reproduces the simple interpretation of the rate as the negative of the time derivative of the highest energy in the ensemble:

$$R(t) \propto -\frac{dE_{max}}{dt} = -\frac{d}{dt} \frac{C_i E'_r}{\ln(\omega t)}. \quad (46)$$

In the following we will dispense with the primes, but the reader should keep in mind the physical interpretation of parameters extracted from experimental measurements. Figure 7 shows the results of a series of simulations using Equation (24) with different values of system parameters. The figure includes a case of an energy distribution consisting of a sum of delta functions spaced equidistantly with a 3 eV separation to simulate photon absorption statistics.

A remark on the zero of time are in place. So far it has been assumed to be equal to the production time in a source. This may need to be modified when one observes the products of decay chains of the form $X_n \rightarrow X_{n+1} + X \rightarrow X_{n-1} + 2X \rightarrow \cdots$. Such decay chains are typical for clusters produced in hot sources without forced post-production cooling. For clusters with sufficiently small heat capacities, consecutive decays involve decay constants with widely different values, with all but the last decay happening in a very short time. In those cases, the accumulated time of all decays prior to that of the measured cluster size can be ignored.

This simple approximation changes when consecutive decay constants in a decay chain are not widely different. This occurs when heat capacities are sufficiently large. The heat...
The size where this value is reached corresponds to clusters of a few hundred atoms for harmonic oscillator heat capacities. For clusters of this and larger heat capacities, the time consumed in the initial decays cannot be ignored. A detailed analysis of the energy distributions produced in ensembles of clusters above such sizes shows that the power law decay appears also for these. This behavior of large clusters is non-trivial and considerations involving energy distributions and any quantity hinging on these distributions require considerations that differ from those used in the main narrative of this work. Details will take us too far astray and the interested reader is referred to (Näher & Hansen, 1994; Hansen & Näher, 1999) for a detailed analysis of the question.

IV. MODIFICATION OF 1/τ RATES: INTRINSIC, SOURCE PROPERTIES

The derivation of the power law decay is fairly general, and it has been observed in a number of experimental studies, most often at relatively short times (Hansen & Echt, 1997; Hansen et al., 1999; Andersen et al., 2001; Hansen et al., 2001; Andersen et al., 2003a, b; Tomita et al., 2003; Andersen, Heber, & Zajfman, 2004; Fedor et al., 2005; Toker et al., 2007; Sundén et al., 2009; Froese et al., 2011; Lange et al., 2012; Goto et al., 2013; Martin et al., 2013; Najafian et al., 2014; Martin et al., 2015; Breitenfeldt et al., 2016; Hansen et al., 2017b; Ji et al., 2017; Martin et al., 2017; Anderson et al., 2018; Bernard et al., 2019). However, corrections may arise to these results, both in the power of −1 and in the long term behavior, caused by factors both intrinsic and external to the decaying system. Below, the short term behavior will be parametrized by replacing the power −1 by the parameter −p and contributions to p calculated.

In this section the effects of deviations of g(E) from a constant will be treated, together with the effect of the variations of the quantity ln(ωt) (or (ωt)^−1/5) jointly with the heat capacity. These two effects are perturbations and will be treated separately. In addition, the effect of a melting transition, which represents a very different situation from the rate constants of Equation (35), will be demonstrated with a theoretical case study.

For decays on the microsecond time scales rates change as a rule of thumb by a factor of 20 for each 10% change in excitation energy. Equivalently, the factor G ≡ ln(ωt)^2 changes 15% over a time interval of a factor 10. This introduces a small, albeit non-zero time dependence into the denominator in Equation (45). Also the heat capacity which appears in the rate has a time dependence through its dependence on G. The heat capacity in general depends on the temperature, or for the microcanonical ensemble here, on energy. The energy in turn depends on the time, because we are considering the decays from the edge of the energy distribution, and this edge changes with time. To account for these variations, p is calculated by taking the double-logarithmic derivative of the expression

\[ R \propto \frac{C_\nu}{G^t} \]  

with respect to t, using the C_\nu and G from Equations (42) and (44). The resulting value is

\[ p = -\frac{\ln(R)}{\ln(t)} = -1 - \frac{1}{\tau} \left( 1 + \frac{2}{G^t} - 1 \right). \]

