Eur. Phys. J. D **9**, 119–122 (1999)

**THE EUROPEAN
PHYSICAL JOURNAL D**
EDP Sciences

Evaporation rates for Na clusters

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Received: 1 September 1998

Abstract. Na clusters in the size range of 50–400 atoms are led to evaporate in a heat bath with controlled temperature. For specific cluster sizes just above closed shells, decay rates are measured as a function of temperature. They agree with an Arrhenius law and allow absolute separation energies to be extracted.

PACS. 61.46.+w Clusters, nanoparticles, and nanocrystalline materials – 36.40.Qv Stability and fragmentation of clusters

1 Introduction

The electronic shell structure of simple metal clusters was originally revealed in measurements of abundance spectra of clusters evaporating in a vacuum [1]. A quantitative relation between mass yields and separation energies was established later, and verified to some degree of accuracy [2–4]. In the present paper, we report on clusters evaporating individual atoms in a thermostated, inert gas, a so-called heat bath. We demonstrate that the decay rate $k(N,T)$ for a few, special Na clusters with an opened electronic shell can be determined as a function of the heat bath temperature, T_{HB}. The present experiment is a further development of the preliminary results of Chandezon, et al. [5]

The description of the evaporation of a single atom from a neutral sodium cluster containing N atoms is based upon statistical decay theory, which states the rate by which clusters of size N are depleted by monomer evaporation. The rate is assumed to be dependent on the available internal energy only,

$$k(N,T) = A(N)\exp\left(-\frac{D(N)}{k_{\mathrm{B}}T}\right), \qquad (1)$$

where $D(N)$ is the separation energy for the Nth atom and T the temperature of the mother cluster, which is assumed equal to that of the heat bath. Measuring k and plotting $\ln k(N,T)$ vs. $1/T$ (Arrhenius plot) yields a value for the separation energy, $D(N)$. In ideal cases, one can obtain a value for the pre-exponential factor, $A(N)$, by extrapolation.

2 Experiments

The experimental apparatus has been described previously [5]. The present experiments are performed with an improved time-of-flight spectrometer, resolving all cluster sizes up to 400. The raw time-of-flight spectra contain an intensity $I_{\mathrm{raw}} = I + I_{\mathrm{bkgr}}$ in each time slot. The background, I_{bkgr}, is assumed to be smooth, with no shell structure. After subtraction, the distribution is converted to mass units, and each peak is integrated to yield $I(N)$. A section of a time-of-flight spectrum, converted to mass units, is shown in Fig. 1.

In the present series, the mass spectra have been measured at five temperatures and at two flow rates of the He carrier gas, and are determined by adjustment of the diameter of the exit nozzle of the heat bath. The lowest temperature is room temperature, $T_{\mathrm{HB}} = 296$ K, where no detectable evaporation occurs during the 60–100 ms residence time in the heat bath. The highest temperature included in this series is 356 K. The evaporation of one atom leaves the remaining cluster colder by 30–40 K for sizes $N = 140$ to 100, i.e., there is a 10% drop in temperature. The subsequent heating by He collisions is very likely to be fast: At a typical pressure of 5 mbar and $T = 323$ K, a Na_{140} cluster collides with $\approx 5\times10^{8}$ He atoms per second; this implies that the temperature of the daughter cluster of size $N = 140$ comes within 0.4 K of the heat bath temperature in ≈ 0.15 ms, somewhat faster for the lighter clusters. This estimate is based on molecular dynamics simulations by Westergren, et al. [6] who use a Lennard–Jones potential for the exchange of energy between the cluster and the inert gas atoms. The temperature

