Doubly Charged Negative Ions of Carbon-60

R. L. Hettich, R. N. Compton,[a] and R. H. Ritchie[a]
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

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We report the observation of long-lived ($\tau > 10^{-3}$ sec) doubly charged negative ions of C_{60} in the gas phase. $C_{60}{}^{-}$ and $C_{60}{}^{2-}$ ions are produced by laser desorption from a surface covered with C_{60} molecules and are believed to be produced by negative surface ionization from the laser-heated surface. Pseudopotential calculations indicate that $C_{60}{}^{2-}$ is slightly bound (electron affinity of $C_{60}{}^{-} \simeq 0.1$–0.4 eV) relative to $C_{60}{}^{-}$.

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In 1985, $C_{60}{}^{+}$ ions were reported to be especially prominent in the laser-ablation mass spectrum of graphite [1]. Unusual stability for C_{60} was suggested. Since that discovery, the relatively facile synthesis of gram quantities of C_{60} has led to a rapid description of many of the fascinating physical properties of this new form of solid carbon [2]. The predicted high symmetry (I_h) of this soccerball-shaped molecule has been verified by the observation of the expected four infrared-active vibrational modes [2], vibrational Raman spectra [3], and the occurrence of a single NMR line for the $^{13}C_{60}$ molecule [4,5]. Scanning-tunneling-microscopy images of C_{60} reveal spherical molecules (the carbon atoms are unresolved, presumably due to rotations) [6,7]. Carbon clusters containing seventy atoms also exhibit stability similar to that of C_{60}. The five-line NMR spectra reported [5] for $^{13}C_{70}$ support an elongated "rugby-ball" shape (D_{5h} symmetry), as predicted earlier.

The isolation of macroscopic quantities of *neat* multiatom clusters allows for the unprecedented study of many phenomena which previously have been complicated by a distribution in cluster size. Among many possibilities are the investigation of surface-plasmon excitations, cage effects in photoabsorption, charge-transfer spectroscopy of C_{60} in electron-donating solvents, and the electrical properties of microspheres. The importance of this new form of solid carbon is underlined by the recent report [8] that potassium-doped carbon-60 (K_xC_{60}) is a superconductor at 18 K. This represents the highest T_c yet observed for a molecular superconductor.

Limited studies of the ionic properties of C_{60} have appeared. The ultraviolet photoelectron spectrum of $C_{60}{}^{-}$ shows bands at ∼3, ∼4.5, and ∼6 eV with a threshold at ∼2.8 eV (electron affinity of C_{60}) [9]. More refined measurements give an electron affinity (EA) of C_{60} $= 2.65 \pm 0.05$ eV [10]. The 3-eV peak is attributed to the removal of the "extra" electron occupying the threefold-degenerate t_u lowest unoccupied molecular orbital.

In this study, we report the observation of the doubly charged ions $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$ in the gas phase. Evidence for $C_{60}{}^{-}$, $C_{60}{}^{2-}$, and $C_{60}{}^{3-}$ in solution has been reported from the fact that three [11] reversible half-wave reduction waves appear in the cyclic voltammetry of C_{60} in CH_2Cl_2. Long-lived doubly charged carbon cluster anions in the gas phase have been reported earlier from sputtering of a graphite surface by Cs^{+} ions [12]. The intensity of the doubly charged clusters ($C_n{}^{2-}$, $n = 7$–28) exhibited a pronounced alternating pattern with even-n clusters being far more intense than their neighboring odd-n clusters.

Two methods were used to prepare the C_{60} and C_{70} samples. In one, C_{60} and C_{70} were generated by laser (xenon chloride laser, 308 nm) ablation of a graphite rod in a quartz vial maintained under a helium atmosphere of 300 Torr. A second method employed an arc (∼80 A at 30 V) between two $\frac{1}{4}$-in. graphite rods (Poco graphite) in ∼100 Torr of helium followed by soxhlet extraction of the particulate into benzene. Commercial samples of C_{60} and C_{70} were also supplied by MER Corporation (Tucson, Arizona). These samples were deposited onto stainless-steel disks and subsequently examined by laser-desorption Fourier-transform mass spectrometry (FTMS). During the course of this study, at least seven different procedures of sample preparation and collection were examined, and in all cases yielded intensity ratios for $C_{60}{}^{2-}/C_{60}{}^{-}$ and $C_{70}{}^{2-}/C_{70}{}^{-}$ in the range of 0.02–0.20.