For systems with large heat capacities, τ ≥ G, this reduces to

\[ p \approx -1 - \frac{1}{\tau} - \frac{2}{G}. \]

The last term on the right hand side is often the dominant correction and is on the order of 5–10%. It is not a priori given that a double-logarithmic derivative gives a sufficiently constant value to make the calculated corrections to the power −1 meaningful, but a numerical estimate shows that this is indeed the case over a broad time interval. For examples, see Figure 7.

The calculation of this correction to p is facilitated by the results on the heat capacities in Equation (44), but it should be stressed that the result will be arrived at independently of this and does not hinge on any definition of the temperature, as required.

There are a few other possible intrinsic effects that may influence the value of p. One possibility is that vibrational degrees of freedom are frozen in for the parts of the excitation energy distribution that are sampled at long times. This will effectively be a change of τ with time. A very clear example of this is shown by the measurements of the thermal electron emission from SF₆ reported in Menk et al. (2014). The electron affinity of the molecule is about 0.5 eV and together with the long measurement time in the experiment, this sets a fairly low value for the energy per degree of freedom. Although the variation of E with time is logarithmically slow, the effect of the decrease with time on the vibrational excitation is boosted because it enters into the determination of the thermal
population. The population, in turn, is proportional to what is effectively a Boltzmann factor, \( \omega \left(-\frac{\hbar \omega}{T}\right) \) \( \exp \), which varies very rapidly when the effective temperature \( T \) decreases below the vibrational frequency.

Another possible intrinsic effect is that the equivalent of freezing occurs in the particle. The result of a maximum of the rate \( \left(-\frac{1}{t}\right) \exp 1 \) also applies to rate constants that are nonmonotonic functions of energy, although the additional peaks that are generated by freezing may not reach the maximum value. Around the melting point at least three more or less resolved peaks will appear in a plot similar to Figure 6.

Figure 8 gives an example of a decay curve that will cause such a behavior. The energy resolved rates are shown in Figure 9 for a range of measurement times that place the energies around the melting point.

The pileup of decays seen in Figure 9 is also seen in the more directly measurable decay rate in the form of an enhanced rate at the times where the decays occur from clusters with energies around the freezing point. Figure 10 shows the decay rate for such a situation. Curves such those in Figure 10 have not yet been measured. As seen from the abscissa values, they require that decay rates are measured over a wide range of times. This is feasible with storage rings, in particular of the cryogenic types, where storage times can reach thousands of seconds. In the choice of cluster material due consideration should be paid to effects of radiative cooling (see below).

Finally, the effect of the source should be considered. Even if the excitation energies acquired in a source are sufficient to induce a spontaneous decay, the excitation energy distributions are rarely completely flat. This will affect the measured decay rates. As this is an external input to the problem, it will vary with the type and operating conditions of the source, as well as the particle type. These effects will be included summarily with a single parameter, \( b \), in the description of the energy distribution which is valid over a limited energy interval,

\[
g(E) = a e^{bE}. \tag{51}\]

The value of \( a \) is uninteresting in this connection. The decay rate will be given by Equation (46) multiplied by the additional factor \( g(E) \). The double-logarithmic derivative gives for the power

\[
\ln p \rightarrow p + b \frac{E_u C_v}{\ln(\omega)}^2. \tag{52}\]

The value of \( b \) is not observed directly, as a rule. However, if one observes the abundances produced by a cascade of decays of a collection of clusters of different sizes, the energy distributions represented by \( b \) can be related to the abundances (see Hansen, 2018b). Ignoring size-to-size variations in \( E_u \)'s, the modification of \( p \) for the size \( N_0 \) is calculated by dividing by \( E_u \) and using the parameter \( b' \) found from fitting the abundances with the function

\[
I_N = a e^{b'(N-N_0)}. \tag{53}\]

Size-to-size variations in \( I_N \) should be ignored in the fits of this kind, and only the smooth part of \( I_N \) vs. \( N \) should be used for this purpose.
The result is then

\[ p \rightarrow p - b' \frac{C_v}{\ln(\omega t)}^2. \]  

(54)

Usually this is not a numerically important correction.

