Photoemission and electron-energy-loss-spectroscopy study of C_{60} monolayers adsorbed on Cs-precovered Au(110) and of bulk distilled Cs_xC_{60}

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The adsorption of C_{60} in submonolayer and monolayer coverages on Cs-precovered Au(110) has been investigated by photoemission and high-resolution electron-energy-loss spectroscopy. Complete fullerene monolayers display discrete molecular oxidation states of approximately -3, -4, and -6 in the presence of Cs. The oxidation states were determined by a comparison of monolayer electronic structure and vibrational mode frequencies with those of the bulk fullerides. There is no evidence for oxidation states of -2 and -5. Surface-specific measurements on bulk vacuum distilled alkali-fulleride samples showed a strong similarity between the properties of the single-layer films and the surface layers of the bulk material. Annealing experiments demonstrated that it was possible to produce a well-ordered, close-packed monolayer of C_{60} with an oxidation state of -3, which may be a useful precursor in producing a metastable fcc Cs_3C_{60} film by epitaxial growth. Bonding with the substrate stabilized this film with respect to bulk samples leading to desorption only at temperatures >900 K. Electron-energy-loss spectroscopy of submonolayer C_{60} in the presence of multilayers of Cs indicates that filling of the lowest unoccupied molecular orbital (LUMO)$+1$ states occurs. Completion of the monolayer results in extra charge occupying the LUMO band only. However, LUMO$+1$ occupation can also be brought about by sandwiching complete fullerene monolayers between Cs layers. [S0163-1829(97)08011-9]

I. INTRODUCTION

The discovery in 1991 that alkali-metal–C_{60} salts (fullerides) form synthetic metals at appropriate stoichiometries[1] and that, furthermore, these metals superconduct[2-7] at temperatures higher than any other organic superconductors, initiated an explosion of research activity into the physical and chemical properties of the fullerides that continues unabated today. It is now known that, when doped with alkali metals, C_{60} forms a number of distinct and separate fulleride phases which have been denoted by the generic formula A_xC_{60}, where A is an alkali metal.

Fullerides of the "heavier" alkali metals (K, Rb, and Cs), obtained by doping a pristine film, saturate at $x=6$, while for Na x values up to about 10 (Ref. 8) have been reported. Pure solid C_{60} has a face-centered-cubic (fcc) crystal structure above about 260 K, with C_{60} molecules located at each of the lattice points of the conventional unit cell. Low levels of doping with the heavier alkali metals leads to the formation of a solid solution, which maintains the fcc structure of the undoped material.[9] These solid solutions appear to saturate at a rather low concentration ($x<0.1$).[10] At concentrations above the solubility limit an A_1C_{60} phase nucleates.[11] For the case of K the $x=1$ phase appears to be thermodynamically stable only above 425 K,[12] although phase separation into a solid solution and K_3C_{60} is not always observed to be complete.[13] A_1C_{60} has a rich variety of phases which have

electronic[14,15] and geometric[16,17] structures which are strongly dependent on the thermal history of the samples.

With increasing dopant concentration, Rb and K form a fcc A_3C_{60} phase,[18,19] with the alkali ions located in the octahedral and tetrahedral interstices of the lattice. It is only this phase of the Rb and K fullerides which exhibits a superconducting transition,[2-6] although it has been suggested that it is in fact a slightly off-stoichiometric composition that forms the superconducting material.[20]

It does not currently appear to be possible to produce a fcc Cs_3C_{60} phase, probably because the ionic radius of Cs is too large for the tetrahedral interstices of the fcc C_{60} matrix, rendering the phase thermodynamically unfavorable. Other cubic phases with a stoichiometry of Cs_3C_{60} have, however, been reported.[21,22] A solid-state reaction technique has produced Cs_3C_{60} with a body-centered-cubic (bcc) structure,[22] while a mixed phase sample was obtained from reaction of Cs and C_{60} in liquid ammonia.[21] The components of this latter material have been identified as having an $A15$ cubic structure [similar to Ba_3C_{60} (Ref. 23)] and a body-centered-tetragonal (bct) structure (similar to A_4C_{60}). It has been suggested that an $A15$ structure is energetically competitive to the fcc structure in A_3C_{60},[24] and the larger atomic volume offered by the former may explain why Cs_3C_{60} adopts this structure. Raman measurements show that, although two phases are present, there is a homogeneous transfer of about three electrons from the Cs atoms to each C_{60} molecule.[21]

The mixed-phase sample is shown to have a superconducting transition at 18 K under ambient pressure, which increases to 40 K under a pressure of 15 kbar. This increase in transition temperature is contrary to that seen for K- and Rb-doped C_{60}, where an increase in pressure leads to a decrease in the superconducting temperature.[25] One possibility is that the increase in the transition temperature for Cs_3C_{60} may be associated with an observed pressure induced phase transition.[21]

Beyond $x=3$ the interstices of a fcc C_{60} matrix can no longer accommodate all the intercalated alkali ions (with the exception of Na, which forms a fcc phase for $x=6$) and the fullerides form a body-centered-tetragonal (bct) A_4C_{60} (Refs. 19, 20, and 26) phase. Simple rigid filling of the C_{60} LUMO (lowest unoccupied molecular orbital) derived conduction band would result in a metallic phase. In contrast, photoemission[27,28] and transport measurements[29] clearly indicate that A_4C_{60} is an insulator (although possibly with an extremely small band gap.[30]).

When alkali doping is increased still further, a body-centered-cubic A_6C_{60} phase[19,31] forms, which represents the saturation doping of alkali fullerides ($A=$ K, Rb, and Cs) produced in this manner. The six electrons donated from the alkali atoms to each C_{60} molecule completely fill the threefold degenerate LUMO-derived conduction band, resulting in an insulating phase.

Further transfer of charge from potassium to C_{60} has been demonstrated,[32,33] but in thin films where there has been a ratio of K atoms to C_{60} molecules of $x>6$, probably resulting from an increased coordination between the C_{60} and potassium arising from disorder and intermixing.[32,34] The extra charge transfer per fullerene molecule results in the filling of the LUMO+1 states, although, unlike the LUMO level below, it does not appear to be possible to completely fill this level.[33]

In an attempt to shed some light on the possible effects of dimensionality on the properties of the alkali fullerides, we investigated the properties of monolayer films of C_{60} coadsorbed on the Au(110) surface with a variety of Cs precoverages. We chose Cs in particular so that it might be possible to prepare a well-ordered, close-packed, first layer of Cs and C_{60} with the fullerene molecules in a -3 oxidation state. A well-defined first layer of appropriate stoichiometry could then provide a foundation on which metastable fcc Cs_3C_{60}, which is predicted to have the very high superconducting transition temperature of 69 K,[35] might be grown.

Photoemission and electronic excitation spectra were also obtained from bulk, single phase, Cs_xC_{60} samples ($x=1$, 4, and 6), prepared by vacuum distillation.[12] Most experimental investigations of electronic structure currently in the literature have involved measurements made on vacuum-doped films, which often exhibit mixed-phase formation.[36] Therefore, spectra from distilled samples provide a clear "benchmark" to which the spectra of the monolayers can be compared. In particular, any effects of hybridization with the substrate and film structure in the C_{60} monolayers can be addressed.