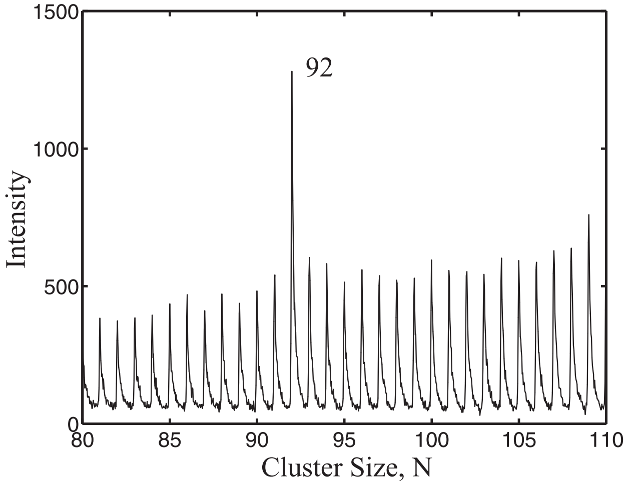

Fig. 1. Time-of-flight spectrum at $T_{\mathrm{HB}} = 328\,\mathrm{K}$ and 100 ms residence time. The mass unit is the Na atom.

$T_{\mathrm{C}}(m)$ of a cluster after m collisions with the gas atoms is

$$T_{\mathrm{C}}(m) = (T_{\mathrm{C}}(0) - T_{\mathrm{HB}}) \times \left(1 - \frac{\kappa}{3Nk_{\mathrm{B}}}\right)^m + T_{\mathrm{HB}}, \qquad (2)$$

where $T_{\mathrm{C}}(0)$ is the initial temperature of the cluster, k_{B} the Boltzman constant, and κ the energy exchange constant for sodium, approximately 31 μeV/K for the present temperature range [7]. The fast equilibration means that macroscopic thermal equilibrium with the temperature given by the macroscopically measured temperature T_{HB} is assured during essentially the entire time of residence in the heat bath.

Two experiments with nozzle sizes 1.5 and 1.9 mm in diameter are performed. The cluster residence times in the heat bath are 100 ± 20 ms and 60 ± 5 ms, respectively, allowing ample time for more than a hundred evaporations with subsequent reheating. The He flow velocity in the heat bath, and hence the residence time, is calculated both from the effective pumping speed and from the assumption of a Poiseuille flow through the nozzle; the uncertainties in the residence times reflect the deviations in the two methods. As argued in [5], the flow in the heat bath tube is laminar, and because of the small diffusivity of the clusters, we have estimated that the mean cluster velocity is 3/2 times the mean gas velocity; this means that the clusters reaching the time-of-flight section are being distributed over the central 50% area of the cross section of the heat bath tube.

The He entering the heat bath possess the temperature of the condensation chamber, $T \approx 123\,\mathrm{K}$. With an ideal gas heat diffusion constant of 0.039 m^2/s, the equilibration time upon entrance into the thermostat cylinder is estimated to be 3 ms. This corresponds to a flight path of 8 and 12 mm – out of a total of 250 mm – for the two nozzles, respectively.

The Na clusters entering the heat bath are presumably all solid. The heating of, say, Na_{139} to its melting point, $T_{\mathrm{m}} = 267\,\mathrm{K}$ [8], the transfer of 2 eV of latent heat, and the subsequent heating to within 0.5 K of the heat bath temperature of $\approx 333\,\mathrm{K}$ can be estimated to last about 0.3 ms, in which time the clusters have moved about 1 mm. From these estimates, we conclude that the effective residence time in the heat bath for evaporations at temperature equilibrium is a few milliseconds shorter than the 60 and 100 ms estimated above.

