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FROM ABUNDANCE SPECTRA TO CLUSTER ENERGIES

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We derive a simple but accurate relation between evaporative activation energies and abundances in ensembles of large, hot clusters. The relation is compared with simulated abundance spectra.

Evaporative processes are frequently used as a tool to probe the internal structure of clusters. These studies allow one to obtain information about both thermal and energetic quantities. This work is concerned with the problem of extracting information from abundances in the special but experimentally easily realized situation of an ensemble of large and evaporatively hot clusters. In an ensemble of this type, the abundances will reflect activation (separation) energies. The connection is unambiguous as far as local variations in the relative separation energies are concerned. Knowing the relation, it is possible to invert abundance spectra to obtain the relative separation energies. These in turn, combined with a reasonable parametrization of the scale, essentially amount to a complete knowledge of the individual cluster energies.[1] The results here are developed for application to the electronic shell structure in metal clusters,[2] but are by no means restricted to these systems.

The scenario is as follows: (i) the clusters are initially hot and cool only by evaporation (hot means that their initial temperature must be more than 10–20% higher than the final),[4] (ii) the abundance distribution is broad. It is only possible to find variations in the separation energy which occurs over a size range small compared to the width of the envelope of the abundance distribution; (iii) the evaporation rate should be reasonably close to the Arrhenius-like expression, $k_N = \omega N^{2/3} \exp(-D_N/T)$, where we have included a surface term, and the temperature is defined as the mean excitation energy per degree of freedom. The separation energy, D_N, will be identified with the evaporation activation energy. The phrase "reasonably close" includes, for example, phase-space theories based on the harmonic approximation for the level densities.[5] Furthermore, we will only treat the case of large clusters for which the distribution of internal energies is so narrow that we can consider the temperature a delta function.[4] We will restrict the treatment to systems where the relative variation in separation energies is sufficiently small. The formulation of the solution allows us to relax the last restriction, but will stick to the simplest case. These restrictions are stated quantitatively below. In spite of all these qualifying remarks, we believe that the theory will cover a major part of the systems that are actually encountered experimentally.

The requirement that clusters cool only by evaporation imposes severe constraints on the possible shapes of the abundance spectra. The temperature and the evaporation rate of a given size is determined in principle by all preceeding evaporation rates. The temperature is determined simply by requiring that all the previous average decay times sum up to give the observation time:

$$t = \sum_{i=N}^{\infty} k_i^{-1} . \qquad (1)$$

Given the separation energies, i.e. the temperature decrease for each evaporation, this equation relates in an average way the final temperature, T_N to t. Equivalently the final rate constant is determined.

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Not all the preceeding decays are equally important. Some happen very fast, either because the cluster is very hot or because the separation energy is very low. The restriction on small separation-energy variations can be formulated quantitatively as

$$\frac{D_{N+1}-D_N}{D_N} \ll \frac{D}{3NT}\,. \tag{2}$$

The ratio $D/T \approx 25$ is the ratio of separation energy to temperature in the absence of any shell structure. Then the only important contributions to the sum in Eq. (1) are the ones from the immediately preceeding sizes. The number of preceeding sizes that give important contributions can be estimated by considering the case of constant separation energies, $D_N = D$, and considering the decrease in temperature for each evaporation.[4] The result is that this characteristic number is $3N(T/D)^2 \simeq N/200$. The size given by $N_\kappa \equiv (D/T)^2/3$ is the characteristic size dividing large and small in evaporative questions. Here we consider $N \geq N_\kappa$.

