Thermionic emission from giant fullerenes

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Abstract. Large even-numbered carbon clusters in the size range from 100 to 600 atoms (giant fullerenes) were generated by laser vaporization and directly injected as positive ions via a supersonic beam into the magnetic trap of an ion cyclotron resonance apparatus. Intense laser excitation of the magnetically levitated fullerenes at 4.0 eV was found to result in production of multiply charged fragments in the trap. Details of the time scale and size dependence of this process suggest it is due to thermionic emission from the superheated gas phase clusters.

1. Introduction

As the study of refractory clusters has matured over the past decade, one of the most promising techniques to emerge has been Fourier transform ion cyclotron resonance, FT-ICR [1–6]. Here cluster ions are effectively levitated in ultrahigh vacuum in a high magnetic field. They may be stored in this field for many minutes, irradiated with lasers, thermalized through collisions with an inert buffer gas, and detected with mass resolutions which can easily exceed 1 part in 10^5. Over the past 5 years experiments have demonstrated the utility of this approach in studies of hydrogen chemisorption on transition metals [1, 2], laser probes of metal containing carbon clusters [7], and extensive studies of the surface chemistry and laser annealing behavior of clusters of silicon [8–11], germanium [8, 11], and gallium arsenide [12].

Recently a much simplified version of such an apparatus was introduced that features direct injection of a supersonic cluster ion beam into the magnetic trap of a FT-ICR apparatus [5]. One of the results is that extremely high mass clusters with many hundreds of atoms are now just as efficiently injected and trapped as the 2–20 atom clusters most readily studied before. These very large clusters are now in the nanometer size range where one may expect to observe phenomena normally thought to occur only on macroscopic particles. We report here one such observation: thermionic emission from carbon cluster positive ions in the 150–600 atom size range.

2. Experimental

The cluster FT-ICR apparatus used in this work has been described in detail elsewhere [5]. Briefly, the carbon clusters were generated by laser vaporization of a graphite disc mounted on the side of a pulsed supersonic nozzle. This supersonic cluster source [5] has been miniaturized such that the entire source fits within a single 6″ conflat cross, pumped by a single 170 l s⁻¹ turbopump. Motion of the graphite target disc in between laser shots was controlled entirely by computer in order to maintain a smooth, flat target surface as it is eroded by successive laser shots. For the experiments reported here the vaporization laser pulse (Nd:YAG 2nd harmonic, 15 mj per shot focussed to a spot 1 mm diameter) was timed to fire 20 microseconds up the rising edge of the helium gas pulse. This was found to produce the most intense C_n^+ ion signal in the ICR trap in the size range near C_{300}^+. Under these conditions the clusters are likely to be quite hot vibrationally in the supersonic beam, though they will cool to near room temperature later in the ICR trap.

The supersonic helium beam, laden with carbon cluster ions, was aimed directly down the central axis of the 6T superconducting magnet of the FT-ICR apparatus. The process of deceleration, trapping, and thermalizing these clusters has been discussed before [5]. The experiments below emphasize the use of a powerful method of selectively ejecting unwanted clusters without exciting the remaining clusters in the trap. This method is known to the
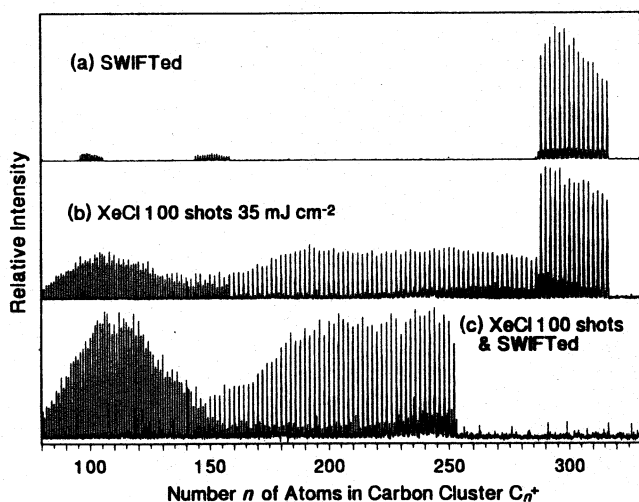
ICR community as "SWIFT" (stored waveform inverse Fourier transform) [6, 11].

