Attachment of Two Electrons to $C_{60}F_{48}$: Coulomb Barriers in Doubly Charged Anions

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The highly fluorinated chiral C_{3h} molecule $C_{60}F_{48}$ was observed to sequentially attach two electrons in the gas phase to produce $C_{60}F_{48}^{2-}$ and $C_{60}F_{46}^{2-} + F_2$. The first electron affinity (EA) of $C_{60}F_{48}$ was measured to be 4.06 ± 0.3 eV. The first and second EA were calculated to be $EA_1 = 5.07$ eV and $EA_2 = 2.27$ eV for the more symmetric D_{3d} isomer. The dianion was found to be *more stable* with respect to electron detachment than the singly charged anion. This remarkable stability of the dianion is attributed to a potential barrier resulting from the long range Coulomb repulsion and short range electron-molecule binding.

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Although singly charged negative ions have received considerable attention during the past thirty years, doubly charged negative ions have remained a curiosity and a matter of some controversy (see, e.g., [1]). Recent studies of doubly charged anions of small carbon clusters C_n^{2-} ($n = 7-28$) [2] and the closed cage fullerenes C_{60}^{2-} and C_{70}^{2-} [3,4] firmly establish the existence of long-lived gas phase dianions. In all of these experiments, the long-lived C_n^{2-} dianions were created at a surface (Cs^+ ion impact on graphite [2] or laser desorption from a surface [3,4]). In fact, the observation of long-lived C_{60}^{2-} is contradicted by existing calculations which yield a negative second electron affinity for C_{60} [5–8]. Doubly charged fullerene anions (C_n^{2-} with $n = 60$, 70, 76, 78, and 84) have also been observed under desorption probe negative chemical ionization conditions with an isobutane plasma [9].

Herein we report studies of the highly fluorinated $C_{60}F_{48}$ doubly charged negative ion. The fluorinated fullerene provides the necessary molecular framework in which to test some rather fundamental concepts in atomic and molecular physics, i.e., the charging of molecular "spheres." This study offers a major advance in the understanding of multiply charged anions for three reasons: (1) We report the observation of nondissociative and dissociative attachment of a second electron to a molecule in the gas phase, making it possible to eventually study the electron energy dependence of such processes; (2) the *second* electron affinity of $C_{60}F_{48}$ is calculated to be positive and large (2.2 eV); and, most importantly, (3) the $C_{60}F_{48}^{2-}$ dianion is more stable toward the loss of either excess electron than the singly charged anion. The unusual stability of the $C_{60}F_{48}^{2-}$ dianion to electron loss is attributed to the relatively large second electron affinity plus the presence of a Coulomb barrier to the removal of either excess electron.

The starting materials for this investigation result from reactions of C_{60} with fluorine gas. This reaction produces $C_{60}F_{2n}$ ($n \leq 24$) mixtures of varying complexity at elevated temperatures [10]. However, elevated temperatures and the use of a sodium fluoride matrix to suppress sublimation yields nearly pure $C_{60}F_{48}$, which was determined by ^{19}F NMR spectroscopy to consist of an enantiomeric pair having the remaining six double bonds arranged in two chirality-generating orientations [11]. For these studies, two different samples were examined: (1) $C_{60}F_x$ (x predominantly 46 and 44) generated at elevated temperature [10], and (2) the enantiomeric pair $C_{60}F_{48}$ [11].

