

# The Charge State of $C_{60}$ (Buckminsterfullerene) Molecules Adsorbed on a Metal Surface: Theoretical Considerations

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## Abstract

The charge state of a  $C_{60}$  molecule is strongly dependent on its environment. We discuss the factors that determine the charge state of  $C_{60}$  molecules adsorbed on metal substrates. An estimate of the charge state of a  $C_{60}$  molecule adsorbed without covalent bonding on a smooth simple metal surface is calculated taking into account the Coulomb interaction of the  $C_{60}^{-n}$  ion with its image charge and the polarization of the molecule, assuming the metal to be a perfect conductor, and the van der Waals interaction, using a Lennard-Jones pairwise potential based on graphite. We find that at most two electrons can be transferred to the molecule regardless of the work function of the metal. The broadening of the LUMO level of the adsorbed molecule due to resonance with the substrate energy levels will allow for a partial charge transfer even for metal substrates with work functions as high as 4.5 eV.

## 1. Introduction

As part of a continuing interest in the electronic structure and properties of molecules adsorbed on metals [1], we have been investigating the electronic structure of  $C_{60}$  molecules adsorbed on metal substrates and, in particular, the nature of the adsorbate-substrate interactions which determine the charge state of the adsorbed  $C_{60}$  molecules. The  $C_{60}$  molecule has a relatively large electron affinity and the three-fold degeneracy of its LUMO level permits it to accommodate up to 6 additional electrons. The charge state of the  $C_{60}$  molecule is dependent upon its "local" environment. In the gas phase, the  $C_{60}$  molecule can take on 2 electrons to form a stable  $C_{60}^{-2}$  ion. In appropriate solvents, the  $C_{60}$  molecule can be reversibly electrochemically reduced in one-electron steps to  $C_{60}^{-4}$ . In the alkali fullerides, the charge state of the  $C_{60}$  molecules, which is determined by the number of alkali metal atoms in the unit cell, i.e.,  $-3e$  in  $K_3C_{60}$  and  $-6e$  in  $K_6C_{60}$ , is stabilized by the Madelung electrostatic energy of the crystal structure. In the case of  $C_{60}$  molecules adsorbed on metals, the charge state will depend on the bonding to the metal substrate, the screening of the electrostatic potential of the negatively charged  $C_{60}^{-n}$  ions ( $n = 1, 2, \dots$ ) by the metal substrate and on the work function of the metal substrate.

In this paper we formulate the factors that, in the absence of any appreciable covalent bonding, determine the charge state of  $C_{60}$  molecules that are adsorbed on surfaces of low and moderately low work function metals. We find on the basis of preliminary theoretical calculations that when  $C_{60}$

molecules are adsorbed on smooth alkali metal substrates, the charge state of the adsorbed molecules is at most  $-2e$ . An adsorbate-substrate system, consisting of a monolayer of  $C_{60}$  molecules adsorbed on an alkali metal substrate in which two electrons are transferred to each  $C_{60}$  molecule, is of considerable interest because of still unresolved questions concerning the role of electron-electron correlations and pairing of the electrons in the alkali fulleride superconductors.

## 2. Background

In 1985, Kroto, *et al.* [2] proposed that the remarkably stable cluster of 60 carbon atoms has a truncated icosahedral "buckminsterfullerene" structure. The proposed structure for the  $C_{60}$  molecule, which consists of twelve pentagon rings and twenty hexagon rings, exhibits two types of carbon-carbon bonds: bonds that form the pentagon rings and bonds that occur on alternate sides of the hexagon rings (Fig. 1). The resonant bonding structure normally exhibited by hexagon rings with conjugated bonds is disrupted by the presence of the single-bonded pentagons.

Molecular orbital calculations of the electronic levels and bond lengths of the  $C_{60}$  molecule were carried out using

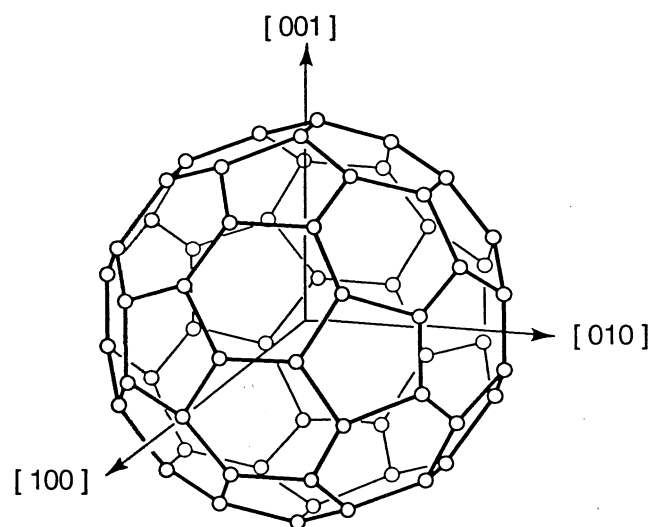


Fig. 1. Geometry of the  $C_{60}$  molecule. There are two different types of C-C bonds, one is on the pentagons, the other is shared by two neighboring hexagons (from Ref. 17)