The distillation methods used to prepare bulk A_xC_{60} naturally lead us to consider the effects of annealing the thin films of Cs and C_{60} coadsorbed on Au. We show that the presence of the Au(110) substrate results in the stabilization

of a composition resulting in a well-ordered film, with C_{60} molecules in an oxidation state of ≈ -3.

Modesti, Cerasari, and Rudolf[37] showed that it is possible from vibrational and electronic excitation spectra to directly estimate the charge state of adsorbed C_{60} molecules. For C_{60} monolayers adsorbed on a Au(110) surface precovered with different amounts of K, they obtained charge states of 1 ± 1, 3 ± 1, and 6 ± 1 electrons. A direct comparison between the results for Cs and K therefore provides a clear indication of the similarities and differences between the interaction of these alkali metals with the C_{60} molecule.

Increased coordination of C_{60} molecules with Cs atoms was achieved by dosing fullerene submonolayers onto a multilayer ($\geqslant 2$ ML) of Cs or "sandwiching" C_{60} layers between Cs multilayers. The electronic excitation spectra from these films show clear features which can be associated with electronic transitions involving filling of the LUMO+1 level of the C_{60} molecules.[32,34]

II. EXPERIMENT

The experiments were carried out in an ultrahigh vacuum (UHV) system consisting of a preparation and a measurement chamber which had base pressures of 1×10^{-10} and 5×10^{-11} mbar, respectively. The sample was prepared by cycles of Ne^+-ion sputtering and annealing. Sample cleanliness was monitored by a Varian Auger electron spectrometer (AES), which was also used to determine adsorbate coverage from the ratio of substrate and overlayer Auger peaks. The C_{60} coverage was calibrated by measuring the Auger peak ratios of the carbon KLL peak at 272 eV to the Au peaks at 69 and 356 eV at a coverage produced by saturating the Au(110) surface with C_{60} at a temperature (≈ 600 K) above that required for desorption of the multilayer. We define the coverage of the resulting *physical* monolayer of C_{60} (which has an areal density of 1.15×10^{18} m^{-2}) as 1 ML.

Cs coverage was calibrated by obtaining a saturated Au(110)-$c(2\times2)$ Cs layer (as observed by low-energy electron diffraction) at 450 K, and by producing Auger growth curves[38] from the ratio of the Cs 563- and 575-eV peaks and Au 69-, 230-, 255-, and 356-eV peaks at 125 K. The coverage of the saturated $c(2\times2)$ Cs overlayer (Cs adatom density 4.2×10^{18} m^{-2}) is taken, for clarity, as 1 ML.[39] Cs coverages for each experiment were then obtained by comparing the Au and Cs peak ratios to the calibration curves, rather than using evaporation time, to eliminate errors brought about by any changes in evaporation rate. This method of coverage calibration gives us an estimated error of $\pm 10\%$ in our measured coverages.

99% pure C_{60}, obtained from Texas Fullerenes and thoroughly degassed in UHV, was sublimated onto the samples from a tantalum crucible at around 700 K. The temperature of the samples could be carefully controlled by resistive heating or by cooling with a liquid-nitrogen flow. A shutter between the source and sample was used to control the deposition time. The pressure during C_{60} evaporation remained between 2×10^{-10} and 6×10^{-10} mbar. Cs was dosed from a commercial SAES getter source, with chamber pressures of 2×10^{-10} mbar during evaporation cycles. Cs coverages of 1 ML and below were obtained both at 298 and 125 K, while higher coverages were stabilized by maintaining the surface

at 125 K during deposition and measurement in analogy with K deposition on Au(110).[40,41]

Thin-film samples of Cs_xC_{60} ($x = 1$, 4, and 6) were prepared by the vacuum distillation method of Poirier, Owens, and Weaver.[12] Multilayer films (>12 ML) of C_{60}, doped to appropriate stoichiometry, were used as the starting point for distillation. For the preparation of Cs_xC_{60} we chose starting compositions of $x = 6$ for Cs_4C_{60} and $x < 0.4$ for Cs_1C_{60}. Alternate dosing of Cs and C_{60} was used to improve the homogeneity of the starting material in the latter case. Distillation was continued until no further changes occurred in either photoemission or Auger spectra, at which point the samples were considered to be homogeneous over the sampling depth of our experimental probes.

After preparation of the samples and characterisation by AES an Omicron low-energy-electron-diffraction (LEED) optics, which like the AES, was mounted in the preparation chamber, was used to determine surface symmetry. Photoemission spectra were obtained using a He lamp and a hemispherical electron analyzer (VG100AX). All spectra presented in this paper were obtained using light from the He I line (21.22 eV), with emission due to the He I satellites subtracted. The Fermi-level position was determined from spectra obtained from the clean Au(110) substrate. All spectra were obtained integrated over the acceptance angle of the analyzer ($\approx 5°$) and in normal-emission geometry.

Vibrational and electronic excitations of the surface could be measured using a Leybold-Hereaus ELS-22 high-resolution electron-energy-loss spectrometer (HREELS) mounted in the measurement chamber. The HREELS also provided a second means of measuring sample cleanliness more sensitive than that provided by AES. Vibrational spectra were acquired at a beam energy of 2 eV (10 eV) with an incident angle of 72° with respect to the surface normal and an analyzer angle of 72°($\approx 20°$) for on- (off-) specular scans. Spectrometer resolution varied between 5 and 10 meV depending upon surface order and composition.

Electronic excitation spectra were acquired in the specular geometry, with incidence and reflection angles of 72° at an incident beam energy of 10 eV. The electronic excitations of a C_{60}-based film have a rather small cross section at low primary beam energies, in comparison to vibrational excitations. Therefore, in order to obtain a good signal-to-noise ratio the spectrometer resolution was degraded to between 30 and 50 meV, when electronic excitation spectra were acquired. The intrinsic widths of electronic excitations measured, apart from the vibrational fine structure of the low-energy excitons,[42] are significantly greater than even this reduced resolution, and are thus not resolution limited. To differentiate between measurements of electronic and vibrational excitations, we shall henceforth refer to them as EELS (electron-energy-loss spectra) and HREELS respectively.

Photoemission spectra and electronic excitation spectra were obtained from the same samples. Vibrational spectra were taken along with electronic excitation spectra in a separate set of runs. Comparison of both the electronic excitation spectra and AES ensured that the photoemission, electronic excitation, and vibrational spectra all refer to samples of the same ''phase'' (or structural/electronic nature) as well as composition.
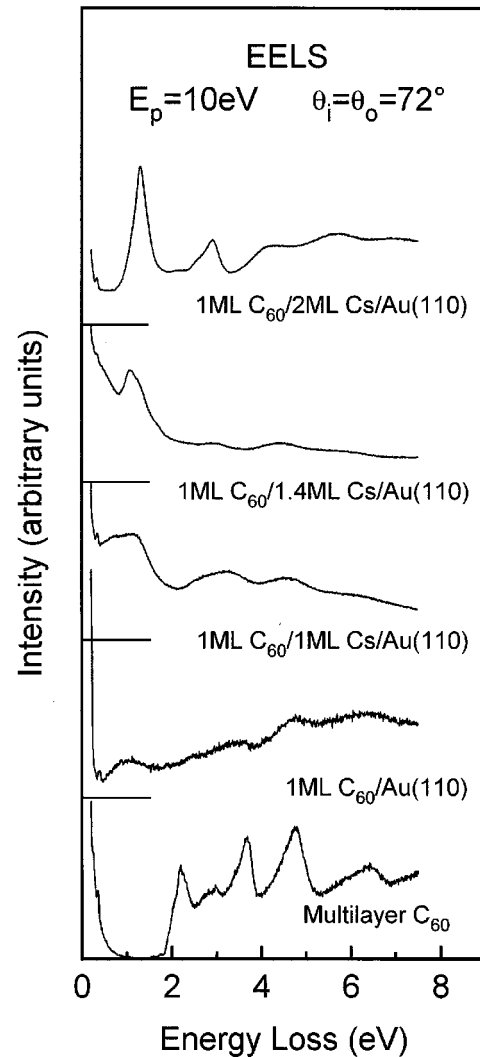

