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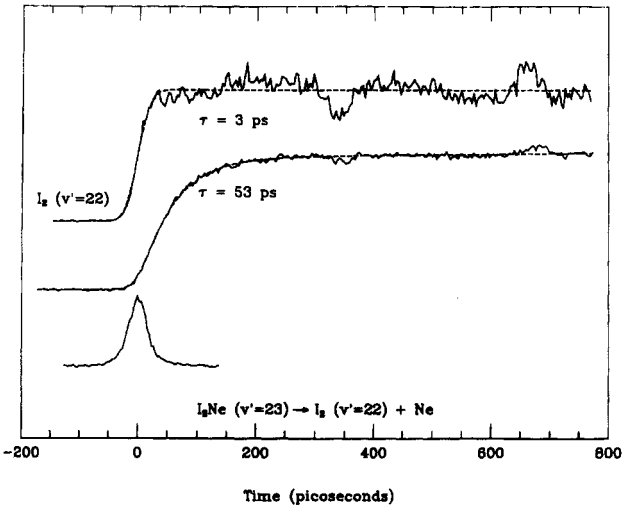

Figure 4. Shown are two transients: (top) transient obtained for the v' vibronic level of I_2; (middle) transient obtained for the vibrational predissociation of the I_2Ne cluster excited to the $v' = 23$ level. In the latter case, the build-up of nascent $I_2(v' = 22)$ is monitored ($\tau = 53$ ps). A cross-correlation of the pump and probe laser pulses is also shown.

of B one can use the entire simulation[1-3]). The differences between full recurrences and half-recurrences are both measured. The error values reported are 1 standard deviation of the value of τ measured for each particular vibrational level. Figure 3 gives a graph plotting both the experimentally determined B constants of this work and those of the literature values[20] as a function of v'.

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Besides the ease with which the rotational constants for individual v' states of I_2 can be extracted by this method, the rotational recurrences observed have proven to be useful in identifying the vibrational levels produced in vibrational predissociation experiments. In a set of experiments described in detail in ref 18, the state-to-state rates of vibrational predissociation have been measured for the I_2X van der Waals clusters (where X = Ne and Ar):

$$I_2X(B,v'_i) \rightarrow I_2(B,v'_f) + X$$

The I_2X cluster is prepared in an excited vibrational level of the B electronic state by the pump laser; energy then transfers from this mode to the van der Waals stretching mode, causing the bond to rupture. The nascent I_2 is excited by the probe laser to an ion-pair state, from which UV fluorescence is detected.

If the predissociation process is fast compared with the rotational period of the molecule (i.e., $\tau_{vp} < \tau_r$), rotational coherence is retained by the nascent $I_2(B,v'_f)$. This is shown in Figure 4 for $v'_i = 23$. In this case, the risetime for nascent I_2 is 53 ± 5 ps, and the criterion of $\tau_{vp} < \tau_r$ ensures a preserved coherence, as shown by Baskin et al.[13] The rotational constant extracted from the rotational recurrences present in this transient is $B = 0.02483 \pm 0.0003$ cm^{-1}, which corresponds well to the literature value of $B = 0.02485$ cm^{-1} for $v' = 22$. Therefore, the observed rotational recurrences confirm that the vibrational predissociation process in this system proceeds via the loss of one quantum of energy in the I_2 stretch mode. The results reported for I_2Ne are part of an ongoing investigation of the dynamics of small clusters involving I_2, and more details are given in ref 18. In the future, we hope to extend these studies to the measurements of rotational recurrences of the larger clusters, I_2X_n.

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Simulations of C_{60} Collisions with a Hydrogen-Terminated Diamond {111} Surface

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The stability of C_{60} during collisions with a hydrogen-terminated diamond {111} surface was studied by using molecular dynamics simulations. At a collision energy of 150 eV only nonreactive collisions occur. At higher energies nonreactive scattering and two types of reactive collisions occur: (1) exchange of one or more atoms between the molecule and the surface; (2) chemisorption of the C_{60} molecule. No dissociation of the rebounding molecules was observed on the time scale of the simulations. However, the scattered molecules contain a large amount of internal energy, which suggests that dissociation may occur at longer times.

