

Radiative cooling of fullerenes

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We have measured the metastable fragmentation of fullerene ions in molecular beams. The rates are significantly smaller than the evaporative ensemble prediction, consistent with an alternative cooling mechanism through emission of electromagnetic radiation. Modeling the competition between radiative and evaporative cooling yields information about the evaporative activation energy and emissivity of the carbon clusters. © 1996 American Institute of Physics. [S0021-9606(96)02011-9]

INTRODUCTION

After the discovery of fullerenes in molecular beams and, in particular, of methods to mass produce these molecules, much effort has been devoted to determining their binding energies. A major tool in this effort has been experiments involving unimolecular fragmentation (see, e.g., Refs. 1–3). The data from experiments of this kind are frequently interpreted in terms of the energies of the involved molecules, applying the powerful theoretical results derived from the so-called evaporative ensemble. These theoretical results include, e.g., relations between relative abundances, evaporation probabilities, and internal energies as measured by kinetic energy releases. In the ideal case, measurement of one set of these quantities should yield predictions for another.

Obviously, studies of this type must be based on diverse assumptions about the state of the molecules, the transition state for the unimolecular reaction and, in general, about the ensemble of evaporating molecules. An essential assumption for the theoretical work and the analysis of experimental data along these lines has been that the molecules cool only by evaporation.

Recently, however, it was realized that radiative energy loss is in fact both observable and important under conditions similar to the ones that prevail in typical mass spectrometric devices.^{4,5} This has, furthermore, been shown not only for fullerenes but also for refractory metals.⁶ Before these investigations, radiative cooling was considered in the context of thermionic emission from metal clusters where it was, however, found to be of secondary importance,⁷ and in Ref. 8 where it was considered in relation to breakdown graphs for C_2 loss from C_{60} .

In the presence of such a cooling channel that may compete significantly with evaporation we can expect a modification of the behavior of the evaporative ensemble. In particular, the energies extracted from experiments must be estimated differently. We present evidence here that the radiative corrections are indeed important. The data can be modeled in a simple but satisfactory way and the model allows us to extract an estimate of the emissivity for the fragments of size $N=38-58$. The value is significantly smaller than one. With some caution it also yields the evaporative activation energies.

EXPERIMENTAL PROCEDURE

The quantity measured in these experiments was the evaporation probability of hot fullerene ions during the free flight part of a TOF mass spectrometer. The quantity varied was the delay between ionization by a UV laser pulse and the acceleration through the TOF extraction stage. Since the ionizing laser also serves to heat the molecules, the delay between heating and acceleration defines a cooling time for the hot molecules. We thus measure the fragmentation probability vs cooling time.

The fullerenes were a homemade mixture of mainly C_{60} and some C_{70} with no more than traces of higher fullerenes. The fullerene source and the mass spectrometer used in these experiments were identical to the ones in Ref. 10 to which the reader is referred for details. Here we just mention that the source is a resistively heated oven from which the fullerenes emerge with thermal velocity towards the ionization and acceleration region. The ions were extracted perpendicular to the neutral beam. The variation in cooling time was achieved by switching on the pulsed extraction field at varying delays after the laser pulse. The laser pulse was a 10–20 ns long pulse from an excimer laser of wavelength 308 nm. The pulse energy entering the ionization chamber was on the order of a few mJ.

After delay and acceleration through two electric fields of different but comparable magnitude (Wiley–MacLaren setup) the ions flew for about 50–100 μ s in the field free region of the TOF after which they entered the two-field reflectron. By a standard procedure it was possible to adjust the reflectron fields to separate the flight times for the molecules that fragmented during free flight from the ones that did not. After exiting the reflectron the ions flew freely towards the MCP detector for a few tens of microseconds.

There are a number of possible instrumental artefacts which could lead to inaccuracies in the measurement of the fragment probability.⁹ In order to make sure that the observed fragmentation probability represented the true value, we subjected the ion beam to several tests. The reflectron voltage was changed, moving the metastable peak from a position close to the prompt peak to a position close to the parent peak. The ratio of the intensities of the metastable peak and the prompt peak should be invariant under such a transformation. This was found to be true to within less than

1.5%. Including the statistical uncertainties, this was the largest source of uncertainties.