V. COMPETING CHANNELS

The power law decay finds its most important use when decays are observed to deviate significantly from the 1/t form. A condition for the power law to occur with the powers calculated so far is that the observed channel represents the main decay. Any major amount of decay through a parallel dark channel will cause modifications, to the point of converting the decay into a different functional form. Any significant deviation from 1/t, viz. one that cannot be assigned to a nonconstant energy distribution or a similar minor effect, can therefore often be taken as indication of the presence of a competing channel.

The most important type of such a dark channel is, somewhat paradoxically, the emission of thermal photons. Emission of thermal photons is an important channel in the decays of molecules and clusters at long times, and the process is attracting increasing attention as an essential part of the description of decays in storage rings and similar devices (Møller, 1997; Dahan et al., 1998; Jinno et al., 2004; Bernard et al., 2008; Pedersen et al., 2015), where cryogenic techniques are pushing storage times into the thousands of seconds regime (Lange et al., 2010; Reinhed et al., 2010; Schmidt et al., 2013; Nakano et al., 2017). It should be stressed that although power law decays appear in their most inestimable form in these types of devices, there is no reason to suspect that they are not present in, for example, single pass devices (Hansen & Campbell, 1996), although the available dynamic time range in these instruments often renders the specific time dependence difficult to disentangle experimentally from a standard exponential decay.

The division of time scales into an early unimolecular regime and a later radiative one is caused by the difference in decay parameters for these two classes of decays. Unimolecular decays have a frequency factor multiplying the ratio of level densities which is essentially given as

\[ \omega = \frac{8\pi\sigma T^2 m}{h^3}. \]  

(55)

where \( \sigma \) is the attachment cross section for the inverse process, \( T \) the microcanonical temperature of the product particle/molecule, \( m \) the mass of the small fragment lost, and \( h \) Planck’s constant. With sticking coefficients around unity, corresponding to geometric cross sections, calculated frequency factors for atomic cluster are in good agreement with those derived from vapor pressure data of the corresponding bulk matter. Figure 11 shows the comparison for a number of metallic elements for which the vapor is predominantly composed of monomers. These values are higher by about two orders of magnitude than the Debye frequencies (also shown) which is often used in heuristic theories.

Equation (55) is derived from detailed balance considerations. This also provides a frequency factor for the thermal electron emission rate constant. The frequency factor is smaller for electron emission due to the much smaller mass of the emitted particle, although it is often boosted by the larger capture cross section and occasionally by the higher temperature at which electron emission tends to be emitted, and it will still be larger than the photon emission value.

The parameters of thermal radiation differ from those two types of unimolecular decays in two respects. First of all the activation energy is much smaller. The activation energy is the energy of the lowest optically active excitation in the system. A low energy of this state is necessary for the process to be observed because also the frequency factor for photon emission is smaller than the atomic emission \( \omega \)'s, which is the second difference. The frequency factor is the Einstein \( A \)-coefficient, which takes values on the order of \( 10^6 \) s\(^{-1} \) for typical electronic transitions, but with a significant spread in values. In a canonical situation the photon emission rate constant \( k_{ph} \) is, in terms of \( T \) and the thermal population of the emitting state, equal to the well-known result

\[ k_{ph}(T) = A \frac{e^{-h\nu/T}}{1 - e^{-h\nu/T}}. \]  

(56)

In a microcanonical situation, this is modified to Andersen, Bonderup, & Hansen (2002)

\[ k_{ph}(E) = A \frac{\rho(E - h\nu)}{\rho(E)} \]  

\[ \frac{1}{1 - \frac{\rho(E - 2h\nu)}{\rho(E - h\nu)}}. \]  

(57)

(At negative energies, level densities are zero.)

