Electron Attachment to a Negative Ion: $e + C_{84}^{-} \rightleftharpoons C_{84}^{-2}$

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The observation of sequential attachment of two electrons to the C_{84} molecule and the subsequent autodetachment of the C_{84} dianion is reported. Remarkably, the cross section for attaching the second electron is estimated to be of the same order as that for adding the first electron. The measured lifetime for autodetachment of C_{84}^{-2} (~ 60 μsec) is in accord with calculations assuming "thermionic emission" from the vibrationally hot dianion. The first (EA_1) and second (EA_2) electron affinities of the two low-lying D_2 and D_{2d} isomers of C_{84} are calculated using density functional theory to be $+3.14$ and $+0.44$ eV, respectively. [S0031-9007(97)03378-4]

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There is considerable current interest in the formation and energetics of gas-phase multiply-charged anions [1,2]. Since the discovery [3] of reasonably high T_c superconductivity in A_3C_{60} salts (A = K, Rb, Cs), attention has focused on the C_{60}^{-n} anions. Interestingly, alkali salts of C_{84}, A_3C_{84} are found to be insulators [4]. Laser desorption of C_{60}^{-2} from a surface is known to produce long-lived ($\tau >$ sec) dianions [5,6]. Although the electron affinity of the C_{60} anion is negative (~ -0.3 eV) [7–10], the long lifetime of this dianion is a result of a Coulomb barrier inhibiting loss of the extra electron [8].

Previous studies of multiply charged anions have been devoted to firmly establishing their existence. Herein we report the observation of sequential attachment of two electrons to gas phase C_{84} fullerene molecules and the first observation of autodetachment of an electron from a dianion, i.e., $(C_{84}^{-2})^{**} \rightarrow C_{84}^{-} + e$ [** denotes vibrational excitation; see Eqs. (1) and (2)].

Of the 24 possible isolated-pentagon structures for C_{84}, predominantly two isomers (D_{2d} and D_2) are produced in the arc-discharge synthesis of fullerenes. The two neutral isomers were found to be energetically degenerate and significantly more stable than the remaining 22 isomers [11,12]. Within the local density approximation to the density-functional theory we also find that the two structures are essentially degenerate for both the neutrals and the anions, with energy differences of only 0.01–0.06 eV, depending on the charge state. In all cases the lower symmetry structure is the more stable (see Table I). Since the lowest unoccupied molecular orbital (LUMO) levels are completely delocalized we have performed spin-unpolarized calculations only. Inclusion of spin polarization will not significantly affect the result. For example, as discussed in Ref. [10], for C_{60} which has LUMO levels that are slightly less delocalized than C_{84}, spin polarization changes the first and second electron affinities by less than 0.02 eV. The structures have similar first and second electron affinities, although there is a slight tendency toward larger electron affinities for the lower symmetry structure. In contrast to the C_{60} fullerene molecule, which has a metastable dianion state, the larger radius associated with the C_{84} molecule leads to an energetically stable dianion.

The attachment of electrons to gas phase C_{84} was carried out in the ion source of a hybrid magnetic-sector/quadrupole mass spectrometer [13], the ZAB-EQ (VG-Analytical, Manchester, UK). High energy electrons ($\sim$70 eV) are moderated to low energy ($\sim$0.5 to 10 eV) via collisions with nitrogen gas, which is present in the source at an estimated pressure of $\sim 5 \times 10^{-3}$ mbar. The energies of the two electrons captured by C_{84} in this source are therefore not precisely known. The negative ion mass spectrum of C_{84} in Fig. 1 clearly shows C_{84} anions starting at m/z 1008, and the dianions starting at m/z 504. For the latter, the isotope cluster peaks ($^{12}C_n{}^{13}C_m; n + m = 84$) are spaced at half-mass intervals, unequivocally identifying the dianion. The intensity ratio of ion signals C_{84}^{-2}/C_{84}^{-} increases linearly with the electron beam current, up to the $\sim$0.5% depicted in Fig. 1, indicative of sequential electron attachment.