Two complementary mass spectrometry techniques were used, each employing low-energy electron attachment. The first experiments involve ion trapping in a Fourier transform ion cyclotron resonance mass spectrometer (FTMS) [4]. The fluorinated fullerene solids were thermally desorbed (250–300 °C) from a stainless steel probe in the vacuum chamber of the FTMS and were then ionized by the attachment of low-energy electrons from an electron beam. The first sample, which is predominantly $C_{60}F_{46,44}$, produced mainly $C_{60}F_{46}^-$ and $C_{60}F_{44}^-$ in the mass spectrum, as shown in Fig. 1(a), along with a small amount of the dianions, primarily $C_{60}F_{44}^{2-}$. To enhance the dynamic range, the more abundant monoanions were ejected from the FTMS cell prior to ion detection. This process not only provided better signal/noise conditions for the detection of the dianions, as shown in Fig. 1(b), but also ruled out the possibilities that the dianion ion signals are due to second harmonics of the abundant monoanions. Examination of the single isomer of $C_{60}F_{48}$ (containing some $C_{60}F_{46}O$) revealed primarily monoanions at $C_{60}F_{48}^-$ [Fig. 1(c)] and dianions of $C_{60}F_{46}^{2-}$ [Fig. 1(d)]. Compared with the first sample, the dianions from $C_{60}F_{48}$ were observed in lower abundance.

In the second technique, a double focusing magnetic-sector–quadrupole-hybrid instrument (MSQH) [10] was used. The monoanions and dianions were generated by electron attachment to gas phase $C_{60}F_{48}$ (thermally

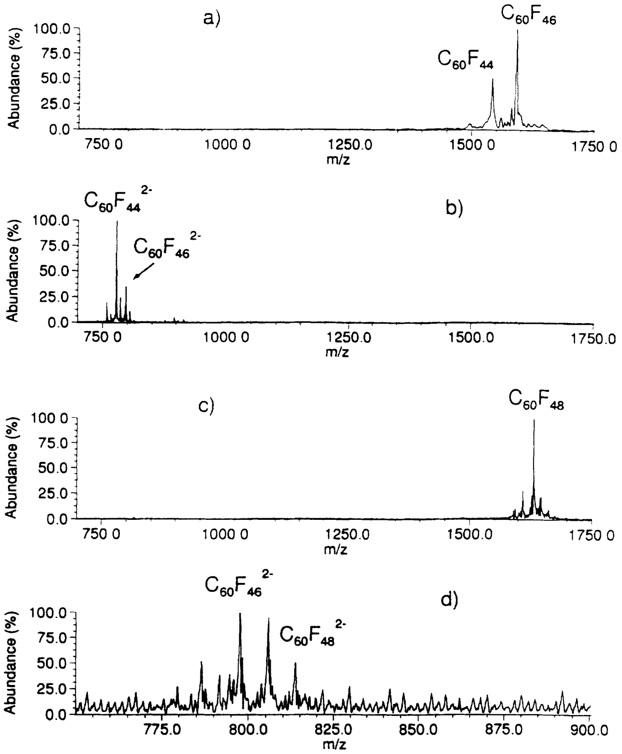

FIG. 1. Thermal desorption (250 °C) electron capture FTMS negative ion mass spectra: (a) $C_{60}F_{46,44}$ mixture (no ion ejection), (b) same as (a), but the monoanions have been ejected prior to ion detection, (c) $C_{60}F_{48}$ sample (no ion ejection), and (d) same as (c), but the monoanions have been ejected prior to ion detection.

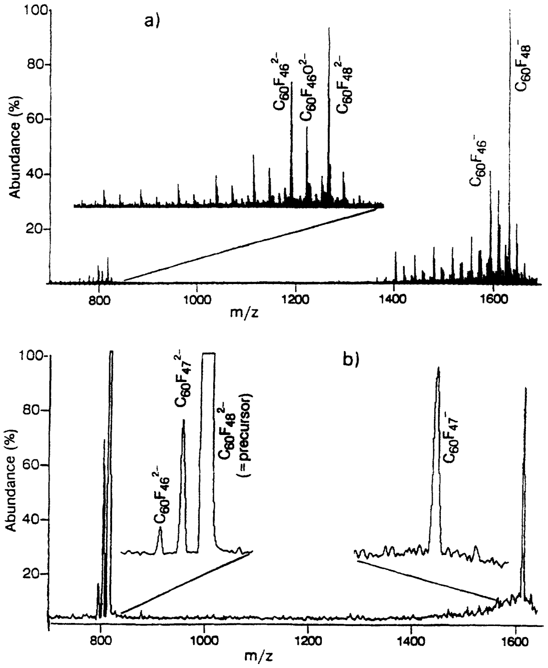

FIG. 2. Thermal desorption electron capture MSQH negative ion mass spectra: (a) $C_{60}F_{48}$ sample with inset detailing the dianion region, and (b) metastable spectrum of $C_{60}F_{48}^{2-}$ with insets expanding the regions of interest. The precursor ion ($C_{60}F_{49}^{2-}$) is overranged; the true intensity is ~3000× that depicted.

