Multilayer Metal Coverage of Fullerene Molecules

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Intensity anomalies in the mass spectra of clusters with composition $C_{60}M_x$ and $C_{70}M_x$ ($x = 0$–500; $M \in \{\mathrm{Ca,Sr,Ba}\}$) seem to be caused by the completion of metal layers around a central fullerene molecule. The first layer is complete when one metal atom is situated above each of the 32 or 37 rings of the fullerene cage. This property appears to make it possible to "count the rings" of fullerenes. The first and additional layers are described in terms of a periodically reoccurring structure having icosahedral symmetry.

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Now that C_{60} is available in macroscopic quantities at rather moderate prices, scientists are encouraged to study the interaction of this fullerene with other molecules and elements. One topic, intercalation compounds of fullerenes and alkali metals, has experienced particular attention since the discovery of superconductivity in solid K_3C_{60} [1,2]. As a possibly helpful approach to a better understanding of the bulk intercalation compounds, the properties of very small metal-fullerene systems, termed clusters, can be studied theoretically and experimentally in the gas phase [3,4].

We recently reported the results of experiments on alkali metal coated C_{60} clusters indicating that the stability of the clusters seemed to be determined by its electronic configuration [5]. The only exception was the high stability of $Li_{12}C_{60}$, which was interpreted to be of geometric origin, with one Li atom above each of the pentagonal faces of C_{60}.

In this Letter we report on clusters having the composition $C_{60}M_x$ and $C_{70}M_x$, $M \in \{\mathrm{Ca,Sr,Ba}\}$. The stability of these clusters seems to be purely geometric in origin. A particularly stable structure is formed each time a layer of metal atoms has been completed around a central fullerene molecule. The first layer contains exactly the same number of metal atoms as there are rings in the fullerene cage. In growing additional layers, the metal might be expected to prefer the icosahedral shell structure observed in pure alkaline earth clusters [6,7]. However, our measurements suggest a different growth pattern.

To study clusters of alkaline earth metal covered fullerenes, we used the technique of photoionization time-of-flight mass spectrometry. The clusters were produced in a low-pressure, inert gas condensation cell filled with 1 torr He gas and cooled by liquid nitrogen. Inside the cell, two ovens, one containing a fullerene and one containing a metal, produce interpenetrating vapor clouds of the respective materials. This mixture is quenched by the cold He gas, causing clusters with various compositions of fullerene and metal to condense out of the vapor. The composition of the clusters can be adjusted by the temperatures of the ovens. By keeping the temperature of the metal oven below the threshold for formation of pure metal clusters and introducing only small amounts of fullerenes as condensation seeds into the metal vapor, we generated cluster distributions consisting almost completely of compositions $C_{60}M_x$ or $C_{70}M_x$ with $M \in \{\mathrm{Ca,Sr,Ba}\}$. The clusters are transported by the He flow through a nozzle and a differential pumping stage into a high vacuum chamber. For ionization of the clusters, we used excimer laser pulses having a wavelength of 308 nm (4.0 eV). The ions were then mass analyzed by a time-of-flight mass spectrometer.

To study the relative stability of clusters, i.e., to enhance mass peaks corresponding to particularly stable clusters, it is useful to heat the clusters until they evaporate atoms and molecules. Clusters of low stability will then decrease in mass and size, in our case by evaporating metal, until a more stable cluster composition is reached, thus causing an increase in abundance of that species. Using sufficiently high laser fluences ($\simeq 60\ \mu\mathrm{J/mm}^2$), we simultaneously heated and ionized the clusters with the excimer laser pulse.

A mass spectrum of $C_{60}Ba_x$ is shown in Fig. 1. The

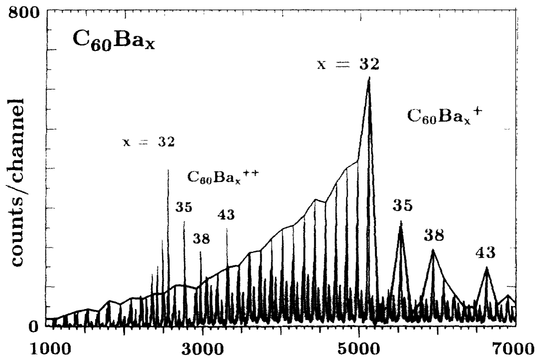

FIG. 1. Mass spectrum of photoionized $C_{60}Ba_x$ clusters containing both singly and doubly ionized species. The solid line connects peaks of singly ionized clusters. The sharp edge occurs at 32 metal atoms, equal to the total number of hexagonal and pentagonal rings of the C_{60} molecule.

