

Surface-enhanced Raman scattering and photoemission of C_{60} on noble-metal surfaces

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Surface-enhanced Raman scattering of monolayer C_{60} deposited in UHV on noble metals yields substantial shifts of the high-frequency, $A_g(2)$ pentagonal pinch mode. These shifts, which increase in the series Au, Cu, and Ag, are attributed, in part, to charge transfer to the fullerene. This behavior is consistent with a decrease in noble-metal work function in this sequence. Confirmation of charge transfer in Cu and Ag is directly obtained by He I, ultraviolet photoemission spectroscopy measurements which indicate formation of a lowest-unoccupied-molecular-orbital (LUMO)-derived band similar to that observed in K_3C_{60} and Rb_3C_{60} . The form and Fermi edge behavior of the LUMO-derived band further imply the formation of a metallic interfacial layer. X-ray photoemission spectroscopy measurements indicate shifts of the C 1s core level which differ from trends noted in Raman scattering, suggesting that interfacial effects beyond charge transfer may be important.

INTRODUCTION

Photoemission and Raman scattering studies of alkali-fullerene materials have demonstrated the sensitivity of electronic and vibrational states derived from C_{60} clusters to charge transfer and possible local bonding effects.^{1,2} In metallic K_3C_{60} and Rb_3C_{60} , as well as insulating K_6C_{60} and Rb_6C_{60} films, charge transfer to C_{60} results in shifts to lower frequency of the intramolecular, $A_g(2)$ pentagonal pinch mode.^{3,4} The origin of this Raman shift, which is similar to that noted in intercalated graphite,⁵ has been attributed to a bond length increase within the graphite intralayer network. Transfer of charge to C_{60} in A_xC_{60} ($A=K, Rb$) systems also modifies the valence-band states, populating in a nonrigid band manner, states derived from the lowest-unoccupied-molecular-orbital (LUMO) π^* states of C_{60} . For $x=3$ the Fermi edge behavior indicates that charge transfer and alkali-C interactions lead to metallic behavior, while for $x=6$ filled band insulating character is found.^{1,2,6}

Recent photoemission studies of C_{60} clusters on selected metal surfaces have also indicated interaction effects on electronic states derived from C_{60} .⁷ Surface-enhanced Raman scattering (SERS) of C_{60} on Au surfaces in solutions have also noted modifications of the intramolecular vibrations.⁸ Of basic interest in these studies is the nature of C_{60} -metal interactions and the role of charge transfer on physical properties of the C_{60} /metal interfacial system. In the present work a combination of SERS and ultraviolet photoemission spectroscopy (UPS) are employed to address these issues. The combination of these methods provides a means of determining when charge transfer occurs and whether the resulting interfacial system is metallic or nonmetallic in character. The results for the noble metals (NM) Cu, Ag, and Au demonstrate variable charge transfer and the formation of an interfacial metallic state whose valence character is qualitatively similar, for Ag and Cu, to that of three-dimensional alkali- C_{60} films. Additional x-ray photo-

emission spectroscopy (XPS) studies of the C 1s core level which is sensitive to changes in valence electron screening are explored.

EXPERIMENT

Thin films of 0.5–2-monolayer (ML) C_{60} were deposited by sublimation at a pressure of $\sim 10^{-8}$ Torr onto magnetron-sputtered, polycrystalline noble-metal substrate films. Thicknesses were calibrated with a quartz crystal monitor. For SERS studies, thin polycrystalline noble-metal films in island form were prepared by both high- and ultrahigh-vacuum magnetron sputtering onto SiO_2 substrates. For Ag and Au the film thickness employed was ~ 50 Å while the Cu thickness was 40 Å. *In situ* SERS measurements at 300 K utilized 514.5-nm excitation, and employed a Spex Triplemate spectrograph with an ITT Mepsicon multichannel detector. Photoemission measurements on these films and on continuous noble-metal films with C_{60} utilized an HA 100 Microsciences hemispherical analyzer with nonmonochromatic He I and Mg K_α radiation for UPS and XPS, with ~ 0.2 and ~ 1.1 eV resolution, respectively. The UHV base pressure for photoemission and Raman measurements was $\sim 2 \times 10^{-10}$ Torr.

