Icosahedra of icosahedra: The stability of $(C_{60})_{13}$

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(Received 5 June 1996; accepted 2 July 1996)

[S0021-9606(96)02038-7]

So-called ''magic numbers'' in mass spectra of clusters have been of interest since the first pioneering days of cluster research. These are mass peaks that are more prominent than their neighbors due to particularly stable structures. One of the most famous examples of a ''magic number'' mass spectrum is the Smalley–Kroto carbon cluster spectrum showing practically only C_{60}^+ and C_{70}^+. This spectrum led to the suggestion of the closed cagelike fullerene structure for these species.[1] As was recently shown by Martin *et al.*[2] it is also possible to obtain mass spectra of clusters of fullerenes which show magic numbers. Particularly intense peaks with intensities of up to a factor of 2 larger than their immediate neighbors were reported for $N=13$ and 55. A careful consideration of the other strong mass peaks in the spectra led to the conclusion that the clusters had icosahedral symmetry with $N=13$ forming the first closed shell. In this note we report on the stability of these fullerene clusters. The stability was probed by studying the dependence of the observed mass spectra on the intensity of a XeCl excimer laser (308 nm, 4 eV) which was used to heat the neutral clusters before single-photon ionization with a F_2 excimer laser (157 nm, 7.9 eV). The cluster source we use is very similar to that used by Martin *et al.*[2] Fullerene vapor is quenched in cold He gas at a pressure of about 1 torr. Clusters condense out of the quenched vapor and are transported by the gas stream through a nozzle at a temperature of 80–110 K. They then cross a differentially pumped region and are subsequently laser-heated and then ionized in the extraction region of a linear time-of-flight mass spectrometer and are detected by dual microchannel plates after acceleration to an energy of 5 keV. The mass spectrum shown at the top of Fig. 1 (without heating) is obtained by a direct single-photon ionization of the clusters ($IP=7.6$ eV for C_{60}). The mass distribution is very smooth with no evidence of magic numbers which indicates that the clusters are cold and have not fragmented to any significant extent. The fall in cluster intensity beyond $N\simeq 20$ is due to the decreasing detection efficiency and does not reflect the true intensity. A small dimer signal can be observed in this mass spectrum which enables us to estimate the temperature of the clusters. The cohesion energy of bulk C_{60} is 1.7 eV.[3] The binding energy per nearest neighbor is 1.7/6 eV=0.28 eV, which then yields a crude estimate of the binding energy of the dimer $(C_{60})_2$. An upper limit for the temperature of the dimer can then be obtained by dividing the binding energy by the Gspann parameter[4] to yield a value of approximately 130 K which is in good agreement with the temperature measured at the nozzle. In order to enhance ''magic'' mass peaks it is necessary to heat the clusters to temperatures at which they evaporate molecules. This was done by exciting the clusters with a XeCl excimer laser, which has a photon energy well below the ionization potential of the clusters, before the ionization laser was switched on. The heating effect can be seen in the remaining mass spectra in Fig. 1. The intensity scales are the same for each spectrum. Clearly all clusters with the exception of $(C_{60})_{13}$ decrease in intensity. The monomer and $(C_{60})_{13}$ peaks become strongly broadened due to fragmentation into these species during acceleration. It is possible to push this evaporation process to such extremes that practically only the monomer and the $N=13$ cluster remain in the mass spectrum as illustrated in Fig. 2. Since this mass spectrum is formed by large scale evaporative processes we can estimate the differences in evaporative activation energy between $(C_{60})_{13}$ and

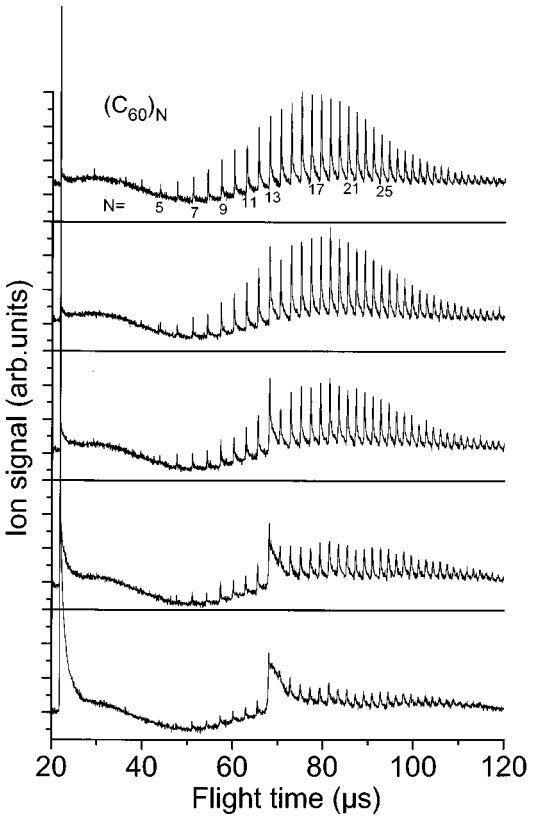

FIG. 1. Abundance spectra of clusters of pure C_{60} for different fluences of the 308 nm heating XeCl laser and constant pulse energy of the ionizing F_2, 157 nm laser. The heating laser fluence increases from top to bottom, the top spectrum being recorded with zero fluence. The heating due to multiple absorption of 157 nm photons is unknown but relatively small. The absolute intensity scales are the same for all spectra.

