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Stability of carbon clusters C_N for $46 \leq N \leq 102$

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Abstract

Relative binding energies for C^+_{N-2}–C_2 have been determined for fullerene ions in the range $46 \leq N \leq 102$. The values were derived from metastable fractions observed in a time-of-flight reflectron mass spectrometer. The timescale of the experiments was such that radiative cooling of the fullerene ions did not play an important role thus simplifying the data analysis. The results are compared with previous values of relative dissociation energies for C_2 loss given in the literature. It was found that the relative C_2 dissociation energies for large fullerenes ($N > 60$) are significantly higher than previously estimated. © 1997 Elsevier Science B.V.

Keywords: Fullerenes; Metastable fragmentation; Dissociation energies

1. Introduction

There have been many investigations of the metastable fragmentation of positively charged fullerene ions carried out in recent years [1–4]. The dominant metastable fragmentation process that occurs on a microsecond timescale is accepted to be C_2 emission. In spite of the large number of studies performed, even the energetics of the simple and most studied dissociation reaction $C^+_{60} \rightarrow C^+_{58} + C_2$ is still a matter of some controversy [5,6] with values ranging from 4 to 12 eV available in the literature. A reliable value for this dissociation energy and the energetics of subsequent C_2 emissions is essential for understanding the fragmentation processes of excited fullerene ions and the competition between C_2 evaporation and other cooling or fragmentation mechanisms. Laskin and Lifshitz [7] have discussed the energetics of subsequent C_2 evaporations, starting with C^+_{60}, in terms of two simple models and interpreted their metastable fraction measurements by RRKM calculations yielding binding energies for C^+_{58}, C^+_{56} and C^+_{54} relative to C^+_{60}. More recently, Märk, Lifshitz, Klots and co-workers [8] have extended these studies down to C^+_{44} and used a new "self consistent" method to determine the consecutive binding energies. In these studies the appearance energies of fragment ions in electron collision experiments were determined and related to the respective binding energies with the help of evaporative ensemble calculations. These binding energies were then used to calculate the breakdown curves for these fragment ions with the help of RRKM

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theory for different transition state models. The calculated and measured breakdown curves were then compared.

It is possible to extend the mass range investigated by using carbon clusters produced from laser vaporisation of graphite. Rate constant data for the metastable fragmentation of such carbon cluster ions were published by Radi et al. [2] before C_{60} soot was made available. The data were then analysed by Klots [9] to extract the relative C_2 dissociation energies. There appeared to be a very dramatic drop in the dissociation energy on going from $N \leq 60$ to $N > 60$. This was interpreted in terms of "magic shells" [9]. However, it was later pointed out that the rate constants extracted from the experimental data were in error due to experimental artefacts [4].

An additional complication has recently come to light in the interpretation of metastable fragmentation measurements. Hansen and Campbell [10] have shown that the metastable fragmentation rates can be significantly smaller than the evaporative ensemble prediction under conditions in which radiative cooling of the fullerenes can become important. It is not clear what consequences this has for the relative dissociation energy values available in the literature.

In this paper we attempt to clear up some of the questions raised by the experiments and interpretations mentioned above, The technique we use is reflectron time-of-flight mass spectrometry. This technique has been used previously to investigate the rate constants for metastable C_2 loss from fullerenes, produced by the laser ablation of polyimide [3]. However, we now know that the conditions in these experiments were such that radiative cooling is likely to have played a significant role and it would not be possible to extract reliable dissociation energies from these data by simply reanalysing them. In the experiments reported here the influence of radiative cooling is unimportant and we have extracted the relative dissociation energies with the help of an evaporative ensemble model. The values are compared with those found in the literature.

2. Experimental set-up

The fullerenes are produced by laser ablation (at 532 nm) of a rotating graphite rod, using the second harmonic of a pulsed Nd:YAG laser. The plasma produced is expanded in helium from a pulsed nozzle (R.M. Jordan and Co.) and clustering occurs. The source is a simple variant of that often used to generate refractory clusters [11]. The ensuing cluster beam, containing a wide mass range of thermally excited carbon clusters, is skimmed before passing into an ionisation region. The fullerenes are ionised and further excited with the third harmonic of a pulsed Nd:YAG laser (352 nm) which is aligned between the two acceleration plates of a reflection time-of-flight mass spectrometer. The pulse energy of the ionising laser is of the order of a few tens of a millijoule.

