

Core-Level Binding Energies of Cs-Doped C₆₀ and Graphite

Stephen P. Kelty, Zhong Lu, and Charles M. Lieber*

Departments of Chemistry and Electrical Engineering, Columbia University, New York, New York 10027, and
 Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138
 (Received: April 30, 1991; In Final Form: July 11, 1991)

The carbon core-level binding energies of C₆₀ and Cs-doped C₆₀ thin films and Cs-graphite intercalation compounds have been characterized by X-ray photoelectron spectroscopy. Thin films of C₆₀ deposited on silicon and gold substrates exhibit systematic increases in the carbon core-level (C 1s) binding energy and peak width with Cs doping. At saturation coverage, which corresponds to a stoichiometry of Cs_{7.2}C₆₀, the binding energy shifts by 1.1 eV. The C 1s binding energy was also found to increase systematically in Cs-intercalated graphite where the maximum shift is 0.5 eV for a stoichiometry of Cs_{0.12}C. The observed increases in binding energy have been explained in terms of an increase in the Fermi level position as a result of Cs charge transfer to a delocalized C₆₀ energy band.

Introduction

The development of efficient methods for the production of macroscopic quantities of C₆₀ has led to an intensive research effort designed to characterize the physical properties and to explore potential applications of this fascinating macromolecule.¹⁻⁷ Molecular solids based on C₆₀ should be a particularly rich area since C₆₀ is robust and can exhibit stable reduced states.³ Indeed, Haddon and co-workers have recently exploited these characteristics to produce alkali-metal-doped thin films of C₆₀ that are conducting.^{7a} In this work they found that the conductivity of pure C₆₀ films ($\sigma < 10^{-5}$ S cm⁻¹) increased over 5 orders of magnitude when doped with Li, Na, K, Rb, or Cs. Even more intriguing is the very recent study reporting the observation of superconductivity at 18 K in potassium-doped C₆₀.^{7b} The observation of enhanced conductivity and superconductivity indicates that the interactions between C₆₀ macromolecules in the solid state are sufficiently strong to form delocalized energy bands.

To develop further this fascinating new class of molecular based conductors requires characterization of the electronic and structural properties of the C₆₀ based solids since they exhibit collective phenomena distinct from the isolated molecular species. Accordingly, we have been investigating thin films and polycrystalline solids of alkali-metal-doped C₆₀ and herein report X-ray photoelectron spectroscopy (XPS) investigations of the carbon core-level binding energies of C₆₀, Cs-doped C₆₀, and Cs-graphite intercalation compounds. We find that the C 1s binding energy increases with Cs doping and have explained these results in terms of a Fermi level shift following charge transfer to a C₆₀ energy band. The C 1s binding energy of graphite also increases during in situ intercalation of Cs, thus showing a striking similarity between these two carbon-based conducting materials.

Experimental Section

C₆₀ was synthesized in a stainless steel chamber, using high-purity graphite electrodes (99.9995%, Johnson Matthey Electronics) as described recently.¹ The soot produced from an arc discharge in 100–150 Torr of He was extracted in benzene to yield a red-brown solution with optical properties in agreement with published results.^{2,3} The C₆₀ was further purified by sublimation, and the purity of the resulting materials was verified by mass spectroscopy. Thin films of C₆₀ were prepared by sublimation of purified material onto polycrystalline gold or Si(111)⁸ surfaces. Notably, we find that these films exhibit a high degree of crystallinity as evidenced by well-defined diffraction peaks that are virtually the same as found for bulk polycrystalline samples of C₆₀.^{1a} The highly oriented pyrolytic graphite (HOPG, Union Carbide) used for in situ Cs intercalation experiments was cleaved immediately prior to insertion into the ultrahigh-vacuum (UHV) chamber.

All of the X-ray photoelectron spectroscopy (XPS) experiments were carried out in UHV using a Kratos spectrometer

TABLE I: Summary of XPS Results for Cs-Doped C₆₀ and Graphite

| sample | C 1s BE, eV | ΔBE, eV |
|--|-------------|---------|
| C ₆₀ /Si(111) | 285.4 | |
| 1% Cs | 285.8 | 0.4 |
| 6.5% Cs | 286.3 | 0.9 |
| 12% Cs | 286.5 | 1.1 |
| C ₆₀ /Si(111)-H | 285.3 | |
| 12% Cs + O ₂ (5 min at 1 × 10 ⁻⁴ Torr) | 286.1 | 0.8 |
| +O ₂ (10 min at 10 Torr) | 285.7 | 0.3 |
| +O ₂ (10 min at 10 Torr) | 285.3 | 0.0 |
| graphite | 284.3 | |
| 4% Cs | 284.7 | 0.4 |
| graphite ^a | 284.4 | |
| 12% Cs ^a | 284.9 | 0.5 |

^a From ref 14.