RESULTS AND DISCUSSION

Shown in Fig. 1 is a comparison of the SERS spectra obtained on ~ 1 ML of C_{60} on Ag and Cu substrates and a thicker C_{60} film. The spectra indicate a number of similar changes, including a general broadening, relative to the 10-ML C_{60} film. Due to the lower enhancement factor found on the Au film, only the higher-energy region of the spectrum is shown in Fig. 1. In addition to the ten Raman-active modes shown, the SERS spectra indicate additional weak features associated with induced scattering. While it might be thought that the induced scattering is due to surface symmetry reductions or local field or field gradient effects in SERS,⁹ induced scattering is also

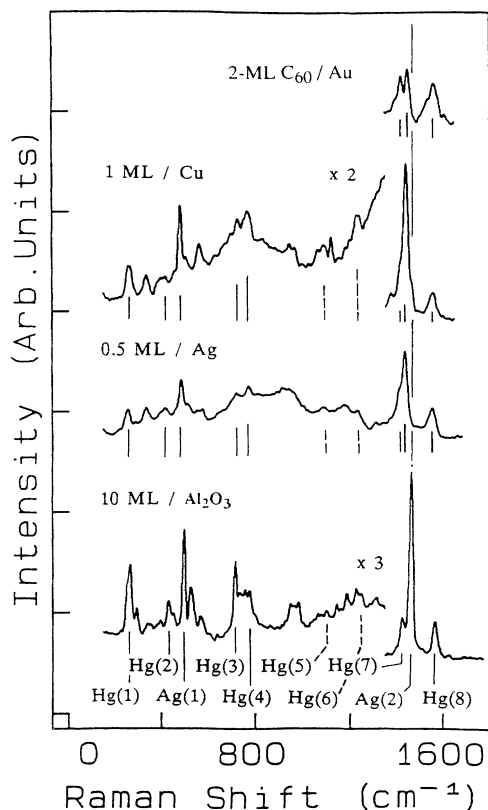


FIG. 1. Comparison of Raman spectra of C_{60} on Au, Cu, and Ag substrates to a thick C_{60} film on Al_2O_3 . The symmetry assignment of the ten Raman allowed modes is given at the bottom.

observed in thicker, 10-ML films of C_{60} , shown in Fig. 1. In addition, certain modes such as that observed at ~ 400 cm^{-1} are suggested by theory to have H_u and G_g symmetry,¹⁰ and thus should not be Raman active for a field gradient mechanism.¹¹ These results indicate that the induced scattering is due to disorder effects within solid C_{60} that remove the pure icosahedral molecular symmetry. While such effects have not been observed in radial distribution function studies of solid C_{60} ,¹² this may be a consequence of quite small radial distortions.

A major change of interest due to substrate interactions is noted in Table I by the decrease in frequency of the intense high-frequency pentagonal pinch, $A_g(2)$, tangential mode relative to pure C_{60} . The largest shift in Table II of this mode of 28 cm^{-1} is observed for C_{60}/Ag , while a smaller shift of 23 cm^{-1} is found for C_{60}/Cu .

TABLE I. Comparison of the Raman frequencies of the $A_g(2)$, $H_g(7)$, and $H_g(8)$ modes of 0.5–2.0-ML C_{60} on different substrates and 10-ML C_{60} on Al_2O_3 .

Substrate	Thickness (ML)	$H_g(7)$ (cm^{-1})	$A_g(2)$ (cm^{-1})	$H_g(8)$ (cm^{-1})
Al_2O_3	10.0	1423.5	1464.0	1567.0
Ag	0.5	1409.0	1435.7	1554.0
Cu	1.0	1415.0	1440.8	1556.0
Au	2.0	1421.0	1448.6	1561.0

TABLE II. Comparison of the Raman shifts of ultrathin films of C_{60} on different substrates relative to thick C_{60} .