The reflectron is tuned in the so-called "hard reflection" mode so that the products of metastable fragmentation in the first few microseconds of flight are observable. The signal is recorded by a fast transient digitiser (LeCroy 9400 oscilloscope) via a set of 40-mm microchannel plates. The spectra are averaged over 4000 shots. In order to rule out the possibility that the parent and fragment beams have different divergences (due to a large kinetic energy release in the decay reaction) a series of spectra were taken with the deflection of the beam varied systematically so that the angle at which the ion beams enter the reflectron is altered from a perceived maximum signal deflection. These spectra showed constant peak ratios, within experimental error. Although no quantitative ionisation laser fluence dependence measurements were made, the parent/daughter ratios were constant from day to day and thus, as shown in [10], perceived to be independent of laser fluence.

Following Hansen and Campbell [10] the metastable fragmentation probabilities were determined as a function of $\log(t_2/t_1)$, where t_1 is the time delay before mass selection and t_2 is the time between laser heating and entry into

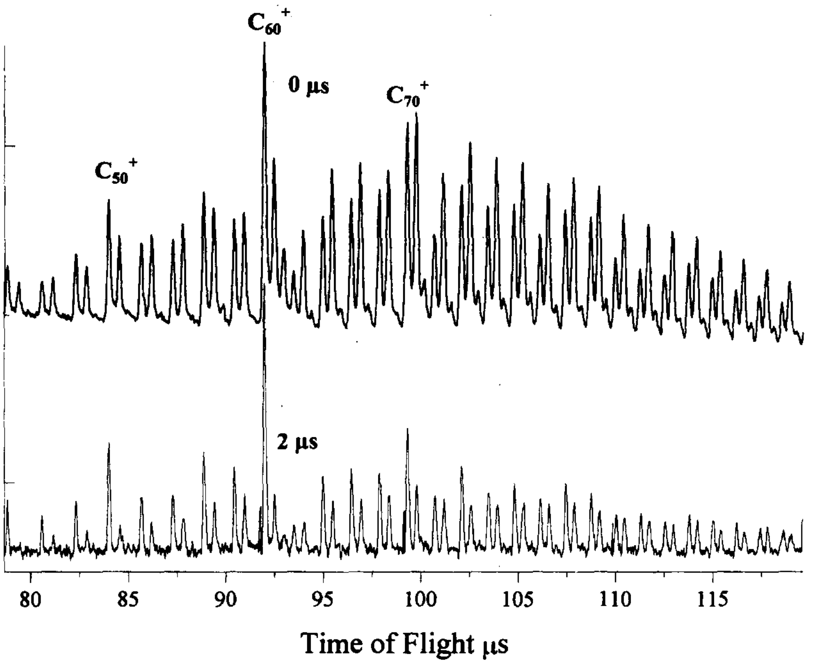

Fig. 1. Time-of-flight mass spectra for two different delay times before ion extraction. Note how the relative intensity of the metastable fragments to parent ions changes with changing delay.

the reflectron, for a range of times. If a linear extrapolation of the fragmentation probability to $\log(t_2/t_1) = 0$ gives a clear negative intercept, that is indicative of significant radiative cooling [10]. This procedure was not useful for the present series of experiments since the range of accessible t_1s was too small to give an accurate extrapolation. Alternatively, we estimated the intercept using the present flight times and the emissivity in [10] to be a factor of three smaller than that found in [10]. Hence the radiative cooling is strongly reduced. In addition, the relative fragmentation probability is considerably higher in the present series of experiments which even further reduces the significance of radiative cooling. The fragmentation probability was taken to be the average of the values obtained for the different time delays t_1 and included the sequential C_2 loss.

Typical time-of-flight spectra obtained for two different times t_1 and fixed $(t_2 - t_1)$ are shown in Fig. 1. The strong metastable fragment peaks for $C_N^+ \rightarrow C_{N-2}^+ + C_2$ can be seen just to the right of the parent C_{N-2}^+ peaks. One can also clearly see the metastable loss of four carbon atoms in the upper spectrum, indicating that the clusters are very hot for the short delay times.