The recent development of techniques for synthesizing and purifying macroscopic quantities of the highly symmetric molecule C_{60} and the related fullerenes[1-7] has intensified experimental and theoretical efforts aimed at determining the properties of these molecules. One property being studied is the stability of the fullerenes with respect to surface-induced dissociation.[8,9] Detection of the charged gas-phase products of collisions of $C_{60}^{\pm}$, C_{70}^{+}, and C_{84}^{+} with silicon and graphite surfaces[8] at energies up to 200 eV and of C_{60}^{+} and C_{60}^{2+} with a stainless steel surface[9] at energies up to 60 and 120 eV, respectively, revealed no fragmentation. This high stability with respect to surface-induced dissociation was unexpected because experiments studying photoinduced dissociation of C_{60}^{+} detected sequential loss of C_2

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fragments from the parent ion.[10] In addition, it is known that small aromatic hydrocarbons readily fragment during collisions with surfaces under similar conditions.[11] The amount of internal energy in C_{60}^+ scattered from a surface should be sufficient to permit dissociation based upon the results of these studies,[11] which showed that 10–20% of the translational energy of an ion is converted to internal energy during a collision with a surface. This suggests that the dynamics of the fragmentation process of buckminsterfullerene is sufficiently slow that it could not be detected in the two series of experiments. Alternatively, there may be processes occurring at the surface such as neutralization, physisorption, or chemisorption that are responsible for the low yield of charged fragments. Direct information about the importance of these processes could not be derived from the experiments.

We performed a series of molecular dynamics (MD) simulations of the collision of buckminsterfullerene with a hydrogen-terminated diamond {111} surface to study the apparent stability of fullerenes during collisions with surfaces. In these calculations the positions and velocities of the atoms comprising the buckminsterfullerene molecule and the surface were determined as a function of time. The potential energy function we used permitted bond breaking and formation among the atoms in the molecule and the surface. Analysis of the trajectories of the atoms in the system yielded detailed information about the dynamics of the collision process during the relatively short time that the molecule was near the surface, a region that is difficult to probe experimentally. The energy threshold for chemical reactions with the surface and the distribution of products of the reactions as a function of the impact energy were calculated by examining the atomic positions at the end of each trajectory. The efficiency of conversion of the center-of-mass translational energy of the incident molecule to internal energy (heating) of the molecule was of particular interest. A low efficiency, if observed, could provide a partial explanation for the low yield of charged fragments observed in the experiments because the rebounding C_{60} would have insufficient internal energy to dissociate. A high conversion efficiency would result in the formation of vibrationally excited molecules that could dissociate at time scales longer than were treated in these simulations. Preliminary details of these simulations were described elsewhere.[12]

The hydrogen-terminated diamond {111} surface was simulated by using a finite cluster of atoms with periodic boundary conditions applied in the directions parallel to the surface. The surface contained 10 layers of carbon atoms with 64 atoms per layer and was topped with a layer of 64 hydrogen atoms. The two bottom layers were held rigid throughout the simulations. The next seven layers of atoms were held at a constant temperature of 300 K by subjecting them to frictional forces by using the method of Berendsen et al.[13] The atoms in the C_{60} molecule were initially located at the vertices of a truncated icosahedron with relative velocities corresponding to a temperature of 300 K. An additional velocity component was added to each atom to give a normal kinetic energy of 150, 200, or 250 eV for the molecule with respect to the surface. The C_{60} was initially located a sufficient distance above the surface to have no interaction with the surface atoms. Fifty trajectories were run at each energy with the impact point on the surface chosen randomly for each trajectory.