Substrate	Thickness (ML)	$A_g(2)$ shift (cm^{-1})
Al_2O_3	10.0	0.0
<i>a</i> -Ge	1.0	-15.0
<i>a</i> -Ge:H	1.0	-2.0
Ag	0.5	-28.3
Cu	1.0	-23.2
Au	2.0	-15.4

SERS spectra of C_{60}/Au , in contrast, indicate a substantial, though somewhat smaller shift of 15 cm^{-1} relative to Ag and Cu surfaces. This latter shift is similar to that observed for solution SERS studies of C_{60}/Au .⁸ If, as suggested by analogy with intercalated graphite, the SERS shift is proportional to the charge transfer, the Raman spectra indicate decreasing transfer in the series Ag, Cu, and Au. Table I shows in addition the high-frequency tangential modes $H_g(7)$ and $H_g(8)$. The same trends are observed with Ag having the largest shift followed by Cu and Au.

It is useful to note that the highest-frequency, $H_g(8)$ mode of C_{60}/NM , shown in Fig. 1, exhibits considerable strength and only a moderate width increase relative to pure C_{60} . This contrasts with Rb_xC_{60} and K_xC_{60} ultrathin films for $x > 1$, which exhibit a substantial $H_g(8)$ broadening and intensity decrease.⁴ These effects have been associated with enhanced electron-phonon coupling of relevance to a phonon-mediated mechanism for superconductivity. Also observed in Fig. 1 are shifts of the $A_g(1)$ mode to lower frequency. This shift, which is larger in Cu than Ag, also differs from the relatively constant $A_g(1)$ frequency of A_xC_{60} films as a function of x .⁴ As such, the observed $A_g(1)$ shift is not simply attributable to charge-transfer effects.

Shown in Figs. 2, 3, and 4 are the He I UPS spectra of C_{60} on Ag, Cu, and Au. All three of the noble-metal substrates have similar UPS spectra, in that there is a very

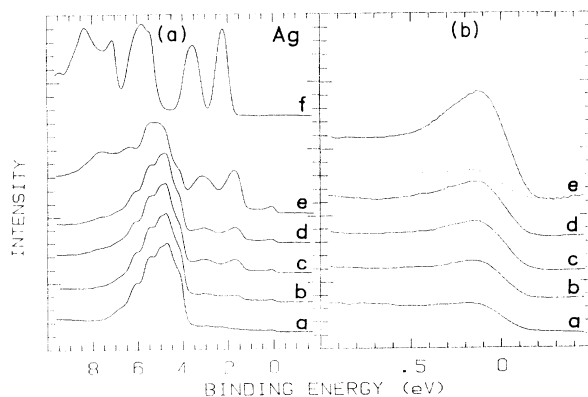


FIG. 2. He I UPS spectra of varying thicknesses of C_{60} on Ag. Curve a, bulk Ag; curve b, 0.25 ML C_{60} ; curve c, 0.5 ML; curve d, 1 ML; curve e, 2 ML; curve f, bulk C_{60} . (a) shows full UPS spectra, (b) shows near-Fermi-edge region. Dotted line shows estimated Ag contribution to spectrum.

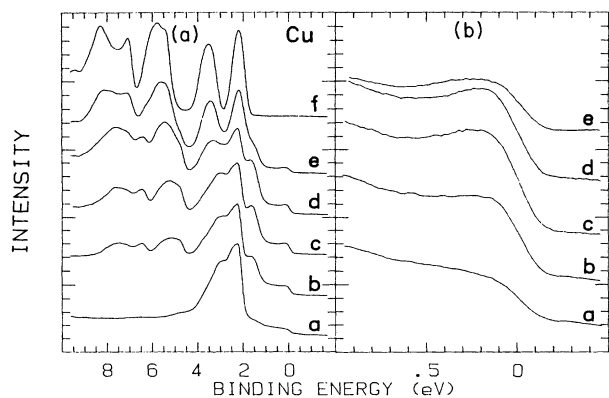


FIG. 3. He I UPS spectra of varying thicknesses of C_{60} on Cu. Curve *a*, bulk Cu; curve *b*, 0.5 ML C_{60} ; curve *c*, 0.75 ML; curve *d*, 1.25 ML; curve *e*, 2 ML; curve *f*, bulk C_{60} . (a) shows full UPS spectra, (b) shows near-Fermi-edge region.

