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International Journal of Mass Spectrometry 233 (2004) 215–221

International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

# Do we know the value of the Gspann parameter?

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Received 15 October 2003; accepted 21 December 2003

## Abstract

We reanalyze some of the data used by Klots to establish an experimental basis for the claim by Gspann that clusters have a highest temperature in molecular beams. The value of this temperature is given by the evaporative activation energy and a dimensionless parameter called the Gspann parameter. The value of the Gspann parameter we derive from the data is higher than the value found by Klots, and is consistent with the predictions from detailed balance theory, although a number of uncertainties persist. More recent data on oxygen clusters are analyzed with the same methods and the model dependent uncertainties are shown to be fairly large.

*Keywords:* Cluster beams; Gspann parameter; Kinetic energy release

## 1. Introduction

The idea that a cluster in a molecular beam possesses a highest temperature has proven to be a very useful approach in the analysis of cluster abundance spectra. The idea is simple and based on a strong separation of timescales, from the very high frequency factor characterizing unimolecular decays, to the typical flight times in a molecular beam experiment [1,2]. The difference between the two timescales can easily amount to 10 orders of magnitude or more. This separation of timescales means that the average amount of energy per degree of freedom in the cluster or, loosely speaking, the temperature is low compared with the smallest activation energy of any of the possible decay channels of the cluster. It also means, and this is the salient point, that even a small increase of the internal excitation energy will increase the decay rate constants dramatically. A 10% increase of the excitation energy leads to an increase in the rate constant with a factor somewhere between 10 and 20. This strong dependence of the rate constants on the excitation energy effectively divides up the clusters into the ones too hot to survive on the observational timescale, and the ones too cold to have evaporated. One consequence of this is that if the clusters have been initially hot enough to undergo at least one evaporation, there will also exist a lowest temperature for the clusters in the ensemble. This temperature is related to the highest temperature and the dissociation energy of the precursor. This concept has provided a simple way to relate relative abundances to relative changes in evaporative activation energy [3,4]. The strong energy dependence is also the root of the non-exponential decay one observes in ensembles with even a very modest spread in excitation energy. In the simplest case the measured decay rate has a $1/t$ profile [5]. Another and very important consequence is that evaporative processes which occur in molecular beams happen from clusters with very similar excitation energies. This kind of 'natural selection' of a certain, but unknown energy opens the door to a determination of the temperature of the cluster since the temperature determines the mean value of the kinetic energy release. Potentially it will also allow a determination of the activation energy of the dominant decay channel, since the activation energy is proportional to the effective temperature of the cluster. The constant of proportionality is essentially the natural logarithm of the product of the evaporative frequency factor and the observation time, and is called the Gspann parameter, $G$.

This parameter can be determined in either of two ways. One may calculate the evaporation rate constant theoretically and use this together with the experimental measurement time to find $G$. This requires that one is able to calculate rate constants, which seems to be a less than trivial task as judged by the numerous different theories available in the literature.

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doi:10.1016/j.ijms.2003.12.021

Alternatively one may base the determination on experimental data, which is at first sight a more appealing approach. However, it requires independent knowledge of one or more dissociation energies and of the temperature of the clusters. The latter can in principle be found from kinetic energy release measurements but that requires separate knowledge about the relation between temperature and kinetic energy release. Although conceptually useful, the value of the Gspann parameter is thus intrinsically difficult to determine. The difficulties in establishing the dissociation energy for the well-studied $C_{60}$ molecule is one demonstration of this [6–8]. Different assumptions concerning either the Gspann parameter or, equivalently, the dissociation rate constant, have produced values for the activation energy that cover more than a factor of two, often with very small stated uncertainties.

Using measured kinetic energy releases and estimated dissociation energies was one of two different means chosen by Klots [9] where the experimental verification of Gspann's prediction was established. The other was a comparison with different experimental temperature determinations. We do not feel qualified to comment on these values, and will concentrate on the interpretation of the kinetic energy releases provided by Stace on Ar [10]. We will also analyze more recent data, on $(O_2)_N^+$ clusters by the Innsbruck group [11].