(XSAM800) equipped with a monochromator on the Al Kα X-ray source as described in detail elsewhere.⁹ The binding energy peaks were calibrated by using the Si 2p and Au 4f peaks of the substrate. The Cs source (SAES getter) was thoroughly outgassed prior to deposition.

Results and Discussion

A typical series of photoelectron spectra for a C₆₀ film deposited on a Si(111) surface recorded as a function of Cs coverage are shown in Figure 1. The C 1s binding energy of the pure film,

- (1) (a) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* 1990, 347, 354. (b) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* 1990, 170, 167.
- (2) Ajie, H.; Alvarez, M. M.; Anz, S. J.; Beck, R. D.; Diederich, F.; Fostiropoulos, K.; Huffman, D. R.; Krätschmer, W.; Rubin, Y.; Schriver, K. E.; Sen Sharma, D.; Whetten, R. L. *J. Phys. Chem.* 1990, 94, 8630.
- (3) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. E.; Smalley, R. E. *J. Phys. Chem.* 1990, 94, 8634.
- (4) Schmalz, T. G. *Chem. Phys. Lett.* 1990, 175, 3.
- (5) Haddon, R. C.; Schneemeyer, L. F.; Waszczak, J. V.; Glarum, S. H.; Tycko, R.; Dabbagh, G.; Kortan, R. A.; Muller, A. J.; Mujica, A. M.; Rosseinsky, M. J.; Zahurak, S. M.; Makhija, A. V.; Thiel, F. A.; Raghavachari, K.; Cockayne, E.; Eiser, V. *Nature* 1991, 350, 46.
- (6) Radi, P. P.; Hsu, M.-T.; Rincon, M. E.; Kemper, P. R.; Bowers, M. T. *Chem. Phys. Lett.* 1990, 174, 223.
- (7) (a) Haddon, R. C.; Hebard, A. F.; Rosseinsky, M. J.; Murphy, D. W.; Duclos, S. J.; Lyons, K. B.; Miller, B.; Rosamilia, J. M.; Fleming, R. M.; Kortan, A. R.; Glarum, S. H.; Makhija, A. V.; Muller, A. J.; Eick, R. H.; Zuhurak, S. M.; Tycko, R.; Dabbagh, G.; Thiel, F. A. *Nature* 1991, 350, 320. (b) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* 1991, 350, 600.
- (8) Kim, Y.; Lieber, C. M. *J. Am. Chem. Soc.* 1991, 113, 2333.
- (9) Lu, Z.; Schmidt, M. T.; Podlesnik, D. V.; Yu, C. F.; Osgood, R. M. *J. Chem. Phys.* 1990, 93, 7951.

* To whom correspondence should be addressed at Harvard University.

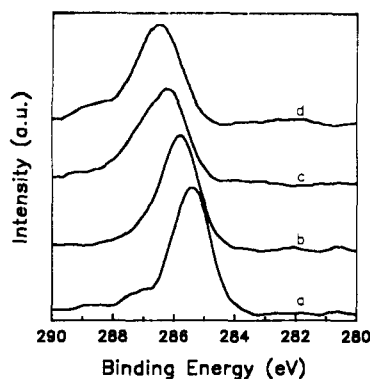


Figure 1. Photoelectron spectra for a C_{60} film on Si(111) as a function of Cs doping. Curves a, b, c, and d correspond to 0, 1.0, 6.5, and 12% cesium, respectively. The carbon 1s peak shifts systematically to higher energy as the Cs coverage increases.

285.4 eV, is similar to the values reported in other XPS studies.^{10,11} The C 1s binding energy observed for C_{60} films deposited on hydrogen-terminated silicon (Si(111)-H)⁸ and on Au often exhibited small variations (± 0.1 eV) compared to our standard Si substrate. These variations could be due to small differences in the film structure or charging effects; however, we believe that in general the substrate has only a minor effect on the XPS spectra of our C_{60} films. Hence, the C 1s binding energies of the pure C_{60} films serve as a reference to assess the role of cesium doping in these materials.