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solid line connects mass peaks corresponding to singly ionized clusters. The peaks not connected by the line correspond to doubly ionized clusters. The sharp edge at $C_{60}Ba_{32}$ observed in both the singly and the doubly ionized series implies that these clusters have a very high stability. Since the number of metal atoms at which this edge occurs is independent of the charge of the cluster, the stability seems to be of geometric origin. The most obvious structure of $C_{60}Ba_{32}$ is obtained by placing a Ba atom onto each of the 12 pentagons and 20 hexagons of the C_{60} molecule, 32 atoms in total. This structure could be visualized as a first metallic layer covering the C_{60} molecule. To get a rough notion of the packing density of this layer, assume the atoms to be hard spheres with the covalence radius of the atoms (0.77 Å for C; 1.98 Å for Ba [8]). Placing the carbon spheres at the vertices of the C_{60} structure with bond lengths 1.40 Å and 1.45 Å [9] and putting the Ba spheres on top of the rings, the Ba spheres placed on neighboring hexagons will almost touch, spheres on neighboring pentagons and hexagons will overlap by a few tenths of an angstrom. In this simple picture the packing of the metal layer is almost perfectly dense, the Ba atoms having just the right size. Not included in this simple picture is, of course, a possible expansion of the double bonds of C_{60} due to electron transfer to the antibonding lowest unoccupied molecular orbital (as was found in the case of $C_{60}Li_{12}$ [3]).

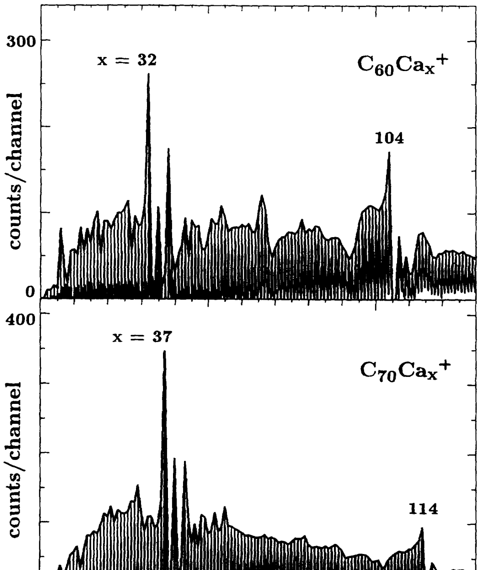

FIG. 2. Mass spectra of photoionized $C_{60}Ca_x{}^+$ (top) and $C_{70}Ca_x{}^+$ (bottom). The lower axis is labeled by the number of metal atoms on the fullerene molecule. The peaks at $x=32$ for $C_{60}Ca_x$ and $x=37$ for $C_{70}Ca_x$ correspond to a first metal layer around the fullerenes with one atom located at each of the rings. The edges at $x=104$ and $x=114$, respectively, signal the completion of a second metal layer.

To verify that our experiment comprises a method of counting the rings of a fullerene, we tested it on C_{70}. Figure 2 shows two mass spectra, the upper one of $C_{60}Ca_x{}^+$, the lower of $C_{70}Ca_x{}^+$. A weak background has been subtracted. In the spectrum containing C_{60}, the coverage with 32 Ca atoms again leads to an extremely pronounced feature. In the spectrum containing C_{70}, we have a very strong peak at $C_{70}Ca_{37}$. C_{70} has 12 pentagons and 25 hexagons, totaling 37, the "ring-counting test" thus being passed.

Further prominent features in Fig. 2 are the edges at $C_{60}Ca_{104}{}^+$ and $C_{70}Ca_{114}{}^+$. We believe these edges signal the completion of the next layer of metal which will be discussed below. Features in the mass spectra below the filling of the first layer and between the filling of the first and the second, perfectly identical for calcium and strontium coverage of the fullerenes, may give some clue to the building process of the layers. However, we do not presently have convincing evidence regarding details of this process.

The fact that the second layer of metal around C_{60} contains exactly the same number, 72 ($=104-32$), of metal atoms for both calcium and strontium leads us to believe that the structure of the second layer may be obtained by packing balls onto the first layer. If the number of atoms in the second layer were only a question of packing as many atoms as possible around a structureless core, the difference in the sizes of Ca and Sr atoms should have resulted in different numbers for layer completion. Note that we speak of layers, not shells. The term "shell" implies self-similarity which, as we will see below, does not apply in our case.

