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Observation of the Doubly Charged, Gas-Phase Fullerene Anions C_{60}^{2-} and C_{70}^{2-}

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Abstract: The fullerenes exhibit a remarkable ability to accommodate excess negative charge. We have observed C_{60}^{2-} and C_{70}^{2-} in a Fourier transform ion cyclotron resonance mass spectrometer by laser desorption (1.064 μm) of raw fullerene material that had been extracted from soot produced from graphite rods. C_{60}^{2-} was distinguished from C_{30}^{-} by the relative abundances and m/z values of its isotopic ions. C_{60}^{2-} was distinguished from the double harmonic of C_{60}^{-} by selective ejection of C_{60}^{-}, selective excitation of C_{60}^{2-}, and by a new and definitive method based upon comparing frequency shifts of singly and doubly charged ions as a function of ICR trapping voltage.

Introduction

The advent of techniques for producing gram quantities of the new form of pure, solid carbon[1,2] (buckminsterfullerene) has made feasible a wide range of new experiments drawn from a variety of scientific disciplines. One notable property of the fullerenes is an unusual ability to accomodate negative charge. On the basis of ab initio calculations,[3] Pitzer and co-workers have suggested that C_{60}^{2-} may be stable in the gas phase. In solution, multiple electrons have been readily added to C_{60} by means of cyclic voltammetry.[4,5] The present investigation focuses on experimental demonstration of the existence of the doubly charged fullerence anions in the gas phase.

Reports of doubly charged, gas-phase anions are fairly rare,[6-10] even though chemists frequently encounter such species in the condensed phases of matter. One strategy for accommodating two like charges is to separate them by as much distance as possible within the molecule, as is illustrated by certain doubly charged gas-phase sulfonates[6] and carboxylates.[7] Another strategy involves the production of gas-phase cluster ions that mimic the solvation of ions in the liquid phase. Solvation provides the stabilization for many familiar doubly charged negative ions that have never been seen in the gas phase as monomers, such as SO_4^{2-}. Clusters also provide opportunities for charge delocalization among equivalent sites. Double negative charges have been reported for oxygen cluster ions.[8] A few small polyatomics may be so electronegative that they can accommodate more than one excess electron, such as NO_2^{2-},[9] and perhaps AuF_6^{3-}.[10] Although there have been reports of doubly charged atomic negative ions, those reports have since been disputed.[6,11,12]

Buckminsterfullerene consists of 60 carbon atoms that assume the shape of a soccer ball. It is aromatic and has icosahedral symmetry, the highest possible symmetry for any molecule. The existence of this molecule was first inferred from laser vaporization studies of carbon clusters by Smalley and co-workers.[13,14] A crucial practical breakthrough occurred when Huffman and co-workers[15] demonstrated that fullerenes could be produced in abundance by evaporating graphite electrodes. Improvements in their technique[16] and an alternative carbon arc technique[17] have

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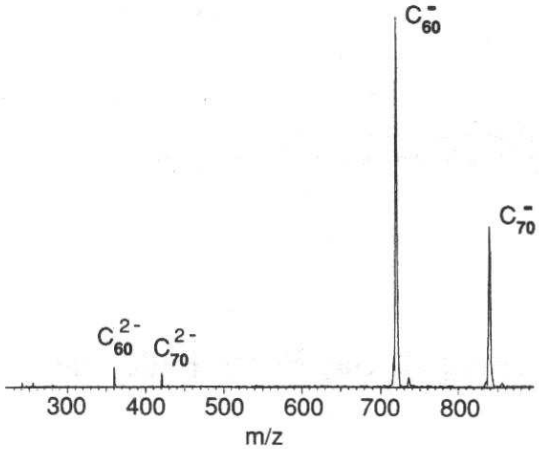

Figure 1. Low-resolution negative ion FT/ICR mass spectrum of ions produced by Nd:YAG laser desorption (1.064 μm) followed 3 s later by broad-band excitation/detection. Identification of the peaks at m/z = 360 and 420 u/e is the subject of this paper.