desorbed from a platinum filament) in the ion source filled with about 1 mTorr of N_2 bath gas. A beam of electrons of nominally 75 eV are first introduced into the ion source. The bath gas serves to thermalize the electrons through ionization and energy loss collisions (especially through the $^2\Pi_g$ N_2^- resonance). Electron impact ionization produces a bimodal distribution of low- and high-energy electrons [12]. The buffer gas also serves to collisionally remove excess vibrational energy of the ions produced upon electron capture. The anions are expelled from the ion source in <1 μs and detected some 90–200 μs later. The mass spectrum, Fig. 2(a), showed the existence of both monoanions and dianions. In contrast to the dianion mass spectrum from the FTMS shown in Fig. 1(d), $C_{60}F_{48}^{2-}$ was found to be the most abundant dianion in the magnetic sector apparatus. However, the dianion to monoanion intensity ratio $I(C_{60}F_n^{2-})/I(C_{60}F_n^{-})$ displayed a maximum at $n = 46$, which is consistent with the FTMS results. The $C_{60}F_{48}^{2-}$ dianion was found to be metastable with respect to F_2, F, and F^- losses. Within the time window of 90 to 145 μs, some of the $C_{60}F_{48}^{2-}$ ions dissociate to $C_{60}F_{46}^{2-}$ (F_2 loss), $C_{60}F_{47}^{2-}$ (F loss), and $C_{60}F_{47}^{-}$ (F^- loss), as shown in Fig. 2(b). Upon medium energy collisions (200 eV) with argon gas, $C_{60}F_{48}^{2-}$ displayed fragments of $C_{60}F_{44}^{2-}$ ($2F_2$ loss), $C_{60}F_{45}^{-}$ (F_2 $+F^-$ loss), and $C_{60}F_{43}^{-}$ ($2F_2$ $+F^-$ loss). *The most significant result from both of these experiments is that electron detachment from* $C_{60}F_{48}^{2-}$ *is* not *observed* in either the metastable decay or collisional dissociation spectra.

For both mass spectral techniques, the $C_{60}F_x^-$ ions were formed by both dissociative and nondissociative electron attachment to gas phase neutral $C_{60}F_x$ molecules. The $C_{60}F_x^{2-}$ dianions are believed to be formed by the sequential addition of two electrons.

The ratio of the intensity of the dianion to the monoanion ($C_{60}F_x^{2-}/C_{60}F_x^{-}$) signal increases linearly with the electron beam current, which is consistent with the postulated sequential two-electron attachment. A third-body collision can remove the excess energy from attachment of the second electron and help stabilize the dianion. The attachment (and subsequent autodetachment) of the second electron will necessarily occur over the top of the Coulomb barrier (tunneling reactions are less probable), which is estimated to be ~1.5 eV (see Fig. 3).