strong *d*-band contribution and a weaker, featureless *s* band that extends to the Fermi edge. Significant changes with the addition of C_{60} are observed for all three systems, with changes near the Fermi energy qualitatively indicating modifications of the band-edge states of the substrates. These modifications are associated with C_{60} -metal interactions. As indicated in Figs. 2(b) and 3(b), both Ag and Cu systems show significant changes near E_F . The shape of the band edge changes dramatically, indicating the formation of a new band. This interface-determined band intensity is significantly stronger in Ag than Cu; however, both systems display a band shape that is similar to that observed for the LUMO-derived band in K_3C_{60} (Refs. 2 and 13) and Rb_3C_{60} .⁶ Au shows essentially no change in the region near the Fermi energy with increasing C_{60} coverage except for the expected decrease in the Au *s*-band signal. However, the Au spectrum does show significant changes in the features at higher binding energy, suggesting interactions with C_{60} .

Figure 2(b) shows an example of the approximate lower limit of the contribution of the Ag substrate (indicated by dotted line) for 2 ML of C_{60} . Since the *s* band of pure Ag has an intensity of $\sim 3\%$ of the *d* band, the signal from

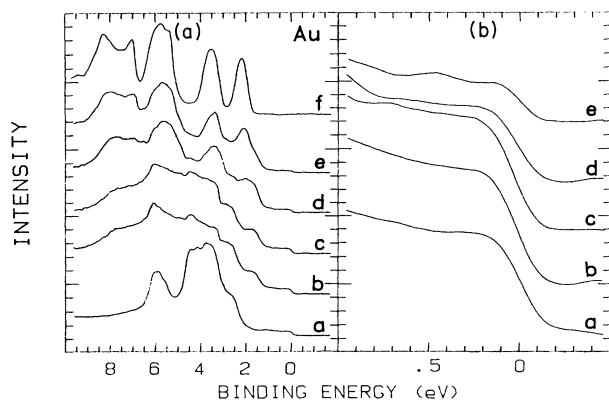


FIG. 4. He I UPS spectra of varying thicknesses of C_{60} on Au. Curve *a*, bulk Au; curve *b*, 0.25 ML C_{60} ; curve *c*, 0.75 ML; curve *d*, 1 ML; curve *e*, 1.5 ML; curve *f*, bulk C_{60} . (a) shows full UPS spectra, (b) shows near-Fermi-edge region.

the substrate *s* band is estimated by comparing the relative intensities of the bulk *d*-band intensity and that of the C_{60} -covered substrate. The spectra show no change in the position of the Fermi edge relative to the highest occupied molecular orbital (HOMO) π_u band of C_{60} with coverage. It is useful to note that the separation of the HOMO band from E_F for C_{60}/Ag of ~ 1.8 eV is smaller than values of 2.0 and 2.2 eV observed in Rb_3C_{60} and K_3C_{60} , respectively.⁶ This is consistent with variations in the degree of metal-carbon hybridization that occurs with LUMO population.