The C_{60} C 1s peak undergoes several significant changes as the film is doped with Cs (Figure 1). In general, we find that the C 1s binding energy increases with increasing Cs doping level. The cesium-to-carbon stoichiometry, which was determined from the relative areas of the Cs 3d to C 1s peaks, typically ranged from a value of 0.01 Cs:C ($Cs_{0.01}C_{60}$) at low coverage to a maximum value with our dosing system of 0.12Cs:C ($Cs_{0.12}C_{60}$). This latter level is referred to hereafter as "saturation coverage" and is not exceeded due to cesium desorption.¹² At saturation coverage the carbon binding energy peak has increased to 286.5 eV (Figure 1), corresponding to a 1.1-eV shift with doping (Table I). We have also found that the C 1s peak becomes broader with increasing Cs doping. The increases in full width at half-maximum (fwhm) from pure C_{60} to the $Cs_{0.12}C_{60}$ in Figure 1 are 0.2, 0.4, and 0.5 eV, respectively. The increase in line width is not unexpected since there are several distinct sites at which the Cs dopant ions can reside in the C_{60} lattice.^{7a} Similar broadening has also been observed in potassium-intercalated graphite.¹³ The broadening in the graphite study was attributed to different interactions of the C 1s electrons with the K^+ ions in the lattice, and thus our explanation is consistent with this work. Since our polycrystalline C_{60} films may also have some degree of structural heterogeneity, further studies will, however, be needed to resolve unambiguously the origin of this broadening.

Similar increases in C 1s binding energy and peak fwhms were also observed for Cs-doped C_{60} films prepared on other substrates (Table I), and thus we suggest that the increases in binding energy and fwhm are intrinsic to Cs doping of the films. Furthermore, we have shown that these significant increases in C 1s binding energy are reversible in that oxidation of the Cs-doped film systematically lowers the binding energy to the value observed for pure C_{60} films (Table I). Specifically, *in situ* treatment of a doped film with oxygen results in a decrease in the C 1s binding energy with increasing oxygen exposure as shown in Figure 2. In addition to demonstrating the reversibility of Cs-induced changes,

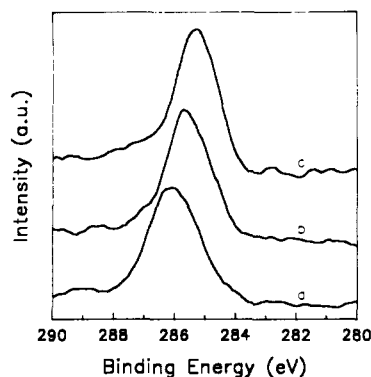


Figure 2. Photoelectron spectra of a Cs-doped C_{60} film on Si(111)-H as a function of oxygen exposure. Curves a, b, and c correspond to a Cs-doped film (saturation coverage) that has been exposed to 10^{-4} Torr of O_2 for 5 min, to an additional 10 Torr of O_2 for 10 min, and 10 Torr of O_2 for 20 min, respectively.

these results strongly suggest that the variations in binding energy determined by XPS reflect systematic reduction (Figure 1) and subsequent oxidation (Figure 2) of the C_{60} films. Since alkali-metal-doped C_{60} films prepared under similar conditions showed changes in bulk conductivity,^{7a} it is likely that Cs deposition results in cesium intercalation into the C_{60} lattice. Direct structural studies will be needed, however, to confirm this point.

To understand further these interesting XPS results obtained for the Cs-doped C_{60} films, it is useful to consider alkali-metal-doped graphite. Alkali-metal doping of graphite leads to the formation of graphite intercalation compounds (GICs) in which the alkali-metal ions lie between the two-dimensional carbon layers of graphite. Previous XPS studies of cleaved bulk materials have shown that the C 1s binding energy and peak fwhm increase in the alkali-metal GICs relative to pure graphite.^{13,14} To check the doping procedures used to prepare our Cs/ C_{60} films, we have also characterized the C 1s binding energy shifts of *in situ* Cs-intercalated HOPG. We find that the C 1s binding energy increases systematically with Cs coverage where the shift in binding energy is 0.4 eV for a coverage corresponding to $Cs_{0.04}C$ (Table I). This coverage corresponds well to the stage two GIC stoichiometry (MC_{24}) for which a 0.4-eV increase in binding energy was also reported in a study of bulk crystals.¹³ Previous studies of lower stage GICs show that at a stoichiometry of $M_{0.12}C$ (MC_8), which corresponds to the saturation stoichiometry of our Cs-doped C_{60} films, the binding energy shift increases to 0.5–0.6 eV.¹⁴ Hence, it is apparent that our procedures are consistent with the other studies of GICs and that Cs intercalates readily into the graphite crystals at room temperature. These results strongly suggest that the observed changes in the Cs-doped C_{60} films are also due to Cs intercalation and not a simple adlayer on the C_{60} surface. The fact that Cs-doped C_{60} prepared under similar conditions also showed changes in bulk conductivity,^{7a} which can only be explained by intercalation, also supports this conclusion.

