Magic alkali-fullerene compound clusters of extreme thermal stability

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The thermal stability of free pure C_{60}-, as well as C_{60}-alkali, and -alkaline-earth metal compound clusters is investigated. We find that small $(C_{60})_m$-clusters ($m \leqslant 6$) decay at comparatively low temperatures below 400 K, as a consequence of weak intermolecular van der Waals interaction. Adding barium or potassium to the clusters dramatically increases the decay temperatures for "magic" configurations of $(C_{60})_m Ba_{2m-1}$ and $(C_{60})_m K_{2m}$, which reach values as high as 1780 K. Contrary to common belief, the superstable compound clusters are not characterized by filled geometrical or electronic shells. Density functional calculations show that the delicate interplay of ionic (K, Ba) and covalent (Ba) interaction between C_{60} and the metal atoms, on the one hand, and entropic contributions to the Gibbs free energy, on the other hand, determine the unusual stability. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2400027]

The appearance of clusters of pronounced stability, so-called magic clusters, is usually associated with the formation of filled geometrical or electronic shells.[1–3] Prominent examples associated with electronic shell filling are the magic alkali metal clusters composed of 8, 20, 40, etc. atoms,[4] while perfect geometry is at the origin of the pronounced stability of icosahedral rare gas clusters of size 13, 55, 147, etc.[5,6] The coincident closure of both the electronic and geometric shell accounts for the magic character of the Al_{13}^- cluster anion.[7] Shell filling has also been used to explain the experimentally observed enhanced stability of some alkali-fullerene compound clusters. This class of materials is particularly interesting because alkali atoms act as electron donor, which can induce superconductivity.[8,9] The stability of $C_{60}Ba_{32}$ was explained by the decoration of all 32 facets of the fullerene molecules with Ba, thus forming a complete geometrical shell.[10] The magic clusters $(C_{60}K_6)_n K^+$, on the other hand, were associated with the complete filling of the lowest unoccupied t_{1u} molecular orbitals of C_{60} with the $4s^1$ valence electrons of K.[11]

The enhanced stability of clusters of a particular size is usually inferred from a substantially increased abundance in the mass spectra of cluster beams. Thermal equilibration of the clusters in these experiments is important to ensure that the observed magic peaks characterize minimum configurations in the Gibbs free energy (GFE). Equilibration is usually strived for by heating the clusters in the beam, e.g., by photon absorption.[10–12] The heating promotes structural ordering of initially disordered clusters, and at the same time causes evaporation of atoms or molecules, reducing the cluster size.[12] As clusters of particularly stable structures resist this evaporation process more strongly, they can thus be identified in the mass spectrum. In the present report we demonstrate by using a novel cluster heating method, that C_{60}-alkali and -alkaline-earth compound clusters with incompletely filled shells are the most stable structures. Magic $(C_{60})_m Ba_{2m-1}$ clusters are found to withstand temperatures as high as 1780 K. The experiments underline the crucial importance of careful thermal equilibration for the determination of the most stable cluster configurations. Metastable structures can easily be mistaken for the global energy minimum, when deduced from the mass spectra of nonequilibrated cluster beams.

The unusual magic configurations in the alkali-fullerene compound clusters arise due to the advantageous interplay between ionic and covalent bonding as well as entropic contributions to the GFE. This is revealed by density functional calculations. Entropic contributions are usually not considered in the determination of the most stable clusters despite the fact that at finite temperatures the most stable clusters minimize the free energy.[13] Our study proves that they are indeed essential in the small size regime and at low temperatures, where they can account for more than 20% of the total free energy. At high temperatures these effects will become more pronounced.

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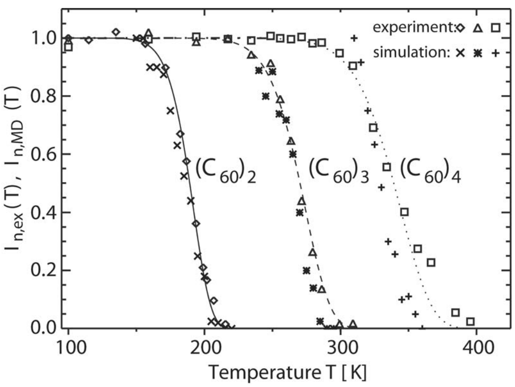

FIG. 1. Thermal decay of small $(C_{60})_m$ clusters ($m=2-4$). The clusters are heated in a He bath with a dwell time of 0.5 ms. The peak intensities from the mass spectra are normalized to the measured intensity at 150 K.

