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Cluster assemblies of metal-coated fullerenes

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Abstract. One of the most appealing aspects of cluster science while it was still in its infancy was the simplicity of the objects studied. More recently, cluster beam experimentalists have begun to direct their interest to more complex condensates which might better be called cluster assemblies. We present mass spectra of Tm-C_{60} and Ho-C_{60} cluster assemblies which indicate that they are composed of subunits of metal-covered fullerene molecules.

PACS. 36.40.-c Atomic and molecular clusters – 61.48.+c Fullerenes and fullerene-related materials

1 Introduction

As the field of cluster science matures, it becomes possible to study increasingly complex structures. The techniques of colloid science have recently been used to study the self-assembly of ligand stabilized clusters into regular arrays [1–5]. Predictions have been made that it may even be possible to construct such arrays using clusters without ligands [6]. Clusters themselves could be used as building blocks in the construction of even more complex condensates which we will refer to as cluster assemblies. In this paper we report evidence for stable assemblies of metal-coated fullerenes.

The technique we use to study structure is mass spectrometry. It may seem overly optimistic to attempt to deduce a complex structure from just one simple number, the mass of a cluster. We are greatly aided in the analysis by the fact that we do not "weigh" just one cluster, but rather a whole series of clusters with various sizes and compositions. In addition, we can establish the relative stability of a cluster within this series by observing which survive after heating to a temperature at which component atoms and molecules begin to evaporate. The cluster building blocks used in the construction of our assemblies are metal-covered fullerenes. Several studies of clusters containing two or more fullerene molecules bonded with alkali metals [7] and transition metals [8–12] have already been reported. The metal we have chosen for the present study is thulium. Why use such an exotic metal? The choice of metal was dictated by the experimental techniques used in the investigation. We favor the use of a resistively-heated oven to produce metal vapor. Such an oven, if placed in a chamber containing 1 mbar of He gas, constitutes a stable source of large clusters. However, the metal must have a high vapor pressure at reasonable temperatures and be unreactive with the oven materials. This requirement limits the choice of metal to groups I and II and a few transition metals. The choice is further limited by the requirement that the metal should have only one natural isotope. Mass spectra of large clusters of elements containing several isotopes are often impossible to interpret unambiguously. Finally, we enhance magic numbers in mass spectra by inducing clusters to evaporate atoms from the "solid phase". Therefore, the metal should "sublime" before melting. Only two metallic elements in the periodic system meet all three requirements (high vapor pressure, one isotope and sublimation) manganese and thulium.

2 Experiment

To study clusters of thulium-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 mbar of 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. 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.

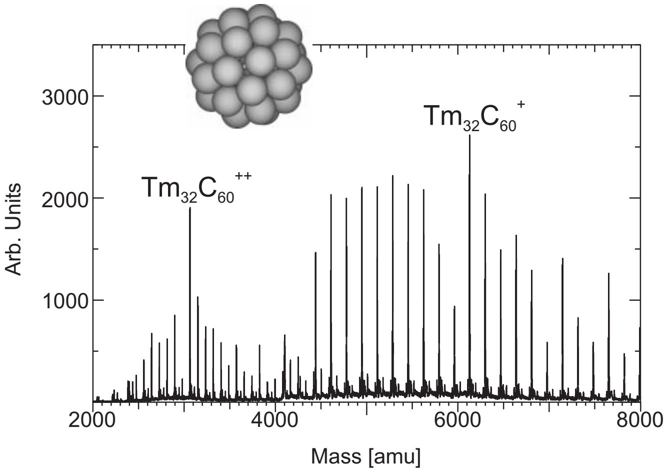

Fig. 1. Mass spectrum of photoionized Tm_xC_{60} clusters containing both singly and doubly ionized species. An unusually strong peak is observed for $x = 32$, equal to the total number of hexagonal and pentagonal rings of the C_{60} molecule.