The determination of $G = 1/0.04$ in reference [9] was later modified slightly downwards to $23.5 \pm 1$ and that value was suggested to be a universal number, provided it referred to a 10 μs experimental timescale. This value has later been used in a large number of studies. Some studies have shown different values, both larger and smaller. Given the importance and widespread use of $G$ to convert experimental data into cluster binding energies it is therefore of great importance to estimate how well we know the value.

The argon data reanalyzed here originally gave a value of $G = 16$, inconsistent with the postulated universal value of 23.5. The reanalysis will give a higher value, although the size—average of the best fit is still below 23.5. The increase in the best estimated value is consistent with the experience from the fullerenes [6–8] for which the number has risen to a value exceeding 30 with time.

The purpose of this contribution is to examine critically the conclusions which can be derived from the data [10,11], and to quantify the effect of an increasing sophistication in the statistical description of the decay. The results will be compared with the predictions of detailed balance theory.

## 2. Reanalysis

The procedure used to fit $G$ in reference [9] was to apply the relation:

$$\mathrm{KER} = \bar{\varepsilon} = cT = c\frac{D}{G} \tag{1}$$

We set $k_B$ to one throughout this work. Consistent with the original analysis we will initially not distinguish between the parent, daughter and effective emission temperatures. This ignores the so-called finite heat bath correction. More about this below. This aside, the relation nevertheless still raises two questions which were not addressed at the time, viz. the values of $c$ and the dissociation energy, $D$. The latter was calculated using the liquid drop model. We note that later use of a $G$ value determined this way to find dissociation energies from e.g., kinetic energy releases obviously depends on the quality of the guess for the initial values of the dissociation energies. The present analysis comes with the same caveat.

The value of $c$ was explicitly assumed to be 1. The justification for this is not clear. The bulk value is 2, which is easily understood as a contribution of 3/2 from the mean kinetic energy of an ideal gas, plus a contribution of 1/2 from the outgoing flux which is biased by the speed ($\upsilon \propto \varepsilon^{1/2}$) [17]. This factor alone would require the value of $G$ to be doubled relative to the original estimate, i.e., $G \simeq 50$. It is clearly important to treat corrections of this magnitude carefully. It turns out that the correction is less than that, but still significant.

A final important effect is caused by the magnitude of the vibrational quantum in the clusters. The measured kinetic energy releases and the calculated temperatures approach this energy scale and this gives important corrections to the expected temperature which will therefore deviate from the naive expectation in Eq. (1).

We start the reanalysis by establishing the dissociation energies from the liquid drop parameters and the extra binding energy due to the polarizability of the cluster atoms. The liquid drop binding energy for neutral clusters is

$$-E_b(N) = AN - BN^{2/3} \tag{2}$$

where $A$ is the bulk binding energy per atom or molecule (80.5 meV for Ar, 71.3 meV for $O_2$). The values of $A$ are found from an Arrhenius plot of the vapor pressure of the solid bulk [12]. The surface tension of Ar gives $B = 44.4$ meV, and for $O_2$ the value 72.9 meV [13]. $B$ is related to the surface tension, $\sigma$, as

$$B = 4\pi\sigma r_1^2 \tag{3}$$

This gives neutral dissociation energies of

$$D_N = A - \tfrac{2}{3}BN^{-1/3} + \mathrm{O}(N^{-2/3}) \tag{4}$$

The third and higher terms are small compared with the first two and the polarization energy derived below, and we will leave them out in the following. The charging energy is calculated with the expression for a classical sphere with dielectric constant $K$. The electric field inside the sphere is

$$-\frac{\mathrm{d}V}{\mathrm{d}r} = \frac{e}{2\pi\varepsilon_0 K r^2}, \quad r \in [r'; r_N] \tag{5}$$

where $r'$ is an effective smallest radius and $r_N = r_1 N^{1/3}$ is the cluster radius. Outside the sphere the field has the vacuum value, i.e., Eq. (5) with $K = 1$. The polarization energy is

$$\begin{aligned} E_{\mathrm{pol},N} &= \frac{K\varepsilon_0}{2}\int\left(\frac{\mathrm{d}V}{\mathrm{d}r}\right)^2 \mathrm{d}^3r \\ &= \frac{1}{2}\int_{r'}^{r_N}\frac{e^2}{4\pi K\varepsilon_0 r^2}\mathrm{d}r + \frac{1}{2}\int_{r_N}^{\infty}\frac{e^2}{4\pi\varepsilon_0 r^2}\mathrm{d}r \\ &= \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{Kr'} + \frac{1}{r_N}\left(1-\frac{1}{K}\right)\right) \qquad (6) \end{aligned}$$