The observation of a distinct LUMO-derived band for C_{60}/Ag demonstrates charge transfer to C_{60} , while the position of the Fermi energy for low coverage indicates formation of a metallic interface state. This indicates that the SERS shift of Table I is associated in part with charge-transfer effects that are similar to that noted in A_xC_{60} films^{3,4} and alkali-graphite intercalates.¹⁴ In the latter charge transfer results in an increase in the bond length¹⁵ and a softening of the bond stretching force constant. For C_{60} theoretical calculations suggest that charge donation results in a relative increase in the hexagon-hexagon, "double bond" length.¹⁶

In the case of C_{60}/Cu and C_{60}/Au the overlap of the noble-metal *d* states and C_{60} π bands renders estimation of the substrate band-edge contribution quite difficult. However, the form of the spectral variations near E_F for Cu is similar to that of Ag, and cannot be derived from the Cu *s* band alone. No such band development at the Fermi energy is observed in Au. Additionally, where the Ag/ C_{60} spectra show a steady increase in the density of states at E_F up to a coverage of ~ 2 monolayers, the density of states at the Au Fermi edge decreases steadily with coverage. This is not due to cross-sectional effects, as the ratio of the cross sections of Ag and Au *s* electrons to *C p* electrons for a photon energy of 21.2 eV are comparable.

UPS spectra for C_{60} on Ag have been reported by Ohno *et al.*,⁷ however, no LUMO-derived bands were observed. A probable explanation lies in the relative cross sections of Fermi edge electrons of silver and carbon at the photon energy used for their measurements, 110 eV. At this energy the carbon *p* electrons have a greatly reduced cross section with respect to the silver *s* electrons than they would at 21.2 eV, the energy used for our experiments. Inverse photoemission measurements for C_{60}/Au (Ref. 7) indicate a LUMO-derived peak at ~ 0.85 eV above the Fermi energy. The spectrum is consistent with population of a tail of LUMO states for C_{60}/Au and the absence of a distinct peak in UPS spectra.

Shown in Table II is a comparison of the SERS shifts for noble metals and IERS (interference-enhanced Raman scattering) (Ref. 17) shifts for amorphous (*a*-) Ge and a hydrogenated *a*-Ge surface. One monolayer of C_{60} on an oxidized Al surface is found to show the same Raman frequencies as a 10-ML-thick film. For the noble metals it is observed that the SERS shift decreases in an approximately linear manner as the polycrystalline work function W increases from Ag (4.3 eV) to Cu (4.7 eV) to Au (5.1 eV). This result is qualitatively reasonable, being consistent with a reduction of charge transfer as W in-

increases for fixed C_{60} electron affinity.¹⁸ Such transfer results from equilibration of substrate and adsorbate Fermi levels.

While work-function changes are expected to primarily influence charge-transfer and SERS shifts, other factors such as covalent interactions, the effects of screened metal-adsorbate interactions and high C_{60} polarizability¹⁹ may be of significance. That covalency effects may modify the SERS shift is noted by the 15-cm^{-1} shift noted for $C_{60}/a\text{-Ge}$. Here interactions between C_{60} clusters and $a\text{-Ge}$ dangling bond p states are suggested. Evidence for this is provided by the small $\sim 2\text{-cm}^{-1}$ shift when the $a\text{-Ge}$ surface dangling bonds are saturated with hydrogen atoms.

The magnitude of the SERS shifts for Ag and Cu substrates are comparable to that observed for thin films of A_xC_{60} for $2 < x < 3$. While this might suggest transfer of up to three electrons in the case of Ag, covalent or other interactions with the metal surface may contribute to the shift. Electrochemical studies of C_{60} in organic solvents have suggested that charge transfers of one and two electrons are more stable.²⁰ It has recently been suggested that the large shift of three to six electrons implied in A_3C_{60} and A_6C_{60} compounds is due to crystal field effects.¹⁸ It has also been found in theoretical studies that for free-electron metals without covalent interactions a maximum of two electrons can be transferred. These results complicate a definitive assignment of the charge transferred. If the ratio of the intensity of the LUMO band at the Fermi energy to the HOMO π band area is evaluated, one finds a ~ 0.6 reduction for C_{60}/Ag relative to K_3C_{60} . This is consistent with less than three electron charge transfer for C_{60}/Ag and C_{60}/Cu interfaces.

