Clusters of Fullerene Molecules

T. P. Martin, U. Näher, H. Schaber, and U. Zimmermann

Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80, Federal Republic of Germany

(Received 9 February 1993)

Intensity anomalies have been observed in the mass spectra of $(C_{60})_n{}^+$ and $(C_{70})_n{}^+$ clusters for $n=13$, 19, 23, 35, 39, 43, 46, 49, and 55. These numbers indicate that the closed shell clusters $n=13$ and 55 are probably icosahedra. The molecules in an incomplete shell seem to undergo a structural transition as the shell fills, similar but not identical to the transition proposed for Ar cluster ions.

PACS numbers: 61.46.+w, 36.40.+d

The identification of C_{60} and the other fullerenes was a product of cluster research [1] (and inspired insight). For several years C_{60} remained one particularly beautiful member of a long list of exotic clusters. Now it has become clear that it is possible to produce vapors and solids [2] containing only C_{60} and it might therefore be regarded as a molecule in the traditional sense of the word. In this paper we report the results of an investigation of clusters of these fullerene molecules; see Fig. 1.

Although the chemical bonding between carbon atoms within a fullerene is very strong, the molecules themselves bond together only weakly through van der Waals forces. The principal difficulty in studying clusters of fullerenes in a mass spectrometer is to ionize them without heating them up to a temperature at which they evaporate into individual molecules. Electron impact has been used [3] to obtain fullerene cluster mass spectra containing up to nine molecules. Photoionization using light just over the ionization threshold might be advantageous. However, if the technique of photoionization is to be used, a wavelength must be chosen for which the cross section for ionization is much greater than that for absorption. The radiation from an F_2 excimer laser fills the requirements necessary to ionize fullerene clusters without destroying them.

The technique we have used to study fullerene clusters is photoionization time-of-flight mass spectrometry. The cluster source is a low pressure inert gas condensation cell. Fullerene vapor was quenched in cold He gas having a pressure of about 1.5 mbar. Clusters condensed out of the quenched vapor and were transported by the gas stream through a nozzle and through two chambers of intermediate pressure into a high vacuum chamber. The size distribution of the clusters could be controlled by varying the oven-to-nozzle distance, the He gas pressure, and the oven temperature. The clusters were photoionized with a 50 mJ, 15 ns, 157 nm (7.9 eV) excimer laser pulse.

In order to enhance mass peaks corresponding to particularly stable clusters, it was necessary to heat them to a temperature at which they evaporate molecules. This heating was achieved in one of two ways. The laser used for ionization could be used also for heating if it was properly attenuated and then focused with a 170 mm focal length CaF_2 lens. Alternatively, a second ArF excimer laser emitting light with energy (6.4 eV) well below the ionization threshold of the fullerenes could be used. Both types of experiments were performed with similar results. In both cases the clusters were heated and ionized in the same 15 ns time interval. The mass spectra of clusters containing a mixture of C_{60} and C_{70} molecules are complicated. This can be seen in Fig. 2, for which

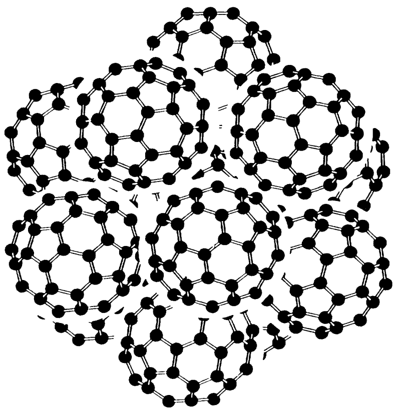

FIG. 1. The icosahedral cluster $(C_{60})_{13}$.