Potentially the fragment ion beam and the parent beam have a different divergence, caused by e.g. the kinetic energy release during evaporation. Disregarding such a difference would of course lead to a misrepresentation of the true evaporation probability. It would also mean that the metastable to prompt peak intensities would depend on the part of the beam that was probed by the detector. It was possible to observe whether this was actually the case by changing the angle between the reflectron axis and the beam axis. We recorded the ratio at four different angular positions, corresponding to the displacements in the horizontal and the vertical planes, respectively, that yielded an intensity of half the maximum. The averages of the ratios from these four (symmetrically located) spectra agreed well with the ones observed for the maximum intensity position, thus ruling out dilution effects of the above type.

As a supplementary control, the focal point of the laser beam was changed along a direction perpendicular to the extraction field and along the direction defined by the expansion from the source. Whereas intensities varied, ratios were unchanged.

The probabilities were found to be reproducible from day to day and the conclusion was that we did indeed measure the absolute magnitude of the fragmentation probabilities of the ions created in the acceleration region.

The measurements were performed with a laser fluence adjusted to be within two extreme limits, namely those of no fragmentation and that of complete depletion of C_{60} . Well within these limits the fragmentation probabilities were independent of the fluence. The fluence-independence as well as the independence of pulse duration and wavelength of the exciting laser was previously observed in Ref. 10. It strongly indicates a situation where the fragmentation process is decoupled from the creation of the excited species, i.e., a statistical fragmentation. The results are presented and discussed in this light.

RESULTS

Within the very broad fluence limits mentioned, the fragmentation probability was found to depend only on the delay between ionization and switching on of the extraction fields, and on the magnitude of the extraction fields. The (nominal) delay was varied from zero to twenty microseconds, the upper limit dictated by the decrease in signal. The magnitude of the extraction fields was changed by a factor of 2, the range limited by intensity considerations and electronics. In the region $N \geq 30$ the only appreciable metastable fragmentation occurred via the dimer channel, although indications of loss of four carbon atoms during the free flight was discernible under some conditions. It was not possible to distinguish between two sequential C_2 losses and one C_4 loss. The magnitude of the signal considered, however, we will refer all evaporation to the single dimer process.

By modifying the switching procedure for the acceleration fields it was possible to measure the amount of ions

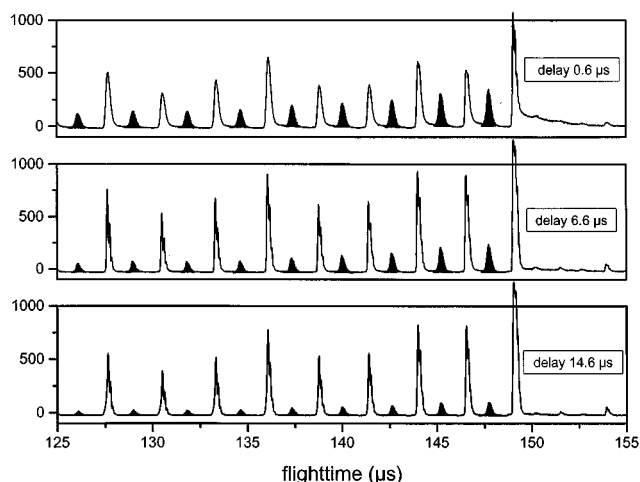


FIG. 1. Time-of-flight spectra for a nominal extraction delay of 0.6, 6.6, and 14.6 μs . The metastable fragment peaks are located between the prompt fragments of the same mass and the parent peaks and have been shaded black. The last prominent peak just below $t = 150 \mu\text{s}$ is C_{60} .

produced by delayed ionization.¹¹ Below $N = 60$ it was found to be small. This is confirmed by the very nearly symmetric peakshape observed when the reflectron was adjusted to the optimal resolution mode and the extraction field was pulsed on without delay. Only C_{60} (and the higher fullerenes present in the soot) display the long time tail characteristic for delayed ionization. In other words, for $N < 60$ statistical (thermal) ionization is essentially completed before the metastable fragmentation is measured. In the following we will only consider the species $36 < N < 58$.