The experiments presented here have been done using a high-resolution reflectron time-of-flight mass spectrometer (TOF-MS).[14] The clusters are formed within a noble gas condensation cell and transported through the system to the detector by a jet of He atoms. A novel heating/cooling stage allowing to adjust the cluster temperature between 150 K and 1800 K is mounted directly after the cluster source.[15] Inside the stage the clusters thermalize with the He bath by collisions, thus assuming the desired temperature. The dwell time of the clusters inside the heating stage can be varied between 0.5 ms and 1 ms by controlling the He pressure inside the source. In all of the experiments the clusters were cooled to 150 K after exiting the heating stage and before photoionization. The setup is similar to Borggreen's[16] with the main difference being the maximum possible annealing temperature. Details of the experiment are published elsewhere.[12,15]

Using this setup the thermal stability of small fullerene clusters was investigated. The peak intensity of $(C_{60})_m$ clusters in the mass spectra was recorded in the temperature range between $T=150$ K to 500 K (Ref. 14). The thermal decay behavior of C_{60} dimers, trimers and tetramers shown in Fig. 1 is obtained by normalization of the peak intensity at T to the intensity at 150 K. It can clearly be seen that $(C_{60})_2$ starts to decay at 160 K and completely vanishes from the mass spectra at 210 K (Ref. 12). At room temperature also the $(C_{60})_3$, and at 400 K the $(C_{60})_4$ clusters completely decay. The decay temperature, which is characterized by $I(\mathrm{T})/I(150\text{ K})=\frac{1}{2}$, is determined to be $T_{1/2}=189$, 270, and 340 K for the dimer, trimer and tetramer, respectively. The low thermal stability indicates weak bonds between the C_{60} molecules. In contrast to the strong covalent intramolecular C—C bonds the intermolecular bonds are due to van der Waals interaction, and can easily be broken by thermal excitation. The decay behavior has been reproduced by canonic molecular dynamic simulations assuming a Pacheco-Ramalho potential to describe the intermolecular interaction.[14] The calculated intensities are superimposed on the experimental results in Fig. 1.

The thermal stability of C_{60} clusters can be significantly enhanced by adding alkali or alkaline-earth metal atoms, such as barium or potassium, to the cluster, thus forming

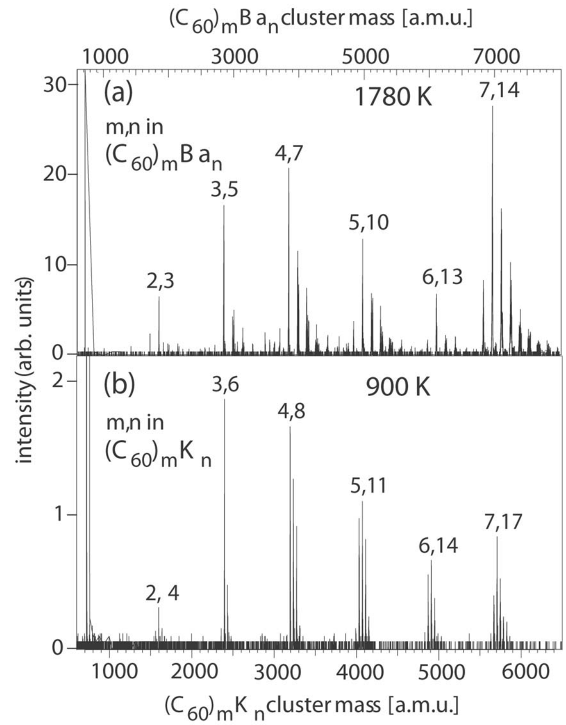

FIG. 2. ToF mass spectra of (a) $(C_{60})_mBa_n$ compound clusters, after annealing to 1780 K, and (b) $(C_{60})_mK_n$ compounds clusters, after annealing to 900 K. The stoichiometries (m,n) of the most stable clusters are indicated. Dwell time: 0.5 ms.

$(C_{60})_m$–metal compound clusters. This is achieved experimentally by simultaneous thermal co-evaporation of fullerenes and metal from two separate crucibles inside the cluster source. The stoichiometry of the clusters depends on the relative vapor pressure of both evaporants and can be adjusted by the crucible temperatures.