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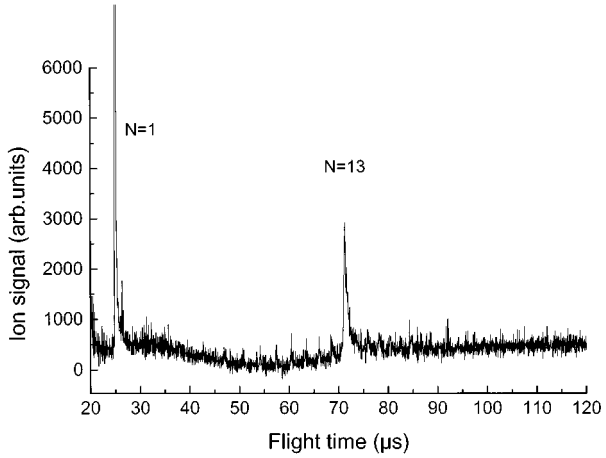

FIG. 2. Spectrum recorded at high XeCl laser fluence and with a good overlap of the two lasers. The $N=13$ peak is the only one which shows such abundance contrasts. The $N=19$ appears to saturate at moderate fluences. The difference between $N=13$ and 14, 15 is estimated to be a factor of 8.

$(C_{60})_{14}$ by using the observed abundance ratio $I_{13}/I_{14}=8$, obtained from Fig. 2. By applying the results from Ref. 5 to the average evaporative rate constant for $(C_{60})_{14}$ and relating the rates for $N=13$ and 14 by a simple Arrhenius expression, it is possible to integrate over the time dependent production and decay of $(C_{60})_{13}$ to obtain the abundance. The result, which holds for $I_{13}/I_{14} \gg 1$, is

$$I_{13}=I_{14}\,\frac{C_v}{G^2}\left[\frac{D_{13}-D_{14}}{D_{14}}G-\gamma-\log\left(\frac{C_v}{G^2}\right)\right], \tag{1}$$

where $C_v \simeq 1300k_B$ is the heat capacity of $(C_{60})_{14}$, $G \simeq 25$ is the Gspann parameter, D_N is the evaporative activation energy of $(C_{60})_N$ and $\gamma \simeq 0.58$ is Euler's constant. We then obtain $D_{13}-D_{14}=0.2D_{14}$. Hence even a relatively small difference in activation energies for evaporation of about 20% is enough to produce the extreme situation illustrated in Fig. 2. This observation suggests that it may be possible to routinely produce macroscopic amounts of large, stable mass-selected clusters for nanoscale applications. Similar effects occur when a mixture of C_{60} and C_{70} is used in the cluster source instead of pure C_{60}. Figure 3 shows a hot mass spectrum for such a mixture. Again, one can see the massive fragmentation into the monomers and the $N=13$ cluster. In this case the second magic number $(C_{60})_{19}$, which corresponds to placing a cap on a vertex of the $N=13$ icosahedron, is also prominent.

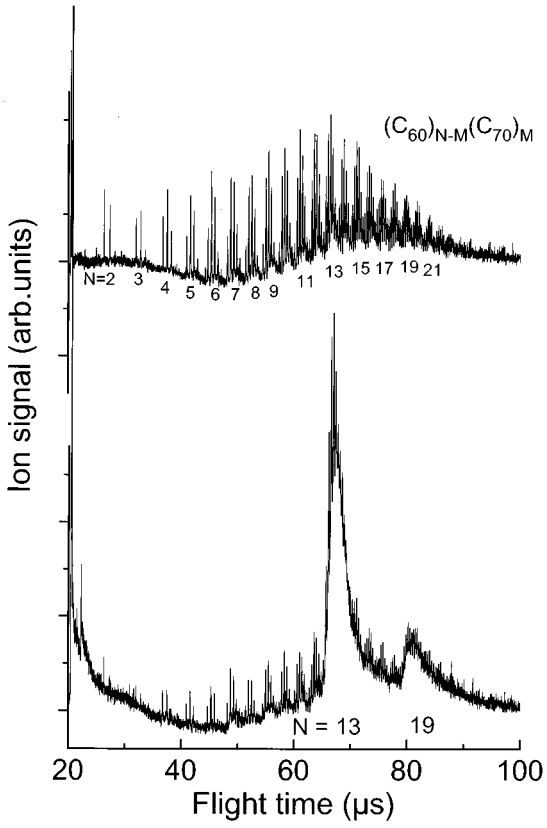

FIG. 3. Abundance spectra similar to Figs. 1 and 2 of mixed C_{60}, C_{70} clusters. In addition to the very strong and partly unresolved $N=13$ peak, $N=19$ is also prominent. The lower spectrum is recorded with a high fluence from the XeCl laser. The intensity scales are the same. The strong increase in the absolute amount of the $N=13$ cluster indicates the presence of higher, undetected clusters in the cold spectrum (top).

Financial support from the EU through the HCM Network ''Formation, Stability and Photophysics of Fullerenes'' and a fellowship for K.H. is gratefully acknowledged. We would also like to thank H. Haberland for help in constructing the cluster source and I. V. Hertel for encouragement.

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