FIG. 1. Electron-energy-loss spectra showing the evolution of the electronic transitions of a monolayer of C_{60} adsorbed on a Cs-precovered Au(110) surface as a function of Cs coverage. The bottom spectrum is that obtained from an undoped, well-ordered, thick film on a bare Au(110) substrate. The solid lines are the zero levels of the spectra.

III. RESULTS AND DISCUSSION

The low-energy (0–7.5 eV) electronic excitation spectra of C_{60} monolayers adsorbed on Au(110) surfaces precovered with representative quantities of Cs are shown in Fig. 1. Spectra from a C_{60} multilayer and 1-ML C_{60} on Au(110), which have already been discussed elsewhere,[37,43] are included for comparison. The spectra clearly demonstrate dramatic changes in the electronic structure of the C_{60} monolayers as a function of the Cs precoverage, and indicate the formation of metallic and insulating phases.

The spectrum from a multilayer of C_{60} (Fig. 1, bottom) shows a clear band gap, which attests to the fact that solid C_{60} (fullerite) is an insulator.[44] The lowest energy electronic transition occurs at 1.55 eV, and corresponds to a Frenkel exciton.[42,45,46] Further peaks, at higher loss energies, have been assigned to excitons, interband transitions, and a π plasmon which has an energy of about 6.3 eV.[47]

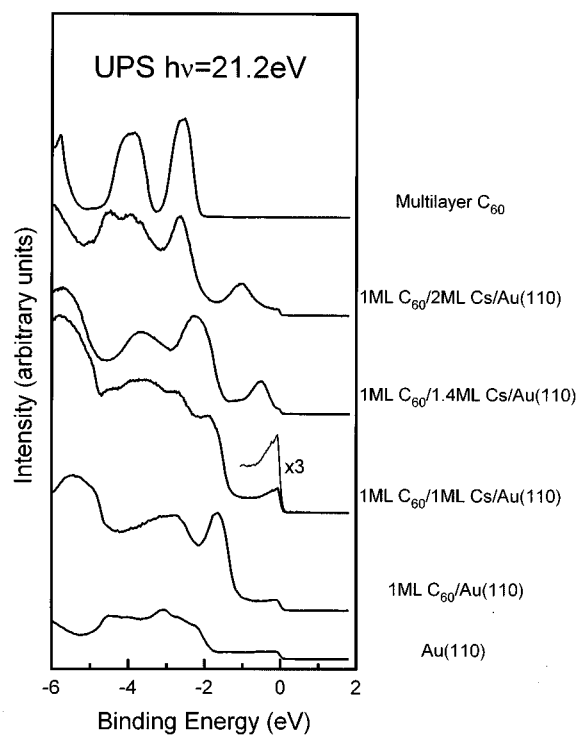When C_{60} is adsorbed on Au(110) it forms a chemisorp-

FIG. 2. Photoemission spectra obtained in normal-emission geometry with He I radiation, from C_{60} monolayers on a Au(110) surface with deffering Cs precoverage. The photoemission spectra from the C_{60} monolayers are normalized to the HOMO peak height. The photoemission spectrum of a bare Au(110) surface and a C_{60} multilayer are shown for comparison. The C_{60} multilayer spectrum is normalized to the LUMO peak height in the same manner as the monolayers, and an arbitrary normalization is used for the spectrum from clean Au(110) to show the photoemission features clearly.
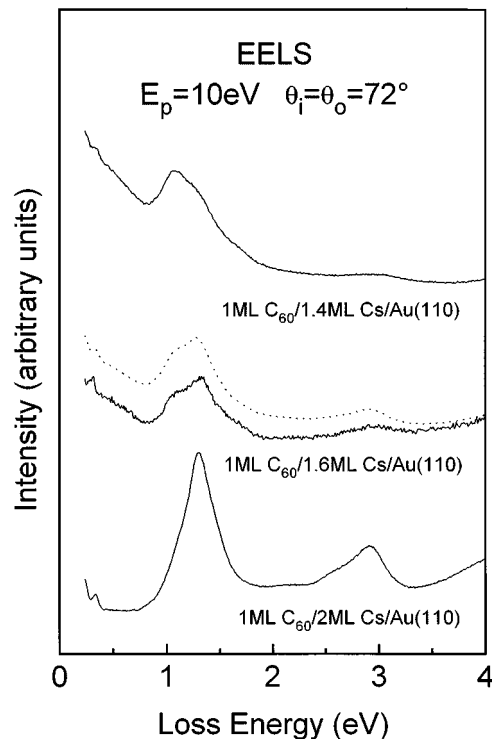

FIG. 3. Electron-energy-loss spectra of C_{60} monolayers on Au(110) precovered with 1.4-, 1.6-, and 2-ML Cs. The shape of the spectrum for C_{60}/1.6-ML Cs indicates the coexistence of the species found at 1.4- and 2-ML coverages, as can clearly be seen by a weighted sum (dashed line) of the top and bottom spectra (1.4 and 2 ML), with weights chosen to fit the low-energy background of the spectrum for 1.6-ML Cs precoverage.

tion bond with the sample surface, resulting in a metallic fullerene monolayer.[37,43,48] The resulting modification of the C_{60} electronic structure is clearly visible in EELS (Fig. 1) and ultraviolet photoemission spectroscopy (UPS) (Fig. 2). However, the presence of coadsorbed Cs further changes the features in the electron spectra with respect to the pristine multilayer, and, as we shall see below, this is the result of an increased transfer of charge to the C_{60} molecules from their environment.

In the presence of Cs three distinct electronic structures are shown both by EELS (Fig. 1) and UPS (Fig. 2). Spectra are seen to have a clearly different form at "low" (1 ML), "medium" (1.4 ML), and "high" (2 ML or more) Cs precoverages. At intermediate Cs precoverages "coexistence," resulting in spectra showing a superposition of the electronic excitations obtained at the Cs coverages above, is observed. We demonstrate coexistence in Fig. 3: The center EEL spectrum (Cs precoverage ≈ 1.6 ML) is clearly a superposition of the spectra above and below, which correspond to Au(110) surfaces predosed with 2 and 1.4 ML of Cs, respectively. Mitch, Chase, and Lannin[49] interpreted Raman spectroscopy data obtained from thin alkali fulleride films as implying that a continuous doping regime[50] exists for fulleride compositions A_xC_{60} of $x < 3$. As we shall show below, the monolayer C_{60} films in this study show oxidation states ≥ -3 (equivalent to $x \geq 3$ for bulk A_xC_{60}); therefore, it appears that three

discrete monolayer C_{60} phases are formed in the presence of Cs, and it is logical that we deal with each of them in turn, before turning to the effects of temperature, and of the presence of a large relative quantity of Cs.