With the lower values of both the frequency factor and the activation energy, radiative cooling is bound to dominate the decays at late times and cause a suppression of the unimolecular decay in that time region (Andersen et al., 1996). The details of the description of this suppression depend on the magnitude of the emitted photons. The systematics of this behavior is summarized in a recent review article (Ferrari et al., 2019), and only a few points concerning the influence of thermal radiation on decay rates will be taken up here.
For sufficiently small photon energies, emission of a single photon is insufficient to cause a major change in the unimolecular rate constant. In the other limit a single photon emitted will quench any further decay. Here only the small photon energy limit will be discussed. The large photon limit is treated in (Ferrari et al., 2019).

In the small photon energy limit, the radiative cooling can be considered a continuous process. We can then rewrite Equation (24) by introducing a time dependence due to the radiation, in addition to the time dependence on the exponential depletion. This can in principle be done either by including time dependence in the population, \( g(E) \rightarrow g(E, t) \) or in the rate constants, \( k(E) \rightarrow k(E, t) \). The latter approach will be used here. With a leading order expansion of the logarithm of the rate constant in the time since creation, one has 

\[
k(E, t) = k(E, 0)e^{-t/\tau},
\]

where \( E \) is the energy the particle is created with, and \( \tau \) is a time constant, defined as

\[
\tau^{-1} = \frac{d\ln k}{dE}P_{em},
\]

where \( P_{em} \) is the emitted power. The expansion of the logarithm of \( k \) and not of \( k \) itself is reasonable because of the strong dependence of \( k \) on energy and its intrinsic non-negative values.

In terms of the average photon energy \( h\nu \), and the photon emission constant \( k_p \), the power is

\[
P_{em} = h\nu k_p.
\]

If we stay with the parametrization in terms of a constant value of \( \tau \), Equation (24) becomes

\[
R(t) \propto \int_0^\infty g(E)k(E)e^{-t/\tau}e^{-k(E)\int_0^t e^{-t'/\tau}dE} dt,
\]

where the exponential of the integral gives the surviving fraction at the initial excitation energy \( E \). All time dependence is given explicitly, and the integral is easily evaluated to give

\[
R(t) \propto \int_0^\infty g(E)k(E)e^{-t/\tau}e^{-k(E)\tau(1-e^{-t/\tau})}dE.
\]

The last equality shows that \( \tau(1 - e^{-t/\tau}) \) acts as an effective time in the integral, which can then be evaluated simply by copying the previous, nonradiative result with the proper substitution for the time. Including the pre-integral exponential, this converts the power law decay to a quasi-exponential form;

\[
R \propto \frac{1}{\tau} \frac{1}{e^{t/\tau} - 1}.
\]

The analogous expression for larger photon energies is (stated without proof),

\[
R \propto e^{-k_p t} / t.
\]

The expression in Equation (63) reduces to a \( t^{-1} \) dependence for short times, as required on physical grounds. At long times it can be approximated by an exponential decay.

The nature of this exponential decay is different from a standard type exponential decay, though, because here the exponential decrease describes the time dependence of the rate constant and not of the population. In fact, at long times, all decays will have ceased but an amount of particles will have been fossilized by the radiation. This is readily observed in storage rings, for example, if the particles are reheated with a laser and resume their decays (Hansen et al., 2001; Kono et al., 2018).