Spectra pertaining to different delays are shown in Fig. 1. The decrease of the metastable peaks with increasing cooling time is clearly visible. At closer inspection one can also see an amount of signal connecting the prompt peak and the metastable peak, most clearly observed for the largest molecules at the shortest delay. This asymmetry is caused by fragmentation during extraction. Not surprisingly, it is more pronounced for short delays. In order to estimate the peak intensities correctly it was necessary to determine the background signal as well as to define a dividing line between the fragment and prompt peaks. The first objective was accomplished by a linear interpolation between the local minima in the spectra between the parent and the metastable peak. The dividing line between prompt and metastable fragment peak was defined as the location of the local minimum between these two peaks. This choice has the virtue that it cancels most of the systematic uncertainty related to the finite width of the peaks from the peak integration. These widths are largest for the shortest delay times, indicating that they are not the result of a spread in the starting position of the ions, but rather due to the spread in energy caused by the initially very rapid fragmentation. The minimum was located at 0.6 times the distance between the peaks and this value was then adopted as the universal dividing point. The peak intensities then followed from a simple numerical integration of the spectra.

The procedure simultaneously fixed the fraction of the

acceleration time that should be considered delay time. The proper delay time is composed of two parts. One is simply the nominal delay between the laser pulse and the switching of the fields. The other is determined by the point during acceleration where mass separation takes place. The TOF parameters used resulted in a linear relation between the geometrical position of a metastable fragmentation during acceleration and the arrival time at the detector, i.e., of the position in the spectrum. Conversely, choosing a dividing line between parent and metastable fragment when integrating peaks then determines a point and hence a time before which the ions are considered not to be accelerated and after which they are accelerated. As an example, this time amounts to 4.2 μs for C_{60} at an acceleration energy of 1.7 keV. In this connection, we want to emphasize that the inclusion of this time is not responsible for the conclusions drawn below concerning the validity of the standard evaporative ensemble description of the experiment, although it will of course be relevant for the precise numbers and relations. In fact, the reduction in evaporation probability will be much more pronounced if it is left out. Actually, the choice of 0.6 represents most of the time spent in the electric field. We beg the reader to understand that the arbitrariness in the definition of the dividing point does not cause a systematic uncertainty: Another choice will simultaneously yield other peak integrals *as well as* another acceleration time. Thus in principle many more points than plotted are available from the spectra. We have, however, restricted the use of these to a single point, namely the one with the smallest systematic uncertainty, as described above. It should also be clear from these remarks that the uncertainty in the acceleration time can be ignored since it will be determined by the digital resolution of the acquisition system. The uncertainties in the other relevant time, i.e., the time between the laser pulse and entry into the reflectron, is less certain in absolute terms. The (systematic) uncertainty corresponds to the passage time through the strong braking field in the reflectron. This value is however still of the order of one percent. The uncertainties that are obviously always present are predominantly connected with the peak intensities and not the times.

An example of the fragmentation probabilities thus determined is shown in Fig. 2 vs the switching delay for $N=50$ and $N=54$. They are chosen since they represent the two extreme curves in this mass region. The delay time is the electronically preset value for the switching times (corrected for a 0.55 μs electronic offset). Also shown is the evaporative ensemble prediction using the relative activation energies cited in Ref. 12 and the expression for the probability from Ref. 2;

$$P = 1 - (\alpha' W'_N)^{-1} \log\{1 + [\exp(\alpha' W'_N) - 1] t_1/t_2\}, \quad (1)$$

where P is the fragmentation probability, t_1 is the proper delay before mass selection, t_2 the total time from laser heating until entry into the reflectron. The size dependent constants $\alpha' W'_N$ are essentially equal to $G^2/C_{v,N} + G(D_N - D_{N+2})/D_N$, where the D_N 's are the evaporative activation energies, $C_{v,N}$ the heat capacities, and G the Gspann parameter for which the value of 23.5 was used.²