In order to determine a general layer-building scheme, evidence for the formation of even larger layers must be considered. Figure 3 shows a spectrum of C_{60} covered with the largest amount of Ca experimentally possible (note the logarithmic scale). We interpret the edges at

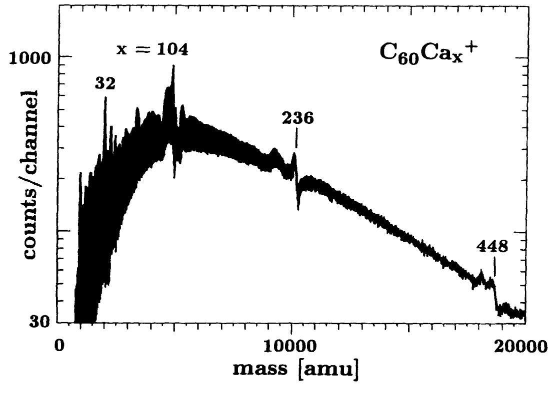

FIG. 3. Mass spectrum of photoionized $C_{60}Ca_x{}^+$ clusters with high metal content. Additional edges, interpreted as completion of a third and fourth layer, are observed at $x=236$ and $x=448$.

$C_{60}Ca_{236}^+$ and $C_{60}Ca_{448}^+$ to correspond to the completion of a third and fourth metal layer. It should be stated that the third and fourth metal layers were only observed for C_{60} covered with calcium ($C_{70}Ca_x^+$ showed a weak edge around $x=260$, possibly signaling the completion of a third layer). In the cases of strontium and barium, the metal content of the clusters could not be increased far enough without also producing pure metal clusters. Because of the various isotopes of the alkaline earth metals, the peaks in the mass spectra become increasingly broad with rising metal content, making it impossible to clearly distinguish between pure metal clusters and clusters containing one fullerene molecule.

We will now turn to proposing the structural arrangement of the atoms in the layers, focusing mainly on the coverage of C_{60} which, due to its high symmetry, can be visualized more easily. The arrangement of the first layer, as previously stated, suggests itself immediately: the 32 metal atoms are situated on the 32 faces of the C_{60} molecule. In the hard sphere picture, their distance to the center of the molecule would be almost equal for atoms on hexagonal and pentagonal faces. More precise predictions would have to rely on *ab initio* calculations, including a change in bond lengths of C_{60}.

In constructing the second layer, it is reasonable to expect this layer to preserve the icosahedral symmetry of the first layer. To make the description of the structures more clear, we will often specify the positions of the metal atoms relative to the central C_{60} molecule. This is not meant to imply any direct interaction between the C_{60} and the atoms of the second layer. The second layer contains 72 atoms. The last digit of this number, being indivisible by 5, requires that each of the fivefold symmetry axes passes through two atoms. Consequently, in the second layer there must be 1 atom perpendicularly above each of the 12 pentagonal faces of C_{60}. The remaining 60 atoms can be arranged basically in two different ways. The first would be to place the atoms such that they are triply coordinated to the atoms of the first layer, i.e., placing them above the carbon atoms as shown in Fig. 4 on the left. The atoms above the pentagons of C_{60} (shaded) constitute the vertices of an icosahedron, the unshaded atoms resemble a C_{60} cage. This structure can also be visualized as twelve caps, each consisting of a five-atom ring around an elevated central atom, placed at the vertices of an icosahedron. This structure, however, does not present an even coverage; there are 20 large openings above the hexagonal faces of C_{60} while neighboring caps overlap along the double bonds of C_{60}. A second way to arrange the 60 atoms, pictured on the right in Fig. 4, is obtained by rotating each cap by one-tenth of a turn (36°) around the fivefold axis through its center. The coordination to the atoms of the first layer will then be only twofold, but the coverage will be quite even. We thus believe the latter of the two structures proposed to be more probable. The resulting structure could be described as an "edge-truncated icosahedron" with 20 slightly vaulted triangular faces. Each face consists of the three icosahedral vertices with a smaller, almost densely packed triangle of three atoms set in between. Note that the first layer can be viewed as a similar construction with only one atom in the smaller "triangle" between the vertices. Using the terminology of Northby [10,11], the second layer would consist of atoms at the 72 FC sites on a 55-atom Mackay icosahedron [12]. Such a layer of 72 atoms put onto a Mackay icosahedron would not result in a stable structure since it only covers the inner part of the triangular faces, leaving large crevices along the edges between the triangular faces. In our case, however, the second layer is built around the core formed by the first layer which is smaller than the corresponding 55-atom icosahedron. The crevices at the edges therefore do not exist, leading to a stable structure.