3. Results and discussion

Figure 1 shows the principal results of this study. The top panel (a) is the FT-ICR mass spectrum obtained after injecting the carbon clusters into the ICR trap, thermalizing with argon for 3 s at $2 \cdot 10^{-5}$ torr, and then using SWIFT to eject out all clusters except those in the range between C_{288}^+ and C_{316}^+. Note that the detection technique also picks up a bit of signal at the 2nd and 3rd harmonic of the fundamental cyclotron motion of the cluster ions in the trap. This makes each peak in the mass spectrum reappear with much reduced intensity at an apparent mass 1/2 and 1/3 of the true mass, respectively.

Note that the mass spectrum in this region consists primarily of just even-numbered carbon clusters. A small amount of what appears to be odd-numbered clusters is evident in this region as well, but these are actually due to doubly-charged even-numbered clusters in the 600 carbon size range. This fact can be verified by detailed examination of the isotopic substructure of the mass peaks in this region. The large peaks that appear to be even-numbered have, as expected from the 1.11% natural abundance of C^{13}, a substructure of sharp peaks spaced at 1.0 amu intervals. However this substructure for the small peaks was found to be spaced at 0.5 amu intervals, showing that they are due to doubly-charged clusters injected in this charge state directly from the supersonic source.

The fact that large carbon clusters tend to be dominated by just even-numbered forms was first noted by

Rohlfing, Cox and Kaldor in 1984 [13]. Although they imagined this may be due to the clusters preferring to form long chain "carbynes", a more interesting hypothesis is currently in vogue. Triggered by the observation that the 60th cluster was preeminently stable [14], a family of hollow geodesic structures was proposed [14–18] each consisting of exactly 12 pentagons and any number of hexagons (except one). This model predicts C_{60} to be specially stable since only for this number of atoms (and 20) is it possible to have perfect icosahedral symmetry with the strains of closure equally distributed. Generalizing from the name "buckminsterfullerene" the entire class of these hollow spheroidal graphitic cages has come to be called "fullerenes". All these fullerenes are even-numbered structures because there is no other way of closing a network of 5- and 6-membered rings than following the rule that the pentagon ring count must be a particular even number (12).

O'Brien et al. [19] found that C_{60}^+ was extremely resistant to photofragmentation, but ultimately it does fragment by the loss of even numbered small carbon radicals. The lowest energy pathway appeared to be the loss of C_2 through a concerted mechanism that involves rearrangement of bonds on the surface of the fullerene so that two pentagons are joined at a common side. The two atoms on this side can then leave to form a free C_2 molecule, leaving behind the next smaller fullerene with one less hexagon but still the required 12 pentagons. This fragmentation mechanism appeared to be followed by all the fullerenes studied in the region from 34 to 80 atoms in size. O'Brien and coworkers [19] showed evidence that loss of larger even-numbered carbon chains must be occurring as well for more highly-excited fullerenes, and presented a concerted mechanism similar to that for C_2 loss.

Here now in Fig. 1 we see the carbon clusters in the size range of 288–316 also fragment by the loss of even-numbered fragments. The middle panel of Fig. 1b shows the result of an equivalent experiment to that of Fig. 1a, except that at the end the clusters were irradiated with 100 shots of a XeCl excimer laser beam (4.0 eV) at a fluence of 35 mJ cm^{-2} per shot over a time period of 2 seconds. This high level of laser fluence through the ICR cell was permissible only because the front and rear "door" electrodes of the cell had 2.5 cm diameter open holes along the central axis without any obstructing grids. Note that extensive fragmentation has occurred.

The laser exposure for the middle panel of Fig. 1 was chosen to show the photofragment distribution pushed down to the region near C_{150}^+. Lower levels of laser excitation were found to produce correspondingly less extensive fragmentation, with the fragment size distribution concentrated near the parent clusters.