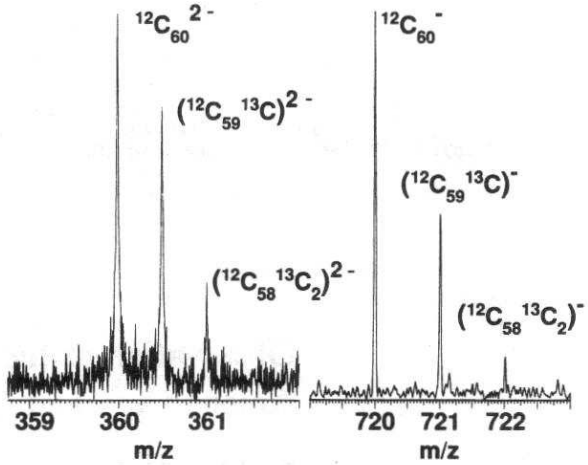

Figure 2. High-resolution FT/ICR mass spectra of C_{60}^- (right) and C_{60}^{2-} (left). (The two spectra have been scaled such that the largest peak in each spectrum has the same magnitude.)

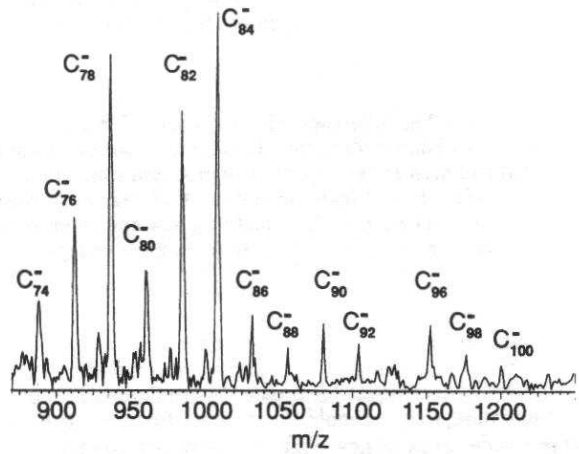

Figure 3. Negative ion FT/ICR mass spectrum showing the fullerene anions C_n^- for $n \geq 74$, which follow the closure rule proposed by Smalley (see text).

produced raw fullerene material (nominally a 6:1 mixture of C_{60} and C_{70}, also containing larger fullerenes and some impurities) that is readily extracted from the resulting soot with a 15% yield. To obtain maximum yields, it is particularly important to perform the graphite evaporation in a 100-Torr atmosphere of helium. The raw fullerene material has been characterized by a variety of techniques including ^{13}C NMR,[11,16] X-ray diffraction,[14] infrared[4,13,15,16,18,19] and UV–visible spectroscopy,[13,15,16,19,20] cyclic voltammetry,[4,5] and mass spectrometry.[13,14,16,21,22] New studies are appearing at an exponentially increasing rate.

In the present work, we report Fourier transform ion cyclotron resonance (FT/ICR) mass spectra of negative ions produced by laser desorption/ionization of raw fullerene material. In the full mass range spectra, we observe signals at m/z = 360 u/e (and 420 u/e), which could arise from C_{60}^{2-} (and C_{70}^{2-}), but which must be distinguished from C_{30}^- (and C_{35}^-) and double harmonics of the signals at the fundamental ICR orbital frequencies of C_{60}^- (and C_{70}^-). The assignment of the doubly charged anions has been established from ^{13}C isotopic distributions, selective ion ejection and excitation experiments, and most definitively by measurement of frequency shifts induced by the ICR trapping voltage. Finally, we also report a negative ion FT/ICR mass spectrum for masses higher than that of C_{70}, as a test of Smalley's proposed "pentagon rule" hypothesis on the closure of fullerenes.[17]