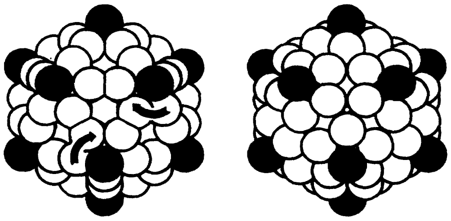

FIG. 4. Two possible geometries for arranging the 72 atoms of the second layer. The atoms above the pentagons of C_{60} are shaded. The structure on the left can be transformed into the more evenly distributed arrangement of atoms on the right by 36° turns of the caps around the fivefold axes.

Additional layers can be constructed in a similar manner: place one atom above each of the icosahedral vertices and increase the length of the edges of the triangles between the vertices by one atom for each additional layer. With respect to the layers underneath, the atoms in these triangles are arranged according to the fcc packing scheme of spheres. The resulting structures of the first four layers are depicted in Fig. 5. The atoms at the icosahedral vertices are shaded.

To express the number of atoms needed to complete such a layer mathematically, let us introduce a layer index K. Define K as the number of atoms along the edge of a triangular face without including the atoms on the vertices above the C_{60} pentagons. The first layer then has $K=1$, the second $K=2$. The number of atoms in the Kth layer can easily be calculated to

$$10K^2+10K+12\,. \tag{1}$$

The total number of atoms $N(K)$ in a cluster composed of K complete layers around C_{60} becomes

$$N(K)=\tfrac{1}{3}(10K^3+30K^2+56K)\,. \tag{2}$$

Note that the coefficient of the leading order in K, determining the shell spacing on an $N^{1/3}$ scale, is equal to that of an icosahedral cluster of the Mackay type [13].

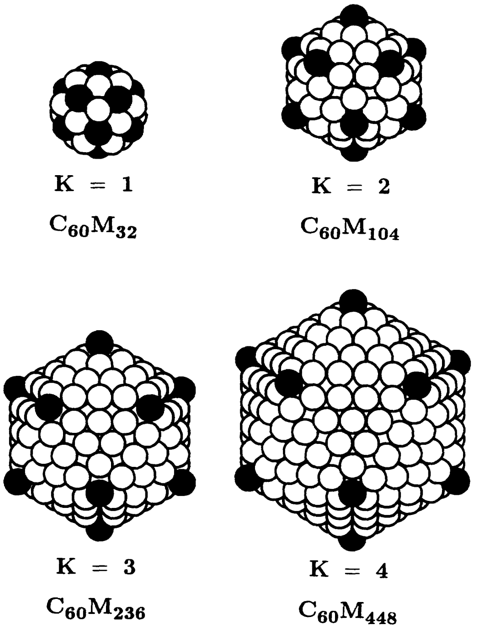

FIG. 5. Proposed arrangements of the atoms in the first four layers around a C_{60} molecule. The atoms at the icosahedral vertices are shaded.

Inserting $K=1$–4 into Eq. (2), we find $N(1)=32$, $N(2)=104$, $N(3)=236$, and $N(4)=448$. These values are identical to the number of atoms observed in clusters having unusually high stability. Obviously, the scheme of building the layers proposed above agrees with the experimental data. Note that the structures depicted in Fig. 5 are not self-similar since the width of the truncated edges remains fixed while their length increases with increasing K. The next layer would be expected at $N(5)=760$. With increasing size the shape of the cluster will converge asymptotically to that of a perfect icosahedron. In the case of C_{70} covered with calcium, the second layer containing 77 atoms could be constructed by placing the six-atom caps above the pentagons as done in the second layer of C_{60}. Putting the remaining 5 atoms above the 5 bonds on the equator around the fivefold axis of C_{70}, an evenly covered second layer results.

In this paper we have shown that the number of alkaline earth atoms in the first layer of metal on C_{60} and C_{70} seems to "count the rings." As the higher fullerenes become available in quantity, it will be interesting to see if this method of counting remains effective. If so it might provide a tool to distinguish between "bucky balls" and "bucky onions" in the mass spectrum by giving a measure for the surface area.

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