All mass spectra were acquired with an Extrel FTMS-2000 Fourier-transform mass spectrometer equipped with a Quanta Ray DCR-11 Nd-doped yttrium-aluminum-garnet pulsed laser. One laser shot (266 nm, 10^{7}–10^{5} W/cm^{2}) of the previously prepared samples generated ions which were trapped for 3–20 ms at a base pressure of 8×10^{-8} Torr and subsequently detected in the FTMS ion cell. The lifetime of $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$ is considerably greater than 1 ms.

Laser desorption of a pure sample of C_{60} and C_{70} (Fig. 1) revealed abundant ions at $m/z = 720$ ($C_{60}{}^{-}$) and 840 ($C_{70}{}^{-}$) and minor ions at $m/z = 360$ and $m/z = 420$, which we believe to be $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$, respectively. The unambiguous identification of the minor ions required examination of several experimental parameters. For example, the signal at $m/z = 360$ could arise from $C_{30}{}^{-}$, $C_{60}{}^{2-}$, or a second-harmonic frequency artifact from the large $C_{60}{}^{-}$ signal at $m/z = 720$. Expansion of the mass region around $m/z = 720$ from Fig. 1 revealed the expected relative isotopic abundance for $C_{60}{}^{-}$ of 720 = 100%, 721 = 67%, and 722 = 24%. Figure 2 illustrates an expansion of the $m/z = 350$–430 region at a resolution of $m/\delta m = 1800$. Notice that the ^{13}C isotopes

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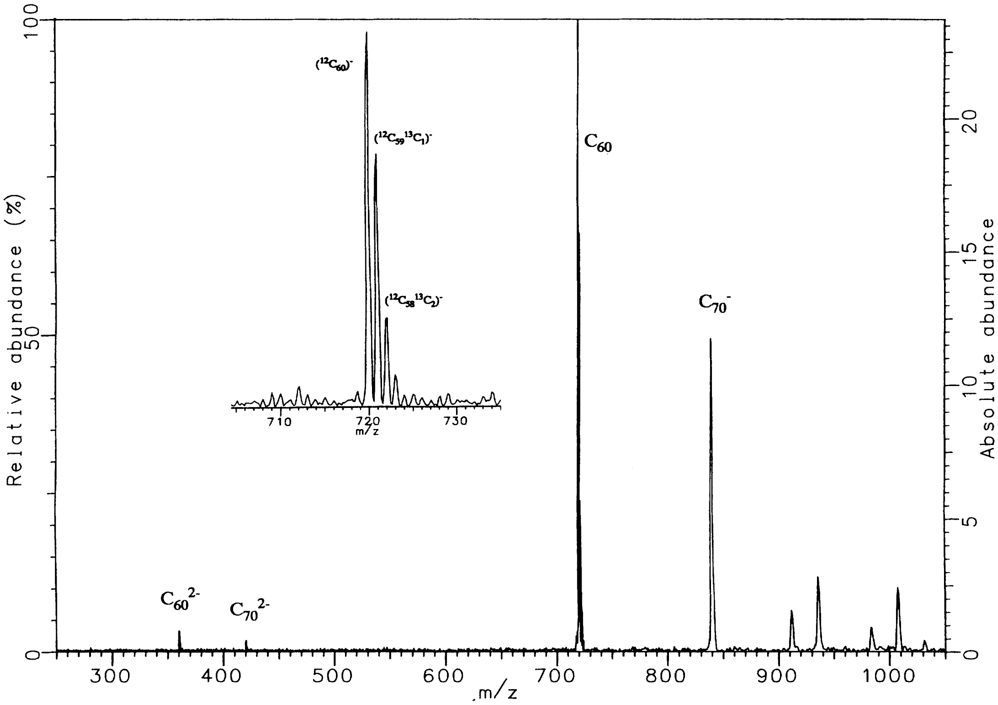

FIG. 1. Laser-desorption negative-ion mass spectrum of C_{60} and C_{70} deposited on a stainless-steel sample plate.

for the ions at nominal $m/z = 360$ and 420 appear at half-integer mass units. This would be the expected isotopic pattern for $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$. In addition, the relative isotopic abundances of the $m/z = 360$-361 ions (360=100%, 360.5=75%, 361=37%) are very similar to the isotopic abundances of the $C_{60}{}^-$ ion outlined above. For comparison, the calculated isotopic pattern of $C_{30}{}^-$ would be 360=100%, 361=34%, and 362=6%. Thus the isotopic patterns of