IV. C_{60} MONOLAYERS ADSORBED ON 2-ML Cs/Au(110)

When a complete monolayer of C_{60} is coadsorbed, at 125 K, with Cs precoverages of between 2.0 ± 0.2 and 4.0 ± 0.4 ML, the electronic excitation spectra (Figure 1, top curve) show a clear "gap" of relatively low background intensity. The gap, which starts below about 0.7 eV, extends down to the vibrational energy region. A series of strong peaks, corresponding to electronic transitions is then observed at higher loss energy. To determine the positions of these features we carried out a Gaussian fit with all parameters free and no background. The fit indicates that the first, strong, peak is at 1.34 eV, followed by a weak peak at 2.7 eV, a doublet with peaks at 2.9 and 3.2 eV, and a broad feature at 5.8 eV.

The first excitation, at 1.34 eV, is in exactly the same position as that measured in transmission electron energy-loss spectroscopy (TEELS) of bulk samples of K_6C_{60} (Refs. 28, 51, and 52) and Rb_6C_{60},[51] and corresponds to dipole-allowed transitions between a filled C_{60} LUMO-derived band and a LUMO+1-derived band. Transitions below this energy are forbidden due to the complete filling of the LUMO
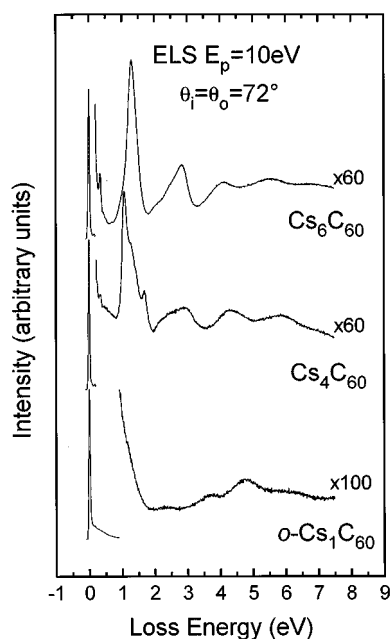
FIG. 4. Electron-energy-loss spectra from bulk Cs_xC_{60} samples, $x=1$, -4, and 6. Spectra were obtained in specular (72°, 72°) geometry at an incident beam energy of 10 eV. Spectra are normalized to elastic peak intensities.

band, which leads to the observed gap in the excitation spectrum, although the loss intensity in the gap is higher than for a pristine C_{60} multilayer, which we shall discuss below. (Loss features in this region *are* observed for submonolayer coverages of C_{60} on surfaces precovered with $\geq$2-ML Cs or when C_{60} monolayers are sandwiched between Cs layers, as discussed in Sec. VII).

The higher-lying peaks in the EEL spectra of 1.0 ± 0.1 ML of C_{60} on the surface precovered with 2.0 ± 0.2-ML Cs agree with the positions of peaks and shoulders in the TEEL spectra of bulk K_6C_{60} (Refs. 28 and 51) to within 0.1 eV, the exception being that a peak at 3.1 eV in the TEELS is resolved into a doublet at 2.9 and 3.2 eV in our spectra. The electronic excitation spectra therefore strongly suggest that the C_{60} molecules adopt an oxidation state of -6 in our monolayer film on a $\geq$2-ML Cs precovered Au(110) surface.

In order to confirm that the observed spectra did indeed imply that the C_{60} molecules had adopted the same charge state as would be seen in bulk Cs_6C_{60}, we produced a bulk sample of this material for measurement. The importance of measuring a bulk sample with the techniques that we apply in this paper, rather than just simply making a comparison with, for example, TEELS (Refs. 28, 51, and 52) and optical[53] results, arises from the bulk sensitivity of these techniques, whereas EELS in reflection geometry is rather surface sensitive, as we shall show below. At present there is no completely conclusive evidence regarding the similarity (or otherwise) of the bulk and surface electronic structure of alkali fullerides. Surface effects have been advanced, for example, to explain the differences in the near-Fermi-edge region between observed photoemission spectra in K_3C_{60} (Ref. 54) and densities of states (DOS) obtained from other techniques.

The Cs_6C_{60} samples we used were prepared by annealing

a multilayer ($>$12 ML) C_{60} film, saturated with Cs, to a temperature of 420 K. This temperature is significantly below that required for "deintercalation" and Cs_4C_{60} formation [700 K (Ref. 12)] to take place, but we found it high enough to desorb excess Cs. As with the vacuum distillation of the other stoichiometries, we ceased annealing when there were no further changes in our spectra (UPS and AES). We show, in Fig. 4, an electronic excitation spectrum obtained from a sample prepared in this manner.

When electron-energy-loss spectra are obtained in the specular geometry from a well-ordered sample, the predominant loss mechanism is the scattering of the incident electrons by the long-range dipole fields arising from elementary excitations of the sample. In the absence of metallic screening, the long range of the electromagnetic field means that electrons can be scattered from excitations arising a significant distance *below* the sample surface[55] and, in consequence, particularly with increasing incident beam energy, the technique becomes less surface sensitive.

Under the experimental conditions used to acquire the electronic excitation spectra presented in this paper, the penetration depth in the specular geometry is calculated to be about 15 Å, for a loss energy of 1 eV. This means that about two-thirds of the observed loss intensity in the low-energy part of the electronic excitation spectra arise from the first two C_{60} molecular layers. The spectra shown in Figs. 1 and 4 indicate that the surface layers of the bulk material possess a strikingly similar electronic structure to that of the monolayer film.

The main difference that exists between the spectra from the bulk Cs_6C_{60} film and the C_{60} monolayer on $\geq$2-ML Cs is that the former shows a significantly lower background loss intensity below about 1 eV, although in both cases the loss intensity is still higher than that in a pristine C_{60} multilayer (Fig. 1, bottom). The increased intensity in the gap region might result from the presence of electronic states between the center of LUMO band and the Fermi level (E_F). States tailing into the band gap have been observed in bulk K_6C_{60} samples by constant final state photoemission yield spectra,[56] and were attributed to disorder in the C_{60} films. The bulk sample displayed a rather narrow, well-defined specular beam, indicating a comparatively high degree of order—in contrast to the monolayer film. Therefore, the difference in low loss background between the spectra from the monolayer C_{60} film and the bulk Cs_6C_{60} sample provides support for the idea that the presence of electronic states in the band gap of Cs_6C_{60} arises from the presence of disorder.

An alternative explanation is that the enhanced background of the C_{60} monolayer on $\geq$2-ML Cs could arise from the presence of unreacted Cs in the film: there are $>$8 Cs atoms per C_{60} molecule in the film. However, EEL spectra from multilayer Cs in the absence of C_{60} (not shown) display a relatively small loss intensity in the loss region under consideration, indicating that if this explanation is correct, the presence of the fulleride monolayer significantly perturbs the electronic structure of the unreacted Cs.