Note that the fragments near the parent clusters mass are primarily just even numbered clusters. Detailed examination of the small peaks in the positions expected for odd-numbered fragments in this region show these are, in fact, not odd clusters at all. Their apparent 0.5 amu isotopic mass spacing proves they are even-numbered fragments of the doubly-charged clusters in the C_{574}^{++} to C_{632}^{++} size range mentioned earlier. Careful study has

Fig. 1a–c. FT-ICR mass spectral study of fullerene cluster laser photolysis: a mass spectrum of selected C_n^+ fullerenes in the $n = 288$ to 316 atom size range, b resulting mass spectrum after irradiation with 100 shots of a XeCl excimer laser at a fluence of 35 mJ cm^{-2}, c expanded vertical scale of same experiment as b except that all clusters larger than C_{252}^+ were swept from the ICR trap prior to detection in order to remove interference from 2nd harmonic detection of the larger clusters

revealed that no odd-numbered photofragments are present in this region with detectable abundance. Note also that these doubly-charged clusters appear to be a bit more photoresistant than the singly-charged fullerenes in this same FT-ICR frequency range. This is likely due simply to their larger size, and the corresponding reduction in the unimolecular fragmentation rate.

3.1. Laser-induced multiple ionization

The FT-ICR mass spectrum of panel (b) in the relatively small mass region (80–150) is the most interesting aspect of this data. Note that here there appear to be both odd and even-numbered clusters. Of course, in this region there is some interference from the second harmonic of the ICR signal of the clusters in the 160–300 size region. This is quite evident in panel (a) in that the highest mass "odd" peak that appears intensely has a "mass" that is exactly one half the mass of the highest mass even numbered parent fullerene, C_{316}^+. However, this second harmonic interference cannot explain all the observed apparent "odd" carbon fragment clusters seen in panel (b). This is proven in the bottom panel (c) which is the FT-ICR mass spectrum after all clusters larger than C_{252}^+ were ejected by a SWIFT waveform. Now there is negligible interference from harmonics of higher mass clusters. But still there are the "odd" peaks.

Figure 2 shows an expanded mass scale version of this same FT-ICR mass spectrum (the same as Fig. 1c). The top panel shows the mass spectrum in the region corresponding to C_{112}^+ C_{120}^+. Note the clear isotopic substructure. Each fine structure peak is found to be spaced from the next by an apparent 0.5 amu interval. These are, therefore, not due to odd-numbered carbon clusters. Instead they are due to even-numbered, but doubly-charged clusters, as labelled in the Figure. They have been gener-
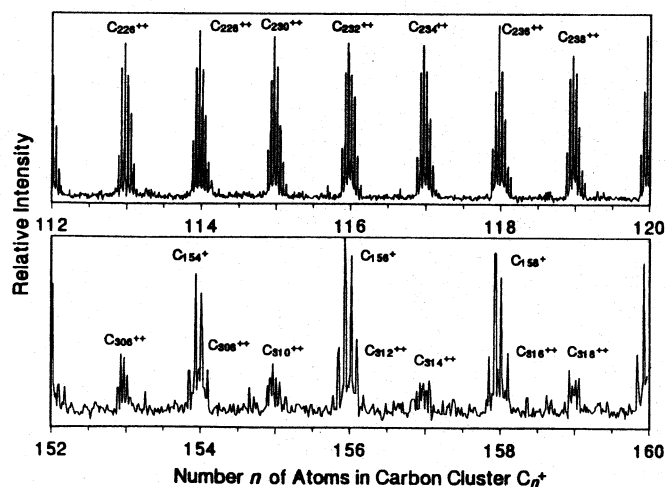
ated here by laser excitation of singly-charged fullerenes in the 288–316 size range. The remarkable feature of this is that the workfunction of bulk graphite is near 4.9 eV, and the laser being used to generate the +2 charge state of these ions has a photon energy of only 4.0 eV. Clearly, this is not a direct one-photon photoionization process.

The lower panel of Fig. 2 shows an expanded view of the mass spectrum of Fig. 1c in the C_{152}^+ to C_{160}^+ size range which is right at the onset of the laser-induced doubly-charged fragment distribution. Note that the interval of the isotopic substructure peaks in clearly 1 amu for the even-numbered clusters in this size range. They are, therefore, the singly-charged fragments as labelled in the Fig.