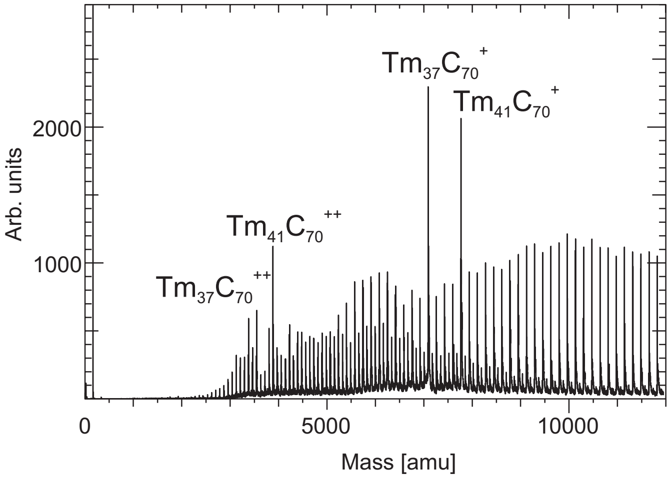

Fig. 2. Mass spectrum of photoionized Tm_xC_{70} clusters containing both singly and doubly ionized species. Unusually strong peaks are observed for $x = 37$ and 41.

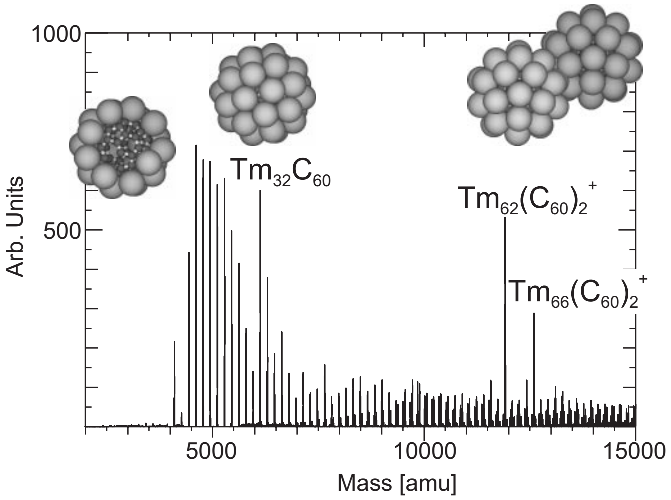

Fig. 3. Mass sectrum of C_{60}-T, clusters containing both one and two fullerene molecules.

Using sufficiently high laser fluences ($\simeq 60\,\mu J/mm^2$), the clusters are simultaneously heated and ionized.

3 Results and discussion

Figure 1 is an example of a mass spectrum obtained if we put C_{60} in one oven and thulium in the other oven. It corresponds to one C_{60} molecule coated with x-thulium atoms, where x varies from about 20 to 42. Notice that one mass peak stands out particularly strongly, $x = 32$. Presumably this peak is strong because the corresponding cluster is resistant to evaporation. That is, this cluster is particularly stable. Now the question arises, why is it stable. Is it because the atoms are arranged in a highly symmetric manner? Or is the cluster stable because it has a closed-shell electronic configuration? We can find the first hint for answering this question by looking at the mass spectrum of clusters with an additional electron removed. The mass spectrum of doubly-ionized clusters can also be extracted from Fig. 1. We see once again that $x = 32$ stands out strongly. This is an indication that the high stability of the cluster has a geometric origin and not an electronic origin.

Why should C_{60} covered with 32 thulium atoms have a particularly high symmetry? C_{60} has 12 pentagonal faces and 20 hexagonal faces, for a total of 32. If we were to place one metal atom in the center of each of the 32 faces, we would have a highly symmetric, icosahedral symmetry, and presumably a highly stable cluster. This explanation immediately suggests a new experiment. C_{70} has 12 pentagonal faces and 25 hexagonal faces for a total of 37. Clearly, we should repeat the experiment using C_{70} as the core molecule. Figure 2 shows a mass spectrum of C_{70} coated with thulium. A strong peak is seen at $x = 37$ and 41.

Usually, the addition of one atom to a cluster having a closed geometric shell results in a relatively unstable cluster. The additional atom must sit on a smooth metallic curved surface and is easily removed. This is evidently not the case for Tm_{33} C_{60}, although $Ba_{33}C_{60}$ did show the expected lack of stability [13]. The reason is that 32 barium atoms on C_{60} form a symmetric layer which is at the same time close-packed. Thulium atoms are considerably smaller than barium atoms. An additional thulium atom can squeeze its way into the first metallic layer without a great loss in stability.

If $Tm_{32}C_{60}$ were a true building block, we would expect the stable dimer to have the composition $Tm_{64}(C_{60})_2$. Figure 3 shows that this is not the case. Two dimer clusters show their high stability by resisting evaporation during the strong laser pulse, $Tm_{62}(C_{60})_2^+$ and $Tm_{66}(C_{60})_2^+$. It would seem that metal atoms can be added or removed at the point of contact between the two "monomers".