In the magnetic sector apparatus, the ions were made in the presence of 1 mTorr of N_2 gas. The metastable $[C_{60}F_{48}^{2-}]^*$ dianions could be stabilized by the high pressure bath gas, while in the FTMS (base pressure 10^{-8} Torr), the main ion formation pathway is dissociative attachment due to the lack of third body collisions. Some of the dianions will escape the source of the MSQH intact, but with sufficient residual internal energy to fragment on the tens- to hundreds-of-microseconds time scale. These are observed as metastable decompositions in the quadrupole sector of the MSQH, as described above. Because of the significantly longer time delay between dianion formation and detection in the FTMS instrument (at least milliseconds), dianions which cannot dissipate their internal energy by collisions will fragment prior to ion detection. Thus, the dianions observed in the FTMS experiment are those which have relaxed primarily through fragmentation, although some of the dianions may have been collisionally stabilized (especially at the elevated pressures). This explains why $C_{60}F_{44}^{2-}$ is the major dianion observed in the FTMS spectrum, as shown in Fig. 1(b), from the sample in which $C_{60}F_{46}^{-}$ was the most abundant monoanion. This is also consistent with the fact that dianions resulting from dissociative electron attachment were observed in greater abundance for the FTMS (low pressure, long time scale) relative to the sector instrument. The $C_{60}F_{48}$ molecule must have a smaller dissociative electron attachment cross section than $C_{60}F_{46}$, as evidenced by the low intensity of $C_{60}F_{46}^{-}$ fragments observed in the mass spectrum from the $C_{60}F_{48}$ sample. As a consequence, it would be relatively difficult for $C_{60}F_{48}^{2-}$ ions to be stabilized by losing F_2 to form $C_{60}F_{46}^{2-}$. The introduction of argon into the FTMS cell at a total pressure of $\sim 2 \times 10^{-6}$ Torr not only aids in thermalizing the electrons but also provides the third body collisions necessary to stabilize the dianions and would therefore be expected to increase the abundance of the dianions, as observed.

Although we believe that the dianions are formed by the attachment of two "free" electrons in both experiments, it is also possible that high Rydberg atoms or molecules (such as N_2^*) formed by electron impact in the magnetic sector ion source may play an important role in dianion formation. The electrons could be transferred from the Rydberg atoms (or molecules) with less excess energy than free electron attachment and therefore produce less fragmentation. The positive ion core of the Rydberg atoms (or molecules) would also lower the Coulomb potential barrier, making it energetically more favorable for dianion formation. The ion core is also known to act as an effective third body for collisional stabilization [13]. This ion formation process via Rydberg charge exchange is not expected to occur in the low pressure FTMS experiments outlined above.

The upper and lower bounds for the first electron affinity of the fluorinated fullerene $C_{60}F_{48}$ were determined in the FTMS by monitoring the occurrence or absence of the charge exchange reaction:

$$C_{60}F_{48} + A^- \rightarrow C_{60}F_{48}^- + A . \tag{1}$$

Reaction (1) was observed to occur for $A = NO_3$ (EA = 3.92 ± 0.24 eV [14]), but was not observed to occur for $A = CF_3COO$ (EA = 4.20 ± 0.3 eV [14]), yielding a bracketed value of $\mathrm{EA}(C_{60}F_{48}) = 4.06 \pm 0.3$ eV. This value is indistinguishable from the bracketed electron affinities of $C_{60}F_{46}$ and $C_{60}F_{44}$ [15] and is ~ 1.5 eV higher than the corresponding value of C_{60} (EA = 2.65 eV [16].

The charge exchange reaction (2) was examined in an attempt to bracket the second electron affinities,

$$C_{60}F_{44}^{2-} + A \rightarrow C_{60}F_{44}^{-} + A^{-} . \tag{2}$$

Specifically, trapping $C_{60}F_{44}^{2-}$ in the presence of gas phase tetrafluoro-1,4-benzoquinone (fluoranil, EA = 2.7 eV [14]) or 7,7,8,8-tetracyanoquino-dimethane (TCNQ, EA = 3.3 eV [15]) for up to 30 s produced no reaction. Also, the doubly charged $C_{60}F_{44}^{2-}$ ions were trapped for several seconds in the presence of gas phase $C_{60}F_x$ neutrals with no appreciable loss of dianion signal or appearance of singly charged $C_{60}F_x^-$ ions. Because the electron affinities of these reagents are almost certainly larger than the electron affinity of $C_{60}F_{44}^-$, the absence of charge exchange provides further evidence for a large exit barrier for electron abstraction from the dianion. The absence of charge exchange reactions suggests that the electron affinity plus the exit barrier for electron abstraction from $C_{60}F_{44}^{2-}$ is equal to or greater than ~ 4.06 eV (the EA of $C_{60}F_{44-48}$).