Of particular interest is just how well the electronic structure of the fullerene monolayer adsorbed on $\approx$2-ML Cs/Au(110) and the surface of vacuum distilled Cs_6C_{60} agrees with results obtained from bulk-sensitive TEELS (Refs. 28, 51, and 52) measurement. This similarity can only
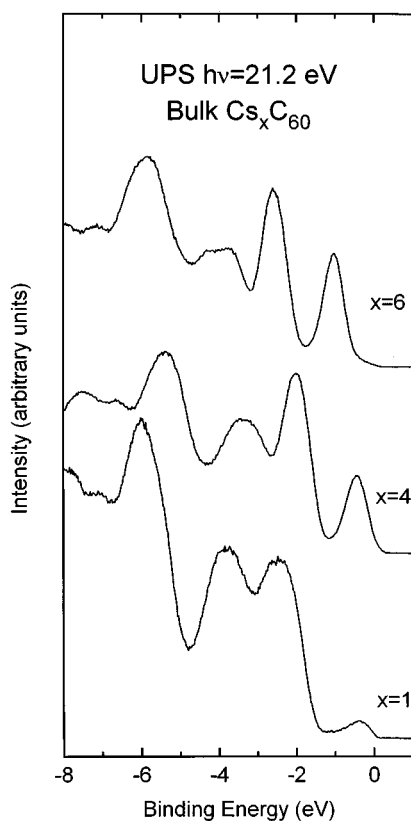
FIG. 5. Photoemission spectra obtained from bulk Cs_xC_{60} samples ($x = 1$, 4, and 6) prepared by vacuum distillation. Spectra are normalized to the HOMO peak height.
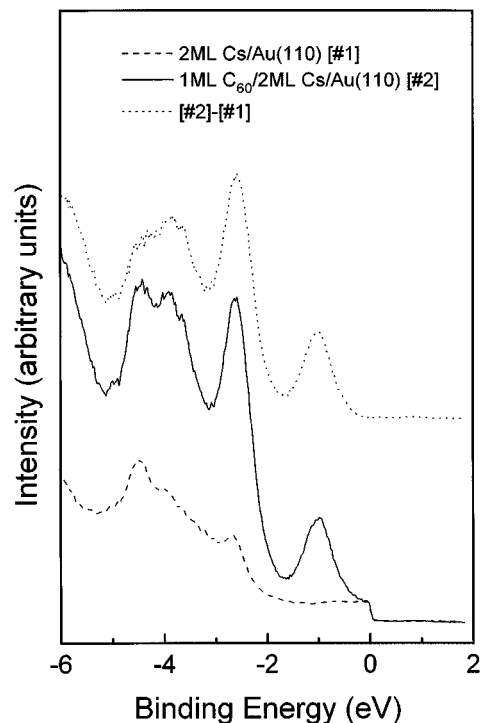

FIG. 6. Difference spectrum (dotted line) obtained by subtracting, a photoemission spectrum of 2-ML Cs/Au(110) (dashed line) from that with a monolayer of C_{60} on top (full line). The former spectrum was normalized to the near-Fermi-edge region of the latter before subtraction. Comparison of this difference spectrum with that of bulk Cs_6C_{60} reported in Fig. 5 indicates the strong similarity between the electronic structure of 1-ML C_{60}/2-ML Cs on Au(110) and the near-surface region of Cs_6C_{60}.

indicate that in A_6C_{60} compounds the differing coordination between the surface and bulk does not strongly perturb the electronic character of the near-surface region in these materials.

Turning to photoemission spectra, let us make a comparison of the valence-band emission of bulk Cs_6C_{60} (Fig. 5, top) to 1 ML of C_{60} on the 2-ML Cs-precovered Au(110) surface (Fig. 2, second spectrum from top). For 1 ML of C_{60} on 2-ML Cs one clearly sees a peak, not present in a pristine thick film (Fig. 2, top) at 1.0 eV below the Fermi level (E_F). The position of this peak and those at higher binding energies are in good agreement with the position of the emission features of a bulk Cs_6C_{60} film [peaks at 1.1-, 2.7-, and 3.8-eV binding energies for LUMO-, HOMO- (highest occupied molecular orbital), and HOMO-1-derived peaks, respectively], shown in Fig. 5.

The photoemission spectra from bulk Cs_6C_{60} (Fig. 5) and the monolayer of C_{60} on the 2-ML Cs precovered surface (Fig. 2) are rather different in the region between the peak at 1-eV binding energy and E_F: The latter displays a flat background in the low-binding-energy region, and a Fermi cutoff is observed. The presence of this plateau and Fermi edge can be attributed to the substrate and those Cs atoms which do not transfer charge to the C_{60} molecules (as mentioned above, there are a total of >8 Cs atoms per fullerene molecule in the film). In fact, the Cs-precovered Au(110) surface shows a similar plateau in photoemission spectra (Fig. 6, dashed curve) between 1-eV binding energy and the Fermi level before C_{60} deposition. If we subtract the substrate con-

tribution from the spectrum of 1-ML C_{60} on 2-ML Cs (drawn again in Fig. 6 as a solid line), weighting the former to the emission just below the Fermi level of the latter, we obtain the dotted spectrum at the top of Fig. 6. The weighting procedure reduces the substrate intensity by about 60% which is consistent with a C_{60} coverage of 1.0 ± 0.1 ML if the photoelectron escape depth is 8 Å (i.e., one C_{60} monolayer) or less.[54] The close agreement between the bulk and monolayer spectra supports the observation from the electron-energy-loss spectra that the C_{60} monolayer is in possession of *exactly* the same electronic structure as the *surface* layer[54] of the bulk material.

The vibrational modes of C_{60} monolayers adsorbed on Au(110) precovered with various quantities of Cs have been measured with HREELS, and spectra from representative coverages are presented in Fig. 7. Examination of the spectrum for a C_{60} monolayer on Au(110) precovered by 2-ML Cs (Fig. 7, top curve) shows a strong softening of the vibrational modes of the C_{60} molecules upon adsorption on the 2-ML Cs-precovered gold surface. This softening has previously been observed in IR measurements from bulk alkali fullerides[53,57,58] and in monolayer films.[37,43] The observed change in both frequency and intensity of the dipole active phonons of the C_{60} molecules was originally described in terms of a charged phonon effect.[59] This description agrees qualitatively with the reported data, but does not reproduce the nonlinearity observed in the frequency changes of the
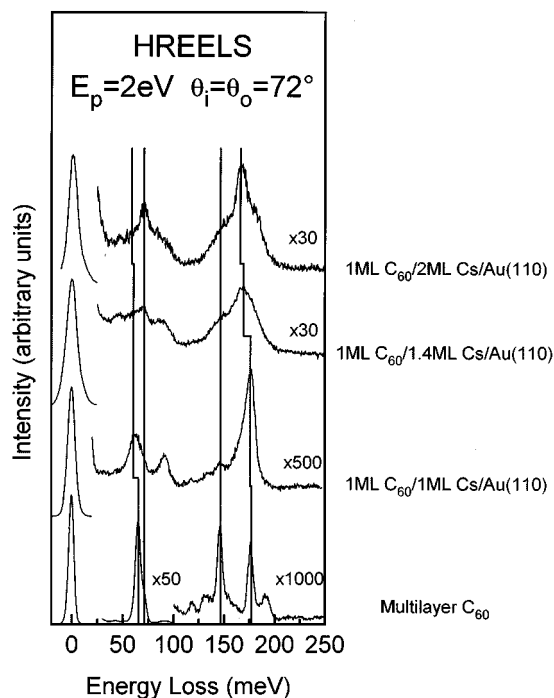
FIG. 7. HREEL spectra, obtained in the specular geometry at a primary energy of 2 eV, from C_{60} monolayers adsorbed on Au(110) with different Cs precoverages. The HREEL spectrum from an undoped thick (6 ML) film is shown at the bottom for comparison. Spectra are normalized to elastic peak intensity.

dipole-active modes as a function of stoichiometry. Giannozzi and Andreoni[60] showed that both charge transfer and structural relaxation are responsible for phonon softening and intensity enhancement in K_6C_{60}, and found a good agreement with experiment for both IR- and Raman-active modes.