3. Extraction of the relative dissociation energies

The evaporative ensemble method which we use is very similar to that used by Klots [9] to extract the relative dissociation energies from the Radi et al. experiment [2]. In the experiment the fullerenes are created with different internal energies in the production and ionisation process. This is taken into account by integrating over all energies when calculating the metastable fragmentation probability. If the energy distribution is smooth and we furthermore make the assumption that all ions that we ultimately detect have undergone at least one fragmentation, we can write the abundance, $I_N(E;t_1)$, for the fullerene C_N at time t_1 after the ionising laser shot as

$$I_N(E;t_1) = c\frac{k_{N+2}(E+D_{N+2})}{k_{N+2}(E+D_{N+2}) - k_N(E)} \times \{\exp(-k_N(E)t_1) - \exp(-k_{N+2}(E+D_{N+2})t_1)\} \quad (1)$$

where c is a normalisation constant to be determined, $k_N(E)$ is the decay rate for C_N^+ with the internal energy E and D_N is the evaporative activation energy for C_2 loss from C_N^+. The rate is then found by averaging $k_N(E)$ over this distribution:

$$< k_N(t_1) > = \int_0^\infty I_N(E;t_1)k_N(E)\mathrm{d}E \quad (2)$$

Accelerating the ions at t_1, the average rate at a later time t_2 is given by a similar integral including an exponential decay:

$$< k_N(t_2,t_1) > = \int_0^\infty I_N(E;t_1)k_N e^{-k_N(t_2-t_1)}\mathrm{d}E \quad (3)$$

$$= \int_0^\infty c\frac{k_{N+2}}{k_{N+2}-k_N}(e^{-k_N t_1} - e^{-k_{N+2}t_1})k_N e^{-k_N(t_2-t_1)}\mathrm{d}E$$

$$= \int_0^\infty c\frac{k_{N+2}}{k_{N+2}-k_N}(e^{-k_N t_2} - e^{-k_{N+2}t_1 - k_N t_2 + k_N t_1})k_N\mathrm{d}E$$

where the rates are to be evaluated at the appropriate energies; $k_N = k_N(E)$ and $k_{N+2} = k_{N+2}(E+D_{N+2})$. The integral can be evaluated by expressing $k_{N+2}(E + D_{N+2})$ in terms of the rate $k_N(E)$. The calculation can be simplified by using the Arrhenius-like expression $k_N(E) = \omega\exp(-D_N C_{v,N}/E)$ where $C_{v,N}$ is the heat capacity in units of k_B. A Taylor expansion of the logarithm of $k_{N+2}(E+D_{N+2})$ in D_N, $C_{v,N}$ and E, retaining terms to first order, yields

$$k_{N+2} = k_{N+2}(E+D_{N+2}) \approx k_N(E) \times \exp\left(-\frac{\Delta_1 C_{v,N}G}{C_{v,N}} - \frac{\Delta_1 D_N G}{D} + \frac{D_N D_{N+2}G^2}{C_{v,N}D^2}\right)$$

$$\equiv k_N(E)A_N = k_N A_N \quad (4)$$

where the average dissociation energy, D, is introduced and the Gspann parameter G is defined as $G = \ln(\omega t_1)$, implying $G = DC_{v,N}/E_1$, where E_1 is simply the energy that gives a fragmentation rate equal to $1/t_1$. The first differences, $\Delta_1 D_N$ are defined as $\Delta_1 D_N = D_{N+2} - D_N$ and analogously for C_v. The definition of the new variable A_N is just for convenience. The value of G is, for our purpose, constant which can be demonstrated by calculating the time dependence of the above relationship between the two rates k_{N+2} and k_N. Accepting this, the average decay rate is then given by

$$< k_N(t_2,t_1) > = \int_0^\infty c\frac{A_N}{A_N-1} \times \left(e^{-k_N t_2} - e^{-k_N(A_N-1)t_1 - k_N t_2}\right)k_N(E)\mathrm{d}E \quad (5)$$

Changing the variable from the energy E to the rate $k_N(E)$, yields

$$< k_N(t_2,t_1) > = c\frac{A_N}{A_N-1}\frac{C_{v,N}D^2}{G^2 D_N} \times \left(\frac{1}{t_2} - \frac{1}{t_2+(A_N-1)t_1}\right) \quad (6)$$

Integrating this rate with respect to time yields the metastable fragmentation probability:

$$P(t_1,t_2) = c\frac{A_N}{A_N-1}\frac{C_{v,N}D^2}{G^2 D_N}\ln\left(\frac{t_2 A_N}{t_2+(A_N-1)t_1}\right) \quad (7)$$