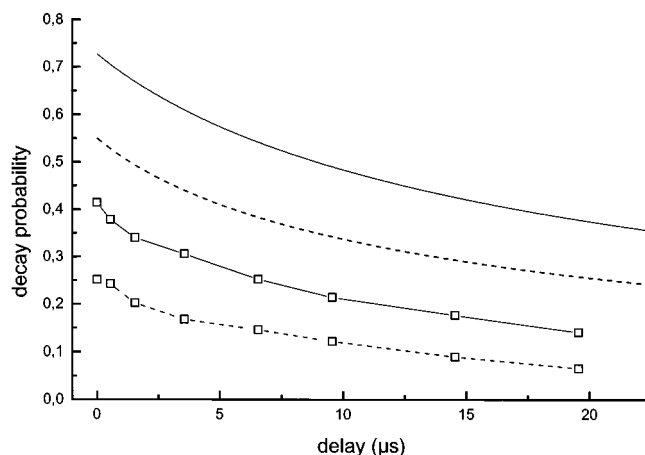


FIG. 2. Probabilities for metastable fragmentation occurring during free flight for parent sizes $N=50$ and $N=54$. The full and the dotted line refers to $N=54$ and 50 , respectively. The curves without symbols are the calculated probabilities using the evaporative ensemble model with standard parameters not accounting for additional cooling mechanisms. (See the main text for the source of these parameters.)

The formula can only be safely applied for species that have undergone at least one evaporation and we will therefore exclude the case of C_{60} . It can also only be applied for species for which the constant $\alpha' W'_N$ is significantly larger than one. Judging by the relative abundances, the latter criterium should be fulfilled by $N \geq 38$.

By inspection of Fig. 2 it is obvious that our data cannot be fitted by this expression using the given parameters. Whereas the general trend in the curves is quite similar, the magnitude is significantly different. A comparable reduction in magnitude has been observed previously¹³ although the issue was obscured by an erroneous estimate of peak intensities in the spectrometer used.^{14,15}

We will argue below that these discrepancies are not just a question of adjusting fitted parameters. Similarly, the disagreement occurs when comparing probabilities for different acceleration energies. Figure 3 shows observed fragmentation probabilities vs $\log(t_2/t_1)$, again for $N=50$ and $N=54$, for the two different acceleration voltages used. The prediction from Eq. (1) that curves pertaining to the same size but different acceleration energies, i.e., different times t_1 and t_2 , should coincide when plotted vs a function of the ratio of the two times, t_2/t_1 is clearly not borne out. The picture is similar for all species. Although the difference between the probabilities pertaining to the two different acceleration energies is small it is significant. For this point it should be kept in mind that this conclusion is independent of the precise procedure used to fit the peak intensities.

Besides the scaling violation, an important observation is that the curves are fairly good straight lines and that the intercept with the ordinate is negative. The analogous plots for the other species (still for $N \leq 58$) show the same behavior down to and including $N=38$ where the intercepts become comparable to the uncertainty. Although both the slope and the intercept of the straight lines vary with size, the values do not change dramatically from one molecule to an-

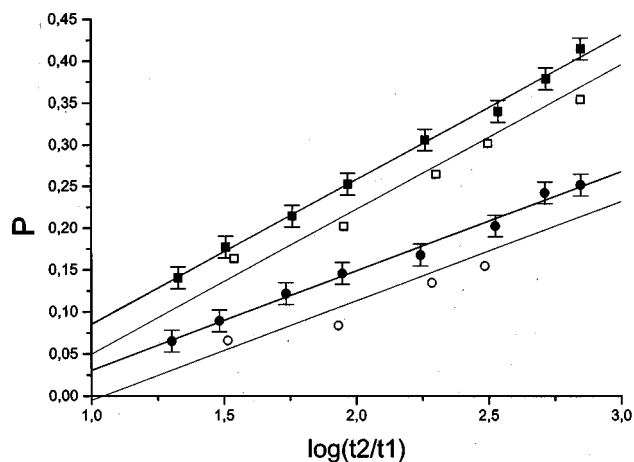


FIG. 3. Probabilities for metastable fragmentation occurring during free flight for $N=54$ (circles) and $N=50$ (triangles) as a function of $\log(t_2/t_1)$. t_1 is the delay before mass selection and t_2 the time between laser heating and entry into the reflectron. The full symbols are strong field data, the open ones results from weak field measurements. The full straight lines are least squares fits to the data obtained with the strong fields. The thinner lines just below are predictions of the weak field data taking into account the additional cooling due to emission of radiation.

other. In particular, the ordinate intercept is always negative. This behavior is the basis of the model that will be discussed in the next section.