Experimental Section

Sample Preparation. The raw fullerene material was prepared by means of the arc welding technique that has been described in great detail by Smalley and co-workers.[17] A small brass tube (10-cm diameter, 15 cm long) was fitted with electrically insulated brass end flanges that had Cajon ultratorr fittings for the manipulation of gas and the insertion of electrodes. Two copper rods (0.250-in. diameter, 20 cm long), which were directed through centrally located fittings, served as high-current electrical feedthroughs and graphite rod holders. This arrangement permitted external manipulation of the spacing between the graphite rods to be arc welded. Graphite rods of 0.156-in. diameter (ultracarbon, UF-4S, 24% porosity) were evaporated by arc welding at 75 A (Lincoln Electric AC-225, $244). The whole apparatus was submerged in cooling water, and the tube had a replaceable window which extended out of the water so that the operator could watch the arc welding (through welder's glasses) and keep the graphite rods almost touching. This operation was performed in an atmosphere of 150 Torr of helium. A 1-g portion of soot could be generated in about 1 h. Raw fullerene material was extracted from the soot with ~10% yield by use of benzene to yield a deep red-brown solution. After evaporation of the benzene, the raw fullerene material was washed with methylethyl ether.

Instrumental Details. FT/ICR mass spectra were obtained with an Extrel FTMS-2000 (Extrel FTMS, Madison, WI) instrument operating at 3.0 T and equipped with dual 2-in. cubic ion traps separated by a conductance limit of 2-mm aperture. The standard diffusion pumps were replaced by Helix Technology CryoTorr-8 cryopumps for both the source and analyzer vacuum chambers. Details of the mechanical and electronic interface between the mass spectrometer and a Continuum Model YG-600A Nd:YAG laser operating at the fundamental wavelength (1.064 μm) with an output of 360 mJ/pulse are described elsewhere.[23]

Mass Spectra. A standard laser desorption FT/ICR event sequence was employed. Ions were formed, trapped, excited, and detected on the source side of the dual trap. A laser pulse of ~10-ns duration was focused by a parabolic aluminum mirror onto a stainless steel probe tip onto which the fullerene solution had been placed and evaporated to dryness. A delay period (typically 3 s) following the laser pulse allowed the pressure to drop to ~6.0×10^{-8} Torr before the excitation event. The trapping voltage was −2 V for all experiments except for those that involved measuring the ICR orbital frequency shift as a function of trap voltage. In those experiments, the trap voltage was either −1 or −2 V. The standard broad-band frequency-sweep excitation mode (200-kHz bandwidth with a 700 Hz/μs sweep rate at an rf amplitude of 80 $V_{(p-p)}$) excited ions to a detectable ICR orbital radius in 0.3 ms. Direct-mode (Figures 1 and 3) or heterodyne-mode (Figure 2) detection (a single 64K time-domain transient, padded with an additional 64K zeroes, and Blackman–Harris apodized for subsequent discrete Fourier transform to yield a magnitude-mode spectrum) was employed in all experiments.

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Table I. Expected Isotopic Distributions, Computed from Known Elemental Abundances

species	isotopic composition	fraction	rel abundance
C_{30}	$^{12}C_{30}$	0.7154	1.000
	$^{12}C_{29}{}^{13}C$	0.2409	0.337
	$^{12}C_{28}{}^{13}C_2$	0.0392	0.055
C_{60}	$^{12}C_{60}$	0.5118	1.000
	$^{12}C_{59}{}^{13}C$	0.3447	0.674
	$^{12}C_{58}{}^{13}C_2$	0.1141	0.223
C_{35}	$^{12}C_{35}$	0.6771	1.000
	$^{12}C_{34}{}^{13}C$	0.2655	0.392
	$^{12}C_{33}{}^{13}C_2$	0.0506	0.075
C_{70}	$^{12}C_{70}$	0.4578	1.000
	$^{12}C_{69}{}^{13}C$	0.3597	0.786
	$^{12}C_{68}{}^{13}C_2$	0.1393	0.304

Table II. Observed Isotopic Distributions, Measured from FT/ICR Magnitude-Mode Mass Spectral Peak Relative Areas

species	isotopic composition	fraction	rel abundance
C_{60}^-	$^{12}C_{60}$	0.51	1.00
	$^{12}C_{59}{}^{13}C$	0.35	0.69
	$^{12}C_{58}{}^{13}C_2$	0.13	0.25
C_{60}^{2-}	$^{12}C_{60}$	0.53	1.00
	$^{12}C_{59}{}^{13}C$	0.37	0.70
	$^{12}C_{58}{}^{13}C_2$	0.10	0.19
C_{70}^-	$^{12}C_{70}$	0.55	1.00
	$^{12}C_{69}{}^{13}C$	0.35	0.64
	$^{12}C_{68}{}^{13}C_2$	0.10	0.18
C_{70}^{2-}	$^{12}C_{70}$	0.63	1.00
	$^{12}C_{69}{}^{13}C$	0.25	0.40
	$^{12}C_{68}{}^{13}C_2$	0.12	0.19