Emission of massive particles may also constitute dark channels. As for photon emission, it will influence the decay rate if it is the main channel, i.e. if the rate constant for this channel is the highest of the two (or more) competing channels on the measurement time scale. One such case is realized in the decay of neutral \( C_60 \) through the channels (Hansen & Echt, 1997)

\[
C_{60} \to C_{60}^+ + e^-.
\]

Experimentally, the decays were produced by laser excitation and the laser power was varied to ensure that \( g(E) \) was flat. It can therefore be left out from the considerations. If the electron yield is dominant, the presence of \( k_a \) in the exponential can be ignored, and one then gets a standard power law decay. This is not what is observed. The electron rate varies as

\[
R \propto t^{-0.65}.
\]

The reduction of the absolute value of the power from unity can only be understood as a consequence of the fact that the \( C_2 \) loss channel is dominant. We can therefore write the rate as

\[
R \propto \int_0^\infty k_e e^{-k_E dE}.
\]

Expressing \( k_e \) in terms of \( k_a \) using exponential expressions for both with a few simplifications, gives that

\[
k_e \propto k_a e^{IE/E_a},
\]

where \( IE \) is the ionization energy measured to be 7.6 eV, and \( E_a \) is the \( C_2 \) loss activation energy. This gives a power law decay

\[
R \propto t^{-IE/E_a}.
\]

Although the ionization energy was well known at the time these experiments were performed, the \( C_2 \) dissociation energy was not. The measured power in this decay allowed a determination of the value, which was in much better agreement with the values produced in the fairly intensive work with quantum chemical calculations that followed the discovery of the Krätschmer-Huffman method of production of macroscopic amounts of the molecules. The value extracted was around 11 eV. With a few later adjustments to 10.8 ± 0.3 eV (Tomita et al., 2003), this is now the generally accepted value.

**VI. ACTION SPECTROSCOPY**

Molecules, in particular large molecules, are occasionally, and clusters very often, found in so low concentrations that standard absorption spectroscopy is not feasible. Although techniques...
such as cavity ring-down spectroscopy will be able to render absorption spectroscopy feasible in some situations, a more convenient spectroscopic technique in cluster studies is action spectroscopy. The principle of this method is to use the easily measured loss of a part of a cluster, typically an atom, as a signature for the absorption of one or more photons.


The application of the technique requires that the quantum yield of the decay process is not too low, and if absolute cross sections are desired it should be known. When the action proceeds via a thermal decay, the quantum yield clearly depends critically on the photon energy. The situation is particularly critical at the red end of a spectrum, where photon energies can be too low to induce the signature decay, and for which a vanishing quantum yield can erroneously be interpreted as a vanishing absorption cross section. Although this problem of insufficient heating can to some extent be bypassed with the use of the messenger molecule technique (see below), it is still particularly severe for vibrational spectroscopy, for which multi-photon absorption is required to provide any yield at all, and techniques have been developed for these experimental conditions, taking into account factors such as the variation of the cross section with internal energy etc. (von Helden, van Heijnsbergen, & Meijer, 2003; Bakker et al., 2010). The problem is most severe and also simplest to examine for one photon processes, and in the following only this situation will be considered.

The problem can be quantified and solved when the internal excitation energy distributions are those that give rise to power law decays. Experimentally, the assumption of a broad energy distribution can be tested by measuring the spontaneously appearing decay fraction and comparing with the results given above. To summarize previous equations, the fractional amount of decay of a mass-selected particle should be given approximately by

\[ M \equiv \frac{I_d}{I_0 + I_d} = \frac{C}{(\ln \omega)^5} \ln \left( \frac{\bar{\tau}}{\bar{\tau}_i} \right), \]  

(72)

where the integrated yield between \( \bar{\tau}_i \) and \( \bar{\tau}_2 \) is measured. The intensities \( I_0 \) and \( I_d \) denote the number of non-decayed and decayed particles, respectively. If these measurements conform to the calculated yields, the decay can safely be described as statistical and from the broad energy distributions assumed here.

The problem of calculating the yield involves several different experimental times, viz. the time between production and measurement, the time lag between photon absorption and the start of the recording of the decay, which may be but not necessarily is zero, and the time where the measurement of the metastable decay ends. If present, radiative cooling will also have to be included in the analysis. We will assume here that radiative cooling is not present. The case where it is present has been treated in (Hansen, 2018a), to which the interested reader is referred.