Table I. Properties of  $C_{60}$  molecules

|                      |         |
|----------------------|---------|
| Diameter of cage     | 7.1 Å   |
| $r_{c-c}$ (pentagon) | 1.47 Å  |
| $r_{c-c}$ (hexagon)  | 1.40 Å  |
| Electron affinity    | 2.65 eV |
| Ionization energy    | 7.75 eV |
| $E(t_{1u}) - E(h_u)$ | 1.7 eV  |
| $E(t_{1g}) - E(h_u)$ | 2.7 eV  |

various semi-empirical approaches as well as the local density approximation (LDA) to density functional theory [3–8]. These calculations showed that the  $C_{60}$  molecule has a closed pi-orbital shell singlet electronic ground state, a relatively large energy gap between the HOMO and LUMO levels, and a relatively large electron affinity (Table I). The pi-orbitals of the occupied and unoccupied levels are delocalized over all of the atomic sites of the molecule. A measurement of the ultraviolet photoelectron spectrum of singly charged  $C_{60}^{-1}$  ions by Yang, *et al.* in 1987 [8] yielded values of 2.6–2.8 eV and 1.5–1.8 for the electron affinity and HOMO-LUMO gap, respectively, of the  $C_{60}$  molecule. More refined measurements have yielded a value for the electron affinity of  $2.65 \pm 0.05$  eV.

The one electron (LDA) level diagram for states within 4 volts of the HOMO level is shown in Fig. 2. The levels are labeled according to their irreducible representations within the icosahedral ( $I_h$ ) point group. The degeneracies of the levels are also indicated. The HOMO level which has  $h_u$  symmetry is 5-fold degenerate. The LUMO level which has  $t_{1u}$  symmetry is 3-fold degenerate. The next higher unoccupied level which has  $t_{1g}$  symmetry is also 3-fold degenerate. Optical transitions are forbidden between the  $h_u$  level and the  $t_{1u}$  level, but are allowed between the  $h_u$  level and the  $t_{1g}$  level.

The development of a simple method for synthesizing gram quantities of  $C_{60}$  by Kratschmer, Huffman and co-

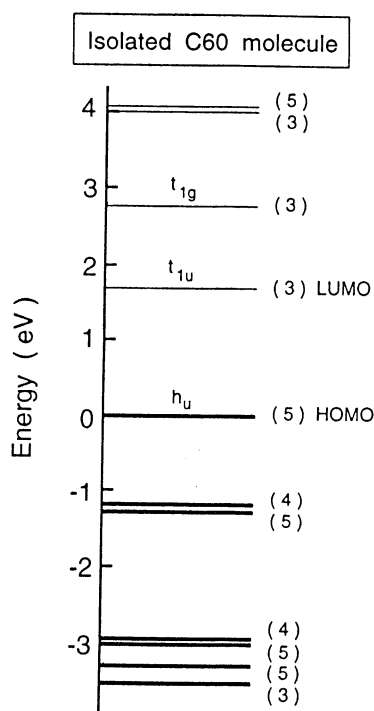


Fig. 2. Energy levels of a free  $C_{60}$  molecule, the numbers in parenthesis indicate the degeneracies of the levels

workers in 1990 [10] has produced an outpouring of experimental and theoretical work on the physical and chemical properties of gaseous and solid  $C_{60}$ . The truncated-icosahedral structure of  $C_{60}$  was verified by the observation of the expected number of infrared active vibration modes [10], by the observation of the Raman active vibration modes [11], by the observation of a single NMR line for the  $^{13}C_{60}$  molecule [12, 13], and by X-ray diffraction [14].  $C_{60}$  was found to form a van der Waals “molecular” fcc crystal at room temperature, which undergoes an orientational-ordering phase transition to a sc crystal at 249 °K [15]. The crystalline  $C_{60}$  is a very low mobility semiconductor with a 1.5 eV energy gap [16]. Band structure calculations for the fcc crystal [17–19] revealed that the energy bands are relatively narrow and bear a close correspondence to the energy levels of free  $C_{60}$  molecules. The calculated optical spectrum exhibits five “disconnected” bands in the 1.4 to 7.0 eV region with sharp features that are attributed to transitions at critical points [20].

The singly charged  $C_{60}^{-1}$  ion is stable in the gas phase, in accord with the relatively large electron affinity of the  $C_{60}$  molecule. Hettich, *et al.* [21] have recently reported the observation of a long-lived doubly charged  $C_{60}^{-2}$  ion in the gas phase (lifetime greater than 1 ms). They estimate a value of 0.1–0.4 eV for the electron affinity of  $C_{60}^{-1}$ , based on a two-particle pseudopotential calculation.