Following each laser shot, the probe was rotated to a new position to expose fresh sample before the next event sequence was initiated. Relative isotopic abundances were obtained from relative FT/ICR magnitude-mode spectral peak areas, which were in turn computed from the areas of an isosceles triangle whose height and width were the magntidue-mode spectral peak height and the interpolated peak width at half-maximum peak height.

Results and Discussion

Both of the doubly charged anions C_{60}^{2-} and C_{70}^{2-} have been detected and identified by the procedures that will now be illustrated for the C_{60}^{2-} case. The FT/ICR mass spectral peak of interest at m/z = 360 u/e (see Figure 1) could arise from C_{30}^-, C_{60}^{2-}, or (due to possible nonlinearities in the detected response)[24,25] a second harmonic of the strong signal from C_{60}^- at m/z = 720 u/e. The following series of experiments provide double-checks on all of the possibilities.

C_{60}^{2-} vs C_{30}^-. Half-Integral m/z Values for Isotopic Ions. Because ^{13}C is present in 1.11% natural abundance, chemically indentical C_n molecules with (say) n = 30 or 60 carbons will produce isotopic ions of detectable abundance at several nominal masses (see Table I and accompanying discussion below).[26] If those ions are singly charged, then their m/z values will be separated by integral multiples of u/e. However, if the ions are doubly charged, then their m/z values will be separated by half-integral u/e multiples. Figure 2 clearly shows that the isotopic ions are observed at m/z = 360, 360.5, and 361 u/e, and therefore cannot arise from C_{30}^-. Similar half-integral m/z multiples were found for the FT/ICR mass spectral peaks from C_{70}^{2-} at m/z = 420, 420.5, and 421 u/e.

Isotopic Abundance Ratios. Independent evidence for the number of carbons is available from the characteristic relative abundances of the various isotopic ions. Table I shows the relative isotopic abundances for C_{30}, C_{60}, and C_{70}, based on the known natural abundance of ^{12}C and ^{13}C. Note that because of the large number of carbon atoms, each system exhibits significant isotopic abundances for $^{12}C_{n-1}{}^{13}C$ and $^{12}C_{n-2}{}^{13}C_2$. Figure 2 shows high-resolution FT/ICR mass spectra for C_{60}^- and for the putative C_{60}^{2-}. The corresponding relative ion abundances are listed in Table II. It is clear that the relative abundances of the isotopic ions at m/z = 360, 360.5, and 361 u/e (Table II) match much more closely the relative abundance of C_{60} than those of C_{30} (Table I), thereby further supporting the identification of the m/z = 360 u/e signal as C_{60}^{2-} rather than C_{30}^-. Moreover, independent of the above arguments, it is highly unlikely that an isolated C_{30}^- fragment would occur without a host of other fragments.

C_{60}^{2-} vs Second Harmonic of C_{60}^-. From all of the above evidence, we conclude that the signal at m/z = 360 u/e cannot arise from C_{30}^-. It therefore remains to distinguish between a doubly charged anion of C_{60} or a second harmonic of the C_{60}^- signal. The following experiments were devised to distinguish between these two remaining possibilities.

The observation of harmonics is a problem inherent in Fourier analysis of nonlinear systems. In FT/ICR experiments, the practical necessity of using finite size electrodes to generate an electrostatic trapping field, and possible nonuniformity in the excitation and detection processes can in practice produce signals at harmonic[24] and combination[27] frequencies that can be enhanced by appropriate detection geometries.[28] For ions whose ICR orbits are centered on the midline z axis of the ion trap (which is in turn colinear with the symmetry axis of the applied static magnetic field), the ICR signal detected from the difference in induced charge between two symmetrically opposed electrodes should contain frequency components only at *odd* integral multiples of the ICR orbital frequency, ω_+. Thus, one would not expect to find a signal at an *even* harmonic frequency (e.g., $2\omega_+$) for ions initially formed (as in this case) on the z axis.