In a spectroscopy experiment, the cross section, \( \sigma \), is obtained from the photo-induced decay count rate \( I \) as

\[ \sigma \propto \frac{I}{\Phi F}. \]  

(73)

where \( F \) is the photon flux and \( \Phi \) is the quantum yield, defined as the number of reactions per absorbed photon. For a thermally induced decay, by nature a delayed reaction, the quantum yield depends on the measurement time, the photon energy, and also on the internal energy. Denoting the differential (energy-specified) quantum yield by \( \phi \), we can write

\[ \phi = \phi(E, h\nu, t_1, t_2), \]  

(74)

where \( t_1, t_2 \) are the beginning and the end of the experimental detection window, i.e. the limits of the time interval during which the decay is measured. The total yield is an integral over the energy dependent contributions from the different excitation energies:

\[ \Phi(h\nu, t_1, t_2) = \int \phi(E, h\nu, t_1, t_2) g(E - h\nu) dE. \]  

(75)

where \( g(E) \) is the distribution of excitation energies immediately before the photon absorption that happens at time \( \nu E \). As before, the zero of time is conveniently set to the time of creation in the source. Setting \( g \) to unity, the quantum yield becomes, after taking depletion up to \( \nu E \) into account,

\[ \Phi(h\nu, t_1, t_2) = \int \phi(E, h\nu, t_1, t_2) e^{-k(E-h\nu)\nu E} dE. \]  

(76)

The fraction \( \sigma F \) of the energy distribution is shifted up by the photon energy \( h\nu \) upon absorption. The energy distribution becomes

\[ P(I_{\text{tot}}, E) = e^{-k(E)\nu E}(1 - \sigma F) + \sigma F e^{-k(E-h\nu)\nu E}. \]  

(77)

This distribution has the time development

\[ P(t, E) = P(I_{\text{tot}}, E) e^{-k(E)(t-\nu E)} = e^{-k(E)(1 - \sigma F)} + \sigma F e^{-k(E-h\nu)\nu E} e^{-k(E)(t-\nu E)}. \]  

(78)

To find the change in population due to photon absorption at the high energy side, which is the relevant one for the question at hand, subtract the non-photo-excited population;

\[ P_p(t, E) \equiv P(t, E) - P_0(t, E) = \sigma F (e^{-k(E-h\nu)\nu E} e^{-k(E)(t-\nu E)} - e^{-k(E)t}). \]  

(79)

This is non-negative anywhere and as the time derivative of it is negative, the differences calculated below for the yields are all non-negative as required, although this may not be immediately apparent from the expression. The energy-specified quantum yield for a photon-enhanced decay is the difference between the populations in Equation (79) at \( t_1 \) and \( t_2 \):

\[ \phi(E, h\nu, t_1, t_2) = P_p(t_1, E) - P_p(t_2, E) \]
\[ = e^{-k(E-h\nu)\nu E} e^{-k(E)(t_1-\nu E)} - e^{-k(E)t_1} - e^{-k(E-h\nu)\nu E} e^{-k(E)(t_2-\nu E)} + e^{-k(E)t_2}. \]  

(80)
The total quantum yield follows from integrating over all energies:

\[
\Phi = \int_0^\infty e^{-k(E-h\nu)\tau_{\text{las}}-k(E)(t_0-\tau_{\text{las}})}e^{-k(E)t_0}\tau_{\text{las}}-k(E)(t_2-\tau_{\text{las}})}+e^{-k(E)t_2}\) dE. \tag{81}
\]

All times entering Equation (81) are instrumental and the quantum yield can be calculated if the functional form for the rate constant is known.