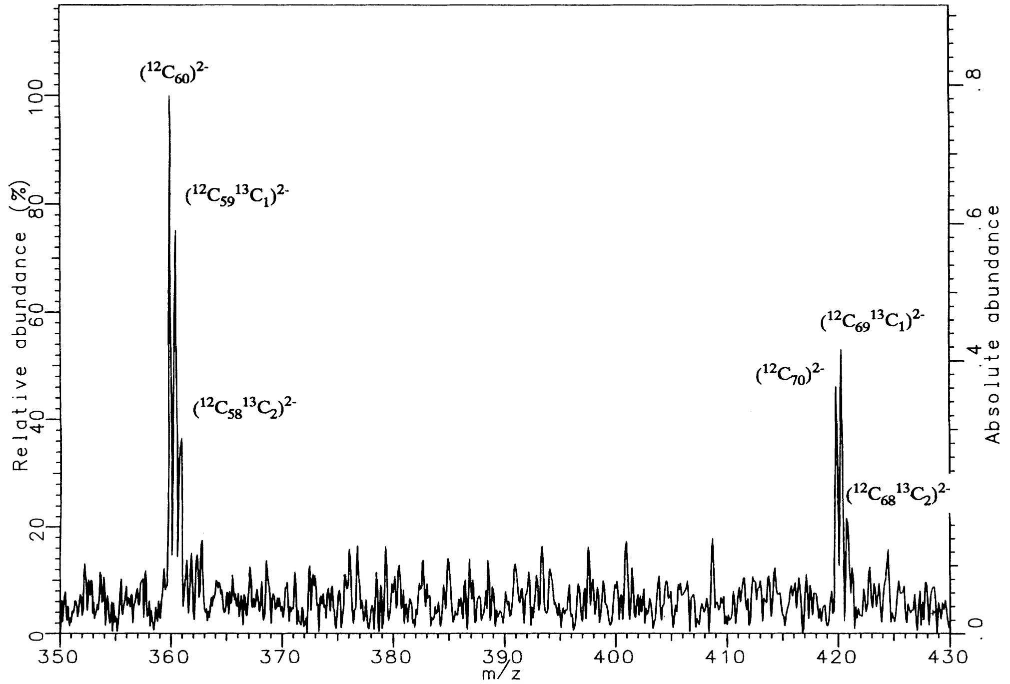

FIG. 2. Expansion of the $m/z = 350$–430 region from Fig. 1. Note that the isotopic spacings and abundances support the assignments of $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$.

the one-half integer masses rule out the possibility that the $m/z = 360$ and 420 were due to singly charged C_{30}^- and C_{35}^- ions.

Signals at harmonic frequencies of abundant ions in a spectrum can sometimes be observed as instrumental artifacts in FTMS experiments [13]. The appearance and intensities of harmonic signals are dependent on trapping plate voltages as well as on the sampling of the time-domain signal and can usually be distinguished from signals resulting from real ions. Varying the ion-detection parameters (number of data points, excitation bandwidth) did not affect the abundances of the $m/z = 360$ and 420 signals. Changing the trapping plate voltages from -2 to -3 V resulted in frequency shifts of 71 Hz for $m/z = 840$, 75 Hz for $m/z = 720$, 65 Hz for $m/z = 420$, and 61 Hz for $m/z = 360$. If $m/z = 360$ and 420 were second-harmonic signals, their frequencies should shift by twice as much as the fundamental frequencies [14]. In addition, ion ejection experiments were used to probe the nature of these signals. For example, if $m/z = 360$ is a real ion (i.e., C_{60}^{2-}), its intensity should be reduced when it is ejected. However, if $m/z = 360$ is due to the second harmonic of the intense $m/z = 720$ signal, then ejection of $m/z = 360$ would have no effect on its intensity because it would be related only to the ion intensity of $m/z = 720$. Ion ejection of $m/z = 360$ resulted in complete loss of the $m/z = 360$ signal while leaving the remainder of the spectrum unaffected (i.e., the large $m/z = 720$, C_{60}^-, is still observed). Similar results were observed for the $m/z = 420$ signal. Thus, these experimental procedures provide direct evidence that the ions at $m/z = 360$ and 420 were not due to second-harmonic frequencies, but are real ions corresponding to C_{60}^{2-} and C_{70}^{2-}.

