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Stability of clusters of fullerenes

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Abstract. We have studied the formation and stability of pure and mixed clusters of C_{60} and C_{60}/C_{70} produced in a gas aggregation source. The source yields very smooth abundance distributions indicating an efficient cooling. The stability of the clusters was probed by varying the degree of heating with a XeCl excimer laser ($h\nu < I.P.$) followed by single photon ionisation with a F_2 excimer laser. The stability patterns show features related to geometrical packing structures but much stronger than previously seen in cluster spectra. The fragmentation patterns for the mixed clusters indicate that C_{60} and C_{70} have similar binding energies in the clusters in contrast to what would be expected from vapour pressure data of macroscopic samples.

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1 Introduction

With a few notable exceptions (see e.g. [1]), experiments on free fullerenes have involved species that are highly excited, typically produced by vapourising material in a effusive source or by laser ablation. The large number of degrees of freedom in the fullerenes make it experimentally very difficult to reach a vibrational temperature low enough to enable investigations of the spectroscopical properties of the free molecules in the gas phase to be carried out. The problem can be solved by vapourising the molecules in a gas aggregation source of the type which has previously been used by a number of groups to produce cold clusters. The main advantage of this type of source is the long thermalisation time and the well controlled source temperature which makes it possible to produce clusters with temperatures very close to the LN_2 temperature of 77 K. At this low temperature the vibrations of even such a large molecule as C_{60} are almost all frozen out and it is therefore meaningful to attempt spectroscopic studies in the gas phase. This was the motivation for building the source with which the results reported here were reached. However, in addition to the possibility of cooling fullerenes to desirable spectroscopic temperatures, the source is capable of, and indeed almost insists on, aggregating these cold fullerenes into clusters of fullerenes. We have recently shown in a short note [2] that it is possible, by heating the clusters before ionisation, to obtain mass spectra from the source where only the monomer and $(C_{60})_{13}$ are present in significant amounts. This extreme behaviour was related to an approximately 20% increase of the activation energy for evapouration of a monomer from $(C_{60})_{13}$ compared to that from $(C_{60})_{14}$. In this paper we continue our investigations on the stability of clusters of fullerenes. We derive the expression used to estimate the relative binding energies of neighbouring clusters and extend our investigations to mixed clusters of C_{60} and C_{70}. Our results indicate that the binding energies of the two fullerenes in the mixed clusters are practically identical. This is rather surprising in view of the significantly different vapour pressures of bulk C_{60} and C_{70} [3].

2 Experimental

The source has been constructed according to the general idea behind a gas aggregation source, found in e.g. [4]. One special feature is worth mentioning, namely the size of the oven. The volume available for the vapourisation material is about 1 cm^3 and the total volume of the oven is 11 cm^3, or ten times the active volume. The difference is taken up by three layers of stainless steel insulation on the side and the bottom of the crucible. This construction makes the source very efficient while still containing enough material to last more than a typical experimental run (1-2 days). It is possible to measure a strong, ionised signal downstream with an electrical heating power of only 15 W. Typically, 25 W or less is used for heating [5]. The small surface of the oven also facilitates the subsequent thermalisation of the molecules. On leaving the oven, the fullerene vapour is quenched in a slowly streaming He or Ar gas ($\approx 1\ torr$), cooled by thermal contact with a liquid nitrogen chamber. The fullerene clusters condense out of the quenched vapour and are transported by the gas stream through a conical nozzle (diameter 2 mm) with a temperature of 80–110 K, measured by a thermocouple mounted in the nozzle. After passing a skimmer (diameter 3 mm) the beam is differentially pumped and then flies freely for about 1 ms before reaching the extraction region of a Wiley-McLaren linear time-of-flight mass spectrometer. Here the clusters can be optionally heated by a XeCl excimer laser (308 nm, 4 eV) and then softly one-photon-ionized by a F_2 excimer laser (157 nm, 7.9 eV). The ionized fullerene clusters are accelerated to an energy of 5 kV and detected by a set of dual microchannel plates after a flight path of 60 cm.