The contribution to the dissociation energy is then

$$\begin{aligned} D_{\mathrm{pol},N} &= -(E_{\mathrm{pol},N} - E_{\mathrm{pol},N-1}) \\ &\approx \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0}\left(1-\frac{1}{K}\right)\frac{1}{r_1}\frac{1}{3N^{4/3}} \qquad (7) \end{aligned}$$

$K$ is related to the atomic polarizability via the Clausius–Mossotti relation [14] with which $\alpha = 1.6411\,\text{Å}^3$, $r_1 = 2.07\,\text{Å}$ (Ar) and $\alpha = 1.5812\,\text{Å}^3$, $r_1 = 2.07\,\text{Å}$ ($O_2$), gives $K = 1.68$ (Ar) and $K = 1.65$ ($O_2$) and hence

$$D_{\mathrm{pol},N} = CN^{-4/3} \qquad (8)$$

with $C = 470\,\mathrm{meV}$ for Ar, and $C = 457\,\mathrm{meV}$ for $O_2$.

The total dissociation energy is then

$$D_N = A - \tfrac{2}{3}BN^{-1/3} + CN^{-4/3} \qquad (9)$$

These values obviously do not include any size-to-size variations like those caused by shell structure, etc., and will not reproduce the special features for e.g., $N = 21$ seen in the mass spectra of the Ar clusters.

As our baseline we will use these dissociation energies to calculate the value of $G$ given by Eq. (1), disregard the finite heat bath correction and set $c = 1$. The value $c = 1$ will be replaced later in the analysis by the more correct value given by Eq. (13). The result for Ar is shown in Fig. 1 as small open circles. The values fitted by Klots are also shown. For the relatively large clusters the agreement is very good, which indicates that the same bulk parameters have been used. For smaller cluster sizes the two values begin to deviate, most likely due to the difference in the polarizability contribution to the dissociation energy. Note that the smallest Ar cluster size has a very low temperature, or equivalently, a large fitted value of $G$. This is an effect of the small heat capacity of the $N = 5$ cluster, and the large difference from the mean value will disappear with the improved treatment below. For the $O_2$ clusters, the analogous fit gives very fluctuating and high values for $G$, approaching 60 for $N = 5$, 6 (open circles in Fig. 2).

The next step in the analysis is to add the finite heat bath correction for a constant heat capacity, $C_v$, which will be set equal to $3N - 7$ for Ar and $6N - 7$ for $O_2$. To leading order it consists of setting the emission temperature, $T_e$, equal to the average of the parent and daughter temperatures, $T_p$, $T_d$: $T_e = (T_p + T_d)/2$. The emission temperature is the relevant temperature for the Gspann parameter, $G \equiv D_N/T_e$. The kinetic energy release is determined by the daughter temperature, $T_d$, which is related to $T_e$ as

$$T_d = T_e - \frac{D_N}{2C_v(N)} \qquad (10)$$

Hence,

$$\bar{\varepsilon} = c\left(\frac{D_N}{G} - \frac{D_N}{2C_v(N)}\right) \qquad (11)$$

These points (with $c = 1$) are also shown in Fig. 1 (crosses, labeled ‘finite heat bath correction’); they lie below those of the baseline points without the correction, and are the lowest values found in this study. One point for $O_2$ is even negative. From Eq. (11) it is clear that the values for $G$ cannot exceed $2C_v$. This is an unphysical constraint which will be removed