In cyclic voltammetry studies of the electrochemical properties of  $C_{60}$  molecules in various solvents (i.e.,  $CH_2Cl_2$ , tetrahydrofuran) the molecules were observed to exhibit one-electron reductions to  $C_{60}^{-1}$ ,  $C_{60}^{-2}$ ,  $C_{60}^{-3}$  and  $C_{60}^{-4}$  anions [22]. Only the first two reductions are fully reversible in controlled potential coulometry. The stability of the  $C_{60}^{-2}$  ion was attributed in part to dielectric screening of the anions by the solvent and in part to the “donicity” nature [23] of the solvent.

Interest in  $C_{60}$  was greatly enhanced by the observation that the incorporation of K into the  $C_{60}$  crystal structure leads to an increase in the room temperature electrical conductivity by several orders of magnitude to a maximum at a composition corresponding to  $K_3C_{60}$ , and then to a decrease in conductivity to a non-conducting phase having a composition of  $K_6C_{60}$  [24]. This was followed by the exciting discovery that the  $K_3C_{60}$  phase, is a superconductor with a  $T_c$  of 18 °K [25, 26] ions. The application of hydrostatic pressure was shown to decrease the  $T_c$  of  $K_3C_{60}$  [27]. The Cs and Rb fullerides,  $Cs_3C_{60}$  and  $Rb_3C_{60}$ , which have larger lattice constants than  $K_3C_{60}$ , were found to have larger  $T_c$  values. The data for various alkali metal fullerides indicate that there is a nearly linear relation between the  $T_c$  of the alkali metal-doped  $C_{60}$  and the lattice constant of the fcc phase [28]. The dependence on lattice constant has been attributed to band narrowing and the associated increase in the density of states at the Fermi level that results from the decreased interaction between the  $C_{60}^{-3}$  ions when the lattice constant is increased.

The electrical conductivity of the alkali metal atom intercalated metallic  $C_{60}$  phases is due to electrons in the  $t_{1u}$  levels of the  $C_{60}$  molecules that were transferred from the alkali metal atoms. Core spectroscopy data for K and C indicate that the conduction electrons reside predominantly on the  $C_{60}$  molecules [29]. The  $K_3C_{60}$  phase has a fcc ionic structure in which the three  $K^{+1}$  ions in the primitive unit

cell occupy two tetrahedral and one octahedral interstitial sites and the  $C_{60}$  ion has a  $-3e$  charge. The insulating  $K_6C_{60}$  phase has a bcc ionic structure in which the six  $K^+$  ions in the primitive unit cell occupy the tetrahedral sites and the  $C_{60}$  ion has a  $-6e$  charge. In  $K_3C_{60}$  the  $t_{1u}$  (LUMO) levels of the  $C_{60}^{3-}$  ion are half-filled [30], and in  $K_6C_{60}$  they are completely filled [31]. The attachment of as many as 6 electrons by the  $C_{60}$  molecules in the alkali fullerenes is stabilized by the Madelung electrostatic energy of the crystal structure, i.e., by the screening of the electrostatic potential of the negatively charged  $C_{60}$  ions by the surrounding alkali metal ions [31, 32].

### 3. $C_{60}$ Molecules adsorbed on metal surfaces

The charge state of the  $C_{60}$  molecule is clearly dependent on the local environment of the molecule. In the gas phase the  $C_{60}$  molecule can take on 2 electrons to form  $C_{60}^{2-}$  ions. In so-called "high donicity" number solvents, the  $C_{60}$  molecule can take on as many as 2 electrons to form stable  $C_{60}^{2-}$  ions. In the alkali metal fullerenes, the charge state of the  $C_{60}$  molecules, which is determined by the number of alkali atoms per unit cell, is stabilized by the Madelung electrostatic energy of the crystal structure, and the  $C_{60}$  molecule can take on as many as 6 electrons. In the case of  $C_{60}$  molecules adsorbed on a metal surface, the charge state of the adsorbed molecule will depend on the character of the bonding to the metal, on the screening of the electrostatic potential of the  $C_{60}^{n-}$  ions by the metal substrate and on the work function of the metal substrate. We note that positive  $C_{60}$  ions only exist in the gas phase, reflecting the large ionization energy of the  $C_{60}$  molecule. Efforts to generate  $C_{60}^+$  ions in various solvents by electrochemical oxidation have not been successful.