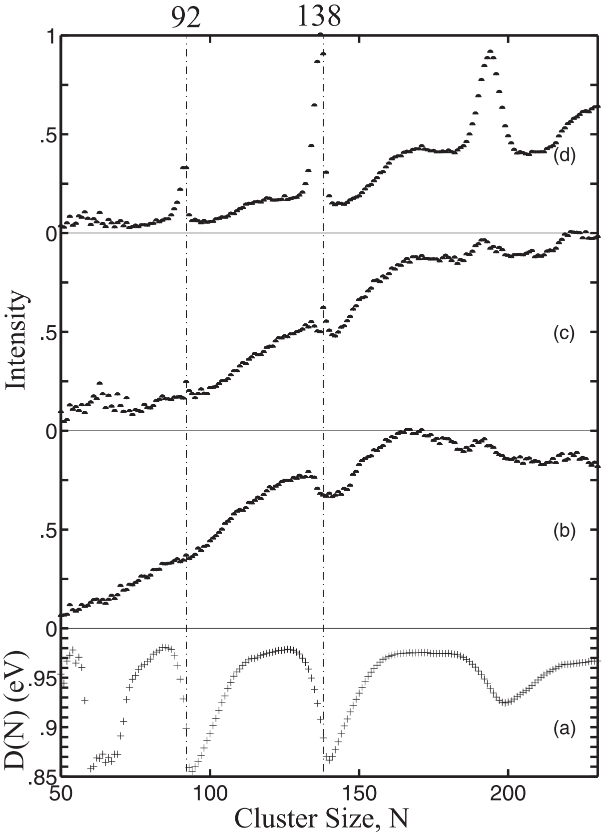

Fig. 2. (a) Separation energies $D(N)$ [4]. (b)–(d) Mass spectra I_N at 296, 316, and 356 K, respectively, for 60 ms residence time. The closed shells, $N_0 = 92$ and 138, are marked.

A sequence of mass spectra is shown in Fig. 2(b–d). The lowest temperature data shows no evaporation. (The reason for the depression around $N \approx 141$ is unknown; it is present at all temperatures and is assumed to have nothing to do with the heat bath, but rather with the formation process itself.) Figure 2(a) shows the separation energies as determined in [4], but now normalized to the more accurate average liquid drop separation energies, including not only the bulk cohesive energy, but also the surface energy, equal to 1.04 and 0.72 eV, respectively [9].

3 Analysis and results

For sufficiently low T_{HB}, there is no measurable evaporation during the time the clusters spend in the heat bath, and thus $k(N, T) \approx 0$. Raising the temperature in small steps eventually leads to a measurable evaporation from the clusters with the lowest separation energies, i.e., clusters just above a closed electronic shell configuration, N_0 (see Fig. 2(c)). At slightly higher temperature, more clusters above N_0 evaporate, all in all leading to an increase of the yield at the closed shell. At even more elevated temperatures, clusters at and below the closed shell also begin to evaporate. For not too high a temperature, the following general picture emerges:

- Evaporation only takes place over a limited range of masses around N_0.
- The summed amount of missing clusters – due to evaporations – above N_0 equals the amount of accumulated clusters at and below N_0.
- There is one cluster size, here taken as N_0+2 for specificity, whose intensity is not, or only very weakly, affected by the evaporation processes. In other words, its gain by accumulation of intensity from heavier clusters equals its loss by evaporation to the lighter ones.
- This particular cluster size is the same for all the temperatures considered. For this transitional cluster, it is feasible to extract a decay rate, because its intensity is constant, and its number of decays during the residence time in the heat bath equals the sum of accumulated clusters below N_0+2 (or missing ones above N_0+2).

The experiment only samples the intensities at one instant, namely after the exit from the heat bath and subsequent cooling. Simulations of decay chains using (1) with $D(N)$ values taken from Fig. 2(a) indeed show that the intensity of the mass peaks in general changes during the time of residence in the heat bath, but they also show that the N_0+2 intensity stays almost constant and that the general picture presented above holds [10].

A plot of the experimental decay rates $k(N,T)$ versus $1/T$ (Fig. 3) exhibits the linear trend expected from the Arrhenius law (1). However, the accuracy of the present results is insufficient to determine both the pre-exponential factor $A(N)$ and the $D(N)$ values at the same time. In this situation, we determine the pre-exponential factor from theory. For the rate, we adopt a classical expression from the kinetic theory [11],

$$k(N,T)=\frac{a}{4}\frac{\bar{\nu}}{k_{\mathrm{B}}T}(P_{\mathrm{sat}}-P_{\mathrm{vap}}), \tag{3}$$

where a is the area of the cluster surface, $\bar{\nu}=(8k_{\mathrm{B}}T/\pi m)^{1/2}$ the mean velocity of the atoms with mass m, and P_{sat} the saturated vapour pressure of the solid at the corresponding temperature. P_{vap} is the actual vapour pressure, which can be neglected here, equivalent to no recondensation in the tube. For P_{sat}, we use a set of bulk-value data [12], which are well approximated by the function

$$P_{\mathrm{sat}}(\mathrm{Pa})=4.7516\times10^{9}\times\exp(-12423.3/T(\mathrm{K})). \tag{4}$$