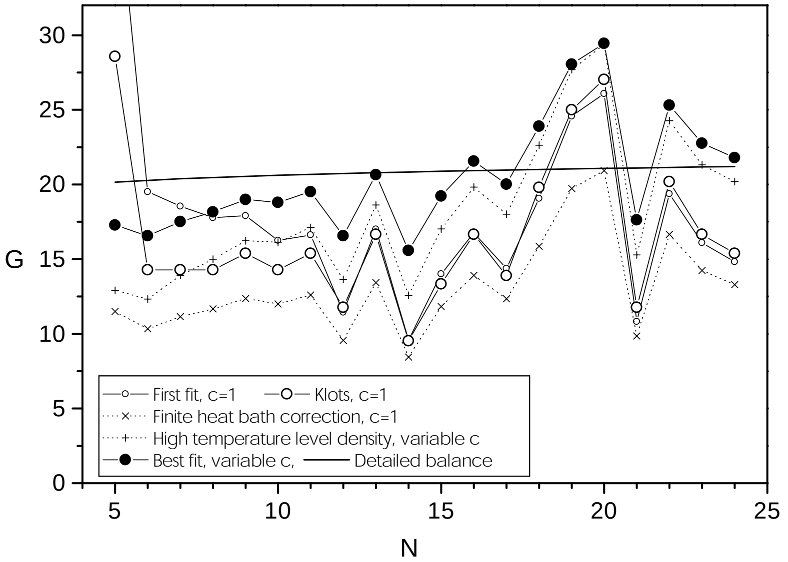

Fig. 1. Calculated values of the Gspann parameter, according to the procedure described in the main text, for $Ar_N^+$ clusters.

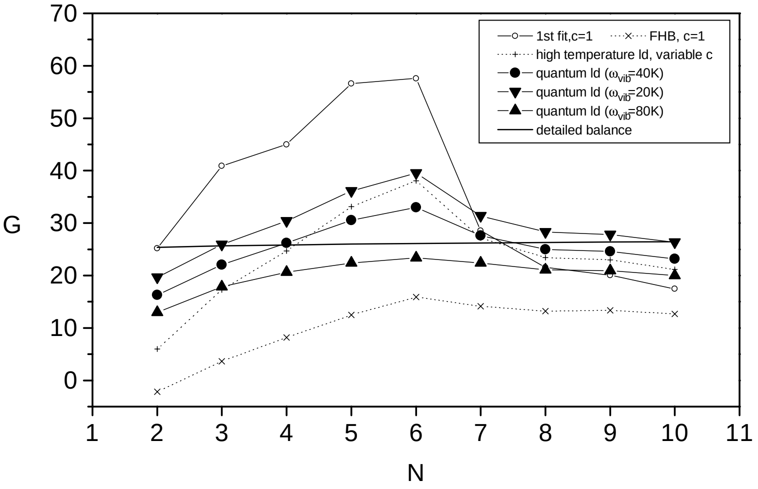

Fig. 2. Calculated values of the Gspann parameter, according to the procedure described in the main text, for $(O_2)_N^+$ clusters. The filled symbols are the values for the low energy level density which is strongly influenced by the magnitude of the vibrational energy quantum. Three different values have been used, $\hbar\omega_{vib}/k_B = 40K$, $20K$ and $80K$.

in the following when specific level densities are introduced into the calculation of the rate constants.

As the second improvement we will calculate a more realistic value of $c$ and use a more precise value of the finite heatbath correction. As mentioned previously, the dark sphere value of $c$ is 2, but the polarizability of the argon atom causes an attraction between the charged cluster and the atom of the form

$$V = -\frac{\alpha e^2}{8\pi\varepsilon_0 r^4} \tag{12}$$

This leads to an increased capture for low energy atoms and, by detailed balance, to a larger emission at those energies and thereby reduced average kinetic energy release. A calculation of the capture cross-section gives a mean kinetic energy release which can be fitted with the form

$$\bar{\varepsilon} = T_d[\tfrac{3}{2} + \tfrac{1}{2}e^{a_1 p + a_2 p^2 + a_3 p^3}] \tag{13}$$

where the dimensionless parameter $p$ is defined as the ratio of the interaction energy between the atom and the cluster at the cluster surface and the (daughter) temperature, $p = |V_0/k_B T_d|$. The value of $V_0$ is given by the polarizability interaction at the surface of the cluster and is calculated as described in reference [15] and derived in detail in reference [19]. The values of the coefficients are $a_1 = -1.892$, $a_2 = 0.311$ and $a_3 = -0.054$. They are the result of a numerical fit to the energy distributions and are independent of cluster material. Eq. (13) limits $c$ in Eq. (1) to values between 1.5 and 2 which is a serious correction to the $c = 1$ value used earlier. For most of the clusters here, both Ar and $O_2$, the value is close to 1.5, i.e., $\varepsilon \approx 1.5T_d$.