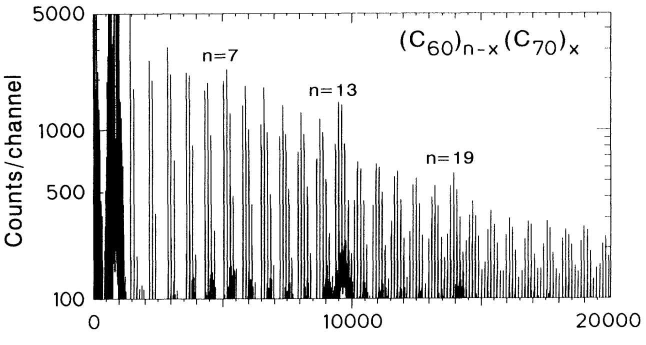

FIG. 2. Mass spectrum of $(C_{60})_{n-x}(C_{70})_x$ clusters produced by cooling in He gas the vapor over carbon black containing fullerenes. Notice that the peaks appear in groups characterized by a particular value of n and that these groups begin to overlap for $n > 20$.

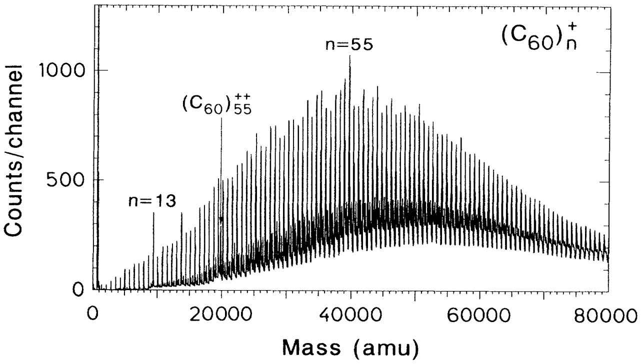

FIG. 3. Unprocessed, low resolution mass spectrum of pure $(C_{60})_n$ clusters. Notice the strong peaks for $n=13$ and 55. Notice also that the mass peak corresponding to doubly ionized $(C_{60})_{55}$ is unusually strong.

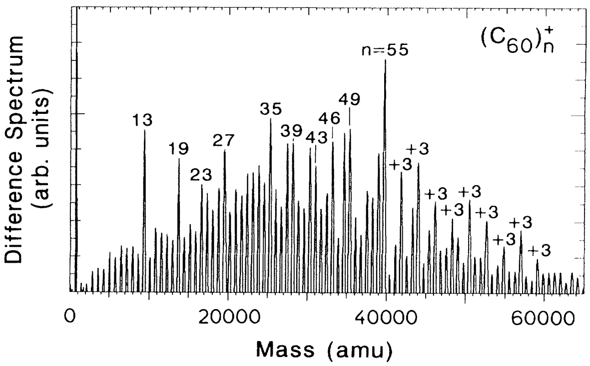

FIG. 4. Difference mass spectrum of pure $(C_{60})_n$ clusters. All of the strong peaks indicated are reproducible.

fullerene-containing soot was used in the oven. At a temperature of about 600 °C the fullerenes evaporated slowly, leaving the graphitic carbon particles as a residue in the crucible. Although some enhanced intensity can be seen in the $(C_{60})_{n-x}(C_{70})_x$ mass peaks for $n=7$, 13, and 19, not too much information can be gained from such spectra. As n becomes larger, so do the possible values of x. The groups of mass peaks for each value of n begin to overlap, making it difficult to extract information for large clusters. For this reason it is highly advantageous to use pure C_{60} or pure C_{70} in these investigations.

A low resolution mass spectrum of pure C_{60} clusters is shown in Fig. 3. The signal-to-noise ratio in this spectrum is very high and even small variations in the peak intensities can be reproduced. Notice that the mass peaks for $(C_{60})_{13}{}^+$ and $(C_{60})_{55}{}^+$ are particularly strong. The series of weak peaks which appear as a dark band running through the spectrum are due to doubly ionized C_{60} clusters. Particularly strong is the peak corresponding to $(C_{60})_{55}{}^{++}$.

In order to enhance the intensity variations the mass spectrum has been processed in the following way. The mass spectrum is averaged with a spline function over 500 32 ns time channels. Thereby information concerning the carbon isotope distribution is lost but signal-to-noise ratio is gained. Next a second spectrum is obtained by averaging the data over 5000 32 ns time channels. A convenient form for display is the difference of these two spectra, which is shown in Fig. 4. Here it is clear that in addition to the intense mass peaks for $n=13$ and 55, several other peaks stand out: $n=19$, 23, 35, 38–39, 43–44, 46, and 48–49. There is some uncertainty concerning $n=27$. This peak may have been enhanced, at least partly, by the underlying doubly ionized $(C_{60})_{54}{}^{++}$ which has a nearly closed shell. For clusters larger than $n=55$ an oscillatory pattern appears, whereby every third peak is strong. A similar difference spectrum for $(C_{70})_n{}^+$ clusters is shown in Fig. 5. High peak intensities occur for almost the same values of n as found in the C_{60} spectra. The main difference is the appearance of a strong peak at $n=32$ and the disappearance of enhancement at $n=46$.

