Cage Destruction in Metal-Fullerene Clusters

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Mass spectrometric studies on free clusters composed of single fullerene molecules and transition metal atoms ($C_{60}M_x$ and $C_{70}M_x$; $x = 0, \dots, 150$, $M \in \{\mathrm{Ti, V, Nb, Ta}\}$) reveal that they undergo a laser induced transformation from metal-fullerene clusters to metal carbide and metallo-carbohedrene clusters. Two types of fragmentation behavior are observed. Fullerenes doped with titanium or vanadium seem to be stable at low laser intensities, whereas tantalum and niobium severely destabilize the fullerene cage. Photofragmentation spectra of preselected $C_{60}Ta_x$ indicate that the C_{60} cage is destroyed for $x \geq 3$. [S0031-9007(96)01478-0]

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In earlier experiments the properties of both group I and group II metal-fullerene clusters have been investigated. The stability of alkali metal coated C_{60} turned out to be predominantly determined by electronic effects [1]. For alkaline earth metals icosahedral metal layers around a central fullerene molecule were observed [2]. In both cases the fullerene molecules remain stable entities that are decorated with metal atoms in different ways. Heating the clusters with a laser pulse results only in the evaporation of metal atoms. Although the metal atoms certainly do influence the fullerene, the interaction is too weak to break the carbon cage. The situtation is quite different for transition metal atoms that interact much more strongly with the carbon atoms. In this Letter we report on transition metal fullerene clusters having the composition $C_{60}M_x$ and $C_{70}M_x$, $M \in \{\mathrm{Ti, V, Nb, Ta}\}$. Exposed to high laser intensities, these metal-fullerene clusters are found to transform into metal carbide and metallo-carbohedrene clusters.

As cluster source we used a modified low-pressure, inert gas condensation cell [3,4]. The transition metals with their very low vapor pressure were evaporated using the second harmonic output of a pulsed Nd:YAG laser focused onto a metal target inside the condensation cell. The laser vaporized material mixes with fullerene vapor from a resistively heated oven. This vapor mixture is quenched in a low pressure helium atmosphere (ca. 1 mbar) cooled by liquid nitrogen. The composition of the resulting clusters can be controlled by changing the temperature of the fullerene oven and the power of the vaporization laser. At moderate fullerene oven temperatures it is possible to find operating conditions where almost exclusively clusters of the composition $C_{60}M_x$ or $C_{70}M_x$ containing only one fullerene molecule and a varying number of metal atoms are formed. The clusters are transported from the condensation cell through a nozzle and a differential pumping stage into a high vacuum chamber where they are photoionized and mass analysed in a time-of-flight mass spectrometer (TOF). For the ionization we used excimer laser pulses at three different laser wavelengths (308 nm, 248 nm, and 193 nm).

A series of mass spectra of C_{60} vanadium clusters exposed to increasing ionization laser intensity is shown in Fig. 1. The spectra were taken at constant source conditions; therefore, they show the ionized fragmentation products of the same neutral cluster distribution. The laser pulse not only ionizes but also heats the clusters, resulting in an increasing degree of fragmentation. At low laser intensities [Fig. 1(a)] we see a distribution of clusters $C_{60}V_x$. Every peak in the mass spectrum corresponds to a cluster composed of one single C_{60} molecule and a varying number, x, of vanadium atoms. The distribution displays sharp edges at $x = 62$, 73, and 86, indicating that the corresponding clusters are especially stable. Similar stability oscillations can be observed for a whole series of different metal-fullerene systems and can be attributed to the formation of a first complete metal layer around the central fullerene molecule [4]. At higher laser intensities [Fig. 1(b)] more heat is deposited in the clusters during the ionisation laser pulse,