Ion Ejection/Single Ion Excitation Experiments. The ejection of ions of a particular m/z value from the ion trap should eliminate signals from any associated harmonic multiples of the fundamental ICR orbital frequency. Accordingly, ions at m/z = 720 u/e were ejected from the trap by single-frequency resonant irradiation at the ICR orbital frequency of C_{60}^-. Subsequent broad-band excitation/detection (not shown) resulted in a reduction of ~95% in the absolute magnitude of the C_{60}^- signal, with virtually no reduction in the magnitude of the signal at m/z = 360 u/e. If the latter signal were a second harmonic, we would have expected it to drop by 95% as well. Conversely, we were able to excite selectively and detect only the signal at m/z = 360 u/e (along with a very small signal at m/z = 720 u/e, possibly arising from some collision-induced loss of the second electron from C_{60}^{2-} during the excitation period) from a sample containing C_{60}^- as the most abundant anionic species; such detection would have been nearly impossible if the m/z = 360 u/e signal were a double harmonic of the (unexcited) signal from C_{60}^-.

Taken together, these experiments based on selective ejection (of C_{60}^-) or selective excitation (of C_{60}^{2-}) strongly suggest that the peak at 360 u/e is a doubly charged anion. (Similar results were obtained for the putative C_{70}^{2-} signal at m/z = 420 u/e.) However, both of these experiments are based on *negative* evidence (i.e., failure to observe an expected signal). Compelling evidence based on *positive* observations is provided by the experiments described below.

Frequency Shift from Trapping Voltage. Analysis of the FT/ICR equations of motion in the presence of a quadrupolar electrostatic trapping potential yields an observed ion cyclotron orbital frequency, ω_+, given by[25,29]

$$\omega_+ = \frac{\omega_c}{2} + \frac{\omega_c}{2}\left(1 - \frac{m}{m_{crit}}\right)^{1/2} \quad (1)$$

in which ω_c is the "true" cyclotron frequency (i.e., the frequency

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Table III. Observed ICR Orbital Frequency Shifts Due to Variation in Trapping Potential[a]

m/z (u/e)	frequency shift (Hz/V)
720	83.7
360	86.4
240	239

[a] These data clearly show that the signal at $m/z = 240$ u/e is a third harmonic of the signal at $m/z = 720$ u/e, whereas the signal at $m/z = 360$ u/e arises from a doubly charged 720-u ion (see text).

of the cyclotron motion in the absence of the trapping electrostatic field). The critical mass, m_{crit}, is the upper mass limit above which the ion trajectories become unstable:

$$m_{crit} = \frac{qa^2B_o^2}{8\alpha V_T} \quad (2)$$

in which q is the ionic charge, a is a trap dimension (e.g., spacing between any two opposed plates for a cubic trap), B_o is the magnetic field induction, α is a trap geometry-dependent factor (e.g., $\alpha = 1.386$ for a cubic trap), and V_T is the trapping voltage applied to each of the trapping electrodes. Clearly, a change in the trapping voltage will shift the observed cyclotron frequency. Since m_{crit} is usually large (e.g., ~200000 u at 3.0 T for a trapping potential of 1 V in the present 2-in. cubic trap), $m/m_{crit} \ll 1$ for the present experiments, and the square root in eq 1 may be Taylor-expanded to produce a first-order "trapping" shift in ICR orbital frequency that is *independent of both ionic mass and charge*. Equation 3 shows that the frequency shift with respect

$$\omega_+ \approx \omega_c - \frac{2\alpha V_T}{a^2B_o} \quad (3)$$

to trapping voltage is $-\frac{2\alpha V_T}{a^2B_o}$ for any ion species. The signal of the nth harmonic thus appears at

$$n\omega_+ \approx n\omega_c - n\left(\frac{2\alpha V_T}{a^2B_o}\right) \quad (4)$$

which demonstrates that the frequency shift with respect to trapping voltage of the nth harmonic signal is n times the frequency shift of the fundamental. Therefore the frequency shift can be used to discriminate between harmonic and ion signals.