3 Results

In the upper part of Fig. 1 we show a mass spectrum of pure $(C_{60})_N$ clusters, obtained by direct single photon ionisation without previous heating. There is no evidence of magic cluster sizes in this very smooth mass spectrum. Since it is known [6] that spectra of fullerene clusters that have undergone evapouration develop strong abundance contrasts ("magic numbers"), the smoothness indicates that only a small amount of fragmentation occurs between the source and the acceleration, i.e that the clusters are cold. The clusters are van der Waals bound with essentially pairwise additive binding energies. Using this, the binding energy of the dimer can be estimated and used to set an upper limit on the temperature of that species when it leaves the source [2]. The result is an upper limit of approximately 130 K, slightly higher than the nozzle temperature. The special stability of certain fullerene clusters is then developed from the smooth spectrum by laser heating the beam. The photon energy of the heating XeCl excimer laser is well below the the ionisation potential of the C_{60} monomer (7.6 eV) and provides an ionisation-free heating for low laser fluences. As we have shown previously [2], it was possible to enhance the relative abundance of the closed shell cluster $(C_{60})_{13}$ to a magnitude not seen before in such large clusters by increasing the fluence of the heating laser. Apart from the monomer, this closed shell cluster, composed of 780 atoms, appears almost alone in the spectrum (lower part of Fig. 1). The reason for this is of course the enhanced stability of the closed shell, i.e. the higher binding energy and thus the higher than average energy needed for fragmentation. It is possible to evaluate quantitatively how much this energy is higher than the average value, represented by the preceeding cluster with N=14. To see how this is possible, note that the strong peak at N=13 is preceeded by a series of almost equally weak peaks, from N=14 to at least N=18 (lower part of Fig. 1). The flatness of the abundance spectra in this region indicates that the evapourative rates and thus the evapourative activation energies D_N for these cluster sizes are similar in magnitude. Therefore and because the heat capacity for these cluster sizes is fairly large ($C_{C_{60})_{13}} \approx 1300 k_B$), we can apply the results concerning the evapourative rate constants of large clusters that were derived in [7]. A single cluster size (here N=14) can be described with a single, time dependent evapouration rate, simply given by

$$k_{14} = C_{14}/(tG^2) \qquad (1)$$

where t is the cooling time elapsed after the heating laser pulse and the Gspann parameter G is about 25 (see [7] and earlier references given there). The evapourative rate for N=14 and the one for the magic cluster 13 are approximately related by

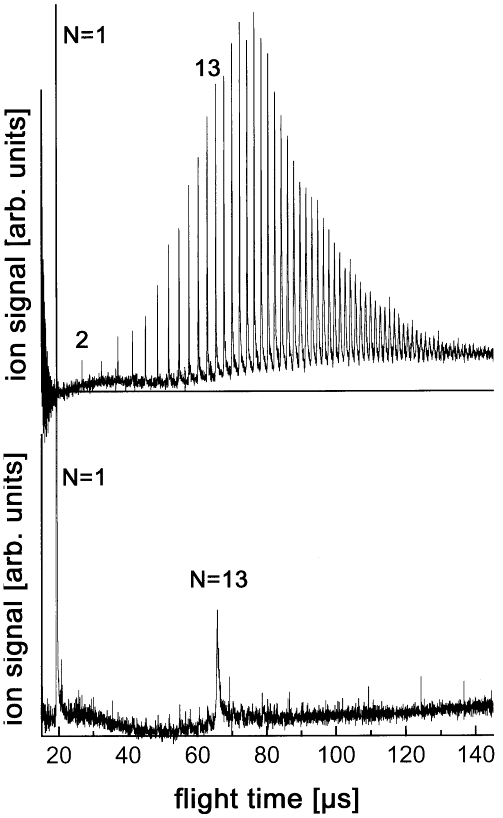

Fig. 1. Abundance spectra of pure C_{60} clusters after single-photon ionisation with a F_2 excimer laser. *Upper part*: without additional heating, estimated temperature 130 K. *Lower part*: distribution obtained on heating with a XeCl excimer laser prior to single-photon ionisation

$$\begin{aligned} k_{13} &\approx k_{14} exp(-(D_{13} - D_{14})/T_{14}) \\ &\equiv k_{14} exp(\Delta_1 D/T_{14}), \end{aligned} \qquad (2)$$