Even larger assemblies can be produced by using higher temperatures in both the C_{60} and thulium ovens. A mass

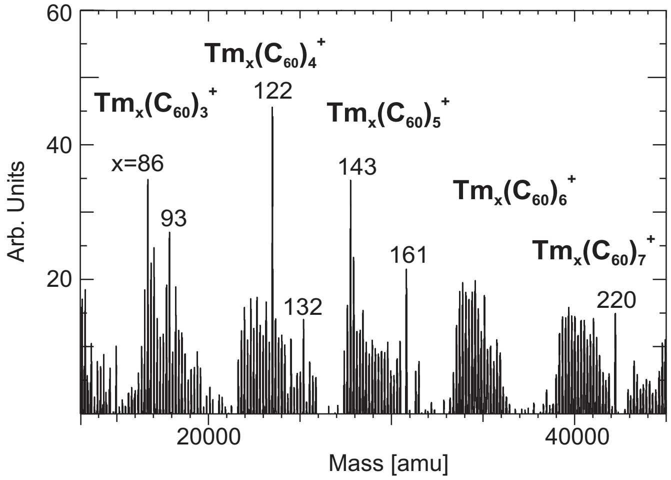

Fig. 4. Mass spectrum of $\mathrm{Tm}_x(\mathrm{C}_{60})_y$ clusters. The average composition of clusters in each group of peaks is about $(\mathrm{Tm}_{31}\mathrm{C}_{60})_y$.

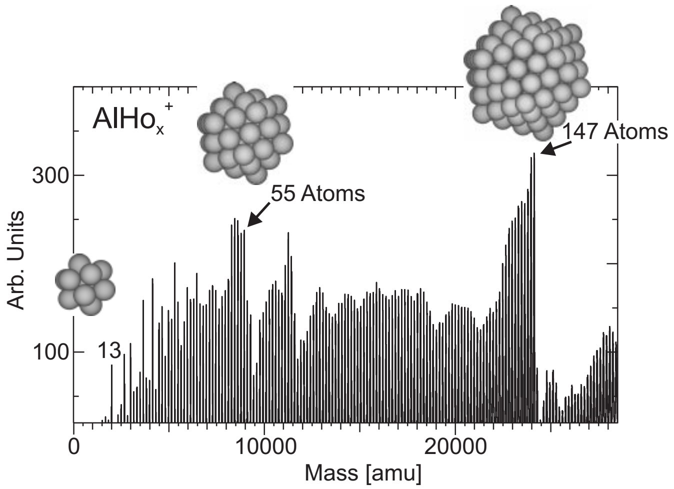

Fig. 6. Mass spectrum of AlHo_x^+ clusters. The aluminum atom provides a seed onto which the holmium vapor condenses. The sequence of strong mass peaks indicates the clusters have icosahedral symmetry.

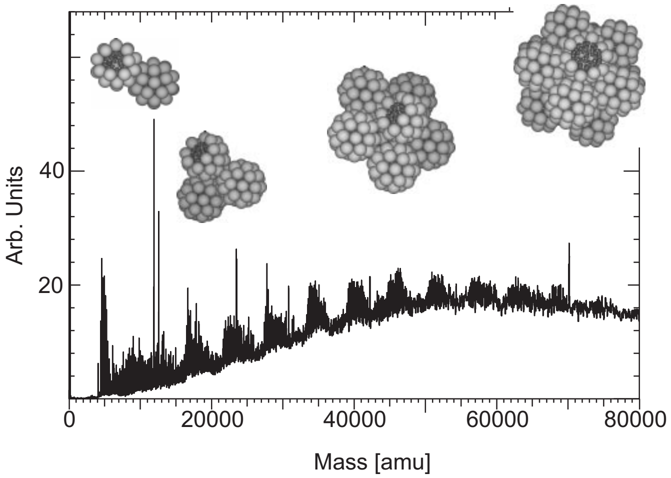

Fig. 5. Mass spectrum of large $\mathrm{Tm}_x(\mathrm{C}_{60})_y^+$ clusters. Each group of peaks corresponds to clusters containing the same number of fullerene molecules. Notice the unusually strong mass peak at 70 180 mass units.

spectrum obtained under such conditions is shown in Fig. 4. The mass peaks appear in bunches, each bunch corresponds to an assembly with a definite number of C_{60} molecules. The average composition of each bunch is approximately $(\mathrm{Tm}_{31}\mathrm{C}_{60})_y$. Individual mass peaks protrude from the bunches indicating that certain cluster sizes and compositions have resisted evaporation and are therefore particularly stable, for example, $\mathrm{Tm}_{122}(\mathrm{C}_{60})_4^+$. It is not possible to uniquely interpret similar mass spectra of clusters containing C_{70} molecules because of a mass coincidence between one C_{70} and five thulium atoms.