Classically, an insulated, perfectly conducting sphere charged with any number of electrons can attach an additional electron when it is close enough to the surface [15]. Quantally, it is not evident that a charged sphere can accept an additional charge. In fact, restricted Hartree-Fock calculations indicate that the C_{60}^{2-} system is unbound [16].

We have taken a semiempirical approach to the problem of estimating the energy of the second electron on the C_{60}^{-2} ion. We assume that the closed-shell C_{60} molecule is approximately spherically symmetric, and that one may represent the interaction of an added electron with the C_{60} molecule by a pseudopotential. We assume that the latter can be written in the simple form $V(r) = -e^2\alpha/[c+2^{1/2}(r-r_c)^2]^2$, where r_c is a radius which is chosen to be approximately equal to the radius of the C_{60} molecule. This potential is attractive at large distances with an asymptote given by $-e^2\alpha/2r^4$. The polarizability α of the C_{60} molecule is calculated to be $\cong 80$ Å^3 using the empirical method of Miller and Savchik [17]. In view of this, the electron of the C_{60}^- negative ion resides in a state not unlike the much-studied image-potential-induced surface states at a metallic surface where a band gap exists [18]. However, the pseudopotential we use is designed to represent, near the molecule, a potential analogous to the inner potential of a solid. We have chosen the value of c in the pseudopotential such that, upon solving Schrödinger's equation, the binding energy of the added electron is found to agree with the measured value of 2.65 ± 0.02 eV.

To treat the added electrons of the C_{60}^{2-} ion, we have solved the Hartree-Fock equations for two electrons in a spherically symmetric, singlet ground state, accounting for exchange and for the Coulomb interaction between them, assuming the same pseudopotential for the electron-C_{60} core interaction as was used in determining the binding energy of the one-electron ion. We find that in this approximation, the binding energy per electron in the singlet state may lie in the range from -0.3 to 0.6 eV as r_c varies from 8 to 12. We note, however, that even in the case where this energy is -0.3 eV, the state found is metastable and that the lifetime of the state is estimated to be ~ 1 μs. This is not long enough to make possible the measurement of the ion in the experiments described here. As discussed previously, our experimental results require that the lifetime of the C_{60}^{2-} ion be greater than 1 ms. In fact, we and others [14] have performed ion trapping experiments which indicate a lifetime of greater than 0.1 s. The state with an EA of -0.3 eV corresponds to r_c about equal to the geometrical size of C_{60} and appears to us to be physically unreasonable.

Figure 3 shows the pseudopotential, the total effective potential seen by one of the singlet electrons in the ground state, and the square of the wave function of one of the singlet electrons. Here r_c was chosen to be 10 a.u., and the resulting binding energy was found to be ≈ 0.3

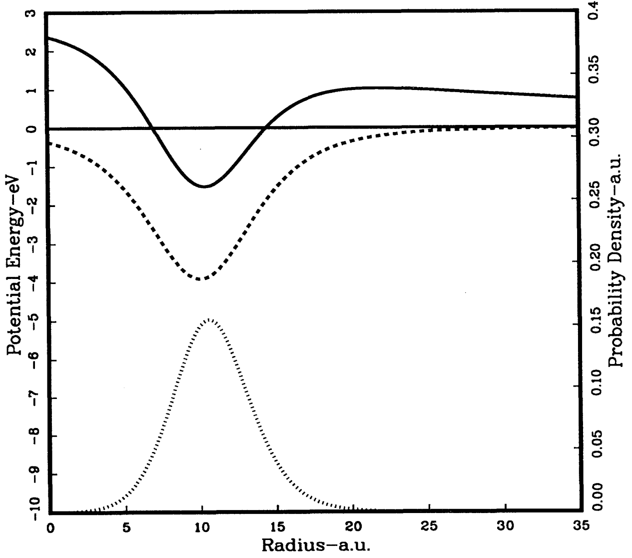

FIG. 3. Schematic pseudopotential for C_{60}^- (dashed curve) and for singlet C_{60}^{2-} (solid curve), and the probability density for one of the singlet electrons of C_{60}^{2-} (dotted curve).

eV. As one sees, the singlet wave function is well localized, as it is for all values of r_c in the range given above. We plan to extend further these theoretical estimates of the properties of the C_{60} ions so as to make the prediction of binding energies more definite.