From (4), we determine the pre-exponential factor in (3), whereas for the exponent, we take the size-sensitive part, $-D(N)/k_{\mathrm{B}}T$ as in (1) and get

$$k(N,T)=1.44\times10^{15}\frac{N^{2/3}}{\sqrt{T}}\exp\Big(-\frac{D(N)}{k_{\mathrm{B}}T}\Big) \tag{5}$$

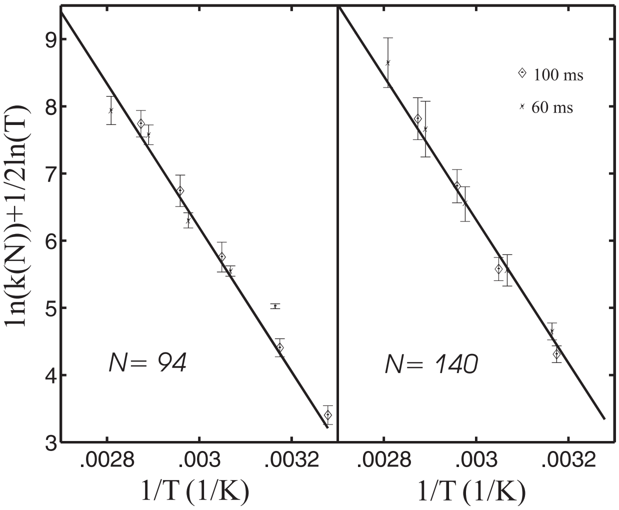

Fig. 3. Arrhenius plot (5) for two cluster sizes, $N=94$ and 140. Residence times are indicated.

(the temperature is in Kelvin). Figure 3 shows $\ln k(N)+1/2\ln T$ vs. $1/T$ for the limited temperature interval of just 53 degrees: For higher T_{HB}, the decay rate becomes too high, meaning that the clusters may not reach T_{HB} between individual evaporations [10], whereas in the temperature region considered, we can assume $T=T_{\mathrm{HB}}$.

The slopes of the lines fitted via (5) convert to $D(94)=0.910\,\mathrm{eV}$ and $D(140)=0.915\,\mathrm{eV}$. The error is here only $\approx0.2\%$, thanks to the approach taken by using (5). The two values are, however, both $\approx0.05\,\mathrm{eV}$ too high compared to the values of Fig. 2(a), a deviation far too big to be accounted for by the uncertainty in the residence time (see Sect. 2). Fits of (1) to the points of Fig. 3 alone give $D(94)=0.86\pm0.04\,\mathrm{eV}$ and $D(140)=1.03\pm0.05\,\mathrm{eV}$, reflecting, among other things, the rather large uncertainties in the present experiments.

4 Discussion

An uncertainty in T_{HB} has a strong influence on the determination of the separation energy; we estimate ΔT_{HB} to be ±3 degrees, or 1%. Since the experiments described above, the temperature control of the heat bath has been improved and is now accurate to within ±1 degree. As a consequence, it should be possible to obtain separation energies with an accuracy of 0.01 eV.

The pre-exponential factor in (5) is several orders of magnitude larger than the one used in [5]. We believe the present approach for evaluating the numerical value is preferable, since it is based upon states of macroscopic equilibrium for obtaining the vapour pressure curves, i.e., (4). This point is discussed in detail by Hansen [13].

In summary, it has been shown that evaporation measurements in a temperature-controlled environment can be performed over a temperature range, and for a considerable length of time. It should be pointed out that the data presented here are in principle absolute determinations of

$D(N,T)$, with the macroscopic thermometers providing the energy unit.

The authors are much obliged to Sven Bjørnholm for his always stimulating and inspiring contributions. They thank Jørgen Schou, of the Risø National Laboratory for lending us his N_2 laser during the initial stages of the experiments. O.E. wishes to thank the Danish National Bank for accommodation during his sabbatical. This work has been supported by the Danish Natural Science Research Council through the research center ACAP, with a grant to K.H., and by the European Commission, Grant No. CHRX-CT94-0612.

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