To perform the sum in the general case, first expand the fractions in the exponentials:

$$\frac{D_{N+1}}{T_{N+1}} \simeq \frac{D_N}{T_N} - \frac{D_N D_{N+1}}{3NT_N^2} + \frac{\Delta_1 D_N}{T_N}\,, \tag{3}$$

where $\Delta_1 D_N \equiv D_{N+1} - D_N$. Next expand the exponentials of the small quantities $\Delta_1 D_N/T_N$ to first order. Resummation of the terms involving the same $\Delta_1 D_i$'s yields

$$t \approx k_N^{-1}\frac{1}{1-q}$$
$$\times(1+q\Delta_1 D_N+q^2\Delta_1 D_{N+1}+q^3\Delta_1 D_{N+2}+\cdots)\,, \tag{4}$$

where the quantity $q \equiv \exp(-N_\kappa/N)$ is close to 1. In other words,

$$k_N = \frac{1}{t}\frac{N}{N_\kappa}\left(1+\sum_{n=N}^{\infty}\frac{\Delta_1 D_n}{T_n}\mathrm{e}^{-(n-N)N_\kappa/N}\right). \tag{5}$$

In particular for constant separation energies we have

$$\mathrm{e}^{-D/T}\left(\frac{T}{D}\right)^2 = t\omega/3N^{1/3}\,, \tag{6}$$

which is easily solved for the ratio D/T.

The k_N's must be related to the abundances in the decay chain. It was shown in Ref. 4 that in the case of constant separation energies, the width of the size distribution for a single decay chain will have a finite width, given by the mean size (and only weakly dependent on the observation time). The larger the size, the larger the absolute width. Consequently, for sizes close to the maximum of the distribution, we will have a constant turnover, similar to the situation in radioactive decay. That is, $k_N I_N$ is approximately constant (I_N is the abundance). Summing over different decay chains will improve this approximation. Since the constant turnover depends only on the width of the distribution, it will also hold when the rate constants are changed within the limit of Eq. (2).

Next we add up decay chains to account for all the different initial temperatures and sizes. By hypothesis of the initial conditions, this gives a smooth factor on the abundances, except for one modification: the density of decay chains that actually stops around a given size is proportional to the separation energy, i.e. $I_N \propto D_N$. Thus

$$\begin{aligned} I_N &\propto k_N^{-1} D_N \\ &\propto D_N\left(1+\sum_{n=N}^{\infty}\frac{\Delta_1 D_n}{T_n}\mathrm{e}^{-(n-N)N_\kappa/N}\right)^{-1} \\ &\simeq D_N\left(1-\sum_{n=N}^{\infty}\frac{\Delta_1 D_n}{T_n}\mathrm{e}^{-(n-N)N_\kappa/N}\right). \end{aligned} \tag{7}$$

Approximating T_n by $D_N T/D$ yields

$$I_N \propto D_N\left(1-\frac{D}{T}\sum_{n=N}^{\infty}\frac{\Delta_1 D_n}{D_n}\mathrm{e}^{-(n-N)N_\kappa/N}\right). \tag{8}$$

Often we are in a situation where the second difference of the separation energy with respect to the size is negligible. Then Eq. (8) can be summed to give

$$I_N \propto D_N - \frac{3NT}{D}\Delta_1 D_N\,. \tag{9}$$

This result is somewhat surprising since the highest abundance does not necessarily coincide with the most stable species. For example, with a sinusoidal varying separation energy, the two maxima are displaced by a quarter of a period. For sharper, more sawtooth-like structures, the two will tend to coincide more closely. Hence the determination of the precise location of, for example, electronic shell closings requires some numerical evaluation.

In order to verify the derived equations, we have simulated hot-cluster ensembles with different sets of separation energies as input. The simulations were performed using the analytical expression for abundances in a single decay chain,

$$k_N I_N = \sum_{j=N}^{N_0} k_j \mathrm{e}^{-k_j t} \prod_{i \neq j} \frac{k_i}{k_i - k_j} . \qquad (10)$$

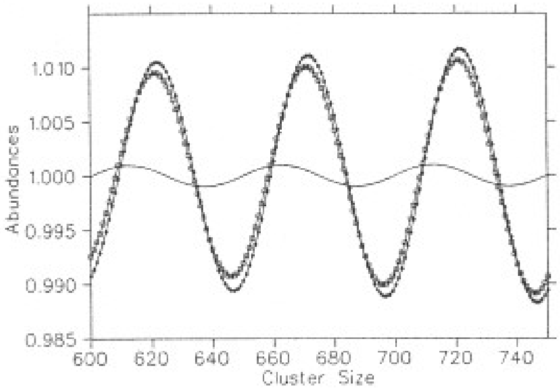

Fig. 1. The abundance spectra as simulated using Eq. (10) and calculated by Eq. (8). The separation energies plotted are sinusoidal with an amplitude of ±0.1%. The shift in phase between separation energies and abundances is clearly seen. N_κ was calculated using Eq. (6) and $N = 200$ to be 240. The parameters in the simulation were $t = 10^{-3}$ s and $\omega = 10^{13}$ s^{-1}. Squares: simulated; diamonds: calculated.