In order to obtain an estimate of the oxidation state of the C_{60} molecules in the coadsorbed monolayer, independent of our previous electronic structure measurements, we make a direct comparison between the vibrational frequencies provided by our HREEL spectra and those measured and calculated for a -6 oxidation state of C_{60} in the bulk alkali fullerides. To determine the frequencies of the IR-active vibrational modes of the C_{60} molecules from our spectra, we perform a nonlinear least-squares Gaussian fit and extract peak positions to an accuracy of ± 0.5 meV. Dipole-active modes were distinguished from dipole-forbidden modes by comparison of on- and off-specular spectra: in *ordered* films dipole-active modes dominate the loss spectrum in the specular geometry. Although the monolayer C_{60} films on Cs precoverages greater than 1.4 ML showed a high degree of disorder due to the low temperature at which they were grown (125 K, compared to room temperature for the other Cs precoverages), some intensity differences (in the regions of the loss energies of the IR-active modes mentioned below) could nevertheless be observed between spectra acquired in nominally on- and off-specular spectra, enabling us to differentiate between modes.

From examination of the fits to the spectra, the lowest dipole-active $T_{1u}(1)$ mode shifts from 66 meV in the pristine multilayer film to 59 meV, a softening of 7 meV. The $T_{1u}(2)$ and $T_{1u}(3)$ modes do not change in position to within experimental error, while the highest-lying dipole-active mode $T_{1u}(4)$ shifts by 13 meV from its multilayer value to 165 meV. Using the *linear* shift in frequencies implied by the charged phonon model of Rice and Choi,[59] and a softening per unit charge of -1.25 meV for the $T_{1u}(1)$ mode and -1.85 meV for the $T_{1u}(4)$ mode,[37,43] we can *estimate* a value for the C_{60} charge state. The shift of the first T_{1u} mode then provides a value of 5.6 ± 0.7 electrons transferred to each C_{60} molecule and the highest a value of 7.0 ± 0.7 electrons per molecule. The average of these results, 6.3 ± 0.7 electrons per molecule, is in good agreement with the conclusions drawn from the electronic excitation and photoemission spectra.

To take into account nonlinearities in the softening of the molecular vibrational modes, we can also compare them directly to IR measurements of the phonons of the bulk material. In K_6C_{60}, Pichler, Matus, and Kuzmany[57] obtained values of approximately 58 and 166 meV for the first and fourth T_{1u} modes, respectively. These values are in close agreement with our results, and further indicate that our assignment of the C_{60} charge state to six extra electrons per molecule is indeed correct.

We can calculate an effective ratio of surface alkali atoms to C_{60} molecules for 1 ML of C_{60} adsorbed on the 2-ML Cs-precovered surface: We assume that the surface density of C_{60} molecules is the same as that of a close-packed fcc $C_{60}(111)$ layer, which is about 1×10^{18} m^{-2}, and that the density of Cs adatoms in the outermost layer of the Cs film is equal to that of a hypothetical hexagonal-close-packed Cs layer, 3.6×10^{18} m^{-2}. This would provide a value of 3.6 Cs atoms per C_{60} molecule in direct contact (compared to >8 Cs atoms per C_{60} molecule in the entire film). Since each Cs atom is unlikely to transfer more than its valence-electron density, the measured charge transfer, of approximately six electrons per molecule, therefore suggests that there is at least some interdiffusion between the Cs and C_{60}, with some Cs ions residing on the vacuum side of the C_{60} film. This kind of interdiffusion has been detected by the presence of two components in the $3p$ core level of K for monolayers of C_{60} adsorbed on a 1-ML K-precovered Au(110) surface.[61] The presence of C_{60}-derived features at a similar energy in photoemission spectra obtained with He II radiation prevented us from unambiguously observing any split components in Cs $5p$ emission.

V. C_{60} MONOLAYERS ON 1-ML Cs/Au(110)

A decrease of the Cs precoverage of the Au(110) surface to 1.0 ± 0.1 ML, corresponding to a $c(2 \times 2)$-Cs overlayer, changes the properties of a coadsorbed C_{60} monolayer quite considerably with respect to the Cs precoverage of 2 ML and the pristine thick film. The gap in the electronic excitations which existed for the saturation-doped insulating C_{60} monolayer disappears, and is replaced by an intense low-energy background which peaks at 0.7 eV, and an additional peak at 1.17 eV is resolved. The strong continuum of electronic excitations indicates that the monolayer is either metallic, or is a semiconductor with a band gap which is masked by the tail of the elastic peak and molecular vibrational excitations. In

the latter case the band gap would need to be less than about 200 meV.

As before, we can make an initial estimate of the chemical state of the C_{60} molecules in the coadsorbed monolayer by making a direct comparison of the electronic excitation spectra with measurements that have been made on bulk samples. We first make a comparison with results from TEELS: The energy of the peak at 1.17 eV differs less than 0.03 eV from that observed in TEELS of Rb_3C_{60} (Refs. 28, 51, and 62) and vacuum-distilled K_3C_{60},[28,63] and is attributed to transitions to the LUMO+1 band from *partly* filled LUMO states. The peak at 0.7 eV is similar to that observed at 0.5 eV in the TEEL spectra, and a plasmon edge observed at 0.73 eV in reflectivity data.[64] The shape of this low-energy-loss region is also extremely similar to the shape of the optical conductivity spectra reported by Iwasa and Kaneyama[53] for K_3C_{60} and Rb_3C_{60}. The TEELS feature observed at 0.5 eV has been interpreted[28,65] as arising from a free-carrier plasmon, shifted in energy from the value predicted by the Drude model by coupling to interband transitions. The plasmon peak width arises from phonon-assisted decay into electron-hole pairs.[65] The loss peak at 0.7 eV in the EEL spectrum from 1-ML C_{60} on Au(110)-$c(2\times2)$ Cs appears significantly broader than that observed at 0.5 eV in EEL (Ref. 66) and TEEL (Ref. 28, 51, 62, and 63) spectra from bulk K_3C_{60}. The exact source of this extra damping and the slight shift in loss energy is not readily apparent. These changes may arise from the reduction from three-dimensional electronic structure in the bulk samples to two-dimensional electronic structure in the monolayer C_{60} film. Such a reduction in dimensionality may increase the efficiency of plasmon decay into electron-hole pairs as seen for ultrathin alkali films adsorbed on Al(111),[67] which account for the increased damping observed for the 0.7-eV feature in the EEL spectrum of the monolayer film. However, this argument is not able to explain the direction of the shift in energy of the plasmon peak. Higher-lying excitation peaks agree with the TEELS results to within 0.2 eV.