An empirical many-body potential energy expression[14] that realistically describes bonding in graphite and diamond lattices and small hydrocarbon molecules was used to describe the interaction of the atoms in the system. In addition to reproducing the structures and energetics of these systems, the potential also provides a proper description of bond breaking and forming, in contrast to traditional force-field potentials. The potential is based upon the Tersoff[15] bond-order expression and includes terms to correct for overbinding of radicals and to account for nonlocal effects. The potential predicts two different bond lengths for C_{60}, 1.45 and 1.48 Å, which agrees with experiment and quantum chemical calculations. The diameter of the molecule is predicted to be 7.27 Å. For diamond the bond length is predicted to be 1.54 Å. The potential yields binding energies of 6.987 and 7.323 eV/atom for C_{60} and diamond, respectively.

TABLE I: Composition of Scattered Molecules and Probability of Their Formation as a Function of Collision Energy

scattered molecule	collision energy, eV 150	200	250
C_{57}	0	0	2
C_{59}	0	2	4
C_{60}	100	86	28
$C_{58}H$	0	0	2
$C_{59}H$	0	4	2
$C_{60}H$	0	4	16
$C_{61}H$	0	0	6
$C_{60}H_2$	0	0	6
$C_{61}H_2$	0	0	2
chemisorption	0	4	32
total reaction probability, %	0	14	72

The classical equations of motion describing the dynamics of the system were integrated by using a third-order Nordsieck predictor–corrector algorithm with variable time steps.[16] Typical time steps were 0.2 fs. The trajectories were integrated until either the interaction between the rebounding molecule and the surface became negligible or it became apparent that the molecule was bound to the surface. Total integration times ranged from 330 to 930 fs.

The chemical composition of the molecule that rebounds from the surface after a collision is strongly dependent on the collision energy. The compositions of the scattered molecules and the probability of observing each of them at the three collision energies studied are shown in Table I. For scattering with 150 eV of normal energy only nonreactive collisions are observed. At 200 eV of incident energy, the majority of the collisions are nonreactive, but 14% of the trajectories resulted in a chemical reaction between the molecule and the surface. At the highest energy treated, reactions occurred for 72% of the trajectories.

Figure 1 shows the atomic positions at several times for a typical nonreactive trajectory with an initial collision energy of 250 eV. Both the molecule and the surface are substantially deformed during the collision. As the molecule approaches the surface (Figure 1b), its lower half flattens and the surface compresses as they experience mutually repulsive forces. At later times (Figure 1c) the upper half of the molecule flattens, also. Although the diamond lattice is very rigid, the collision is sufficiently hard to push the layer of hydrogen atoms and the top two layers of carbon atoms a substantial distance into the bulk. Figure 1d,e depicts the system as the top layers of surface atoms return to their equilibrium positions and exert forces on the atoms causing desorption. As the molecule rebounds, it regains its original shape but is in a vibrationally excited state (Figure 1f). This ability of buckminsterfullerene to experience a severe structural distortion and return to its original shape has been referred to as *resilience*.[8]

The predicted low reactivity of buckminsterfullerene observed for collisions at 200 eV and below is consistent with experimental observations. Beck et al.[8] detected a negligible yield of charged fragments resulting from the impact of $C_{60}^{\pm}$, C_{70}^+, and C_{84}^+ with silicon (111) and graphite (0001) surfaces with collision energies in the range 0–200 eV. A weakness of the initial experiments was the inability to detect neutral species (molecules neutralized via charge transfer with the surface or neutral fragments, if they exist)