where we have approximated T_{13} by T_{14}, consistent with the large heat capacity limit and we have parametrised all 'magic' effects into the single number D_N. With the two relations above we can now find the abundance of $(C_{60})_{13}$ by integrating over the temporal development

$$I_{13} = \int_0^t dt' I_{14} k_{14}(t') exp(-k_{13}(t')(t - t')). \qquad (3)$$

It can be argued that I_{14} is almost time-independent [8] on fairly general grounds, and it seems also quite unsurprising since the abundances for the higher N are so similar. Combining the above relations and treating the ratio k_{13}/k_{14} as time independent, the abundance for the $(C_{60})_{13}$ is

$$\begin{aligned} I_{13} &= I_{14} \frac{C_v}{G^2} exp\Big(\frac{C_v}{G^2} e^{\Delta_1 D/T_{14}}\Big) \\ &\times \int_0^t dt' t'^{-1} exp\Big(-\frac{C_v}{G^2} e^{\Delta_1 D/T_{14}} t/t'\Big). \end{aligned} \qquad (4)$$

The integral can be performed and yields a result in terms of the exponential integral, E_1. In the limit where $C_v exp(\Delta_1 D/T_{14})/G^2$ is small, i.e. for large contrasts, this reduces to the approximate result:

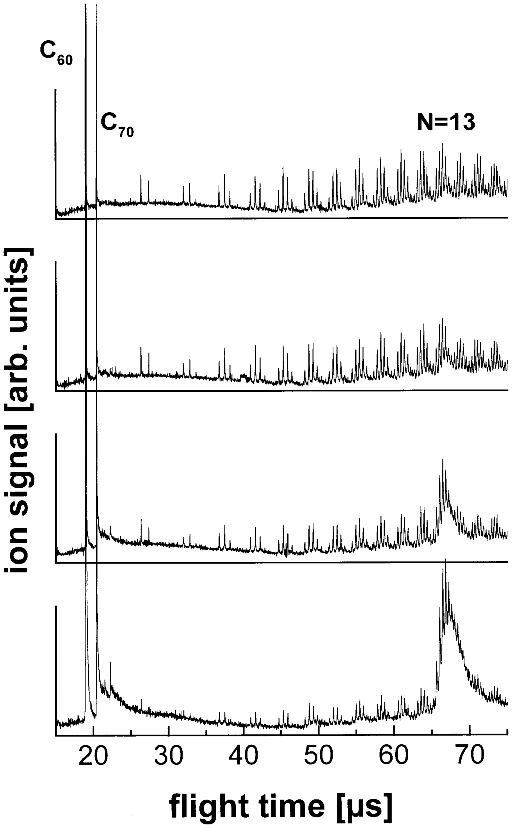

Fig. 2. Abundance spectra of mixed C_{60}/C_{70} clusters as a function of the fluence of the pre-ionisation heating laser

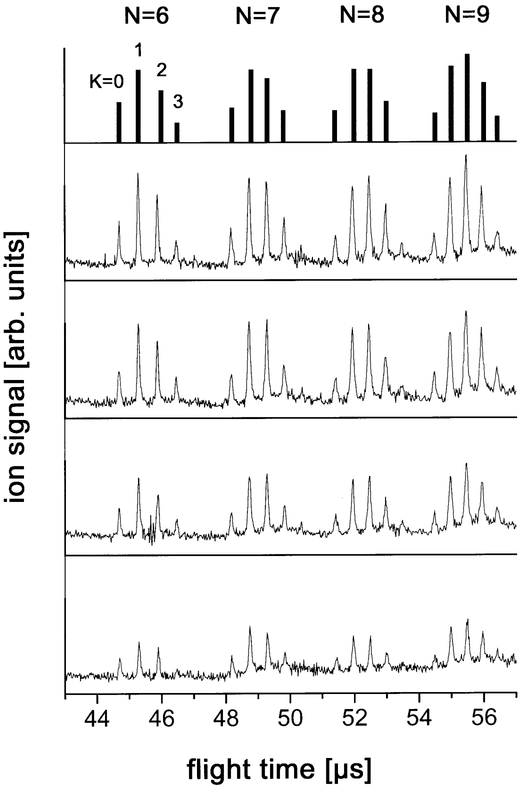

Fig. 3. Expanded section of Fig. 2. The distributions of C_{60} and C_{70} for a given cluster size are compared with the binomial distribution expected for $C_{60} : C_{70} \equiv 0.775 : 0.225$. The distributions do not change as the amount of fragmentation is increased showing that the binding energies of the two fullerenes within the clusters are very similar