It is thus important to consider the implications of the C 1s binding energy shifts in Cs-doped C_{60} and the similarity of these results to data obtained for the alkali-metal GICs. For an isolated molecule it is expected that reduction (e.g. Cs doping) would cause a decrease in binding energy due to Coulombic effects; however, since XPS measures the binding energy relative to the Fermi level, the observed increase in binding energy is not unreasonable. Specifically, the recent studies of conductivity and superconductivity in alkali-metal-doped C_{60} show that these materials should have well-defined Fermi levels and energy bands. Assuming that reductive Cs doping simply increases the conduction electron density without a major change in the electronic structure (i.e., rigid band approximation), then it is expected that the Fermi level and hence the C 1s binding energy will increase systematically with doping (Figure 3). This explanation is also consistent with the results for alkali-metal GICs where the increase in Fermi level

(10) Lichtenberger, D. L.; Nebesny, K. W.; Ray, C. D.; Huffman, D. R.; Lamb, L. D. *Chem. Phys. Lett.* **1991**, *176*, 203.

(11) Weaver, J. H.; Martins, J. L.; Komeda, T.; Chen, Y.; Ohno, T. R.; Kroll, G. H.; Troullier, N.; Hauffler, R. E.; Smalley, R. E. *Phys. Rev. Lett.* **1991**, *66*, 1741.

(12) Derrien, J.; D'Avitaya, F. A. *Surf. Sci.* **1977**, *65*, 668.

(13) DiCenzo, S. B.; Basu, S.; Wertheim, G. K.; Buchanan, D. N. E.; Fischer, J. E. *Phys. Rev. B* **1982**, *25*, 620.

(14) Estrade-Szwarczkopf, H.; Rousseau, B. *Synth. Met.* **1988**, *23*, 191.

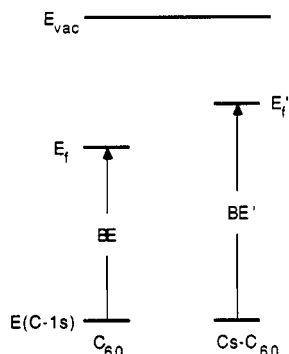


Figure 3. Schematic diagram illustrating the shift in the Fermi level (E_F) and corresponding increase in C 1s binding energy (BE) due to charge transfer doping of C_{60} by Cs.

is well-documented.¹⁵ Although it will be important to confirm the Fermi level shifts in alkali-metal-doped C_{60} , our results clearly support the idea that these films exhibit delocalized energy bands that can be doped.^{7a}

Lastly, it is also interesting to compare the relative C 1s binding energy shifts at saturation coverage for Cs-doped C_{60} and graphite. In the $Cs_{7.2}C_{60}$ film there is a 1.1-eV shift while at a similar Cs

concentration the shift for Cs-GIC is 0.6 eV. Within the context of the simple charge-transfer doping model discussed above, the greater shift in C_{60} indicates that the density of electronic states near the Fermi level may be significantly lower in C_{60} than in graphite.

Conclusions

In summary, we have used XPS to characterize in situ the changes in C 1s binding energy of C_{60} films upon Cs doping. We showed that increasing Cs coverage results in an increase in the C 1s binding energy and that subsequent oxidation yields a binding energy characteristic of undoped C_{60} films. Similar studies carried out on Cs-intercalated graphite, which also show an increase in C 1s binding energy, demonstrate that Cs doping causes strikingly similar changes in these two carbon-based materials. The C 1s binding energy shifts are consistent with Cs charge donation to a C_{60} (or graphite) energy band that results in an increase in the Fermi level position. Hence, our results further confirm the idea that thin-film C_{60} has the well-developed energy bands characteristic of a delocalized solid.