The largest cluster observed to be unusually stable has a mass of 70 180 dalton, Fig. 5. At this point, a discussion of the mass calibration and resolution of our instrument is appropriate. Under optimal conditions our time-of-flight spectrometer has a mass resolution, $M/\Delta M$, of 40 000. "Optimal conditions" means the cluster does not lose mass through thermal evaporation once it leaves a small volume within the acceleration field. However, we must heat the clusters to a temperature at which they evaporate in order to enhance magic numbers, i.e. the intensities of particularly stable clusters. Large clusters have stored so much thermal energy that they continue to evaporate even after leaving the ionization volume. This greatly reduces the mass resolution, in this case to only 1000. The broadening of the mass peaks in turn makes difficult a precise mass calibration because the sequence of clusters cannot be followed continuously from small clusters, which can be uniquely identified, to large clusters. For this reason we must assign the mass peak at nominally 70 180 amu to either $\mathrm{Tm}_{364}(\mathrm{C}_{60})_{12}$ or $\mathrm{Tm}_{360}(\mathrm{C}_{60})_{13}$. The potentially high symmetry of this latter assembly has not escaped our notice.

It was mentioned at the beginning that only two metallic elements possess the three requirements of optimal experiments of this type. The element holmium has just one disadvantage. Sufficient vapor pressure can be attained only for temperatures at which the oven self-destructs. Still, it was possible to obtain a few spectra. The comparison is of interest because Tm and Ho are neighbors in the periodic table, Ho having 11 f-electrons and Tm having 13. Despite this similarity their behavior as a cluster component is quite different.

We cannot show a mass spectrum of pure Ho clusters: apparently it does not self-nucleate easily. However, the presence of just one impurity; Al, O, or F, for example, provides the seed for cluster growth. A mass spectrum of AlHo_x^+ is shown in Fig. 6. Discontinuities in the mass spectrum at clusters containing 13, 55 and 147 atoms most likely reflect geometric shell structure. The additional strong mass peaks for 19, 23 26 and 29 atoms indicate that

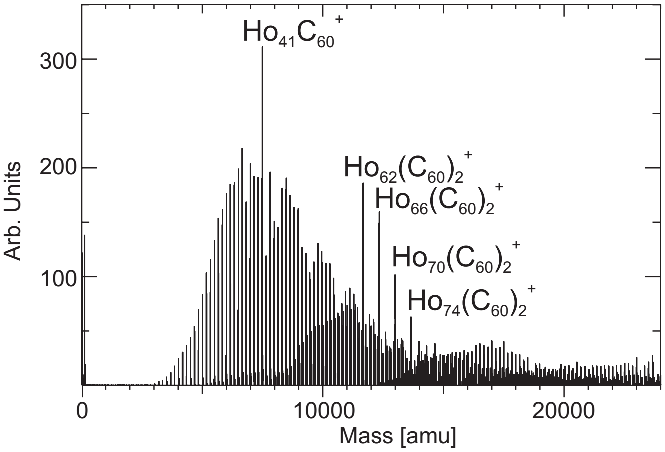

Fig. 7. Mass spectrum of $Ho_x(C_{60})_y^+$ clusters for $y = 1$ and 2.

the symmetry is probably icosahedral, at least for small clusters. The thulium metal mass spectra do not show icosahedral shell structure.

C_{60} also provides a seed for the condensation of Ho vapor. A mass spectrum of clusters containing one and two fullerene molecules is shown in Fig. 7. Notice that $Ho_{32}C_{60}^+$ is not a magic number. Instead, a strong peak occurs at $Ho_{41}C_{60}^+$. We can give no plausible explanation for this disimilarity with Tm-C_{60}. It is particularly surprising in light of the dimer magic numbers, $Ho_{62}(C_{60})_2$ and $Ho_{66}(C_{60})_2$, which are identical to those for the Tm-C_{60} system.

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