Autodetachment of an electron from $(C_{84}^{-2})^{**}$ was observed in two separate experiments. In the first experiment the ZAB-EQ was operated as a single-focusing magnetic-sector instrument by observing the signal at the

TABLE I. Energies of the tri- and bi-staggered isomers of C_{84} molecules as a function of charge state as calculated within the local (LDA) and nonlocal (GGA) approximations to the density-functional theory. Energies are in eV. For computational details, see Ref. [10].

	LDA		CGA	
Z	D_{2d} (Tristaggered)	D_2 (Bistaggered)	D_{2d} (Tristaggered)	D_2 (Bistaggered)
0	0.00	0.00	0.00	0.00
1	−3.40	−3.41	−3.13	−3.14
2	−4.07	−4.11	−3.54	−3.58

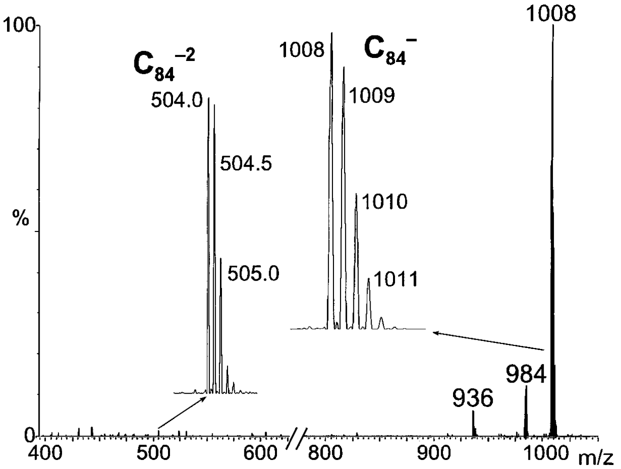

FIG. 1. Singly and doubly charged negative ions of C_{84} produced by the reaction of free electrons and gaseous C_{84}.

detector located between the magnetic and electrostatic sectors. In such an instrument, ions leaving the source with mass m_1 and charge z_1, which decay between the source and the magnet (the field free region, FFR) into ions of mass m_2 and charge z_2, will appear at an apparent mass corresponding to $(m_2^2/m_1)\,(z_1/z_2^2)$. In this mode, the transition $(C_{84}{}^{-2})^{**} \longrightarrow C_{84}{}^{-}$ was observed at the expected apparent mass of 2016 Da [i.e., $(1008^2/1008)\,(2/1^2)$]. Some of the ions corresponding to this transition presumably occur as a result of collisions with nitrogen gas escaping from the source into the FFR through the exit slit. Others may result from metastable autodetachment in the FFR. A similar observation was made for the transition $(C_{82}{}^{-2})^{**} \longrightarrow C_{82}{}^{-}$. Figure 1 shows the small amounts of C_{78} and C_{82} present in the commercial C_{84} sample. Of these, only C_{82} was observed to form a long-lived dianion.

In the second experiment, one of the dianion isotope peaks $({}^{12}C_{84}{}^{-2})$ was mass separated in the sector portion of the ZAB-EQ, decelerated from 16 to 12 eV kinetic energy, and passed through a short (12 cm) drift cell which was devoid of collision gas (pressure $<10^{-7}$ mbar). After traversing this region (FFR3; drift time $\sim$83 μsec) the resulting ions were mass analyzed with a quadrupole mass filter. The results of this tandem mass spectrometry experiment are displayed in Fig. 2, where both the ${}^{12}C_{84}{}^{-2}$ and its decay product ${}^{12}C_{84}{}^{-}$ are detected. From the known drift time and the intensity ratio of $C_{84}{}^{-2}$ to $C_{84}{}^{-}$ (1:3; see Fig. 2), we calculate the lifetime for the $(C_{84}{}^{-2})^{**} \longrightarrow C_{84}{}^{-}$ decay to be about 60 μsec. It should be noted that the lifetime determined here is a "mean" lifetime of those dianions which have survived the transition from the exit of the ion source to the entrance of FFR3, a flight requiring about 75 μsec. Dianions which decay during that flight are lost to the analysis. Ions exiting the source have a distribution of internal energies, and the "hotter" dianions are more likely to autodetach an electron before entering FFR3 than are the "cooler" ones surviving the 75 μsec. Therefore, the mean lifetime of the dianions exiting the source is expected to be somewhat shorter than that measured in FFR3.