The normalisation constant c is found by letting t_2 go to infinity since then $P = 1$. The resulting expression is

$$P(t_1,t_2) = \ln\left(\frac{t_2 A_N}{t_2+(A_N-1)t_1}\right)/\ln(A_N) \quad (8)$$

Note that this only holds in the absence of radiative cooling and that the only time dependence enters through the ratio t_2/t_1. This result differs from the one used by Klots [9] on several points. One is the starting point (Eq. (1)) for which Klots

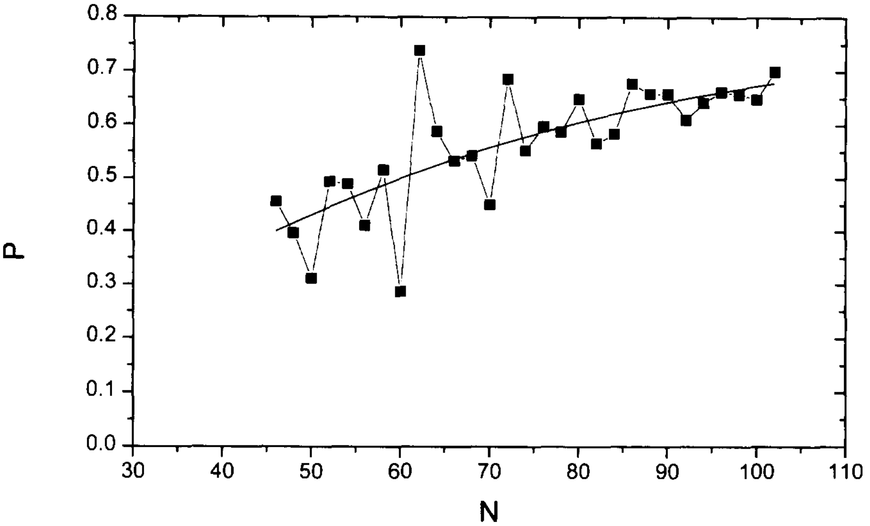

Fig. 2. Experimental metastable fragmentation probability as a function of fullerene ion size. The full line is a fit to the experimental data for an average dissociation energy D in order to extract the Gspann parameter G from the data. For the results shown, $G = 30$.

uses an approximate result. On the other hand, we use the simplified Arrhenius rate which fails in the limit of very small particles.

A more correct energy dependence would be $k_N(E) = \omega \exp(-D_N C_{v,N}(E - D_N/2))$, but since, as will be shown below, the value of G is such that $E \gg D_N/2$, the ions have sufficiently high internal energies to justify our neglect of this complication.

A mean curve for P can be found if all the fullerenes are equally stable, $\Delta_1 D_N = 0$. With $\Delta_1 C_{v,N}/C_{v,N} = 2/N$,

$$A_N^{\text{smooth}} = \exp(-2G/N + G^2/C_{v,N}) \quad (9)$$

For reasonable heat capacities $2G/N \ll G^2/C_{v,N}$ so that we can get a first fit of the experimental data. Since the delays in extraction in our experiment were all small, the ratio t_2/t_1 is practically independent of mass. Using the experimental value for t_2/t_1, the fragmentation probability vs. N can be fitted to a first approximation with only a single free parameter, namely the Gspann parameter G. Once G has been found it is possible to extract the dissociation energies D_N relative to the average value D. The procedure is to use Eq. (8) with the known ratio t_2/t_1 to solve for A_N. Using the definition of A_N (Eq. (4)) we can then find $\Delta_1 D_N$. Approximating $D_N D_{N+2}$ by the average value D^2 yields

$$\Delta_1 D_N/D = \left(-\ln(A_N) + \frac{G^2}{C_{v,N}} - \frac{2G}{N}\right)/G \quad (10)$$

A numerical integration (summation) of the resulting first differences $\Delta_1 D_N$ then yields the value of the dissociation energy relative to the average value.