The electron affinity of an adsorbed  $C_{60}^0$  molecule,  $E_a^*(C_{60}^0)$ , corresponds to the difference between the ground state energy of the adsorbed  $C_{60}^0$  molecule and the ground state energy of the adsorbed  $C_{60}^{-1}$  ion. It corresponds also to the ionization energy of the adsorbed  $C_{60}^{-1}$  ion,  $E_i^*(C_{60}^{-1})$ , i.e., the energy required to remove an electron from the  $t_{1u}^*$  level of the  $C_{60}^{-1}$  ion, leaving the  $C_{60}$  molecule in its ground state. Similarly the electron affinity of an adsorbed  $C_{60}^{n-}$  ion is the difference in the energy of an adsorbed  $C_{60}^{n-}$  ion and the energy of an adsorbed  $C_{60}^{(n+1)-}$  ion. In the absence of sizeable covalent bonding of  $C_{60}$  by the metal substrate,  $E_a^*(C_{60}^0)$  will be appreciably larger than the electron affinity of the "free" molecules,  $E_a(C_{60}^0)$ , primarily because of the attractive Coulomb interaction between the adsorbed  $C_{60}^{-1}$  ion and its image charge in the metal, i.e., because of screening of the electric charge of the  $C_{60}^{-1}$  ion by the metal substrate. In general, the electron affinity of an adsorbed  $C_{60}^{n-}$  ion will be larger than the electron affinity of the free  $C_{60}^{n-}$  ion.

The charge state of an adsorbed  $C_{60}$  molecule on a given metal substrate is determined by the relative magnitudes of the electron affinities of the adsorbed  $C_{60}^0$  molecule and adsorbed  $C_{60}^{n-}$  ions and the work function  $W$  of the metal substrate [33]. When the work function of the substrate is larger than the electron affinity of the adsorbed  $C_{60}^0$  molecule (i.e.,  $W > E_a^*(C_{60}^0)$ ), the adsorbed  $C_{60}^{-1}$  ion will be unstable with respect to transfer of the "extra" electron to the metal substrate. The adsorbed  $C_{60}$  molecule will be

neutral. When the work function is smaller than the electron affinity of the adsorbed  $C_{60}^0$  molecule (i.e.,  $W < E_a^*(C_{60}^0)$ ), the adsorbed  $C_{60}^{-1}$  ion will be stable. Correspondingly, an adsorbed  $C_{60}^{2-}$  ion will be unstable, with respect to the transfer of an electron to the metal substrate, when  $W > E_a^*(C_{60}^{-1})$ , but will be stable when  $W < E_a^*(C_{60}^{-1})$ .

The ground state energies of the adsorbed  $C_{60}^0$  molecule and  $C_{60}^{n-}$  ions depend on the nature of their interactions with the metal substrate, which also determine their equilibrium distance from the metal. The binding energy curve (i.e., energy versus distance of the center of the  $C_{60}$  molecule from the metal substrate,  $z$ ) for the  $C_{60}^0$  molecule involves contributions from the attractive van der Waals interaction, the repulsive Pauli exclusion and the covalent bonding interaction which are all short-range. The Pauli exclusion and covalent bonding interactions are localized at the  $C_{60}$  carbon orbitals lying closest to the metal substrate. The corresponding binding energy curve for an  $C_{60}^{n-}$  ion involves contributions from the long range attractive Coulomb interaction with the positive image charge in the substrate and from the short range exchange-Coulomb interaction with the correlation hole in the substrate [34], as well as contributions from the van der Waals attractive interaction, the Pauli repulsive interaction and the covalent bonding interactions. As discussed in the next section on Covalent Interactions, covalent bonding is expected to be relatively weak for  $C_{60}$  molecules adsorbed on smooth surfaces of simple metals, such as the alkali metals and Al, but may be significant in the case of  $C_{60}$  molecules adsorbed on transition metal substrates, and on "rough" surfaces of noble metals and transition metals.

In the absence of any appreciable covalent bonding, the binding energy curves for the  $C_{60}$  molecule, the  $C_{60}^{-1}$  ion and the  $C_{60}^{2-}$  ion, each taken to be in their ground state, take the form shown schematically in Fig. 3. Three spatial regions are designated: a far region,  $z$  greater than  $6R \approx 30 \text{ \AA}$  (where  $R$  is the radius of the  $C_{60}$  molecule); a near region,  $z$  between  $6R$  and  $3R$ ; and a "close" region,  $z < 3R$  where the "tail" of the electron distribution of the metal substrate overlaps the pi and sigma orbitals of the  $C_{60}$  molecule. In the case of the  $C_{60}^0$  molecule, the interaction with the metal substrate is appreciable only in the "close" region where the overlap of the electron wavefunction of the metal with the pi and sigma orbitals of the  $C_{60}$  molecule gives rise to the Pauli repulsion. In the case of the  $C_{60}^{n-}$  ion, there is an attractive