In order to calculate the first and second electron affinities of the fluorinated fullerenes, the geometry of a D_{3d} isomer of $C_{60}F_{48}$ was optimized by using the method of partial retention of diatomic differential overlap [17], which is an approximate molecular orbital method that can reproduce the results of STO-3G Hartree-Fock calculations. At the optimized geometry, local density functional [18] vertical electron affinities were calculated using a triple-zeta plus polarization Gaussian basis [19] and a variational principle that eliminates the need for four-center integrals [20]. The electronic structure of the neutral molecule is $a_{1g}^{74}a_{1u}^{60}a_{2u}^{58}a_{2u}^{72}e_{g}^{264}e_{1u}^{264}$, and the anions involve partial and full occupation of the $37a_{2u}$ orbital whose eigenvalue is -0.9 eV in the dianion. The computed first and second electron affinities (EAs) are 5.07 and 2.27 eV, respectively. The first EA is approximately 25% greater than the experimental value determined above. This discrepancy is consistent with the fact that LDF and experimental EAs of atomic fluorine are 3.97 and 3.40 eV, respectively [21]. In addition, the theoretical calculations also provide a vertical EA, since nuclear geometries are not adjusted. The experimental bracketing technique more closely approximates the adiabatic EA.

Additional stability occurs as a result of the Coulomb barrier to the removal of either excess electron. This can best be illustrated by considering the interaction potential for an electron with a singly charged sphere of radius a and dielectric constant k, i.e.,

$$V(r) = -\frac{e^2(k-1)a^3}{2(k+2)r^2(r^2-a^2)} + \frac{e^2}{r} + \frac{l(l+1)\hbar^2}{2mr^2}, \tag{3}$$

where the last term represents the centrifugal potential for an approaching electron with angular momentum

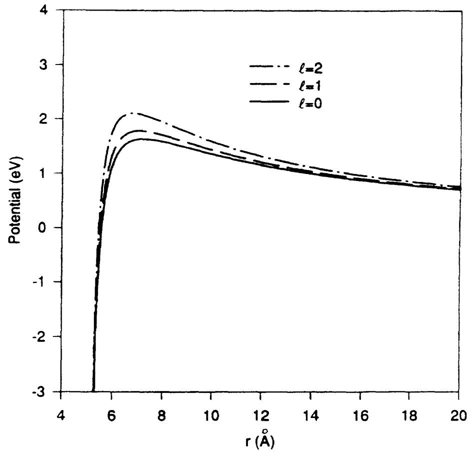

FIG. 3. Effective interaction potential between an electron with orbital angular momentum quantum number l and a singly charged dielectric sphere [defined in Eq. (3)], illustrating the Coulomb and angular momentum barrier to the removal of either excess electron from $C_{60}F_{48}{}^{2-}$.

$[l(l+1)]^{1/2}\hbar$. We estimate the polarizability of $C_{60}F_{48}$ to be 84 Å^3, as compared to 80 Å^3 for C_{60}, and thus take k to be the same as that of C_{60} (4.4) [22]. The radius of the sphere is taken as that of C_{60} plus a C-F bond length (~ 5 Å). The effective potentials for $l = 0, 1, 2$ are shown in Fig. 3. One can see that the ($l = 0$) Coulomb barrier is on the order of 1.5 eV, and the total energy required to remove either excess electron is on the order of 3.5 eV. This simple but realistic model provides a rationalization for the exceptional stability of $C_{60}F_{48}{}^{2-}$ with respect to electron detachment as a result of collisions or reactions. This result is generally applicable to molecular dianions.

It is interesting to note the analogy between the shape resonances for multiply charged anions and that of the shape potential experienced by the alpha particle in the nucleus. Alpha decay occurs via tunneling through the potential barrier resulting from the combined nuclear force and the Coulomb repulsion of the receding nuclei. Finally, multiply charged anions are routinely employed in electrospray mass spectroscopy [23] of macromolecules and biomolecules, such as DNA. This study provides a rationale for their special stability.

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