Figure 5 shows the effect of C_{60} -noble-metal interactions on XPS spectra of the C 1s core line. Comparisons were made for all three substrate systems between 0.5 ML C_{60} and thick films (> 6 ML). The observed shifts to higher binding energy with increased coverage are 0.4 eV for Ag, 0.6 eV for Cu, and 0.5 eV for Au. These C 1s shifts are qualitatively similar to those observed by Ohno *et al.*⁷ on Cr and Au substrates. The observed shift behavior differs from the SERS trends of Table II, suggest-

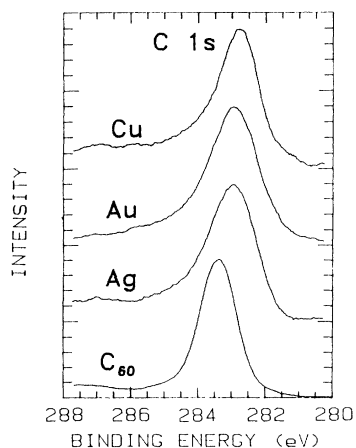


FIG. 5. Mg $K\alpha$ XPS spectra of 0.5-ML C_{60} on Cu, Au, and Ag substrates compared to bulk C_{60} .

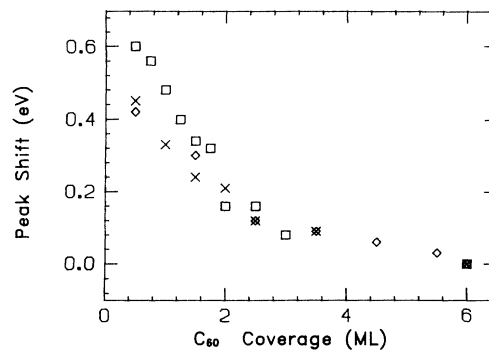


FIG. 6. Shift in C 1s peak with increasing C_{60} coverage, compared to bulk C_{60} . Ag substrate (diamonds), Cu substrate (box), Au substrate (\times). Bulk C_{60} (6 ML) for all three substrates is given the same energy value.

ing that effects other than charge transfer⁷ occur. It is possible that both screened long-range and short-range exchange-Coulomb interactions of C_{60} with substrate itinerant electrons may influence the core shifts.

Comparison of the shifts in the C 1s band as a function of C_{60} thickness is shown in Fig. 6 for all three substrate systems. There is a clear change in slope at ~ 2 ML, which appears to indicate the approximate point at which C-C interactions, as opposed to C-substrate interactions, dominate. It is believed that this transition occurs at ~ 2 ML, rather than 1 ML, due to surface roughness in the substrates increasing the surface area available to the C_{60} molecules.

In summary, a combination of surface-enhanced Raman scattering and UPS spectra has indicated formation of metalliclike interfacial states for C_{60} on Ag and Cu. The SERS shift for these surfaces has been primarily attributed to charge transfer to the C_{60} cluster with decreasing noble-metal work function. This transfer results in a substantial decrease in the frequency of the $A_g(2)$ pentagonal pinch mode due to force constant reductions attributable, by analogy with intercalated graphite, to an increase in C-C bond lengths. UPS spectra for Ag and Cu substrates demonstrate that the charge transfer as in A_3C_{60} results in the formation of a metallic, rather than insulating, surface layer. In contrast, the smaller SERS shift and the absence of a distinct LUMO-derived band observed for C_{60}/Au has been attributed to a reduced charge transfer possibly due to increased covalent interactions or additional metal-substrate interactions. While for C_{60}/Ag and C_{60}/Cu the observed frequency shifts are comparable to those observed in Rb_3C_{60} and K_3C_{60} , additional substrate interactions might possibly result in a transfer of less than three electrons per molecule. XPS measurements indicate shifts of the C 1s core levels that qualitatively differ from the SERS trends. This suggests the presence of adsorbate-substrate interactions other than those due to charge transfer.

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