Without heating of the cluster beam the observed spectrum appears smooth, with no pronounced peaks, as it is characteristic for a statistical size distribution. At high temperatures less stable clusters decay while clusters of high stability remain visible in the spectrum as peaks of distinct intensity. A mass spectrum of $(C_{60})_mBa_n$ clusters taken at 1780 K is shown in Fig. 2(a). The most stable configurations $(C_{60})_mBa_n$ at 1780 K are found to be those with $(m,n)=(2,3)$, (3,5), (4,7), (5,10), (6,13) and (7,14). It appears that clusters are magic which consist of m C_{60} molecules and $n=2m-1$ Ba atoms if $m\leqslant 4$, and $2m$ or more Ba atoms if $m>4$. The cluster decay results only in an increase of the abundance of monomers of C_{60} and Ba. Larger fragments, such as the dimers C_{60}–C_{60}, C_{60}–Ba or Ba–Ba, are not found to have noticeable intensity in the mass spectrum at elevated temperatures. However, this does not mean that the evaporation of bigger fragments from the clusters is excluded as the fragments themselves may continue to decay further.

Clearly, the thermal stability of small C_{60} clusters in combination with Ba is significantly enhanced with respect to pure C_{60} clusters. To determine the origin of the increased stability, comparative experiments have been performed with K instead of Ba. Since K has a similar ionic radius as Ba ($r_{Ba^+}=1.53$ Å, $r_{Ba^{2+}}=1.34$ Å, $r_{K^+}=1.33$ Å) but only half as many valence electrons ($Ba:[Xe]6s^2; K:[Ar]4s^1$), it should help to distinguish between electronic and geometrical effects.

A mass spectrum of $(C_{60})_mK_n$ clusters taken at 900 K is shown in Fig. 2(b). Here, different magic numbers (m,n) as compared to the C_{60}–Ba clusters are observed at elevated temperatures. The most stable clusters consist of m C_{60} molecules and $n=2m$ K atoms for $m\leqslant 4$ and $2m+1$ or more K atoms for $m>4$, respectively. The following conclusions can be drawn from the experiments. (i) The observed magic numbers for $(C_{60})_mBa_n$ and $(C_{60})_mK_n$ clusters at high temperatures are neither in agreement with geometrical nor with electronic shell filling. (ii) For a given number of C_{60}'s in the cluster those with Ba are more stable than those with K, whereas the most stable configuration contains more atoms of K than of Ba.

The experiments clearly show that the heating method has significant influence on the observed result. In this work electrically *neutral* clusters have been thermalized with a He bath of given temperature by a sufficient amount of collisions ($\sim 10^5-10^6$), over a comparatively long time on the order of $\leqslant 1ms$. The obtained magic numbers differ from those observed in previous experiments, where the clusters have been heated by short laser pulses.[10,11] During photon absorption the energy is transferred to the cluster within nanoseconds, thus causing excitations of the vibrational modes similar to the striking of a bell. Due to the high photon flux more than one photon is absorbed per cluster, heating and ionizing the cluster at the same time. In such experiments, thermal stability of *ionized* clusters is probed and geometrical shell filling and electronic shell filling is found to govern the stability of $(C_{60})_mBa_n$ and $(C_{60})_mK_n$, respectively. As can be seen in Fig. 2, the clusters with closed shells, which would be $(C_{60})_mBa_{3m}$ and $(C_{60})_mK_{6m}$ under the assumption of complete ionization of the metals, are not visible here, meaning that they are less stable than other configurations.

Thermal stability is therefore not only determined by the annealing temperature alone, but also by the exposure time. The probability to enter the cluster configuration of global energy minimum on the potential energy surface (PES) increases with temperature and heating time. This, in turn, also promotes evaporation of atoms, resulting in cooling of the cluster and even in a change of its PES. The balance between temperature and annealing time can be exploited to perform a wealth of new experiments probing the PES, as was demonstrated on large clusters of C_{60} molecules.[12]