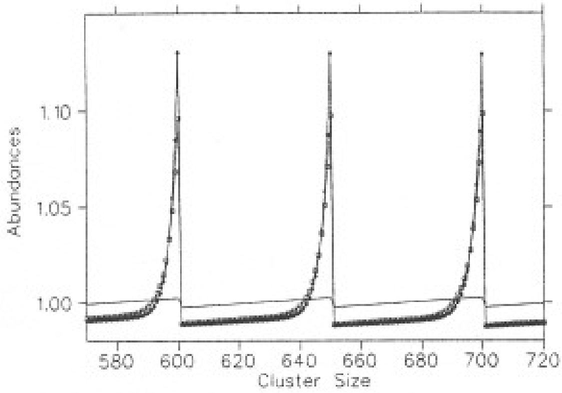

Fig. 2. Abundance spectra in the extreme case of sawtooth-like separation energies. The sawtooth amplitude is 0.5% of the total. The details of the calculations are similar to those of Fig. 1. The transient due to a sudden change in separation energy is clearly seen as a low-mass tail [see Eq. (8)]. The difference in amplitude between simulated and calculated spectra at the *magic number* is roughly one quarter.

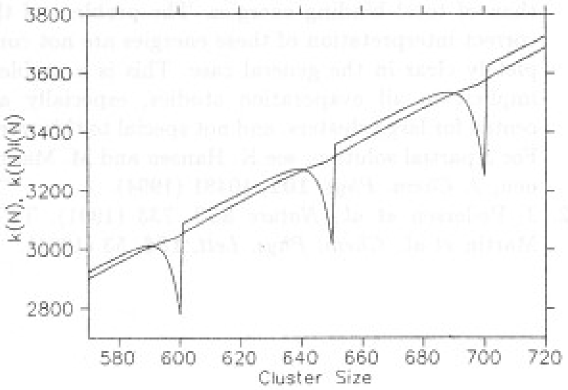

Fig. 3. The average rate constant and the product of the average rate constant and the abundances. The data are the simulated results corresponding to Fig. 2. The product $k_N T_N$ is the almost straight line, confirming the argument for a constant turnover.

Please note that the k_N's here are not average values, as used previously. Rather, the decay chain originates at $t = 0$ with the size N_0 and the temperature T_{N_0}. This determines all the rate constants in that particular chain (the kinetic energy of the fragment is ignored). For each N_0 a broad ensemble of chains with different T_0 was simulated and the resulting abundances properly summed. The abundances are shown in the Figs. 1 and 2 and compared with the ones calculated from Eq. (8). In Fig. 3 the relation $k_N I_N \approx$ *constant* is demonstrated.

In conclusion, we have derived a relation between evaporative activation energies and abundances in an ensemble of large, hot clusters. The relation is simple and greatly facilitates the problem of finding systematic trends in the energies of the homologous series of large clusters. It is possible to use simple evaporative spectra to locate the particularly stable species. This is a nontrivial problem for large clusters. In particular, we see that local maxima in abundances do not necessarily coincide with the locally most stable species. With a reasonable assumption about the mean separation energy as a scale parameter, it is possible to find the magnitude of the local variations in separation energy. The theory is susceptible to improvements, whether the reason is the desire to have higher precision or to treat more extreme cases.

References

1. For completeness we should add that these energies should be understood in terms of free energies rather

than of total binding energies. The problem of the correct interpretation of these energies are not completely clear in the general case. This is a problem implicit in all evaporation studies, especially accented for large clusters, and not special to this work. For a partial solution, see K. Hansen and M. Manninen, *J. Chem. Phys.* **101**, 10481 (1994).

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