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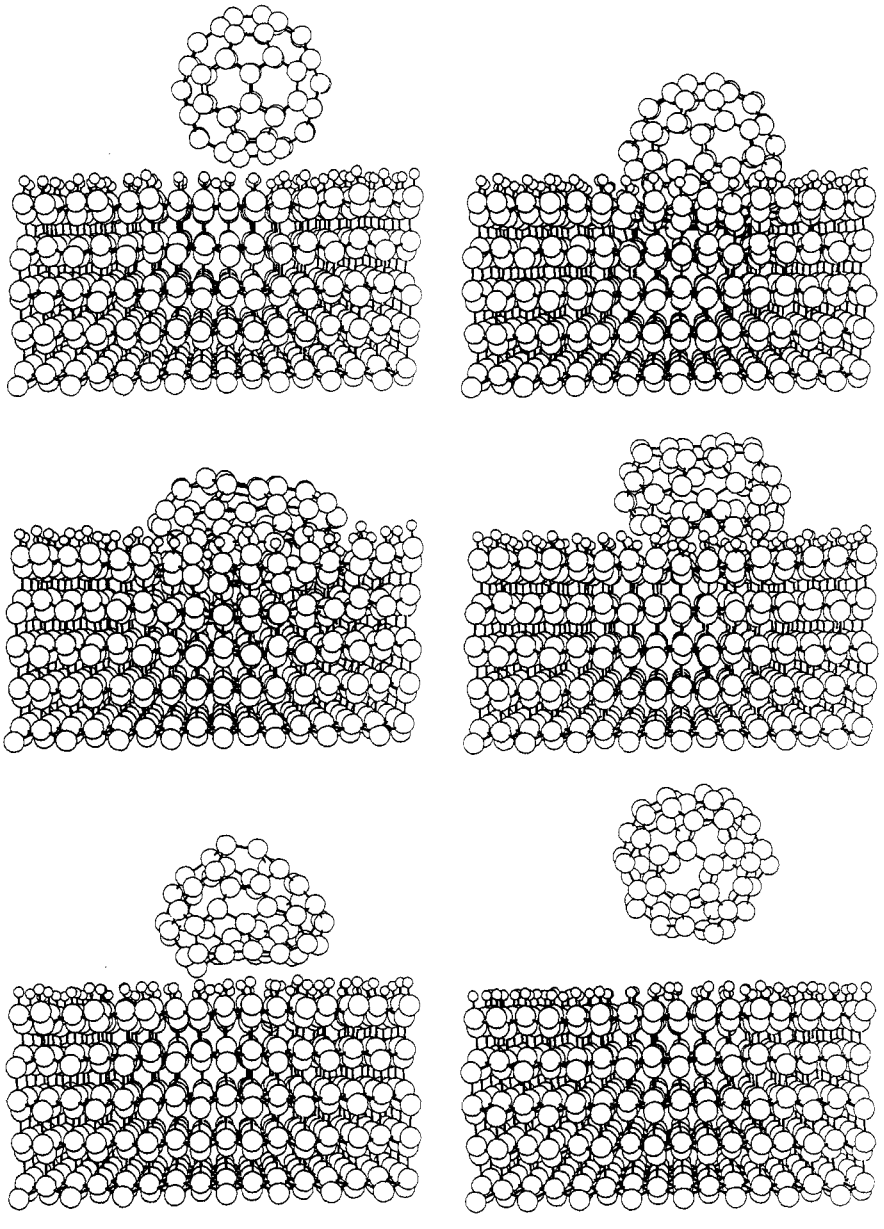

Figure 1. Atomic positions for a trajectory resulting in nonreactive scattering at various times: (a) 14, (b) 54, (c) 114, (d) 174, (e) 215, and (f) 294 fs. The initial collision energy is 250 eV.

that desorbed from the surface. More recently, the yield and translational energy distributions of desorbed C_{60} formed by neutralization of C_{60}^+ at the Si (100) surface were measured by reionizing the molecule as it rebounds from the surface and using time-of-flight mass spectroscopy for detection and energy analysis.[17] These later experiments indicate that C_{60} can survive collisions with incident energies at least as great as 100 eV. In a related series of experiments, McElvany et al.[9] collided C_{60}^+ and C_{60}^{2+} with a stainless steel surface. For the singly and doubly charged ions with collision energies of 60 and 120 eV, respectively, only inelastic, nonreactive scattering was observed. These experiments further demonstrate the resilience of the C_{60} cluster.