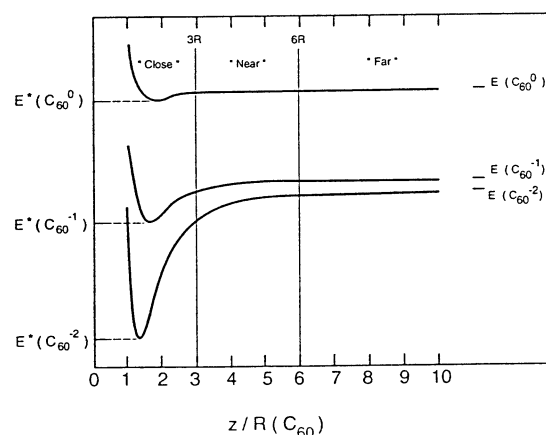


Fig. 3. Schematic diagram of the ground state energies of  $C_{60}^0$ ,  $C_{60}^{-1}$ ,  $C_{60}^{2-}$  in the "far", "near" and "close" regions of interaction with a metal substrate

interaction of the ion with its image charge, which corresponds to a point-charge interaction in the far region i.e., the potential energy varies as  $n^2/4z$ . In the near region, the spatial distribution of the electronic charge of the molecule and that of its image charge is comparable to their distance from each other. Moreover, there may be a significant polarization of the spherical charge distribution along the  $z$  direction. As a consequence, the potential energy in this region may vary somewhat faster than  $n^2/4z$ . In the "close" region there is, in addition to the Pauli repulsion, another quantum mechanical effect, namely the exchange interaction of the electrons in the  $t_{1u}^*$  level of the  $C_{60}^{-n}$  ion with their (image) correlation holes. Since the binding energy of the  $C_{60}^{-1}$  ion is greater than that of the  $C_{60}^0$  molecule, the equilibrium distance of the  $C_{60}^{-1}$  ion from the metal substrate (providing it is stable),  $z_{\text{eq}}(C_{60}^{-1})$ , will be smaller than that of the  $C_{60}^0$  molecule,  $z_{\text{eq}}(C_{60}^0)$ . Similarly,  $z_{\text{eq}}(C_{60}^{-n})$  will be smaller than  $z_{\text{eq}}(C_{60}^{-(n-1)})$ .

The difference in energy of the  $C_{60}$  molecule and the  $C_{60}^{-1}$  ion at large  $z$  is the electron affinity energy of the free  $C_{60}$  molecule. The difference in the energies of the adsorbed  $C_{60}$  molecule and adsorbed  $C_{60}^{-1}$  ion, each at their equilibrium positions, is the "adiabatic" electron affinity energy of the adsorbed  $C_{60}$  molecule. Correspondingly, the difference in the energies of the adsorbed  $C_{60}^{-1}$  ion and the adsorbed  $C_{60}^{-2}$  ion at large  $z$  is the electron affinity energy of the free  $C_{60}^{-1}$  ion and the difference in energy of the adsorbed  $C_{60}^{-1}$  ion and the adsorbed  $C_{60}^{-2}$  ion is the electron affinity energy of the adsorbed  $C_{60}^{-1}$  ion.

The binding of the  $C_{60}^0$  molecule and  $C_{60}^{-n}$  ion to the metal leads to a reduction in the symmetry of the molecular energy levels and to a lifting of their degeneracies. The removal of the center of inversion of the adsorbate modifies the selection rules for optical transitions. In particular optical transitions between the HOMO and LUMO levels can be induced by electric fields with a  $z$  component, i.e., by  $p$ -polarized photons and by the Coulomb field of electrons. The originally sharp molecular energy levels will broaden appreciably and shift as a result of their resonance with substrate energy levels [35].

We note that, as a consequence of the 3-fold degeneracy of the  $t_{1u}$  level, there will be, even in the absence of  $t_{1u}^*$  level broadening, a fractional filling of the LUMO level of the adsorbed  $C_{60}^0$  molecule when  $E_a^*(C_{60}^0) > W$ . The resulting charge on the adsorbed ion will be  $-(1 + \Delta q)$  where the magnitude of  $\Delta q$  will be such that the Fermi level of the adsorbate and Fermi level of the substrate are aligned. Fractional filling will also occur when  $E_a^*(C_{60}^{-n}) > W$ . As a result of the broadening of the  $t_{1u}^*$  level, there can also be a fractional filling of the LUMO level even when  $E_a^*(C_{60}^0) < W$ .