It has previously been pointed out that experimentally observed magic peaks deviate from those predicted by electronic and geometrical shell filling arguments, and it has been suggested that entropy might be responsible for this.[17–19] Here, we present the first evidence from *ab initio* calculations that entropy is indeed important in determining absolute cluster stability. Density functional calculations have been performed on $(C_{60})_2M_n$ $(1\leqslant n\leqslant 6, M=K,Ba)$ clusters.[20] We consider only monomer evaporation since other decay channels have not been observed and cannot be quantified. Due to the formidable computational cost, the calculations were limited to clusters containing two C_{60}'s and two main sets of geometries. In Set A, all of the metal atoms were sandwiched between the fullerenes, whereas in Set B they had an $M-C_{60}-M_{n-2}-C_{60}-M$ arrangement. In addition, finite temperature contributions to the GFE were computed for the most energetically stable clusters for a given n at the temperatures of the heating and of the cooling stage (150 K). If we allow for uncertainties in the calculated entropy per metal atom by only up to 4%, the temperature at which the clusters will start to decompose (i.e., $\Delta G\approx 0$), is in agreement with experimental observations. Errors of this magnitude in ΔS are to be expected due to the fact that the harmonic approximation has been applied and that small errors in the entropy inflate errors in the GFE at high temperatures (S is multiplied by T). However, at low temperatures the cluster distribution can be predicted accurately, and we have accordingly calculated the cluster stabilities at 150 K. The agreement between theory and experiment indicates that the clusters that are frozen out upon cooling are the most stable structures at 150 K, not metastable structures that have accidentally survived the heating/cooling process. Other affordable computational methods could not provide superior results; molecular dynamics (MD) requires the use of unknown interaction potentials, and *ab initio* MD would be prohibitively expensive.

Figure 3(b) shows the dependence of the main bonding mechanisms[20,21] on n for the energetically most stable Ba clusters, which all belonged to Set A. For $1\leqslant n\leqslant 3$ and $n=5,6$ the dominant interaction is ionic and covalent bonding, respectively. The magnitude of the former decreases steadily with increasing n, as does the average Mulliken charge per Ba [Fig. 3(a)]. For large n, full electron donation to the unoccupied C_{60} orbitals cannot occur, since the electrostatic repulsion between the Ba^{2+} ions would be too large for the cluster to be stable. Instead, as n increases, so does back donation into the empty Ba $5d$ orbitals. Thus, the d-element character of Ba (Ref. 22) is essential in determining the bonding and geometries of these clusters.

The total binding energy per metal atom (BEM) confirms that $(C_{60})_2Ba_3$ is the most stable cluster. This is a result of the balance between a decreasing stabilization from the $Ba\rightarrow C_{60}$ electron transfer and an increasing stability from $C_{60}\rightarrow Ba$ back donation, as n increases. However, the BEM reveals that $(C_{60})_2Ba$ is only 50 meV less stable. In order to explain the magic character of $(C_{60})_2Ba_3$, one needs to consider the entropic and enthalpic contributions to the Gibbs free energy (GFE) change per metal atom (see Ref. 23). Figure 3(c) shows that the former has a greater destabilizing effect on smaller clusters than on larger ones. This can be explained by considering the production of the largest and smallest possible clusters from the reaction of $2n(C_{60})$ and n(Ba). Clearly, the former is entropically favored since it yields $Ba_n(C_{60})_2$ and $(2n-2)C_{60}$, a total of $2n-1$ molecules, while the latter yields$n(Ba(C_{60})_2)$, a total of n molecules. At higher temperatures the entropic contribution to the GFM is expected to become even more important. The $H_{EC}M$ (see Ref. 23) is about one order of magnitude smaller than TSM and has little effect on the total GFM. The GFM, given in Fig. 3(d), shows a distinct minimum for $(C_{60})_2Ba_3$, confirming the stability of this configuration.