DISCUSSION

Before discussion of the possible explanation for the observed behavior of the decay probability, it is important to realize that it cannot be contained in the standard evaporative ensemble framework. Whereas some improvement between Eq. (1) and the experimental results can be achieved by assuming a completely unrealistic value of the Gspann parameter, a more careful consideration of the trends reveal that even such a desperate measure does not explain the observations. The decay probabilities as described by Eq. (1) are simple proportionalities of $\log(t_2/t_1)$, at least for short fragment times and small heat capacities. We note that this statement is independent of the value of the Gspann parameter and in general of the value of the parameter $\alpha' W'_N$. Any uncertainty in this quantity will affect the slope. With larger heat capacities or longer fragment times, the curves can still be approximated by straight lines, but now with a positive ordinate intercept. From Eq. (1) it can be seen that this result does not depend on the precise values of the parameters, whether they be activation energies or heat capacities, as long as they can be considered constant. The reader can verify this statement by evaluating the function $P[\log(t_2/t_1)]$ in zero, and calculating the first and the second derivatives. The results are zero, positive and negative, respectively, independent of the value of the finite and positive parameter $\alpha' W'_N$. Approximating a function with these properties by a straight line, it is easily seen that the intercept must be non-negative. Hence the above conclusion. In this context we mention that the estimated energy content is below the heat capacity peak around 4000 K observed in simulations,¹⁶ but,

on the other hand, not so low that corrections due to quenching of vibrational degrees of freedom are significant.¹⁷ Hence a description in terms of a constant heat capacity appears justified.

The fragment probability can obviously be modelled differently than in Eq. (1). However, due to the nature of the evaporation as an activated process the restrictions on the possible models are so severe that any realistic model based on similar kinds of assumptions will give qualitatively similar results. (The easiest way of realizing this is perhaps to attempt to construct a counterexample.) In particular the negative intercepts will not appear. Hence, whereas the straight line behavior in Fig. 3 can be contained in a standard theory of this type, the negative intercepts pose a serious challenge. Even relaxing the idealized assumptions about the ensemble, the intercepts are difficult to understand in terms of, e.g., modifications of rate constants or by inclusion of competing fragmentation channels, whether these consist of emission of electrons, atoms or molecules. The basic reason is that all these explanations, while logically possible, require a precisely concerted fine-tuning of parameters for all the observed fullerenes simultaneously. We will therefore disregard these explanations.

Instead we note that the molecules in the beam cool not only by evaporation but also by radiation.⁴ This additional cooling obviously must reduce the evaporation probability. The quantitative statement of this is derived in the Appendix.

The leading order result for the evaporation probability found in the Appendix reproduces the experimentally observed behavior. The validity of the result can be tested further by a comparison of the probabilities at the two different acceleration energies. Reducing the extraction voltage by a known factor (in case the factor of 2.00 for the lower curves in Fig. 3) yields a prediction for the evaporation probability in terms of those of the previous setting. A proper rescaling of the fitted parameters describing the radiative energy loss, Δ , obtained for the strong fields taking into account the different flight times yields a prediction for the weak field Δ 's and hence the evaporation probability. (See the Appendix for the definition of Δ .) To be specific, we have compared the predicted and observed decrease in probability at a delay corresponding to the value of $\log(t_2/t_1)=2.2$, making use of the fitted straight lines for the strong field. The observed changes are of the order of -4×10^{-2} . Among the sizes for which the statistics make a comparison meaningful, $N=38-50$, only the value for $N=38$ shows a major disagreement of a factor of 3 between predicted and observed decreases. Averaging the ratio of observed to predicted decreases for the other ten values yields a value of 1.24 ± 0.08 . We consider this result very satisfactory. The deviation from one is likely to be related to an equivalent difference in the values of the fitted slopes for the weak field results as compared with the strong field results. This difference is again of the same order of magnitude as the higher order terms ignored in the derivation in the Appendix, i.e., comparable to $t_1/t_2 \sim 0.1$.