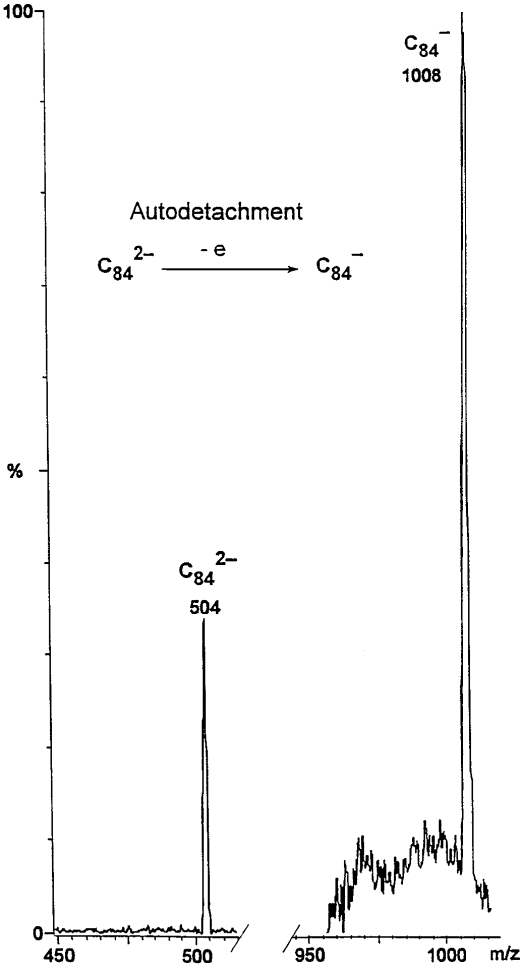

FIG. 2. Negative ion tandem mass spectrum of ${}^{12}C_{84}{}^{-2}$ showing ${}^{12}C_{84}{}^{-}$ resulting from autodetachment of an electron from the precursor dianion within the third field free region of the mass spectrometer.

The experimental observations of attachment and autodetachment are consistent with a sequential electron attachment process, i.e.,

$$e(\epsilon_1) + C_{84} \underset{\tau_1}{\overset{\sigma_1}{\rightleftharpoons}} (C_{84}{}^{-})^{*}, \tag{1}$$

$$e(\epsilon_2) + (C_{84}{}^{-})^{*} \underset{\tau_2}{\overset{\sigma_2}{\rightleftharpoons}} (C_{84}{}^{-2})^{**}, \tag{2}$$

where the asterisk(s) denote considerable internal energy in the anions. The attachment of the first electron results in $C_{84}{}^{-}$ with an internal energy equal to the incident electron energy (ϵ_1) plus the electron affinity energy ($\sim$3 eV; see Table I). In addition, the ion source is operated at 200 °C, leading to an internal vibrational energy of $\sim$2.08 eV for neutral C_{84} (calculated from the estimated vibrational frequencies of C_{84}). Because C_{60} captures electrons with a large cross section from $\sim$1 to 15 eV with a peak at $\sim$8 eV [14,15], we estimate the average internal energy in $(C_{84}{}^{-})^{*}$ to be on the order of 10 eV. Because the second electron affinity of C_{84} is ~0.4 eV, we further estimate the total internal energy in $(C_{84}{}^{-2})^{**}$ to be ~15 eV (10 eV + 0.4 + ϵ_2). ϵ_2, the kinetic energy of the second electron, must be greater than the Coulomb barrier (see below) of ~1.75 eV. We estimate this energy to be ~5 eV. Based upon comparisons with $(C_{60}{}^{-})^{*}$ [14] we expect the lifetime of $(C_{84}{}^{-})^{*}$ formed in our experiments to be very long ($\gg$msec) because both the electron affinity and the number of degrees of freedom for C_{84} are larger than that for C_{60}.