#### 4. Covalent interactions

Conjugated five- and six-membered carbon rings (cyclopentadiene,  $C_5H_5$  and benzene,  $C_6H_6$ ) are known to bond covalently to single transition-metal atoms [36]. Examples are the sandwich compounds  $Fe(C_5H_5)_2$  and  $Cr(C_6H_6)_2$ . Since the  $C_{60}$  molecule is a network of such rings, one might anticipate that similar covalent bonding would take place between the  $C_{60}$  molecule and appropriate metal atoms, and that such bonding may also occur for the case of  $C_{60}$  molecules adsorbed on a metal surface. Another

covalent bonding situation at a metal surface may also be possible. The recent synthesis of discrete molecules of  $C_{60}$  with Pt show that a metal can bond to *two sites* of the  $C_{60}$  molecule [37]. The two sites to which the Pt atom is bound are the two carbon atoms of the  $C_{60}$  molecule that are shared by two neighboring six-membered rings. As such a bonding interaction will require fewer coordination sites around the metal atom at the surface, it may be preferred in some cases over the bonding to the *face* of a five-membered or six-membered ring. These two possibilities do not, however, exhaust the bonding situations which might exist. The type of covalent interaction which might obtain in any situation will clearly depend on the nature of the metal substrate and on the local surface topography. The adsorbed  $C_{60}$  molecule (or ion) may migrate a large distance until they encounter a proper local site for forming covalent bonding (dictated by the local electronic structure) – at which point they become immobilized.

The occurrence of either type of covalent interactions between  $C_{60}$  and a metal substrate would make the largest perturbation of the  $C_{60}$  molecule. However, it seems unlikely that on a smooth metal substrate the requisite number of coordination sites will be available around a single atom of a smooth metal surface. In heterogeneous catalysis, the low index faces of transition metals (e.g., Pt) are not active. However, roughened surfaces or high index planes, with many steps and ledges, are reactive. Assuming that appropriate adsorption sites for covalent interactions are present, i.e., on a rough surface, the strength of the interaction will depend strongly on the nature of the metal substrate. For example, it is expected that rough alkali metals, and other metals whose atoms in the gas phase have low ionization potentials, will not form strong covalent bonds with  $C_{60}$ . The metal atoms at steps must be able to share electrons effectively with the  $C_{60}$  molecule to form a covalent bond. Al and the noble metals should be more effective than the alkali metals, but the transition metals would be the most effective. The atoms at steps will have lost some of their valence electrons to the substrate, so that the resulting partially screened ions are the actual species with which the  $C_{60}$  molecules interact. The nature of these ions can only be determined by detailed calculations and the same is true for the nature of their covalent interactions. Nevertheless, a few general observations can be made. One would expect that the electron affinity of the covalently bonded  $C_{60}$  molecule (in comparison with the isolated  $C_{60}$  molecule) would be smaller the stronger the covalent interaction of the molecule with the metal. The Pauli repulsion, between the extra electron and the electron pairs of the covalent bond, confines the added electron to a smaller region of the molecule, raising its kinetic energy and making it easier to remove. One would also expect that the 1s core level of the C atoms involved in the covalent bonding to be shifted (to higher binding energy) from the other carbon atoms of the  $C_{60}$  molecule and that the magnitude of the shift would reflect the strength of the covalent interaction.

#### 5. Theoretical formulation of binding energy and charge state

For metals not exhibiting any covalent interaction with  $C_{60}$ , one can begin to formulate a quantitative description of the relevant energetics and possible charge-transfer reac-

tions, using only elementary theoretical ideas. This aspect of the discussion is preliminary, and although it provides a reasonable estimate of the important energetics in  $C_{60}$  adsorption, the results should not be considered definitive.

We want to find the stable charge states and associated binding energies of a  $C_{60}$  molecule adsorbed on a metal surface, where the metal is defined solely by its work function. The binding energy, with respect to infinite separation from the metal, will be described by a family of curves,  $E(Q; z)$ , where  $Q$  is the total charge transferred from the metal to the  $C_{60}$  molecule, and  $z$  is the distance from the center of the  $C_{60}$  to the idealized abrupt metal surface.

The binding energy as a function of  $Q$  and  $z$  may, for the purposes of the computation, be arbitrarily divided into three primary contributions: The ground-state energy,  $E_0(Q)$ , of a gas-phase  $C_{60}$  molecule carrying excess charge  $Q$ ; a van der Waals interaction,  $E_{vdW}(z)$  between the  $C_{60}$  and the substrate atoms, which is a combination of a weak van der Waals attraction and a Pauli repulsion; and the simple electrostatic Coulomb attraction between the excess charge  $Q$  and its image charge in the metal (assumed perfectly conducting). A fourth term, describing the effects of polarization of the excess charge, is added perturbatively:

$$E(Q; z) = E_0(Q) + E_{vdW}(z) + E_{elec.}(Q; z) + E_{polar.}(Q; z) \quad (1)$$

It is known from first-principles total-energy LDA calculations [32] that for  $Q$  between 0 and 6,  $E_0(Q)$  can be accurately fitted to a quadratic in  $Q$ :

$$E_0(Q) = a + b(Q - Q_0)^2 \quad (2)$$

where  $E_0(0) - E_0(1) = E_a(C_{60})$ , the affinity energy of the  $C_{60}$  molecule, etc. The close resemblance of this expression to the energy required to charge a "spherical capacitor" is a reflection of the delocalized nature of the LUMO states. This term represents the largest contribution to the binding energy, roughly 3 eV for  $Q = 1$ .