The fitted Δ 's and the flight times combine to yield estimates of the products $\epsilon_N D_N^3$, where ϵ_N is the emissivity and D_N the activation energy for C_2 emission from C_N^+ (see Ap-

TABLE I. The table gives the values of Δ_N and the derived quantities, $\epsilon_N D_N^3$ (eV³) and (relative values of) D_N , from this work in columns 2–4. Columns 5–7 are the relative values of D_N given in Ref. 12 for the model referred to as TS-1, TS-2, and TS-3, respectively. The last column gives the values found in Ref. 2. Please note that our D_N 's have been normalized differently from the other values.

N	Δ_N	$\epsilon_N D_N^3$ (eV ³)	D_N (rel)	D_N (TS-1)	D_N (TS-2)	D_N (TS-3)	D_N
			This work	Ref. 12	Ref. 12	Ref. 12	Ref. 2
36	0.169	0.095	0.78
38	0.252	0.138	0.85
40	0.296	0.159	0.88
42	0.373	0.196	0.92
44	0.544	0.279	1.00
46	0.387	0.195	0.91
48	0.417	0.206	0.92	0.9051	0.8637	0.7528	0.869
50	0.504	0.245	0.95	0.9306	0.8936	0.7931	0.930
52	0.339	0.161	0.85	0.8881	0.8557	0.7657	0.907
54	0.339	0.158	0.85	0.9150	0.8885	0.8132	0.954
56	0.473	0.218	0.91	0.9348	0.9154	0.8591	0.982
58	0.468	0.212	0.90	0.9603	0.9496	0.9178	0.992
60	1.0000	1.0000	1.0000	1.000

pendix). The values vary around 0.2 eV³ (a complete listing is found in Table I). This value is close to a factor hundred bigger than the one found in Ref. 5. Obviously the main part of this difference must be due to differences in emissivity and not in activation energy. Whether this disagreement can be traced to the substantial difference in time scales in the two experiments, the molecule and/or charge state or to the choice of ensemble is not clear to us. Experiments where radiation from a mixture of hot fragments are observed, such as Ref. 4, should thus be interpreted in terms of the higher emissivities found here, rather than the value given in Ref. 5. This observation does not alter any of the conclusions drawn in Ref. 4 concerning the competition between radiative cooling, evaporation, and ionization. Cooling by fragmentation and ionization will still dominate for temperatures in excess of 3000 K as discussed in Ref. 4. Although the energy loss due to radiation is much larger than assumed in that work, it would still not be observable under the experimental conditions.

We note that the differences in emissivity are compatible with the (classical) description of the problem given in Ref. 18. Differences in emissivities refer in this theory to differences in the complex index of refraction of the particle. Apart from this dependence, the emissivity is found to be reduced by essentially the ratio between the particle diameter and the wavelength of the emitted photon.

Fixing the index of refraction similarly to Ref. 7 yields an estimate of the absolute evaporative activation energies. The magnitude of these values obviously depend on the precise choice of index of refraction and should of course be taken with a grain of salt, at least with respect to the absolute magnitude which is around 4 eV. The order of magnitude of this value is, however, in nice agreement with typical chemical binding energies. We consider this order of magnitude agreement a corroborating fact for the general interpretation of our data. The relative values should be far more reliable. They are included in Table I.