Assuming the reaction scheme (1, 2), the ratio of ion signals $C_{84}{}^{-2}/C_{84}{}^{-}$ can be approximated by $[e]\sigma_2\ell$, where $[e]$ represents the electron density, and ℓ the interaction length, respectively. Using the measured ratio of ion signals (correcting for the decay of $C_{84}{}^{-2}$) along with estimated electron densities, we find that σ_2 is on the same order of magnitude as σ_1. If we make the reasonable assumption that the attachment rates for C_{84} and C_{60} are comparable, we estimate the attachment cross section σ_2 to be at least 1 Å^2. This is a surprising result. Such a large cross section must involve the long range $e + C_{84}{}^{-}$ Coulomb repulsion and polarization attraction interaction. The precise long-range behavior of the interaction between the negative anion and the electron was determined from first-principles density-functional-based calculations on the C_{84} anion in an electric field. The D_2 molecule has three nonequivalent principle axes leading to polarizabilities of 127.9, 120.8, and 112.4 Å^3, respectively. However, for the D_{2d} molecule, two of the three axes are equivalent, leading to polarizabilities of 116.9, 121.1, and 121.1 Å^3, respectively. The average values for these isomers are given in Table II, along with an estimate for the average polarizability of the neutral C_{84} molecule, obtained by scaling the C_{60} calculations of Pederson and Quong [10].

The potential energy of interaction between an electron and a charged conducting or semiconducting sphere is given in any advanced text in electromagnetism (see also Ref. [16]). Here we employ a simple classical interaction using a point charge polarizability. The nonspherical corrections to the polarizability are negligible, hence the long-range polarization attraction plus Coulomb electron-anion repulsion is given by

$$W = -A/R^4 + B/R\,, \tag{3}$$

where R is the distance from the center of the $C_{84}{}^{-}$ anion to the second electron. The expansion coefficients (A, B) are also included in the table for both D_2 and D_{2d} geometries. The position and height of the Coulomb barrier is given by $(4A/B)^{1/3} = 6.22$ Å and $(3B/4)(B/4A)^{1/3} = 1.74$ eV, respectively. These numbers are weakly dependent on polarizability and are therefore effectively the same for both the D_{2d} and D_2 isomers. Because the $C_{84}{}^{-2}$ state lies 0.44 eV below the $C_{84}{}^{-}$ state, we expect that the net Coulomb barrier for reemission of an electron would be 2.18 eV, as illustrated in Fig. 3.

The metastable decay of $C_{84}{}^{-2}$ is attributed to vibrational autodetachment (thermoionic emission) of thermally hot $C_{84}{}^{-2}$ ions over the top of the Coulomb barrier. We calculate rate constants for reemission of a second electron from $C_{84}{}^{-2}$ much as was done earlier [16] for vibrational autodetachment from $C_{60}{}^{-}$. The potential described in Eq. (3) goes through a pronounced maximum at a distance $R_c \simeq 6.2$ Å. The addition of an angular momentum component does not significantly change the location of that maximum. Therefore, we assume that the cross section for attachment of a second electron with energy ϵ is given by a step function, i.e.,

$$\sigma = 0, \qquad \epsilon < E^0, \tag{4a}$$

$$\sigma = \pi R_c^2, \qquad \epsilon > E^0, \tag{4b}$$

where E^0 is the height of the barrier at R_c, estimated above to be 1.74 eV. Note that πR_c^2 is approximately 100 Å^2 which can be related to the electron capture cross section. We expect this number to represent a geometrical cross section and an approximate upper limit since every interaction at this impact parameter will not necessarily lead to capture. Our experimental estimate of the capture cross section is ~1 Å^2, as compared with the geometrical upper limit of ~100 Å^2. The true value is expected to lie somewhere in between.

Using microscopic reversibility, the rate constant for electron emission, $k(T)$, is given by

$$k(T) = (2k_BT/h)(2\mu R_c^2 k_BT/\hbar^2)(g_1/g_2) \times \exp(-E_0/k_BT)\,, \tag{5}$$

where E_0 is the barrier for remission, equal to $\mathrm{EA}_2 + E^0$, k_B is the Boltzmann constant, and g_1/g_2 is the ratio of the electronic degeneracies of the singly and doubly charged ions, assumed below to equal $\frac{2}{3}$ (C_{84} in either D_2 or D_{2d} symmetry has a doubly degenerate LUMO). In deriving Eq. (5) we have assumed that the vibrational partition

TABLE II. Average C_{84} polarizabilities (LDA) as a function of the charge state and conformation as calculated within the first-principles density-functional-based cluster codes. The A and B coefficients are defined by Eq. (3).