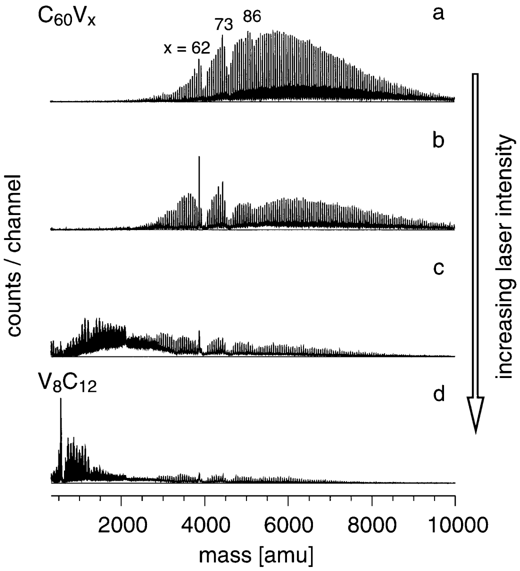

FIG. 1. Fragmentation spectra of $C_{60}V_x$ clusters exposed to different laser intensities.

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leading to a stronger evaporation of metal atoms from the clusters. As a result the relative abundance of the more stable magic number clusters is enhanced. Going one step further [Fig. 1(c)] we start to see additional peaks in the spectrum which can no longer be assigned to the original series $C_{60}V_x$. At even higher laser intensities these peaks become stronger and finally dominate the spectrum [Fig. 1(d)]. One peak is especially strong and can be assigned to V_8C_{12}, a so-called met-car cluster. The special stability of this species was observed for the first time by Castleman and co-workers [5,6]. They created this cluster in a plasma reaction from hydrocarbon gas and metal vapor and coined the name metallo-carbohedrene (met-car). Analogous clusters M_8C_{12} containing other transition metals were also observed in similar experiments [7,8]. In our experiments, these clusters appear as photofragmentation products of metal coated fullerene molecules.

The met-car is the most abundant but not the only observable photofragmentation product. Figure 2 shows an expanded view of the fragmentation products [Fig. 1(d)]. Besides the strong met-car peak, we find a whole series of peaks which can be assigned to vanadium carbide clusters V_nC_m. Peaks corresponding to clusters with the same number n of vanadium atoms are connected with lines to guide the eye. An instructive way of presenting this data is the plot shown in Fig. 3. Here, the peaks of the mass spectrum are represented by dots in a vanadium-carbon composition plane. The size of the dots corresponds to the intensity of the associated peaks in the mass spectrum. In this composition plane a representation of the observed V_nC_m clusters forms a straight line with a slope of about 1.44. This is a surprising result since there is no known bulk vanadium carbide phase with a carbon content higher than 50%.

Essentially the same composition distribution can be observed if we start with $C_{70}V_x$ instead of $C_{60}V_x$ clusters. Again the met-car V_8C_{12} is the dominant fragmentation product, accompanied with V_nC_m clusters falling on the same staight line in the composition plane. This is even true if the V_nC_m clusters are not produced by photofragmentation of metal-fullerene clusters, but directly by laser vaporization of bulk vanadium carbide. Apparently, the V_nC_m clusters produced by photofragmentation of vanadium coated fullerenes have no memory of their origin. The straight line in Fig. 3, although incompatible with the bulk stoichiometry, obviously represents the preferred composition ratio of vanadium carbide clusters in this size regime.

The transformation process from metal-fullerene clusters to met-cars can be monitored in more detail using a tandem mass spectrometer. In a first TOF mass spectrometer, a single cluster species can be preselected, followed by controlled photofragmentation with a second laser pulse and subsequent mass analysis of the fragmentation products in the main TOF. Figure 4 shows the fragmentation spectra of preselected $C_{60}V_{20}$ clusters exposed to a series of increasingly strong fragmentation laser pulses. Starting from the spectrum in Fig. 4(a) which was recorded without the additional fragmentation laser, the first fragmentation process that can be observed is the successive loss of single metal atoms [Fig. 4(b)]. With increasing laser intensity this metal loss sequence becomes stronger. In Fig. 4(c) we already start to see weak additional peaks, which do not belong to the metal loss series. They become stronger at higher laser intensities [Fig. 4(d)] and can be identified with metal-carbon clusters V_nC_m having a composition in agreement with the stability line in Fig. 3. For even higher laser intensities [Fig. 4(e)] the met-car V_8C_{12} is observed as the dominant fragmentation product. This sequence clearly confirms the proposed transformation process. At low laser intensity the fullerene seems to be still intact. Heating the clusters results in evaporation of metal atoms. In the mass spectra without preselection discussed above (Fig. 1), we observe at this stage an enhancement of the more stable magic number clusters for which the evaporation process is slower. At higher laser intensities the