The finite heatbath correction can be calculated as an expansion in the reciprocal heat capacity. We have used only the leading order term above. As an alternative to calculating corrections, we will use the high temperature expansion of the harmonic oscillator level densities of the clusters,

$$\rho_N(E) \propto \frac{(E + E_0)^{C_v(N)-1}}{(C_v(N) - 1)!} \tag{14}$$

where $E_0$ is numerically equal to the zero point motion of the oscillators in the cluster and $C_v(N)$ is the canonical heat capacity. We will summarily set $E_0(N-1) = E_0(N) = E_0$. The use of the level density avoids the assumption of a constant heat capacity and is also not more complicated. The rate constant is given by [17]

$$k(E) = \omega\frac{\rho_{N-1}(E - D)}{\rho_N(E)} \tag{15}$$

where the frequency factor $\omega$ only varies slowly with energy and can be set to a constant.

With the chosen level density the daughter microcanonical temperature becomes

$$\begin{aligned} T_d^{-1} &= \frac{d\ln((E - E_0 - D_N)^{C_v(N-1)-1})}{dE} \\ &\Rightarrow T_d = \frac{E + E_0 - D_N}{C_v(N-1) - 1} \end{aligned} \tag{16}$$

This is the temperature we fit from the kinetic energy releases. Hence, the equation can be solved for $E + E_0 - D_N$ and $E + E_0$ and the rate constant can be calculated.

The rate constants can be written as

$$\begin{aligned} k &\approx \omega\left(\hbar\omega_v\frac{(C_v(N-1) + C_v(N) - 1)}{2}\right)^{C_v(N)-C_v(N-1)} \\ &\quad\times\frac{(E + E_0(N-1) - D_N)^{C_v(N-1)-1}}{\hbar\omega_v(E + E_0)^{C_v(N)}} \\ &= \omega\left(\frac{\hbar\omega_v(C_v(N-1) + C_v(N) - 1)/2}{E + E_0}\right)^{C_v(N)-C_v(N-1)} \\ &\quad\times\left(\frac{E + E_0(N-1) - D_N}{E + E_0}\right)^{C_v(N-1)-1} \end{aligned} \tag{17}$$

where the $((C_v(N-1)+C_v(N)-1)/2)^{C_v(N)-C_v(N-1)}$ arises as an approximation to $(C_v(N)-1)!/(C_v(N-1)-1)!$. The $\omega_v$ is the proper average vibrational frequency of the cluster. Heat capacities are measured in units of $k_B$. The frequency factor $\omega$ is a slowly varying function of energy and can, for our purpose, be set equal to a constant. Also the factor to the power $C_v(N) - C_v(N-1)$ will vary relatively slowly and can to a good approximation be set equal to a constant, since it is essentially a small power of the microcanonical temperature in units of the vibrational frequency. In fact, the variation of $\omega$ will compensate for much of the variation of this factor. It will therefore be absorbed into $\omega$. We will therefore write the rate constant as

$$k \approx \omega \left( \frac{E + E_0 - D_N}{E + E_0} \right)^{C_v(N-1)-1} \tag{18}$$

With this change in point of view, it is more meaningful to define the Gspann parameter as

$$G \equiv \ln \left( \frac{\omega}{k} \right) = \ln(\omega t) \tag{19}$$

where $k = 1/t$ is the typical rate constant at the observation time $t$. For the argon experiments this timescale was given as a few μs [10] and for the $O_2$ experiments 30–60 μs, but we do not really need this information at this point. Inserting the value of $E + E_0$ into Eq. (19) one obtains

$$G = C_v(N-1) \ln \left( \frac{(C_v(N-1)-1)T_d + D}{(C_v(N-1)-1)T_d} \right) \tag{20}$$

These values are also shown in Figs. 1 and 2 (crosses, labeled 'high temperature level density'). The Ar numbers are similar to the values in [9] for small $N$, but systematically higher for $N > 11$. The increase can be traced back to the behavior of the value of $c$. Only at small $N$ is this 50% increase partially offset by the corrections due to the finite heat bath. For the oxygen clusters, the change is significant, with values that are now close to realistic numbers, at least for some sizes.