Results similar to these have been obtained for all fullerene clusters in the size range from 150 through 600 atoms. All appear to fragment simply by C_2 and larger even-numbered carbon radical loss. The larger clusters do require somewhat more laser excitation to produce equivalent extents of fragmentation, but no more so than would be expected from a simple size effect on the absorption cross section and the unimolecular statistical fragmentation rate as a function of total energy. However the production of doubly charged fragments was found to be very sensitive to fullerene cluster size. The clusters in the 150 atom size range produced only a trace of doubly charged fragments, while those in the 600 atom size range were found to be dominated by +2 charged fragments. In fact the production of fragments with a +3 charge was found to be quite efficient from the 600 atom fullerenes.

3.2. Dependence of time scale

We were particularly surprised to observe this laser production of multiply charged fullerene fragments since this research group has studied laser excitation of fullerenes for many years with even considerably higher levels of excitation than those used here. However, most experiments were primarily done on a tandem time-of-flight apparatus (TTOF) where multiple ionization would only have been detected only if it had occurred within 10–30 microseconds.

As a double check just to make sure we had not missed such a dramatic effect on the large fullerenes, an experiment was performed on the TTOF machine for fullerenes in the C_{650}^+ mass range. No multiply charged photofragments were observed at equivalent levels of excitation. Laser production of multiply charged fullerene fragments observed in these ICR experiments must therefore be due to a long time scale process observable only in the magnetic trap of the ICR.

3.3. Thermionic emission

In the ICR apparatus the clusters are levitated in high vacuum. After the laser excitation their only effective cooling mechanisms are (1) infrared emission, (2) evaporative loss of C_2 and larger even-numbered carbon fragments, and (if they are hot enough) (3) thermionic emission. We believe there is no reasonable explanation for the

Fig. 2. Expanded mass scale of the FT-ICR spectrum shown in Fig. 1c. Note the isotopic substructure of the peaks in the top panel appear to be spaced at 0.5 amu intervals. This proves they are due to clusters with a charge of +2

observation of $+2$ and $+3$ charged clusters in these laser photolysis experiments other than *(3)* – a process that is certainly very familiar for very hot macroscopic objects, but has never been seen before (to our knowledge) from a gas phase molecule.

Ordinarily, molecules fragment far too rapidly at high levels of excitation to ever see the slow process of coupling vibrational energy that is broadly distributed in the many modes of the molecule into the motion of a single electron so that it can escape. However, if these carbon clusters really are giant fullerenes, efficient thermionic emission is not hard to understand.

A fullerene in the size range of 300 atoms is a hollow, nearly spherical object roughly 2 nm in diameter. This is large enough that the second ionization potential should not be more than 2–3 eV higher than the first. There are 300 pi electrons delocalized around the surface of this spheroid. The molecular orbital pattern of this 300 atom fullerene may be quite reminiscent of the surface band structure of the basal plane of graphite. It therefore seems reasonable to try a simple macroscopic treatment of the process of thermionic emission from such an object. Estimates of the rate of thermionic emission based on the traditional Richardson-Dushman approach [20] do indeed predict that the rate for the production of $+2$ ions could easily become high enough to compete with infrared emission on the millisecond time scale provided the effective temperature of the cluster is kept high enough. To be precise it will be necessary to measure the ionization potential, IP, of carbon clusters in this region [21]. However, assuming for the moment that the IP of C_{300}^+ is 7–8 eV, this crude approach would predict substantial formation of C_{300}^{++} if the cluster temperature is above 3000 K.

For ordinary clusters, fragmentation at this high temperature would be so rapid that thermionic emission would not be a concern: they would be destroyed by fragmentation long before they had a significant chance to boil off an electron*. But if these carbon clusters are indeed fullerenes, long lifetimes at such high temperatures are expected [19, 22]. Detailed study of these giant molecular carbon shells may reveal some beautiful physics.

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* The mechanistically more elaborate but energetically much favored process of ejection of a C_2^- or some larger even-numbered C_n^- fragment should also be considered on these long time scales