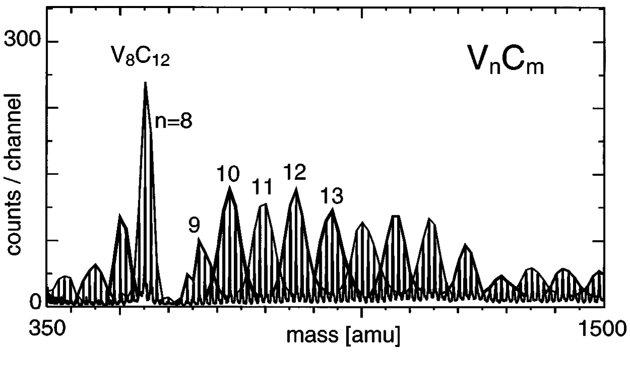

FIG. 2. Expanded view of Fig. 1(d) showing the photofragmentation products obtained from $C_{60}V_x$ clusters exposed to intense laser radiation (≈1 mJ/mm^2).

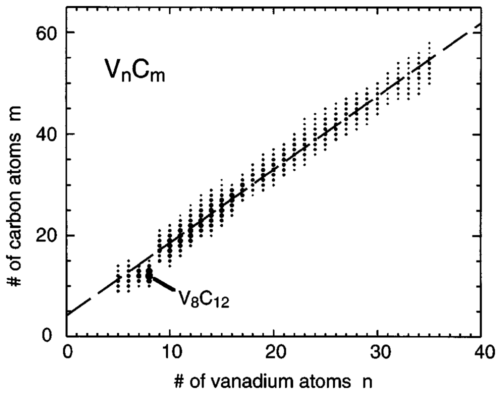

FIG. 3. Composition plane representation of the photofragmentation products obtained from $C_{60}V_x$ clusters exposed to intense laser radiation. The size of the dots represents the intensity of the corresponding peaks in the mass spectrum (Fig. 2). The slope of the dashed line is about 1.44.

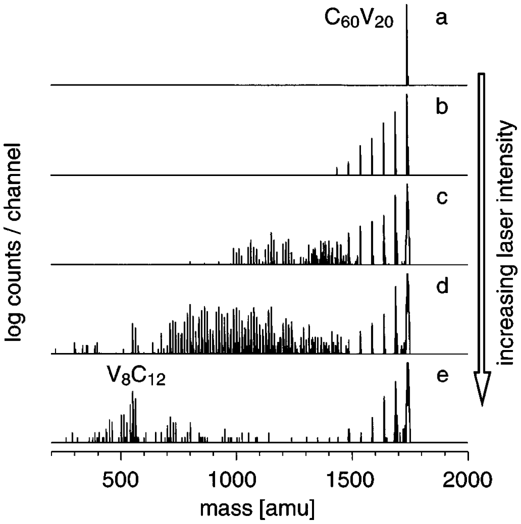

FIG. 4. Fragmentation spectra of preselected $C_{60}V_{20}$ exposed to different laser intensities showing the transformation from a single metal-fullerene cluster species into a series of metal-carbon and met-car clusters.