A photoemission spectrum of 1-ML C_{60} on the 1-ML Cs-precovered Au(110) surface is shown in Fig. 2. The general shape of the spectrum in the near-Fermi-edge region (below about 1.1 eV) displays a sharp peak near the Fermi cutoff followed by a broad and featureless tail extending to higher binding energies. This spectral profile is very similar to that obtained by Wang et al.[68] from a KC_{60}^- complex in the gas phase. The spectral shape was interpreted in terms of the excitation of vibrations in the photoemission process. A change in photoemission intensity between spectra from gas phase C_{60}^- and KC_{60}^- was noted and explained by the excitation of more low-frequency vibrations related to the presence of K, in addition to the already numerous intramolecular vibrations possessed by the fullerene molecules. When the C_{60} monolayer on 1-ML Cs/Au(110) is cooled to 98 K, we observe a slight sharpening of the spectral profile and a clear and reproducible sideband at a binding energy about 180 meV greater than the sharp peak in photoemission intensity, which can be ascribed to the excitation of just such intramolecular C_{60} modes.

Comparison of the photoemission spectra from bulk K_3C_{60} obtained at 100 K (Ref. 64) (putting aside for a moment the temperature dependence of the bulk photoemission spectra) with those from 1-ML C_{60} on Au(110)-$c(2\times2)$ Cs shows that the spectra have the same general shape, but with an important difference, that is the width: In bulk K_3C_{60},[69] the total width of the LUMO-related feature amounts to 1.3 eV, compared to 0.8 eV for the C_{60} monolayer film, as demonstrated in Fig. 2. The extra spectral width in the bulk samples arises from the presence of a broad satellite feature at about 0.7-eV binding energy, which appears to be absent in the spectrum from the two-dimensional film. There are two possible explanations for the observed differences in photoemission line shape between the two-dimensional film and three-dimensional bulk fulleride, which we shall consider in turn since each explanation is based upon a particular interpretation of the photoemission profile of the bulk material.

Knupfer et al.[69] interpreted, with the help of calculations, the observed photoemission profile as arising from the presence of phonon and charge carrier plasmon satellites. If one adopts this interpretation of the photoemission profile, it has to be concluded that the charge-carrier plasmon is not identifiable in the photoemission spectrum from the monolayer film, although it is clearly visible in the electronic excitation spectra from this system (Fig. 1), albeit with a broader line shape than for K_3C_{60}.[63] The absence of a clear plasmon satellite in the photoemission spectrum does not contradict the observation of a clear charge-carrier plasmon-related feature in the electronic excitation spectrum: The time dependencies of the perturbation a moving electron exerts on the plasmon field is very different if the electron is an external particle, as in EELS rather than a particle created in the material, as in the photoemission process, as seen by following the reasoning of Lucas and Šunjic.[70] In particular, the perturbation exerted on the plasmon field should be considerably stronger for an external electron than for a photoelectron.

Finally, it should be noted that the escape depth of photoelectrons from a bulk film is estimated to be one molecular layer or less.[54] Hence the 0.7-eV satellite observed in the photoemission spectra obtained from bulk K_3C_{60} (Ref. 69) is likely to arise from, or be contributed to primarily, by the outermost layer of the bulk fulleride. The absence of the satellite feature from spectra of 1-ML C_{60}/1-ML Cs may therefore suggest that the coupling between the emitted photoelectron and the charge-carrier plasmon is rather weaker in the monolayer film than in the outermost layer of bulk K_3C_{60}. Upon going from a three-dimensional system to a two-dimensional system on a metallic substrate, the electron-plasmon coupling will be influenced by several factors, namely, the presence of substrate electrons, which can participate in screening processes, and by the different density of states likely to exist in two dimensions.

Alternatively, it has been suggested that the bulk photoemission spectrum arises from a nonstoichiometry of K_3C_{60} compounds,[20,71] and for a fixed on-site electron repulsion energy U, good agreement between calculated and observed photoemission spectra have been observed for slightly off-stoichiometric compositions.[71] Calculation of the photoemission spectrum for a highly correlated system depends on the values of two parameters U, the above-mentioned on-site electron-electron repulsion energy, and V, the *intersite* Cou-

lomb interaction. Both of these values will change in going from a bulk compound to our single adsorbed C_{60} monolayer, even if the oxidation state of the fullerene molecules remains exactly the same. First, consider U. In the absence of a metal substrate a bidimensional C_{60} layer would have a higher effective on-site repulsion due to a reduction in screening,[72] and and a smaller bandwidth due to reduced coordination. However, the presence of the metal substrate will change the situation due to the presence of substrate electrons, which can participate in screening. The presence of these electrons means that the polarizability of the surroundings, which will be different to that of the bulk material, must explicitly be included in a calculation of the monolayer photoemission spectrum.[72] The effect of screening will also be to reduce the value of the intersite interaction potential V significantly, and taking both the changes in U and V together, it is clear that significant changes in the photoemission profile can occur in going from the bulk material to the two-dimensional film, and these may well explain the differences we observe in the photoemission spectra of the bulk material and monolayer film.

We noted above that the photoemission spectrum obtained from a monolayer C_{60} film at room temperature is rather similar to that from a bulk K_3C_{60} sample measured at 100 K,[69] rather than at room temperature. In fact, the spectra from 1-ML C_{60} on Au(110)-$c(2\times2)$ Cs retain the same form even at 600 K. The origin of the temperature dependence of the photoemission spectra from the bulk material is not clear—it has been suggested that the large-scale excitation of alkali-atom optic modes, librations of the fullerene molecules, or low-energy anharmonic phonons may be involved. It is also quite possible that the changes in correlation effects outlined above are implicated. Whatever the exact cause, it is absolutely clear that *if* C_{60} molecules in the bulk and monolayer films have the same oxidation state, then the temperature-induced changes in photoemission intensity, and any energy-loss channels associated with them, are strongly suppressed by going from three to two dimensions and/or by the presence of the alkali-precovered gold substrate.

The narrowness of the photoemission feature near E_F in the spectrum from the monolayer film of C_{60} on the Au(110) surface precovered with 1-ML Cs in comparison with that from bulk K_3C_{60} (Refs. 28 and 69) has been remarked upon above. This difference indicates that, if the integrated density of states under this feature is the same in both spectra from the monolayer and the bulk potassium fulleride, there is an increase in the Fermi-level DOS in the monolayer film. This increase in the DOS at E_F has been estimated by normalizing the Fermi-level emission in the photoemission spectra from the monolayer, and from bulk K_3C_{60} measured at 10, 100, and 300 K,[28] to the total integrated intensity between -1.18 and $+0.5$ eV. It is found that the monolayer spectrum, measured at 300 K, has a Fermi-level DOS approximately twice as high as that measured from the bulk sample at 300 K, and approximately 1.3 times higher than that measured from the bulk at 100 and 10 K.