It is possible to reduce the number of parameters needed to calculate the yield. Define the fictitious time \(t_0\) as

\[
k(E-h\nu)\tau_{\text{las}} \equiv k(E)t_0. \tag{82}
\]

It is clear from the definition that \(t_0\) is positive. It does not depend on the frequency factor that appears in the description of the rate constant (it appears on both sides of the equation as a multiplicative factor and cancels). The value of \(t_0\) can therefore be calculated from level densities and activation energies alone. Although \(t_0\) is introduced as a fictitious time, it has a measurable physical meaning as the zero of time for the photo-excited part of the ensemble. If the time-resolved decay after laser excitation is measured, it is found as the offset in the photo-induced decay as \(1/(t-\tau_{\text{las}}+t_0)\). This is particularly easy to measure in storage ring experiments, see e.g. (Sundén et al., 2009), but it is not unique to such experiments; also single pass experiments may accomplish this. The identification of \(t_0\) with the experimental time offset is derived below after some simplifications of the equations.

With the parametrization of the rate constant in Equation (82) for the shifted signal, the signal becomes

\[
\Phi \propto \int_0^\infty e^{-k(E)(t_1-\tau_{\text{las}}+t_0)}e^{-k(E)(t_2-\tau_{\text{las}}+t_0)}+e^{-k(E)t_2} \] dE. \tag{83}
\]

All four terms in the exponent in the integrand of Eq. (83) contain the factor \(k(E)\), but are multiplied by different times. As argued, the arguments of the exponentials are strongly varying functions of energy, providing fairly sharp cutoffs in the energy distributions. The cutoff energies, \(E_m\), for the energy distribution for the laser excited species are

\[
E_m(t) = \frac{E_{a,\text{atom}}}{{\ln(\omega t)}} + E_{0,\nu}, \tag{84}
\]

where \(t\) may be either of the times \(t_1, t_2, t_1-\tau_{\text{las}}+t_0, t_2-\tau_{\text{las}}+t_0\) in Equation (83).

The presence of such a cutoff energy greatly facilitates the calculation of the integral, because these can be calculated as the pairwise differences between the two cutoff energies. The energy offset \(E_{0,\nu}\) cancels in the process and the integral is approximately proportional to

\[
\Phi \propto \frac{1}{\ln(\omega(t_1-\tau_{\text{las}}+t_0))} - \frac{1}{\ln(\omega(t_2-\tau_{\text{las}}+t_0))} + \frac{1}{\ln(\omega t_2)} - \frac{1}{\ln(\omega t_1)}. \tag{85}
\]

The factor \(E_{a,\text{atom}}\) is independent of the photon energy and has been left out. The contribution of the last two terms can be approximated by an expansion to first order in \(\ln(t_2/t_1)\). This gives the (unnormalized) quantum yield;

\[
\Phi \propto \frac{1}{\ln(\omega(t_1-\tau_{\text{las}}+t_0))} - \frac{1}{\ln(\omega(t_2-\tau_{\text{las}}+t_0))} - \frac{1}{\ln(t_2/t_1)}. \tag{86}
\]

The value of \(t_0\) can be calculated if some information about the energy dependence of the decay constant is available. Alternatively, it is possible, as mentioned above, to relate \(t_0\) to the experimentally observable decay rate after the photon absorption. The photon-enhanced decay rate is the derivative of \(\Phi\) with respect to \(t_1\):

\[
R = \frac{d\Phi}{dt_1} \propto \frac{1}{(\ln(\omega t_0))^2} \frac{1}{t-\tau_{\text{las}}+t_0} - \frac{1}{(\ln(\omega t_0))^2} \frac{1}{t-\tau_{\text{las}}+t_0}. \tag{87}
\]

A fit of the measured \(R\) versus \(t-\tau_{\text{las}}\) will give \(t_0\) directly. It may be more convenient to fit \(R^{-1}\),

\[
R^{-1} \propto t-\tau_{\text{las}}+t_0. \tag{88}
\]