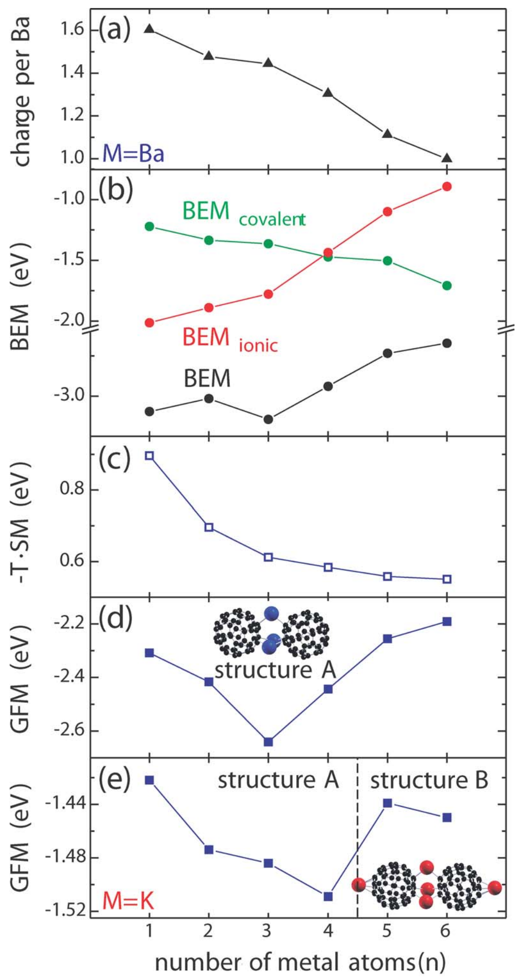

FIG. 3. (Color online) DFT calculations of the alkali- and alkali-earth-fullerene compound clusters. (a) average Mulliken charge per Ba, (b) relevant contributions to BEM, (c) -TSM, and (d) GFM of the most stable $(C_{60})_2Ba_n$, $1 \leq n \leq 6$, clusters, (e) GFM of the most stable $(C_{60})_2K_n$, $1 \leq n \leq 6$, clusters. (See Refs. 21 and 23.)

A similar analysis for the $(C_{60})_2K_n$ clusters showed that the bonding is purely ionic, with an almost full transfer of the valence K $4s^1$ electrons to the unoccupied orbitals of the C_{60}'s. The GFM shown in Fig. 3(e) agrees with the experimental observation that $(C_{60})_2K_4$ is magic. Here, consideration of finite temperature effects changes the order of stability of the clusters. $(C_{60})_2K$ and $(C_{60})_2K_4$ are predicted to be the most stable at 0 K and 150 K. The calculations show a structural transition for $(C_{60})_2K_n$ from Set A to Set B for $n \geq 5$ in order to reduce the electrostatic energy between the positively charged metal ions. Thus, the preferred geometries of the potassium clusters are mainly determined by the strong tendency of the alkaline atoms to ionize almost completely and to distribute over the C_{60} surface. However, it is necessary to take into account the entropic contribution to the GFE in order to identify the most stable structure.

In summary, the thermalization of $(C_{60})_mBa_n$ and $(C_{60})_mK_n$ with a He bath yields a series of magic clusters with distinctively high thermal stability, which cannot be explained by common shell filling models. For K clusters, DFT calculations identified metal-to-C_{60} electron transfer as the main bonding mechanism and the geometries of these clusters could be explained with comparatively simple electrostatic models. For the Ba clusters, an interplay between ionic and covalent bonding was found. In agreement with experimental results, the GFM indicate that $(C_{60})_2Ba_3$ and $(C_{60})_2K_4$ are the most stable structures and therefore appear as magic clusters at the experimental temperatures and pressures. Magic clusters are hence not only a result of the distinctive nature of the electron transfer but also of entropic effects.

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[20] See EPAPS Document No. E-JCPSA6-125-022645 for a description of the computational details. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).
[21] BEM is the total binding energy per metal atom. The $(C_{60})_2Ba_n$ clusters exhibited ionic bonding due to a charge transfer from the Ba 6s to the unoccupied C_{60} molecular orbitals (BEM_{ionic}), covalent bonding between the Ba 5d and $C_{60}-\pi^*$ orbitals ($BEM_{covalent}$) and metal-metal bonding between the Ba atoms ($BEM_{Ba\text{-}Ba}$). Also, the C_{60}'s did not retain icosahedral symmetry in the optimized clusters (BEM_{geo}). BEM_{geo} and ($BEM_{Ba\text{-}Ba}$) were found to be small, and a systematic trend could not be observed. In a latter publication it will be shown that the GFM/BEM give a means to globally compare the fragmentation energies of the clusters.
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[23] GFM is the Gibbs free energy change per metal atom for the cluster formation and is calculated by $GFM = BEM + H_{EC}M - TSM$, where T is the temperature, and $H_{EC}M$ and SM are the change in the finite temperature enthalpy correction and in the entropy per metal atom for the reaction: $2(C_{60}) + n(Ba) \rightarrow Ba_n(C_{60})_2$.