	Tristaggered (D_{2d})			Bistaggered (D_2)		
Z	α [Å^3]	A [eV Å^4]	B[eV Å^4]	α [Å^3]	A [eV Å^4]	B[eV Å^4]
0	115.9	834.5	0	116.4	837.8	0
1	119.7	861.5	14.4	120.4	866.6	14.4

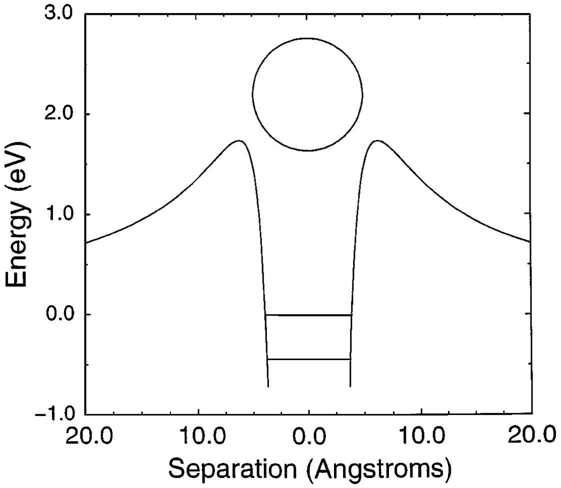

FIG. 3. Classical interaction energy between an electron and a point charge with a polarizability equal to that of C_{84}^- (120 Å^3), Eq. (3). The sphere represents the size of the C_{84} fullerene molecule. The horizontal lines represent the relative energies of C_{84}^- (0 eV) and C_{84}^{-2} (−0.44 eV).

functions of the two ions are equal and hence cancel. Rate constants calculated in this way are converted to the energy domain using the isokinetic relation [17] and plotted in Fig. 4. Above we estimate the total internal energy in $(C_{84}^{-2})^{**}$ to be 15 eV. From Fig. 4 the calculate lifetime of an ion with this internal energy is ~25 μsec, which is in good agreement with the measured lifetime.

In summary, we present the first experimental observation of electron attachment to a gas phase anion and of autodetachment from a gas phase dianion. The estimated attachment and detachment rates are consistent with calculations of the lifetime employing quasiequilibrium theory assuming thermoionic emission over the Coulomb barrier of the dianion. The electron attachment is facilitated by efficient coupling of electronic and vibrational (phonons) motion partly as a result of the large polarizability of C_{84}^-. In this connection, Auerbach [18] and Friedberg *et al.* [19] have discussed electron-vibron interactions in charged fullerenes and related this to superconductivity in alkali fullerenes. The results presented herein provide a possible window to the study of "Cooper pairs" in the gas phase.

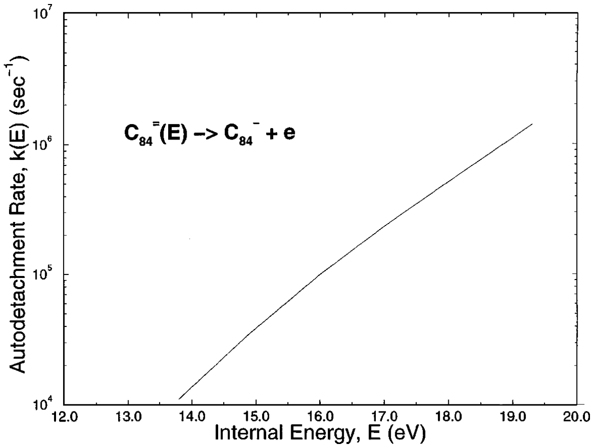

FIG. 4. Rate constant for electron autodetachment from C_{84}^{-2} as a function of its total internal energy. Autodetachment is assumed to occur over the top of the Coulomb barrier shown in Fig. 3.

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