The attractive part of the van der Waals interaction between the adsorbed  $C_{60}$  and a simple metal involves the interaction of the virtual dipole excitations of the  $C_{60}$  molecule with the virtual excitation of surface plasmons. In the absence of a detailed formulation, we model the van der Waals interaction using Lennard-Jones potentials taken directly from graphite work [38]. This pairwise-additive potential has been used to calculate the bulk lattice constant and compressibility of fcc  $C_{60}$  to within 1% of the experimental values [39]. Although the van der Waals term con-

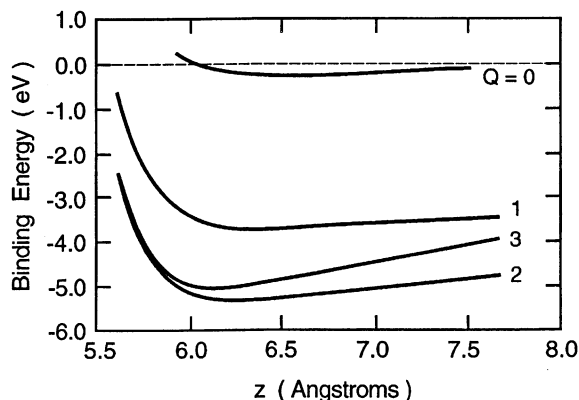


Fig. 4. Calculated binding energy curves,  $E(Q; z)$  vs.  $z$ , for  $C_{60}^{n-}$  ( $n = 0, 1, 2, 3$ ) in the "close" region of interaction

tributes only slightly (0.5 eV) to the binding energy of the adsorbed  $C_{60}$  molecule, it is the strongly repulsive "hard core" part of the van der Waals interaction, which is the primary factor that determines the equilibrium position of the adsorbed  $C_{60}$  molecule.

The Coulomb term is calculated by treating the charge  $q_i$  on each carbon atom as an independent parameter, subject to the constraint that the  $q_i$  are all positive and sum to  $Q$ :

$$E_{elec.}(\{q_i\}; z) = \frac{1}{2} \sum_i \frac{q_i^2 - q^2}{R_c} + \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j - q^2}{|r_i - r_j|} + \frac{1}{2} \sum_{ik} \frac{q_i q_k}{|r_i - r_k|}, \quad (3)$$

where  $q = Q/60$ ,  $R_c$  is the effective "radius" of a single C atom,  $i$  and  $j$  run over 60 C atoms, and  $k$  runs over the 60 C atom in the image molecule.

Equation (3) includes the electrostatic contribution to the polarization term; it remains to define a quantum-mechanical contribution. This is done perturbatively, through a simple Hückel calculation of the total energy as a function of the  $q_i$ . In this approach, the Hückel on-site parameters are perturbed by an amount proportional to  $q_i$  and the deviation,  $E_{Hückel}(\{q_i\})$ , of the resulting total energy from the unperturbed case is defined as the quantum contribution to the polarization energy. Together, the electrostatic and quantum polarization contributions are quite small, typically less than 0.1 eV at  $z_{eq}$ , justifying the perturbative treatment.

Finally, we gather together all of the above results, and redefine the binding energy of Eq. (1) by

$$E(Q; z) = E_0(Q) + E_{vdW}(z) + E_{elec.}(\{q_i\}; z) + E_{Hückel}(\{q_i\}) \quad (4)$$

By requiring that the  $q_i$  satisfy the condition of minimizing the total energy  $E(Q; z)$ , the approach mimics that of the density functional theory.

Typical binding-energy curves for  $E(Q; z)$  are shown in Fig. 4 for  $0 \leq Q \leq 3$ . Within this picture, in order for the transfer of  $Q$  electrons to be energetically favorable, the following condition must be satisfied:

$$|E(Q; z_{eq}(Q)) - E(Q-1; z_{eq}(Q-1))| > W_{loc}^* \quad (5)$$

where  $W_{loc}^*$  is the local work function in the vicinity of the adsorbed  $C_{60}^0$  molecule. For work functions  $W$  less than roughly 3.5 eV, a transfer of one electron is expected; For  $W$  of 1.5 eV or less, two electrons may be transferred. The transfer of more than two electrons appears extremely unlikely, regardless of the value of the work function of the alkali metals. However, we caution that the present description is tentative. It does not account for work-function modification by the adsorbed  $C_{60}$  molecule and  $C_{60}^n$  ions, or for quantum-mechanical  $C_{60}$ -adsorbate interactions more complex than the ( $Q$ -independent) van der Waals.