The above numerical conversions are based on an estimate of the Gspann parameter. This was obtained from the

data using Eq. (7) in the Appendix and the slopes of the P vs $\log(t_2/t_1)$ curves for the sizes $N=44-58$. The value thus fitted was $G=31$. This is somewhat higher than the usual value of 23.5 (for a 10 μ s time scale), presumed valid for our time scales, even considering that the molecules are colder than evaporatively predicted. In our opinion, however, neither the present fragmentation models for fullerenes nor the results derived in the Appendix are so exact that they rule out either of these values. For example we do not want to rule out that the quantity that we experimentally identify with the Gspann parameter is in fact the result of a radiative correction of the true value; such a correction would be expected to have a typical magnitude comparable to the first term ignored in the theory, i.e., 10%–20%. A clarification of this problem must await a more thorough theoretical treatment.

We have included a comparison of estimated relative values of the activation energy from Refs. 2 and 12 in Table I. The curves share a falling trend from $N=60$ to $N=52$, and an increased stability for $N=50$. It is not clear what effect the inclusion of radiative cooling will have on the data used to derive the results in Ref. 12.

In principle, the data presented here allow a comparison between the size dependence of the abundances, the radiative constant, and the size dependence of the metastable peaks. Analogous to the nonradiative evaporative ensemble, relations should exist between these quantities although reduced in number because of the introduction of a new parameter (the radiation constant). We consider the development of such a complete model beyond the scope of this work, particularly since we do not have the possibility of excluding or quantifying the potentially disturbing effects of parallel decay channels such as C₄ loss during the initial stages of the ensemble life. We will therefore restrict the discussion of this subject and just point out that abundances, metastable fragment intensities, and radiation constants are related empirically as shown in Fig. 4. Abundances correlate almost perfectly with the fitted values of Δ . Similarly, the metastable fragment intensities for $N+2$ correlate positively with both of the others, although the size-to-size variations are smaller.

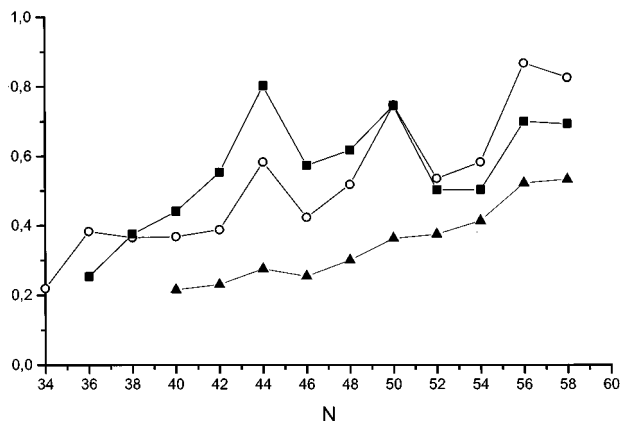


FIG. 4. Comparison of prompt fragment abundances (open circles), metastable fragmentation intensities (filled triangles), and radiation constants (filled squares) as a function of N . The latter is defined as minus the ratio of the intercept and the slope of the fitted straight lines. It is modeled by the constant term in the parenthesis on the right-hand side of Eq. (A7) and is dimensionless. The prompt and the metastable signals have been scaled with a different factor for display purposes and the metastable fragment intensities have been shifted down by two carbon atoms.

CONCLUSION

The data presented here show that radiative cooling can influence the unimolecular reaction rates of fullerene ions in a significant way. We have modeled the behavior of an ensemble of such evaporating molecules and found good agreement between our experimental results and the model predictions. Using a theoretically calculated emissivity we can estimate the values of the evaporative activation energies. An important side result is that these energies are determined in absolute values due to the introduction of a nondimensional parameter, viz. the Stefan–Boltzmann constant. We will defer a detailed comparison of the activation energies derived here with results from literature to a situation where a better theoretical understanding has been obtained. We just want to point out that the experimental method used here has the advantage that only molecules that actually do evaporate during the experiment are used to extract physical quantities. This procedure should reduce the assumptions implicitly required concerning the earlier stages of the ensemble formation, e.g. about the stage at which competing decay channels are quenched.