Beyond 100000 amu the signal in the mass spectrum becomes weak. This is not because larger clusters are not produced in abundance, but because they are difficult to detect. Evidence of this is seen in the measured distribution of doubly ionized clusters; see Fig. 2. It can be seen that the distribution reaches a maximum around $m/z=50000$, i.e., $m=100000$ amu. In order that a cluster be registered as a count in the detector it must produce secondary electrons on impact with the channel plate. Apparently the buckyballs are more inclined to bounce on impact than, for example, sodium atoms. The high mass limit is determined by the post acceleration voltage and charged state of the clusters. The doubly charged clusters hit the detector with higher kinetic energy and are, therefore, more likely to be registered.

The observation of these doubly charged clusters allows us to study the stability of large clusters. For even values of n the mass peaks of $(C_{60})_n{}^{++}$ coincide with the peaks

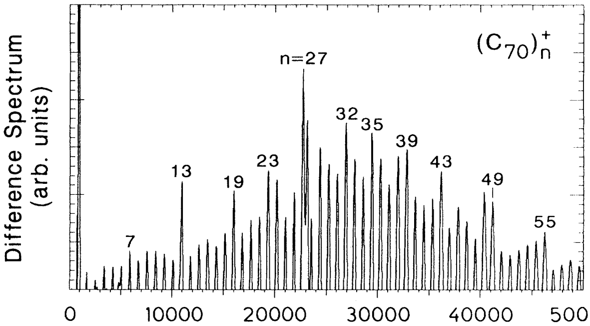

FIG. 5. Difference mass spectrum of pure $(C_{70})_n$ clusters. The peak just to the right of $n=27$ corresponds to doubly ionized $(C_{70})_{55}$ which is also unusually strong.

of singly ionized clusters. No information can be extracted from our mass spectra for doubly ionized clusters containing an even number of molecules. Therefore, the results have been presented in Fig. 6 by connecting the mass peaks in a difference spectrum of $(C_{60})_n{}^{++}$ for odd n only. Notice the reproducible structure in this curve for values of n between the shell closings at 55 and 147. The strong mass peaks at $n=13$, 55, and 147 are very suggestive but far from definitive. Three types of structures have major shell closings for these numbers; icosahedra, cuboctahedra, and square-faced truncated decahedra. A cuboctahedron of any size can be cut out of an fcc crystal. Since bulk C_{60} has fcc structure, the occurrence of a cuboctahedron already at size 13 molecules would not be surprising. However, the noncrystalline icosahedron and truncated decahedron cannot be dismissed at this point in the discussion, particularly in light of the fact that CH_4 molecules show a local icosahedral symmetry when they are condensed into clusters [4].

So let us move on to the next magic number, 19. The fcc packing is not ruled out because the cluster could conceivably undergo a transformation to perfect octahedron which also can be cut out of an fcc crystal. On the other hand, with six molecules a "cap" can be placed on the vertex of an icosahedron or a decahedron. So the magic number 19 has not brought us closer to a determination of the probable structure of these clusters. Fortunately, the remaining magic numbers do provide the information we need to deduce the probable structure.

Considerable insight into the growth of an icosahedral structure is provided by the work of Farges *et al.* [4] and Northby [5]. We would like to summarize some of their most relevant results. The central idea is that an icosahedral core of thirteen atoms can support two mutually exclusive lattices. These two lattices, called IC and FC by Northby, are quite distinct. They do not even contain the same number of sites. The IC lattice consists of all sites for the next larger Mackay icosahedron [6]. There are 42 such sites. A closer examination of an atom in one of these IC sites shows that it makes contact with only two underlying atoms. For low coverage of the thirteen atom core it is not plausible that an atom balances itself in such a precarious position. It is more likely to fall into a triangular hole, thus making contact with three substrate atoms. This triangular hole is an FC site. More detailed consideration using a Lennard-Jones potential [5] indicates that the FC sites will be preferred for low coverage and the IC sites for high coverage. According to Northby, $n=19$, 23, 26, and 29 correspond to highly stable fillings of the FC lattice and $n=39$, 43, 46, and 49 to favorable fillings of the IC lattice. For example, the removal of one triangular face from the second shell leaves a total of 49 atoms.