Specifically, in the present experiments, the frequency shift computed from eq 3 should be ~65 Hz/V, independent of m/z: i.e., if the signal at $m/z = 360$ u/e arises from C_{60}^{2-}, then its frequency shift should be the same as that for C_{60}^-. However, if the signal at $m/z = 360$ u/e represents the nth harmonic of the signal at $m/z = 720$ u/e, then the apparent frequency shift at $m/z = 360$ u/e should be n times that for $m/z = 720$ u/e. The experimental results listed in Table III unequivocally show that the signal at $m/z = 240$ u/e is a third harmonic of the C_{60}^- signal (since the frequency shift is 3 times larger for the former than the latter). In contrast, the signal at $m/z = 360$ u/e has the *same* frequency shift as the signal from C_{60}^- at $m/z = 720$ u/e. Thus, the $m/z = 360$ u/e signal cannot be a second harmonic of the C_{60}^- signal, and must be due to the doubly charged anion C_{60}^{2-}.

Taken together, the preceding tests consistently confirm that we have produced and detected the doubly charged anion of buckminsterfullerene in the gas phase. In similar fashion, we have observed and confirmed the identity of C_{70}^{2-}. We strongly suspect that an additional signal observed at $m/z = 504$ is due to C_{84}^{2-}, but the above-listed procedures were inconclusive due to too low signal-to-noise ratio.

Finally, FT/ICR signals from C_{60}^{2-} and C_{70}^{2-} could be excited and detected up to 3 min after their production by the laser pulse. Thus, these species are more than just metastable; i.e., C_{60}^- and C_{70}^- must have positive adiabatic electron affinities.

Higher Mass Fullerene Anions. An FT/ICR mass spectrum in the mass region above C_{70}^- (840 u/e) is presented in Figure 3. This mass spectrum is quite interesting when interpreted in the context of a recent proposal by Smalley and co-workers regarding the closure of fullerenes.[17] They presented a plot of the number of dangling bonds vs the number of carbon atoms in both graphite sheet fragments and fragments that incorporate pentagons to reduce dangling bonds (thereby curving the sheet). There is a one to one correspondence between the masses we have observed and the masses on their "pentagon rule" plot, resulting in zero dangling bonds. These are the fragments that totally eliminate dangling bonds by closing, including C_n^-, where $n = 60$, 70, and any even $n > 70$. The validity of the pentagon rule picture is nicely supported by the various ions observed in the mass spectrum of Figure 3.

Conclusion

All of the positive and negative evidence reported here is self-consistent and verifies the existence of gas-phase C_{60}^{2-} and C_{70}^{2-}. Our general technique of measuring frequency shifts as a function of trapping voltage should prove especially useful when (as in this case) it is necessary to distinguish multiply charged species from harmonic artifacts. In future work, it should prove interesting to collisionally dissociate the various fullerene singly and doubly charged anions, and to bracket the electron affinity of C_{60}^- (or C_{70}^-) by observing charge-transfer reactions between the corresponding doubly charged anions and neutrals of varying electron affinity.

Acknowledgment. In the course of this work, we learned that R. L. Hettich and R. N. Compton (Oak Ridge National Laboratories, Oak Ridge, TN) had independently observed C_{60}^{2-} and C_{70}^{2-} by laser desorption (at 266 nm rather than 1.064 μm) of a fullerene mixture. Their results will be published elsewhere, along with some theoretical calculations for the anion species. We thank these investigators for sharing their work in progress. We thank R. McCreery for providing graphite and for helpful discussions. We also thank R. M. Pitzer and collaborators for sharing, in advance of publication, their theoretical calculations on the stability of C_{60}, C_{60}^-, and C_{60}^{2-}. This work was supported by grants from the National Science Foundation (A. G. M., Grant CHE-8721498) and The Ohio State University (J.V.C. and A. G.M.).