$$I_{13} = I_{14}\frac{C_v}{G^2}\Big(- \gamma - log(C_v/G^2) - \Delta_1 D/T_{14}\Big), \tag{5}$$

where γ is Euler's constant 0.57... and log is the natural logarithm. Using the relation $T_{14} = D_{14}/G$ and inserting the experimentally observed ratio $I_{13}/I_{14} = 8$ yields for the relative difference in dissociation energies, $(D_{13} - D_{14})/D_{14}$, the value 0.2. This value is noteworthy, because on the one hand it gives rise to the very strong abundance contrast, but on the other hand it is of realistic magnitude when considering the structure and binding patterns of the clusters in question.

Aggregation of the vapour from a mixture of C_{60} and C_{70} yields mixed clusters of the type $(C_{60})_{N-K}(C_{70})_K$. This makes it possible to compare the aggregation and stability of these mixed clusters, not only as a function of N but also of K. The upper part of Fig. 2 shows a mass spectrum of such mixed clusters with no heating by the 308 nm XeCl laser. The smoothness of the mass distribution indicates as before a size-independent sticking coefficient and no subsequent fragmentation during and after the cluster formation. Thus, the composition of the mixed clusters with respect to the amount of C_{60} and C_{70} is fixed only by the available amount of these two species in the vapour in the source. Such conditions produce binomial distributions of the K values, i.e. of the distribution of C_{70} in the cluster for a given cluster size N. Furthermore, the single parameter needed to describe such distributions should be identical for all cluster sizes and equal to the mole fraction of one of the species in the source. This is indeed the case in the size range examined as will be shown below (see Fig. 3). On heating, one again sees a clear fragmentation into the monomer species and the "magic number" cluster containing 13 fullerenes. The two molecules, C_{60} and C_{70} may have different binding energies in a given cluster. Such a difference in binding energy can also be revealed by the experimental procedure used to explore the size-dependent binding energies of the pure clusters. Somewhat surprisingly, the mixed clusters did not show any relative enrichment of either C_{60} or C_{70}, even after extensive fragmentation (see the lower panels of Fig. 2). The amount of fragmentation is easily documented by noting the very large contrasts between clusters composed of different numbers of molecules, quite similar to the case for pure C_{60} clusters (see e.g. [2]). An expanded section of the spectra shown in Fig. 2 is reproduced from N=6 to N=9 in Fig. 3. Here one can very clearly see that the C_{60}/C_{70} distributions within a given cluster size are practically independent of the degree of heating. The distributions can be fitted in each spectrum by using the binomial distribution with a mole fraction of C_{70} of 0.225 as indicated at the top of the figure. This independence of the amount of heating implies that the clusters fragment statistically similar to their aggregation; that is, the evapouration process does not distinguish between C_{60} and C_{70}. This means that the difference in evapourative activation energy is small compared to the effective temperature. Quantitatively this can be stated as the inequality

$$(D_{N,60} - D_{N,70})/D_N \ < \ 1/G \ \approx 0.04 \tag{6}$$

where the subscript $N, 60$ refers to evapouration of C_{60} from cluster size N etc. and the denominator is the average value. This should be compared with the relative difference in the values of the sublimation enthalpies of the pure bulk materials, which is about 0.13.

4 Conclusion

Clusters of fullerenes have stability patterns that give rise to some of the most extreme abundance variations seen in large clusters. The very strong selection of the icosahedral closed shell cluster with 13 molecules indicates that the production of large monodisperse clusters may be possible by taking advantage of evapourative processes. The binding of mixed clusters, on the other hand, shows a remarkable insensitivity to the species; C_{60} and C_{70} seems to be bound equally well in the clusters. The large ratio between the radius of the molecule and the range of the intermolecular potential makes such clusters interesting model systems for the study of finite size thermodynamics.

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