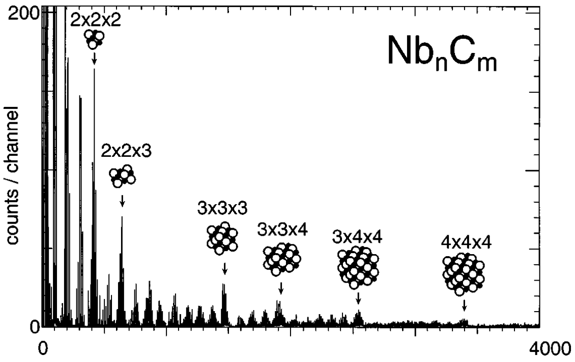

FIG. 5. Mass spectrum of the photofragmentation products of $C_{60}Nb_x$ clusters. The peaks can be assigned to Nb_nC_m clusters with a metal carbon ratio of about 1:1. Peaks corresponding to complete, cube-shaped nanocrystals are especially strong.

fullerene cage is broken and the cluster quickly loses its carbon surplus until a V_nC_m cluster near the stability line in Fig. 3 is formed. Further fragmentation along the stability line then preferentially leads to the especially stable met-car cluster.

An analogous transformation behavior can be observed using titanium instead of vanadium. At low laser intensities we find a distribution of metal-fullerene clusters $C_{60}Ti_x$ or $C_{70}Ti_x$. Intensity anomalies in the mass spectra can be attributed to stability oscillations due to the formation of a first metal layer around the fullerene molecule [4]. Exposed to high laser intensities, the clusters transform to titanium met-car Ti_8C_{12}. Despite the numerous natural isotopes of titanium and the mass coincidence between the most abundant isotope ^{48}Ti and $^{12}C_4$, the strong met-car peak can be easily identified.

We also investigated fullerene molecules doped with tantalum and niobium. Here the fragmentation behavior is different. Starting from a distribution of $C_{60}Nb_x$ clusters, we obtain Nb_nC_m clusters at high laser intensities. Figure 5 shows a mass spectrum of the photofragmentation products. As in the case of vanadium and titanium, the peaks in the spectrum form groups corresponding to clusters with a fixed number n of metal atoms and a varying number m of carbon atoms. In this case, however, the average metal-carbon ratio is about 1:1 in agreement with the stoichiometry of bulk NbC. Some groups are especially strong. They can be assigned to complete cubic nanocrystals cut out of the bulk lattice structure. Again, the composition of the fragmentation products is the same when we use C_{70} instead of C_{60}, indicating that the clusters do not remember their fullerene origin. A similar result is observed for the fragmentation products of $C_{60}Ta_x$ and $C_{70}Ta_x$ clusters. In both cases we obtain carbide clusters with bulk stoichiometry and magic numbers in accordance with the bulk lattice structure.

Another difference when compared with vanadium or titanium is the fact that for both niobium and tantalum we do not observe intensity anomalies in the metal-fullerene cluster distribution that could be attributed to a metal layer formation around the fullerene molecule. This can be explained by the results of the tandem-TOF photodissociation experiments. They reveal that the fragmentation of $C_{60}Ta_x$ clusters starts with carbon loss and not with the evaporation of metal atoms as in the case of $C_{60}V_x$. As discussed above, the evaporation of metal atoms is responsible for the formation of the intensity oscillations in the titanium and vanadium mass spectra. Therefore, it is clear why we cannot observe similar features in the mass spectrum of $C_{60}Ta_x$ clusters.

Figure 6 shows, for example, the fragmentation spectra of preselected $C_{60}Ta_{19}$ for two different fragmentation laser intensities. At low laser intensities [Fig. 6(a)] the first observable decay channel is the successive loss of C_3

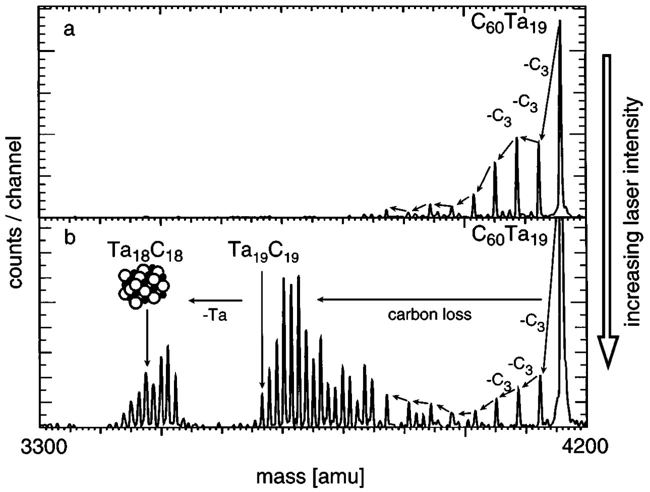

FIG. 6. Fragmentation spectra of preselected $C_{60}Ta_{19}$ for two different fragmentation laser intensities.