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APPENDIX: FRAGMENTATION RATES AND RADIATIVE COOLING

The fragmentation probability during the experimental time window can be estimated in the presence of radiative cooling by observing that the radiative cooling changes much slower with the molecules internal energy than does

the evaporative cooling. The probability that a molecule with a certain energy, E , survives until time t is given by

$$P = \exp\left\{-\int_0^t k[E(\tau)]d\tau\right\} \quad (\text{A1})$$

assuming that we can use the small molecule/cluster approximation and extend the integral to zero time (see Ref. 19 for the difference between small and large molecules). The energy depends on time through the radiative loss. Ignoring quantization of photons,

$$(dE/dt)_{\text{rad}} = -\epsilon\sigma_{\text{SB}}AT^4. \quad (\text{A2})$$

Here ϵ is the (dimensionless and possibly temperature dependent) emissivity, σ_{SB} the Stefan–Boltzmann constant, A the surface area of the molecule, and T the equivalent temperature. The proper definition of T is the canonical ensemble temperature for which the mean excitation energy equals the actual (microcanonical) one. For our purpose the relation $E = (3N-6)T - E_0$ is sufficient.²⁰ The constant E_0 is included for completeness. It incorporates, e.g., the zero point energies of the vibrations and will drop out of all subsequent results. The expression for the energy loss and in particular the power of four is chosen here exclusively in order to compare the results with the macroscopic black body result. It will not appear in the final result below since the radiative energy loss will be approximated by a constant. Performing a cumulant expansion on $k[E(\tau)]$ with respect to τ and then the integral with respect to time yields

$$P(t) \approx \exp\left[-k \frac{1}{w} (1 - e^{-wt})\right], \quad (\text{A3})$$

where w is defined as $w \equiv \epsilon\sigma_{\text{SB}}AD^3/[G^2(3N-6)]$, D is the activation energy for evaporation which until further notice will be considered size-independent. (All time dependent quantities without an argument refer to the values at time t .) The quantity w has the dimension of a rate constant and is, apart from a numerical factor, the radiative energy loss in units of the activation energy, D .

As for the case of a radiationless ensemble, the survival probability P considered as a function of energy will have a well defined cross over from essentially one to essentially zero at a certain energy. After subtraction of the radiative energy loss, the motion of this crossover point determines the fragmentation rate. It is found by implicit differentiation,

$$\begin{aligned} k(t) &= -\frac{1}{D} [dE/dt - (dE/dt)_{\text{rad}}] \\ &= -\frac{1}{D} \left[\frac{df/dt}{df/dE} + w \frac{D(3N-6)}{G^2} \right], \end{aligned} \quad (\text{A4})$$

where $f \equiv -k(1/w)(1 - e^{-wt})$. Here $k(t)$ is the ensemble (observable) value of the rate constant as opposed to the energy specified Arrhenius expression above. The division by D accounts for the width of the energy distribution in an average way. Performing the differentiations and making use of the fact that the energy per d.o.f. is much smaller than the separation energy [$E/(3N-6)D = 1/G$], the ensemble rate can be approximated by

$$k(t) \approx \frac{3N-6}{G^2} \left(\frac{1}{t} \frac{wte^{-wt}}{1-e^{-wt}} - w \right). \quad (\text{A5})$$

Provided multiple evaporations do not occur, the observable evaporation probability is then the integral of this ensemble rate constant during the relevant time window from t_1 to t_2 . Performing the integral and changing variables to $r \equiv t_1/t_2$ and $\Delta \equiv w(t_2 - t_1)$ yields after an expansion in r ,

$$P_f = \frac{3N-6}{G^2} \{ -\log(r) + \log[(1 - e^{-\Delta})/\Delta] - \Delta + O(r) \}, \quad (\text{A6})$$

or, since r is small,

$$P_f \approx \frac{3N-6}{G^2} \{ \log(t_2/t_1) + \log[(1 - e^{-\Delta})/\Delta] - \Delta \}. \quad (\text{A7})$$

Since Δ is independent of the delay, terms involving only this quantity are constant for a given accelerating potential.

This result has been derived without regard for any size dependence in the activation energies. We consider a proper treatment of such effects to be beyond the scope of this work. With a simple generalization we will, however, define a radiative cooling rate in the presence of a nontrivial size dependence as

$$w_N = D_N^3 \epsilon_N \sigma_{\text{SB}} A_N / [G^2(3N-6)]. \quad (\text{A8})$$

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