4. Results and discussion

Fig. 2 shows the fit of the Gspann parameter G to the observed metastable fragmentation probabilities P_N. The fit gives a value of $G = 30$ for $C_{v,N} = 3N$. This value is somewhat higher than the value suggested by Klots and frequently used to interpret experimental data but within the limit of plausible values. The relative dissociation energies, extracted using the method described above, are summarised in Table 1 and shown in Fig. 3. In this plot D_N has been plotted relative to D_{54}. This

Table 1
Relative dissociation energies D_N/D_{54} for the reaction $C_N^+ \rightarrow C_{N-2}^+ + C_2$

N	Present results	[10]	[8]		[9]
			TS1	TS3	
46	0.99	1.07			
48	1.02	1.08	0.99	0.93	0.91
50	1.08	1.12	1.02	0.98	0.97
52	0.99	1.00	0.97	0.94	0.95
54	1.00	1.00	1.00	1.00	1.00
56	1.04	1.07	1.02	1.06	1.03
58	1.00	1.06	1.05	1.13	1.04
60	1.13		1.09	1.23	1.05
62	0.94				0.81
64	0.99				0.89
66	1.01				0.90
68	1.01				0.88
70	1.05				0.91
72	0.98				0.82
74	1.02				0.88
76	1.01				0.87
78	1.02				0.88
80	1.00				0.87
82	1.03				
84	1.02				
86	1.00				
88	1.01				
90	1.01				
92	1.03				
94	1.02				
96	1.01				
98	1.02				
100	1.02				
102	1.01				

has been done in order to compare the results with results from other experiments. C_{54}^+ has been investigated in all the related work and has the advantage of being a "non-magic" cluster. Care has to be taken when comparing the values for C_{60}^+ and C_{70}^+ since the relative intensities of these two "magic" species compared to the other fullerenes can vary dramatically under different experimental conditions [12]. This may lead to saturation effects which will distort the values obtained.

The crosses plotted on Fig. 3 are the results from the Klots' analysis of the Radi et al. experiments [9]. The results from Radi et al. [2], although showing the same trends as our results, considerably underestimate the values of the dissociation energies for $N > 60$ by about 10–15% compared to the results from the present experiments. A discrepancy with the present results is expected considering the problems in the analysis of their data due to experimental artefacts [4]. The "magic shell" discussed by Klots [9] where the dissociation energies of all the fullerenes for $N \leq 60$ were significantly larger than those for $N > 60$ is no longer apparent. Note, however, that the two parts of the plot are connected through the fragmentation probability of C_{60}

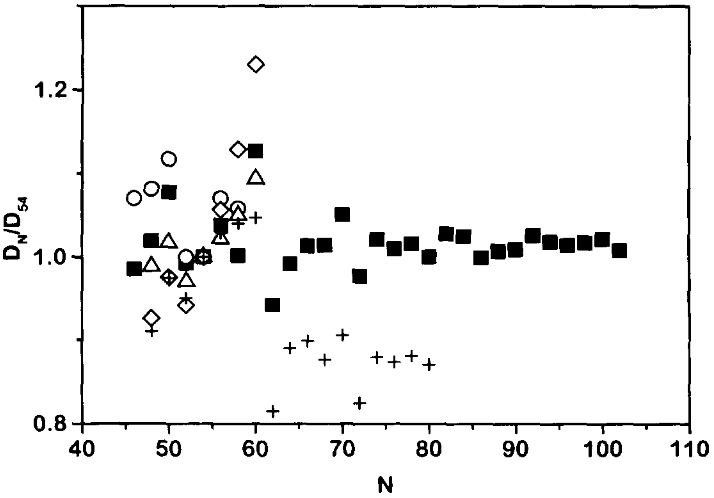

Fig. 3. Relative dissociation energies, normalised to the value for C_{54}^+: (■) present results; (+) from [9]; (△) TS1 from [8]; (◇) TS3 from [8]; (○) from [10].

which links D_{60} and D_{62}. Due to the potential saturation of the C_{60} abundance the difference between D_{60} and D_{62} may be misrepresented and we can therefore not entirely rule out the presence of a small ''magic shell''.

The triangles and diamonds in Fig. 3 are the results from Wörgötter et al. [8] for two different transition state models (TS1 and TS3 in [8] respectively). Better agreement is seen for the TS1 model, as would be expected from the discussion in [8]. Finally, the open circles give the results reported by Hansen and Campbell [10]. These show the same trend as the present results but are consistently higher (using C_{54}^+ for normalisation). The agreement is, however, still surprisingly good considering that the data from [10] were obtained under conditions in which radiative cooling is significant. The parameter which can be extracted from the experimental data in this case is the product of the emissivity and the cube of the dissociation energy, $\varepsilon_N D_N^3$ [10]. Assumptions were made as to the dependence of emissivity with N in order to extract the relative dissociation energies. A direct comparison of results with and without radiative cooling should provide fairly accurate values for the cluster emissivity.

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