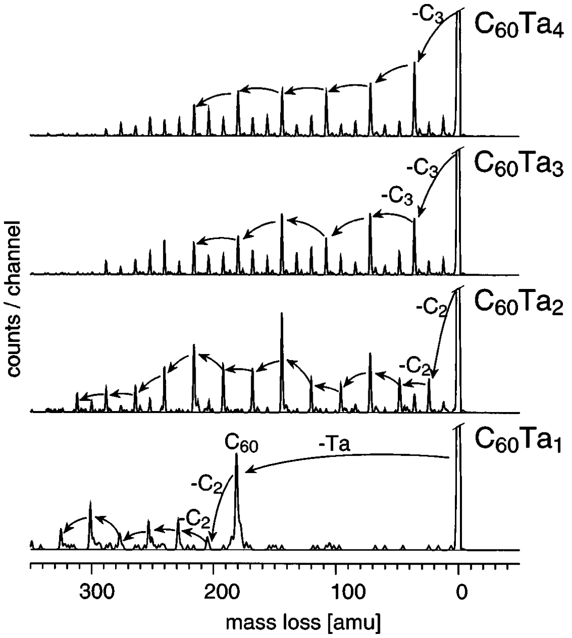

FIG. 7. Fragmentation spectra of preselected $C_{60}Ta_x$ with $x = 1, \ldots, 4$.

units. At higher laser intensities [Fig. 6(b)] other carbon loss steps also occur and a group of peaks close to the 1:1 composition ratio of TaC is formed. Then, a first metal loss step can be observed and a second group of peaks corresponding to clusters containing 18 tantalum atoms appears in the spectrum. As the fragmentation continues, smaller Ta_nC_m clusters with approximately 1:1 stoichiometry are formed successively.

The observed C_3 loss sequence is a surprising result, indicating the destruction of the fullerene structure. Fullerenes generally fragment by losing C_2 units. An evaporation of the very stable C_3 molecule would result in a cluster with an odd number of carbon atoms which is incompatible with the energetically very stable fullerene cage structure. The predominant decay channel of nonfullerene C_n clusters with $n \leq 20$ has also been shown to be the evaporation of a C_3 molecule [9]. The photofragmentation results for $C_{60}Ta_x$ clusters therefore indicate that in these clusters the fullerene cage is already broken when the first fragmentation step occurs. This is true for $x \geq 3$ where the preferential loss of C_3 units can be observed. From Fig. 7, which shows the first fragmentation steps of preselected $C_{60}Ta_x$ for $x = 1, \ldots, 4$, we can see that the situation is different for $x = 2$ and $x = 1$. $C_{60}Ta_2$ shows a C_2 loss sequence, signaling that here carbon retains a cage structure even while the cluster shrinks in size. During the fragmentation process the two metal atoms remain firmly bonded to the cluster, demonstrating the strong interaction between the two tantalum atoms and the fullerene. In the case of $C_{60}Ta_1$, the metal fullerene bond is weaker compared to the stability of the carbon cage, and the cluster first loses its tantalum atom. Further fragmentation of the remaining C_{60} results in the expected C_2 loss.

In this paper we have investigated the fragmentation behavior of transition metal-fullerene clusters. The metal-carbon interaction turns out to be strong enough to allow the breaking of the fullerene cage. Upon heating with a laser pulse, the metal-fullerene clusters transform into metal carbides and met-car clusters. The latter can be produced from C_{60} and C_{70} molecules coated with vanadium or titanium atoms, whereas niobium or tantalum doped fullerenes transform into bulk-like metal carbide clusters. Photofragmentation measurements on preselected tantalum doped C_{60} reveal a severe destabilization of the fullerene cage in clusters with more than two metal atoms.

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