The definition in Eq. (19) may need explanation. If we use Eq. (15) to calculate the canonical rate constant at temperature $T$ we get

$$\begin{aligned} k(T) &= \omega \int_0^\infty \frac{\rho_{N-1}(E-D)}{\rho_N(E)} \frac{\rho_N(E)}{Z_N} e^{-\beta E} \, dE \\ &= \omega \frac{Z_{N-1}}{Z_N} e^{-\beta D} \end{aligned} \tag{21}$$

where $Z_N$ is the canonical partition function for the internal degrees of freedom of cluster size $N$. A comparison of Eqs. (15) and (21) shows that the frequency factors in the two cases are identical apart from the ratio of partition functions, which is of magnitude $(T/\hbar\omega_v)^\gamma$, where $\omega_v$ is the vibrational frequency and $\gamma$ a low power. We will ignore the difference of this factor from unity. Then our definition of $G$ is identical to Klots' definition in terms of the so-called isokinetic temperature.

The final improvement we will make here is to replace the Kassel level density of Eq. (17) with a function which better handles small excitation energies. To get this better approximation, we need to know the vibrational frequencies of the cluster. The vibrational frequency of the neutral argon dimer can be found from the Lennard–Jones potential:

$$U(r) = 4\varepsilon_{LJ} \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right) \tag{22}$$

and the two parameters $\varepsilon_{LJ} = 119.4K$ and $\sigma = 3.4$ Å [18], which gives a value of $\omega_v = 37.9K/\hbar$. This will be an overestimate of the vibrational frequency of the average frequency of a neutral cluster. On the other hand it is likely to underestimate the frequency for a charged cluster because the added attraction will pull the atoms closer to the charge and into the more highly curved $r^{-12}$ part of the potential. For simplicity we will simply set all vibrational frequencies to the same value. For Ar it will be the dimer value, and for oxygen we will use three different values for illustration, $20K/\hbar$, $40K/\hbar$ and $80K/\hbar$.

This allows an explicit evaluation of the vibrational level density. If we express all energies in units of $\hbar\omega_v$ the problem reduces to the combinatoric question of how many ways $\varepsilon \in Z_+$ indistinguishable units can be distributed in $n$ boxes. The answer is

$$\rho(\varepsilon; n) = \frac{(\varepsilon + n - 1)!}{(n-1)!\varepsilon!} \tag{23}$$

One can calculate the daughter temperature with this level density with a logarithmic derivative defined as the finite difference;

$$\frac{\hbar\omega_v}{T_d} = \ln(\rho(\varepsilon; n)) - \ln(\rho(\varepsilon - 1; n)) \tag{24}$$

With the identifications $\varepsilon\hbar\omega_v = E - D_N$ and

$$n(N; \text{Ar}) = 3N - 9 \quad \text{and} \quad n(N, O_2) = 6N - 12 \tag{25}$$

one has

$$\frac{\hbar\omega_v}{T_d} = \ln \left( \frac{E - D_N + (n-1)\hbar\omega_v}{E - D_N} \right) \tag{26}$$

where the remaining energy units have been reintroduced. This is easily solved for the energy:

$$E - D_N = \frac{(n-1)\hbar\omega_v}{e^{\hbar\omega_v/T_d} - 1} \tag{27}$$

This relation is more interesting than suggested by the ease with which it was derived. It relates the energy of a microcanonical system with non-constant heat capacity to the microcanonical temperature. The relation is identical to the canonical relation, apart from the fact that there is one less oscillator here compared to the canonical system at the temperature $T_d$, and it has the well known form of the thermal energy of a collection of harmonic oscillators. All that is required to derive the relation is that the total excitation energy is large compared with the quantum energy of vibration. At high temperatures it reduces correctly to Eq. (16).