We have analyzed the scattered molecules in our simulations to determine the amount of energy retained as they rebound into the gas phase and the distribution of energy among their translational, rotational, and vibrational degrees of freedom. The fraction of energy transferred into internal motions of the molecule is of interest because highly excited molecules could possibly dissociate at times longer than can readily be treated in the simulations. The average final center-of-mass kinetic energies of unreacted molecules with incident energies of 150, 200, and 250 eV were 45.5, 53.9, and 57.4 eV, respectively. Although the final center-of-mass energy increases with increasing incident energy, the fraction of the incident center-of-mass energy retained during the collision decreases. The average increases in the internal energy of the unreactive molecules were 43.4, 51.5, and 60.7 eV for incident energies of 150, 200, and 250 eV, respectively. The majority of the internal energy is in the vibrational degrees of freedom rather than rotational motion. These internal energies correspond to temperatures in the range 3000–4000 K. It seems likely that these molecules will ultimately dissociate, although large times, compared to the propagation times used in these simulations, will be required for energy to be sufficiently localized for bonds to begin to break. Experiments studying laser-induced[10] and surface-induced[8] dissociation of fullerenes suggest that times on the order of microseconds are required before fragmentation occurs.

At the highest collision energy studied most impacts resulted in a chemical reaction between the molecule and the surface. As Table I shows, most reactions involved the transfer of one or more hydrogen atoms from the surface to the molecule. This is not surprising because the exposed position of the hydrogen atoms in the top layer of the surface puts them in close proximity to the

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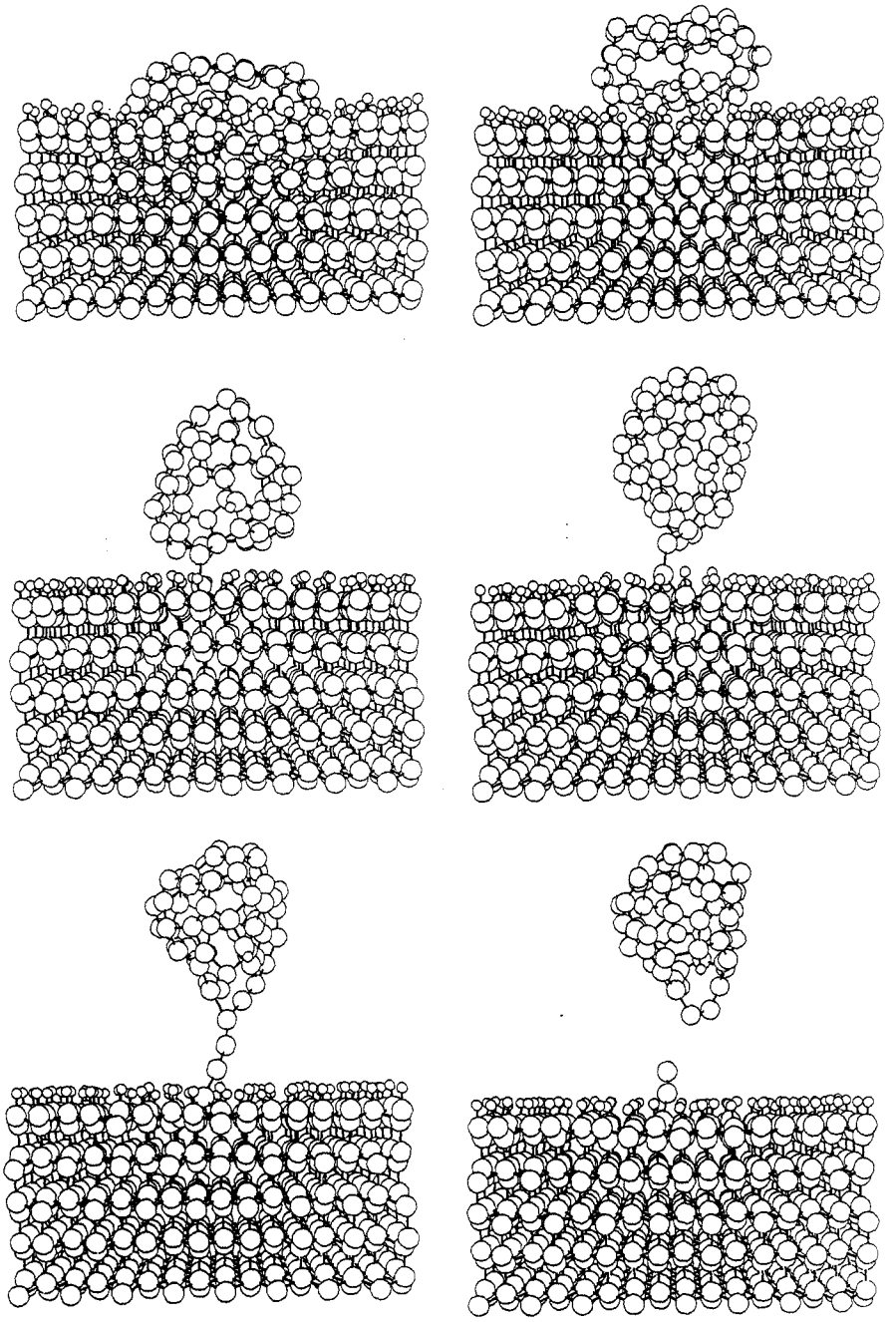