Acknowledgment. We thank Dr. A. W. Moore (Union Carbide) for the generous donation of highly oriented pyrolytic graphite and Columbia's Microelectronics Sciences Laboratory for use the XPS instrumentation. C.M.L. acknowledges support of this work by the National Science and David and Lucille Packard Foundations.

(15) Dresselhaus, M. S.; Dresselhaus, G. *Adv. Phys.* **1981**, *30*, 139.

Solvent Effects on the Adiabatic Free Energy Difference between the Ground and Excited States of Methylindole in Water

Ronald M. Levy,* John D. Westbrook, Douglas B. Kitchen, and Karsten Krogh-Jespersen*

Department of Chemistry, Rutgers University, New Brunswick, New Jersey 08903 (Received: June 17, 1991)

Molecular dynamics simulations have been used to compute the adiabatic free energy difference between the electronic ground and 1L_a excited states of 3-methylindole in water. Partial atomic charges for the two electronic states were derived from fits to the (gas phase) quantum mechanical electrostatic potentials produced by semiempirical INDO/S wave functions. The computed solvent reorganization energy (~ 3 kcal/mol) is smaller than values deduced from experimental spectroscopic data for various indole derivatives in polar solvents (4–12 kcal/mol). The solvent reorganization energy computed from the simulations is close to the value estimated from the Onsager dipole cavity reaction field model when a previously suggested, but ad hoc, molecular volume parameter is used with the model. However, this model is shown to generally not approximate reaction field energies well for a large planar molecule like indole, since it does not distinguish among different charge distributions which produce the same change in the magnitude of the chromophore dipole moment but very different reaction fields. Additional free energy simulations are carried out to demonstrate this point. In contrast, a recently proposed molecular dielectric model, which explicitly incorporates the effects of the solute structure and charge on the solvent dielectric response, is found to agree with the simulated free energy changes to within a few percent.

Analysis of medium effects on optical absorption and emission bands of indole and its derivatives continues to receive considerable attention.^{1–8} Reasons for this interest include the following: indole is the chromophore of the amino acid tryptophan and is of basic importance for optical studies of proteins; the near-ultraviolet absorption and emission spectra of indole are extremely sensitive to solvent interactions and the solvent-induced Stokes shifts provide

information about the excited-state energetics and charge-transfer dynamics; indole is used as a model system for studying electronic structure aspects of two energetically proximal, low-lying (π , π^*) excited states (1L_a , 1L_b). The 1L_a state has a considerably larger dipole moment than the 1L_b state and is the lower excited state in polar solvent.^{3,4} From a theoretical perspective, the development of models for interpreting optical experiments on indoles in solution has two principal components: (1) modeling the ground- and excited-state charge distributions of the chromophore, and (2) modeling the solvent reaction fields induced by these charge distributions. The Onsager dipole cavity reaction field model has often been used to estimate the energetic effects of solvation, including the analysis of optical spectra.^{9–11} This is a continuum solvent model. While recent molecular dynamics free energy

- (1) Beecham, J. R.; Brand, L. *Annu. Rev. Biochem.* **1985**, *54*, 43.
- (2) Eftink, M. R.; Selvidge, L. A.; Callis, P. R.; Rehms, A. A. *J. Phys. Chem.* **1990**, *94*, 3469.
- (3) Rehms, A. A.; Callis, P. R. *Chem. Phys. Lett.* **1987**, *140*, 83.
- (4) Lami, H.; Glasser, N. J. *Chem. Phys.* **1986**, *84*, 597.
- (5) Lakowicz, J. R.; Szmajda, H.; Gryczynski, I. *Photochem. Photobiol.* **1988**, *47*, 31.
- (6) Ilich, P.; Haydock, C.; Prendergast, F. G. *Chem. Phys. Lett.* **1989**, *158*, 129.
- (7) Ludescher, R.; Johnson, I.; Volwerk, J.; deHaas, G.; Jost, P.; Hudson, B. *Biochemistry* **1988**, *27*, 6618.
- (8) Petrich, J. W.; Longworth, J. W.; Fleming, G. R. *Biochemistry* **1987**, *26*, 2711.

- (9) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
- (10) McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562.
- (11) Birks, J. B. *Photophysics of Aromatic Molecules*; John Wiley: New York, 1970.