## 6. Discussion

Based on the alkali metal work functions (Table II), our preliminary calculations indicate that, when a  $C_{60}$  molecule is adsorbed on a smooth alkali metal surface, no more than two electrons may be transferred to the molecule from the metal substrate. As a result of the broadening of the LUMO

Table II. Work function of metals

|    | $W$ (eV) | $r_s/a_b$ |
|----|----------|-----------|
| Li | 3.1      | 3.1       |
| Na | 2.7      | 3.9       |
| K  | 2.4      | 4.9       |
| Cs | 1.8      | 3.3       |
| Al | 4.2      | 2.1       |
| Ag | 4.3      | 3.0       |
| Cu | 4.7      | 2.7       |
| Au | 5.1      | 3.0       |

level, which may be as much as 1 eV depending on the overlap of the pi-orbital wavefunctions and the tail of the electron density of the metal substrate, there will be an appreciable fractional filling of the level for smooth metal surfaces with work functions as large as 4.5 eV (i.e., Al and the noble metals).

As a further consequence of the negative charge transferred from the metal to the  $C_{60}$  molecule, and the associated electrostatic potential of the resulting dipole, which is much larger than the "polarization dipole" of opposite sign in the adsorbed  $C_{60}$  molecule, the work function of the substrate at the site of the adsorbed  $C_{60}$  ion, is expected to increase by an amount which depends on the charge transferred. The average work function  $W^*$  will increase with adsorbate coverage, as well as with the amount of charge transfer. A measurement of the work function of the adsorbate-substrate system and its dependence on coverage for different substrates would provide information about the charge state of the  $C_{60}$  molecule and its dependence on the nature of the substrate. We note that with increasing coverage, the Coulomb repulsion between the negatively charged  $C_{60}$  ions will play a role in the formation of an ordered monolayer, particularly in the case of a smooth alkali metal substrate.

As noted earlier, the symmetry of the adsorbed molecules is reduced and the degeneracies of the energy levels are lifted. The broadening and shifting of the  $h_u^*$ ,  $t_{1u}^*$  and  $t_{1g}^*$  levels resulting from their interaction with the substrate is expected to be different, due to differences in spatial symmetry and resonances with the electronic energy levels of the substrate. The energy separations between the levels will therefore be different from those in the free molecule. Also as a result of the reduced symmetry (e.g., the removal of the center of inversion, etc.), the selection rules for optical transitions between the levels are modified (i.e., the normally forbidden transitions between the  $h_u^*$  and  $t_{1u}^*$  levels become allowed in the adsorbed  $C_{60}$  molecule and can be induced by  $p$ -polarized photons), and the selection rules for infrared absorption and Raman scattering are relaxed.

## 7. Concluding remarks

Ohno, *et al.* [40] have recently carried out photoemission and (C 1s) core level spectroscopic measurements on monolayers and multilayers of  $C_{60}$  adsorbed on films of Ag ( $W = 4.3$ ); Au ( $W = 5.1$ ), Mg ( $W = 3.6$ ), Bi ( $W = 4.2$ ) and Cr ( $W = 4.5$ ) evaporated onto a cleaved GaAs crystal in UHV. Their data indicates that in each case, despite differences in the metal work functions by as much as 1.5 eV, there is a partial filling (0.1 to 0.5 eV) of the LUMO level of the adsorbed  $C_{60}$  molecules, and that the LUMO level is

pinned at the Fermi level. These results are in reasonable agreement with our own conclusions.

We have initiated at Univ. of Pennsylvania an experimental research program to study the electronic and optical properties of  $C_{60}$  molecules adsorbed on various single crystal metal surfaces, including vicinal surfaces. We plan to measure the changes in the surface work function upon adsorption of  $C_{60}$  molecules on different metal substrates, which would yield useful information about the charge state of the adsorbed molecules. Measurements of the Raman scattering by  $C_{60}$  molecules adsorbed on Ag island films have already been carried out. An additional vibrational mode at  $350\text{ cm}^{-1}$  has been observed, which we attribute as the silent octupolar mode of the molecule whose Raman scattering becomes allowed due to the reduced symmetry of the adsorbed  $C_{60}$  molecules. Measurements of the nonlinear optical response of  $C_{60}$  molecules on alkali metal and noble metal substrates are now under way. The use of three wave mixing spectroscopy has proven to be a useful probe of surface electronic structure and excitations, namely, the electronic energy level distribution within a few eV of the Fermi level, and the transition selection rules of surface electronic transitions [41]. Three-wave mixing would provide direct information on the nature of the chemical bonding and on the position of energy levels of the adsorbed molecule. We will also use three-wave mixing to determine the thermal desorption temperature of the  $C_{60}$  molecules by monitoring the change in the three-wave mixing signal upon heating of the sample.

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