Figure 2. Atomic positions for a reactive trajectory resulting in formation of $C_{58}H$ at various times: (a) 114, (b) 174, (c) 241, (d) 299, (e) 354, and (f) 381 fs. The initial collision energy is 250 eV.

impacting molecule and subjects them to strong forces that can break the hydrogen–carbon bond while forming a new bond with the molecule. Experimental observations of reactive collisions of buckminsterfullerene with surfaces have not been reported. However, the hydrogen-terminated diamond {111} surface with its exposed hydrogen atoms may be more reactive than the surfaces used in the experiments.

In some collisions carbon atoms were transferred from the surface to the molecule or vice versa. Figure 2 shows the atomic positions at several times beginning near the midpoint of one such reaction in which $C_{58}H$ was the product. In Figure 2a, a hydrogen atom has been abstracted from the surface by the buckminsterfullerene, a process that created a radical carbon atom at the surface. Figure 2b shows that this surface carbon atom reacted with a carbon atom in the molecule. Figure 2c–e shows that as the molecule rebounded from the surface the atoms in the neighborhood of the bond started to "unravel" and form a chain. Interestingly, carbon chains were also found to play an important role in a mechanism for the formation of C_{60} recently demonstrated by Chelikowsky in a series of molecular dynamics calculations.[18]

The bond linking the molecule and the surface stretched as the molecule continued moving away from the surface and eventually broke allowing the molecule to desorb (Figure 2f). Collisions occurring via this mechanism created molecules with relatively low center-of-mass translational energies but high internal energies. As the molecule rebounded, the bond between the surface and the molecule exerted a decelerating force on the molecule that was not felt evenly by all the atoms. The atoms closest to the surface were slowed to a greater extent than those atoms farther away, thus producing an elongation in the molecule leading to vibrational excitation. In addition, some bonds between atoms were broken, resulting in an increase in the internal energy. Many of the trajectories that led to reactions via this mechanism produced molecules with substantial amounts of rotational energy. In these collisions the bond linking the molecule and the surface did not lie on a line passing through the center-of-mass of the molecule. The decelerating force exerted on the molecule through

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this bond is not directed through the center-of-mass of the molecule and created a torque that starts it spinning as it moves away from the surface.

The most frequent event that occurred for a collision energy of 250 eV was chemisorption. The trajectories that led to chemisorption looked qualitatively like the one depicted in Figure 2a–e. However, these molecules had insufficient center-of-mass translational energy to break the bonds linking them to the surface and remained bonded to the surface. If such events do in fact occur during collisions of C_{60} with diamond surfaces, it should be possible to detect the chemisorbed molecules with surface microscopy techniques.

In conclusion, these MD simulations and the experimental observations[8,9] yield complementary information that, taken together, provides a relatively complete and consistent description of the collision process. The simulations predict that for collision energies up to 150 eV C_{60} does not fragment immediately after colliding with a diamond surface, which is consistent with experimental observations of the stability of fullerene ions during collisions with solid surfaces. We find that during the collision the buckminsterfullerene cage is severely distorted but remains intact. Scattered molecules contain large amounts of internal energy, which suggests that they may fragment at time scales longer than were examined in the simulations. At higher collision energies both nonreactive and reactive scattering occur. The lack of evidence of reactive collisions in the experimental studies may be caused by the inertness of the surfaces used relative to the hydrogen-terminated diamond surface used in the simulations or to the lower collision energies used in the experiments.