We will explore a self-energy model in which the long-range part of the pseudopotential is characterized in terms of the dynamic response function of an equivalent jellium spherical shell, and the short-range part is expressed through an exchange-correlation potential.

It is interesting to speculate on possible mechanisms for producing $C_{60}{}^-$ and $C_{60}{}^{2-}$. Unimolecular attachment of slow electrons to C_{60} ($e + C_{60} \rightleftarrows C_{60}{}^-$) can lead to very long-lived $C_{60}{}^-$ ions. The lifetime of $C_{60}{}^-$ formed under such conditions can be calculated from the model by Compton *et al.* [19], in which the electron energy (thermal) and electron affinity energy are shared equally among the 174 degrees of freedom of the anion. Using previously calculated [20] vibrational frequencies for C_{60} and the accepted $\mathrm{EA}(C_{60}) = 2.65$ eV, an autodetachment lifetime of 10^5–10^6 s is obtained if one assumes the maximum s-wave electron-capture cross section [$\pi(\lambda + a)^2$, λ denotes the de Broglie wavelength of the electron]. Thermal electron attachment to $C_{60}{}^-$ to produce $C_{60}{}^{2-}$, however, would require tunneling through a long-range Coulomb barrier of the type shown in Fig. 3. The probability of such tunneling is small. We have examined this possibility by thermally desorbing C_{60} and C_{70} into the gas phase and interacting this vapor with a low-energy electron beam. Slow electrons are observed to attach to C_{60} and C_{70}, forming $C_{60}{}^-$ and $C_{70}{}^-$ but not the doubly charged anions. The lifetimes of these ions are greater than 1 ms.

A likely mechanism for forming $C_{60}{}^{2-}$ involves negative surface ionization [21]. If one assumes that $C_{60}{}^{2-}$ and $C_{60}{}^-$ are produced by negative (Saha-Langmuir) surface ionization, the ratio of the $C_{60}{}^{2-}/C_{60}{}^-$ signal can be calculated from

$$\frac{I(C_{60}{}^{2-})}{I(C_{60}{}^-)} = \frac{g^{2-}}{g^-} e^{-\Delta E/kT},$$

where g is the ion statistical weight, ΔE represents the difference in the electron binding energies for $C_{60}{}^{2-}$ and $C_{60}{}^-$ (~ 2.2 eV), and T is the surface temperature. g^{2-}/g^- would be 1 for singlet $C_{60}{}^{2-}$, 3 for triplet $C_{60}{}^{2-}$, and 4 if the ion is a mixture of the two. Laser heating of the surface is expected to raise the temperature of the surface to a few thousand degrees. At these temperatures, the $C_{60}{}^{2-}$ ions are probably an admixture of singlet and triplet ions (spacing $\simeq 0.3$ eV [18]) so that $g^{2-}/g^- = 4$. Taking g^{2-}/g^- to be 4, $\Delta E \simeq 2.2$ eV, and the surface temperature to be ~ 3000 K (the approximate melting point of graphite), the ratio of $C_{60}{}^{2-}$ to $C_{60}{}^-$ becomes ~ 0.001. This factor appears too low to explain our observed ratios; however, this ratio is strongly dependent upon the assumed binding energy of $C_{60}{}^{2-}$, and the surface temperature (e.g., for $T = 5000$ K, the ratio becomes 0.05). Our conclusion is that the surface temperature must be large in order to make $C_{60}{}^{2-}$ comparable to $C_{60}{}^-$.

During the course of these studies we learned that the authors of Ref. [14] have also observed long-lived $C_{60}{}^{2-}$ and $C_{70}{}^{2-}$ using 1.064-μm laser irradiation of C_{60} and C_{70} on a surface in a FTMS. We are very grateful to P. A. Limbach and A. G. Marshall for providing us with a preprint of their results (Ref. [14]) and to R. M. Pitzer for an advanced copy of their theoretical results on $C_{60}{}^{2-}$ (Ref. [16]). Also, we acknowledge helpful discussions with R. S. Berry, C. E. Klots, John Bartmess, and A. Tuinman. This publication is based on work performed through the Laboratory Exploratory Studies Program and research sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under Contract No. DE-AC0584OR21400 with Martin Marietta Energy Systems, Inc.

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[a] Also at The University of Tennessee, Knoxville, TN 37996.

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