Once the value of $E - D$ is found from the values of $T_\mathrm{d}$ fitted with Eq. (13), the rate constant is calculated as

$$k = \omega \frac{(E - D_N/\hbar\omega_v + n(N-1) - 1)!(n(N) - 1)!(E/\hbar\omega_v)!}{(E/\hbar\omega_v + n(N) - 1)!(n(N-1) - 1)!(E - D_N/\hbar\omega_v)!} \tag{28}$$

where the number of oscillators of cluster size $N$, $n(N)$, are given in Eq. (25) for the two different types of clusters. For non-integer values of the factorial we use the gamma function, for which simple and precise numerical approximations exist [16]. The value of $G$ is then found by application of Eq. (19) with the relevant flight times of the ions. The results are shown in Figs. 1 and 2 (filled symbols). There is a general increase in the fitted value of $G$, strongest for the smallest clusters, relative to the previous fit which used the high energy level density. The difference to the values fitted by Klots for Ar is an average of 4.5 ($N = 5$ excluded). There is an increasing trend in the fitted values with size for these clusters. This may either be due to a problem with the parametrization of the binding energies, or be an effect of higher vibrational frequencies for the smaller clusters. Atoms in small clusters will on the average be closer to the charge and therefore feel a stronger electric field than those in larger clusters. This is likely to produce higher vibrational frequencies, as discussed briefly above. This would cause the low energy corrections in the level density to be more severe for small clusters and hence to increase the fitted $G$. For the oxygen clusters there is an increase from $N = 2$ to a maximum at $N = 6$ after which the fitted $G$ levels off somewhere between 20 and 30. This non-constant value may be due to geometric effects in the packing of the molecules and the resulting variation in the dissociation energy.

The figures also include the prediction from detailed balance, shown as a line. In this theory the frequency factor is given approximately as [17]

$$\omega = \frac{gm}{\pi^2\hbar^3}\frac{T_\mathrm{d}}{B_\mathrm{rot}}\int_0^\infty \sigma(\varepsilon)\varepsilon\, \mathrm{e}^{-\varepsilon/T_\mathrm{d}}\,\mathrm{d}\varepsilon \tag{29}$$

where $g$ is the atomic degeneracy and $m$ is the reduced mass. To a sufficient precision one can calculate the logarithm of this factor by setting the integral equal to the product of the geometric cross-section, $\sigma_\mathrm{geo} = \pi r_1^2 N^{2/3}$ and $T_\mathrm{d}^2$. For simplicity we set to $T_\mathrm{d} = 5\,\mathrm{meV}/1.6$ for Ar and to $T_\mathrm{d} = 3\,\mathrm{meV}/1.5$ for $O_2$. The frequency factors for the oxygen clusters also include the rotational contribution, given by the rotational partition function of the small fragment. This is not included for the Ar clusters i.e. the factor $\mathrm{T_d/B_{rot}}$ is absent for Ar clusters. The size dependence of the cross-section gives a weak size dependence of $G$, but the value is essentially constant, as expected. For Ar the mean value is 20.8, which should be compared with the 20.6 of the analysis presented here, and the 16.1 found by Klots. For $O_2$ the theoretical mean is 26.0, whereas the experimental values fit to an average of 20.2 ($\hbar\omega_\mathrm{vib} = 80K$), 25.4 ($40K$) and 29.4 ($20K$).

## 3. Conclusion

The value of the Gspann parameter one can extract from experimental data on kinetic energy releases depends crucially on a number of assumptions about the clusters. Two of the most important factors are the treatment of the kinetic energy release and the parametrization of the level density of the clusters. The kinetic energy release is likely to be higher than was originally anticipated by Klots, by a factor which amounts to 1.5 in the cases analyzed here, which as a first estimate increases the expected value of the Gspann parameter by the same factor. The other critical point, the level densities, is much more uncertain but plays an equally important part numerically. For the $O_2$ clusters, the difference in the fitted value of $G$ between a vibrational frequency of $20K$ and $80K$ was 9. Although the calculation here was somewhat schematic, it does not seem possible to rule out systematic uncertainties of this magnitude without a very good knowledge of the system. For Ar we found that the best estimate increased $G$ by 4.5. The overall value was found to be in good agreement with the one predicted from detailed balance theory.

Other studies, on sodium clusters [20,21], and fullerenes have indicated that the value of $G$ for these systems is higher than the otherwise generally accepted value of 23.5. For these systems the uncertainty in the level density is strongly reduced because they fragment at temperatures well above the vibrational energy quantum. The analysis of the two examples here shows that the sodium and fullerene cases are not necessarily exceptions, but that one should treat the canonical value of $G$ as a more provisional number. In particular the development of the correct understanding of the fragmentation dynamics of fullerenes during the last decade illustrates the danger of preconceived notions in this field.

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