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Production, Spectroscopy, and Electronic Structure of Soluble Fullerene Ions

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Taking advantage of the well-separated redox potentials of the mono-, di-, and trianions of C_{60} and C_{70}, their room-temperature-stable, soluble monoanion radicals have been selectively prepared in bulk quantities by controlled-potential coulometry. Upon reduction, strong bands in the near-IR are observed for C_{60}^- but not for C_{70}^-. Absorptions at 1064, 995, and 917 nm are tentatively assigned to the allowed HOMO–LUMO t_{1u}–t_{1g} transition of C_{60}^-, in agreement with theoretical calculations. Vibrational (Raman) bands of excited C_{60}^- radical anions at 1507 and 652 cm^{-1} and/or t_{1g} orbital splittings of similar magnitudes can be calculated from the electronic spectrum. For C_{70}^- the allowed HOMO–LUMO e_1''–a_1'' transition is calculated to occur in the IR region. ESR signals with *g* values below the free electron value are observed for solutions of both C_{60}^- and C_{70}^-. For C_{60}^- the occurrence of facile electron self-exchange in solution is suggested.

The availability of carbon clusters in large quantities[1-4] has triggered an explosive research effort. Limited information, however, is available on the reduced aggregates whose electronic structure is of great interest due, inter alia, to the recently reported superconductivity properties of metal-doped C_{60} and bulk K_3C_{60}.[4] We[6] and others[7] have recently reported the electrochemical detection of at least three anions of C_{60} and C_{70}. The ESR and electronic spectra of these anions are direct probes of their structure and of the electron transfer and ion pairing that occurs in solution. A new, fully allowed, near IR absorption in C_{60}^- measures the HOMO–LUMO gap of the anion and agrees well with Xα calculations. The absence of such bands in the near IR spectrum of C_{70}^- can be rationalized on the basis of recent ab initio SCF-HF calculations of C_{70}. The bulk preparation of the stable fullerene ions in solution should allow not only examination of their unusual physical properties but also the synthesis of numerous derivatives using fullerene anions as a starting point.

Purified C_{60} and C_{70} were obtained as described previously.[6b,8] Their spectroscopic and chromatographic properties match the literature data and will not be reported again here. Soluble C_{60} and C_{70} anions are efficiently and selectively produced in bulk in organic solvents via controlled-potential coulometry.[9] Solutions

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(9) (a) A Princeton Applied Research Model 173 potentiostat and a Model 179 digital coulometer were used. The electrochemical cell consists of a Pt mesh working electrode, a Pt auxillary electrode isolated in a separate bridge tube, and a standard calomel reference electrode (SCE). Degassed methylene chloride/toluene solutions of C_n were electrolized at −0.7 V vs SCE until the current reached approximately 90% of its limiting value; the supporting electrolyte was Bu_4NPF_6. Under similar conditions, our previous cyclic voltammetry and differential pulse polarography experiments[6] indicated that a potential of −0.7 V vs SCE results in the reversible and selective production of the monoreduced C_{60} and C_{70}. At this potential lower nuclearity aromatic hydrocarbons are not expected to be reduced (see ref 6b). No EPR signals were observed prior to reduction or after reoxidation. The di- and trianions are currently being produced using the same technique. Samples were transferred under anaerobic conditions to UV–vis/EPR cells by syringe. The *reversible* bulk reduction process has been monitored by ESR and electronic spectroscopy. Samples kept under N_2 did not change their color or deposit a precipitate for extended periods of time. (b) Reductions of fullerene with alkali metals in solution yield less well defined anions: Gorun, S. M., to be submitted; Bausch, J.-W.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1991**, *113*, 3205.

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