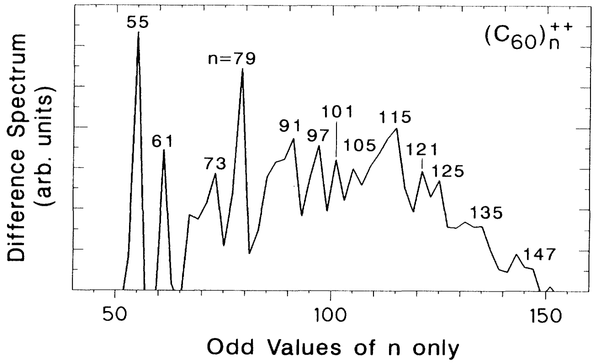

FIG. 6. Line connecting the mass peaks of $(C_{60})_n{}^{++}$ for odd values of n in a difference spectrum.

The oscillatory pattern after $n=55$ might be designated the "filled face sequence." With three molecules the FC sites of one triangular icosahedral face can be filled. It would appear from Fig. 4 that at least nine such faces are covered without adding any vertex molecules. This can be seen even more clearly in the data for the doubly ionized clusters; see Fig. 6. Since only odd values of n can be observed, the filled face sequence shows up at 61, 67, 73, and 79. The sequence seems to be broken at 85, but then continues with 91 and 97. The last member of this sequence is $n=115$. For this cluster it would seem that each of the twenty triangular faces has accepted three molecules at close-packing sites. This forms a structure with perfect icosahedral symmetry even though it does not belong to the series of Mackay icosahedra. A representation of this cluster can be found in the review by Hoare who has called it a rhombicosidodecahedron [7].

It would not have been surprising to have found that C_{60} molecules pack together in clusters as if they were hard spheres. After all, fcc packing is the preferred structure of the solid. It appears, however, that for the small clusters studied in this investigation, the icosahedral symmetry is preferred. The magic numbers are very similar to those observed for xenon [8] and argon [9] clusters; similar but not identical. A determination of the exact structure, including the relative orientation of the molecules, will have to await detailed calculations. Such calculations should take into consideration the fact that in these experiments evaporation has revealed the stability of charged clusters. In the meantime we could gain insight by referring to previous theoretical studies on Ar clusters. It would appear that the first molecules to condense onto a 13 or 55 molecule icosahedron take dense packing sites. Only when the new shell is about half filled do the molecules rearrange themselves onto Mackay icosahedral sites.

We would like to thank A. Mittelbach for providing the C_{70} used in these experiments.

---

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and

R. E. Smalley, Nature (London) **318**, 162 (1985).
[2] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature (London) **347**, 354 (1990).
[3] T. Jerger, D. Kreisle, E. Recknagel, and A. Weidinger (private communication).
[4] J. Farges, M. F. de Feraudy, B.Raoult, and G. Torchet, J. Chem. Phys. **84**, 3491 (1986); Ber. Bunsenges. Phys. Chem. **88**, 211 (1984).
[5] J. A. Northby, J. Chem. Phys. **87**, 6166 (1987).
[6] A. L. Mackay, Acta Crystallogr. **15**, 916 (1962).
[7] M. R. Hoare, Adv. Chem. Phys. **40**, 49 (1979).
[8] O. Echt, K. Sattler, and E. Recknagel, Phys. Rev. Lett. **47**, 1121 (1981); W. Miehle, O. Kandler, T. Leisner, and O. Echt, J. Chem. Phys. **91**, 5940 (1989).
[9] I. A. Harris, R. S. Kidwell, and J. A. Northby, Phys. Rev. Lett. **53**, 2390 (1984).