The derivation here provides the quantum yield for thermal, photo-induced decays from an ensemble of clusters with broad energy distributions, and can be applied directly to convert yields to relative cross sections for these situations. It works also when the messenger atom technique is used, in which a weakly bound atom is detached at a lower energy than the threshold for unimolecular reaction of the undressed cluster. See, e.g., Cismesia et al. (2017) and Gorlova et al. (2017) for two recent examples of work using this technique. The benefit of the messenger atom technique is that it extends the sensitivity of the spectroscopy to a photon energy smaller than the naked cluster technique by a factor \(E_{a,\text{atom}}/E_{a,\text{naked}}\). However, the low internal energies required for an efficient sticking of a messenger atom may be incompatible with the requirement of a broad cluster excitation energy distribution. This is paty an experimental issue which is best addressed for the specific experiment undertaken.

It should also be mentioned that the results can be used when the decaying systems radiate, with the proper modifications of the equations. A detailed analysis of these cases is given in Hansen (2018a).

The main result presented here is an equation for the quantum yield for a given photon energy in an ensemble possessing a broad energy distribution. In this situation the action yields need to be corrected with the quantum yields to give the correct absorption cross section. This is achieved by division with the expression in Equations (86) or (85). The procedure for the nonradiative cases described here involve the determination of the frequency factor of the measured process.

This will usually be by theoretical means, but as it enters only logarithmically, the uncertainty associated with this will have a minor effect. All times except \(t_0\) that enter the expression are experimental values. The value of \(t_0\) is either measured as described, or it is calculated with Equation (82).

**VII. CONCLUSIONS AND OUTLOOK**

Decays of free particles, without contact with a thermalizing heat bath, will often occur with a power law time dependence,
in spite of being completely statistical and exponential at the level of individual particles. A power law decay does not contain any characteristic time and consequently also no characteristic energy that can be related to the activation energy of the process. It does, however, have a zero of time, in contrast to exponential decays.

The systematics associated with the power law decay has consequences for a number of phenomena. One is the amount of metastable decays, another the relation of hot cluster beam abundances to binding energies. It also has importance when it breaks down. The presence of a competing channel is one such situation. Such a channel will, if dominant, cause distortions of the decay which can be used to identify the characteristics of this dark decay. Frequently observed cases involve thermal photon emission.

The technique of using deviations from power law decays to infer the properties of a dark competing channel has been used for the decay spectra of metal cluster anions in some of the presently longest storage time experiments at electrostatic ion storage rings (Hansen et al., 2017b; Andersen et al., 2018). In these experiments, made possible by the low device temperatures which reduce the pressure and hence the limiting factor of restgas collisions, the ions can be stored for a good fraction of an hour. This permits the identification of more than one radiatively suppressed power law decay in the decay of an ion species. Small copper clusters, for example, have been observed to decay with two such curves (Breitenfeldt et al., 2016; Hansen et al., 2017b). They have been identified as originating from two different populations of the cluster ions, differing by their angular momenta (Hansen et al., 2017b). This conserved quantity acts as a very efficient barrier, blocking the conversion between the two types of isomers and ending them with different radiative properties, making their observation possible by simple measurements of the decay rates.

In summary, the power law decay of isolated and highly excited ions is both well established and useful for the interpretation of a number of phenomena. It appears in its most insistent form in long term storage devices, but is often present in single pass devices also, even if much harder to distinguish from the more commonly used fitting functions of exponential decays.

REFERENCES


Klavs Hansen, born 1958, received his PhD degree from the Niels Bohr Institute in his native Denmark in 1991, with a thesis on the electronic shells and supershells in metal clusters. His main interests are thermal and quantal effects in gas phase clusters and molecules, including fullerenes. His work is both experimental and theoretical and involves dynamics on time scales from femtoseconds to hours, studied with short pulse lasers, mass spectrometers and electrostatic storage rings. Since 2016 he is professor at Tianjin University and from 2020 also at Lanzhou University, China. He has a senior visiting professorship at KU Leuven, Belgium.