It has been demonstrated that there is a strong dependence of the superconducting transition temperature on the DOS at the Fermi level.[73] In the bulk superconducting alkali fullerides this has been manifested by an increase in superconducting transition temperature with increasing lattice

parameter.[6,73] An increase in lattice parameter results, in a tight-binding model, in a reduction of the conduction-bandwidth. Since the number of states in the band is constant, the net result is to increase the DOS at the Fermi level which, for the superconducting fullerides, must lie in the conduction band. An increase in the Fermi-level DOS leads, within the well-known BCS model,[73] to an increase in the superconducting transition temperature. The increased density of states at E_F in the C_{60} monolayer on 1-ML Cs/Au(110) in comparison to bulk K_3C_{60},[69] estimated above, may arise either from the larger ionic size of Cs in comparison to K, or the reduction of dimensionality in the monolayer film. In the former case, given that an 11% increase in the DOS at E_F in going from K_3C_{60} to Rb_3C_{60} brings about an increase in superconducting transition temperature of 10 K,[73] there is the possibility that a metastable fcc Cs_3C_{60} film will, as predicted,[35] possess a much higher transition than the existing fulleride superconductors.

Both the electronic excitation and photoemission spectra of 1-ML C_{60} on Au(110)-$c(2\times2)$ Cs suggest that the adsorbed C_{60} molecules are in an oxidation state of ≈-3. In the same manner as for the Cs precoverage of 2 ML, we may use the softening of the IR-active vibrational modes of the molecule as an independent estimate of the molecular charge state.

A least-squares fit to the spectrum for 1-ML C_{60} on Au(110)-$c(2\times2)$ Cs, shown in Fig. 7, shows that, as before, only the first and fourth dipole-active T_{1u} mode soften. The $T_{1u}(1)$ mode shifts downwards in frequency by 6 meV, while the $T_{1u}(4)$ mode moves by 1 meV to lower frequency. Applying the charged-phonon model,[59] we find a charge transfer of 4.8 ± 0.7 electrons per molecule from the $T_{1u}(1)$ mode, and 0.5 ± 0.7 electrons from the $T_{1u}(4)$ mode. While the ''average'' value of charge transfer provided by the two modes, 2.7 electrons/molecule, agrees well with the conclusions from photoemission and electronic excitation spectra, the difference between the charge transfers estimated from the first and fourth dipole-active modes is quite considerable. Direct comparison with IR spectra[54,58,59] shows that the $T_{1u}(4)$ mode in the monolayer C_{60} film softens much less than the same mode in bulk A_3C_{60}.

It is notable that the fourth T_{1u} mode is ''stiff'' for all the adsorption systems examined by this method so far,[37,43] except for the C_{60} monolayers on two or more monolayers of alkali metal, and underestimates the C_{60} charge state in each case. The cause of this nonlinearity is not certain but, given the importance of molecular distortion in determining mode softening,[60] is likely to arise from anisotropies induced in the molecule by bonding with the surface.

While the electronic excitations of a monolayer C_{60} on a 1.0 ± 0.1-ML Cs-precovered Au(110) surface agree closely with those for C_{60} monolayers at similar K precoverages, there is an important difference which arises when a quantitative analysis of the vibrational excitation spectra is undertaken. In both systems only the first and fourth T_{1u} modes shift, as expected. In both systems the $T_{1u}(1)$ mode shifts downward in frequency by 6 meV. However, for the Cs-precovered surface the $T_{1u}(4)$ mode softens by only 1 meV compared to 3 meV for the K-precovered surface. The charged-phonon model[59] indicates that the frequency change of the $T_{1u}(4)$ mode implies a C_{60} charge state of 0.5 extra

electrons per fullerene molecule for the Cs-precoated surface, compared to 1.6 electrons for the K-precovered surface.[37]

A possible explanation for the differences between the positions of the fourth T_{1u} modes for C_{60} monolayers on Au(110) surfaces precovered by 1 ML of Cs or 1 ML of K arises from the observation that the vibrational spectra from the 1-ML K-precovered surfaces display a poorer resolution that those for the 1-ML Cs-precovered surfaces. In consequence, it is possible that, for the former, the observed dipole active peak position may in fact be a convolution of two $T_{1u}(4)$ peaks—one from C_{60} molecules in a -3 oxidation state, and the other from molecules in a -4 oxidation state, which, as we shall see below, manifest a larger softening of the $T_{1u}(4)$ mode.

Cs forms a variety of ordered phases on Au(110) for coverages at or below 1 ML,[74] which represents the saturation coverage at room temperature. These ordered phases enable us to explore the possibility of producing ordered C_{60} films which have a well-characterized oxidation state. In particular the formation of a well-ordered close-packed layer of C_{60} molecules with an oxidation state of -3 could provide the foundation on which a metastable fcc Cs_3C_{60} film, which is likely to show a higher superconducting transition temperature than the current fulleride superconductors,[35] may be grown.

We first deposited a C_{60} monolayer at room temperature on a Au(110) surface precovered by 0.25 ML of Cs. The Cs-precovered Au surface displayed a ''streaky'' 1×2 diffraction pattern, indicative of disordered Cs adatoms distributed in the rows of the Au(110) 1×2 reconstruction. Upon deposition of 1 ML of C_{60}, we obtained a rather high-quality hexagonal LEED pattern with a C_{60}-C_{60} spacing of 10 ± 1 Å, consistent with the formation of a close-packed $C_{60}(111)$ layer on the substrate.

When starting with a 1-ML Cs-precovered Au(110) surface displaying a $c(2 \times 2)$ LEED pattern with relatively broad diffraction spots, prepared by dosing Cs at room temperature, deposition of a monolayer of C_{60} at room temperature leads to a relatively disordered overlayer structure. Diffraction patterns from a surface prepared by dosing Cs and C_{60} under these conditions display a liquidlike ring about the (00) spot. However, it was found to be possible to prepare a better-ordered monolayer of C_{60} in the -3 oxidation state, which displayed a clear well-defined hexagonal LEED pattern characteristic of a close-packed C_{60} structure: A well-ordered $c(2 \times 2)$ Cs layer was prepared by dosing Cs with the Au(110) sample at 373 K. A C_{60} multilayer was deposited on this surface, and annealed to 420 K for about an hour. The ratios between Au, Cs, and C peaks in Auger spectra taken after annealing showed the same ratios as in the monolayer prepared at room temperature. Similarly, photoemission and electron-energy-loss spectra were indistinguishable from 1-ML C_{60} on the 1-ML Cs-precovered Au surface prepared at room temperature. This strongly indicates that the annealing process produces well-ordered monolayer films with C_{60} molecules in an ≈ -3 charge state, which may be able to act as templates in the growth of fcc Cs_3C_{60} thin films.

While distillation procedures[11] produce a K_4C_{60} phase upon annealing, an ''overdoped'' C_{60} film to the appropriate temperature, it has been noted[70] that it is also possible to produce an A_4C_{70} stoichiometry from lower alkali-doping levels by preferential fullerene desorption, indicating that A_4C_m ($m = 60$ or 70) phases may be particularly stable in the bulk. However, the presence of a substrate can change this result considerably when one comes to consider monolayer films. When distilled, bulk samples of composition Cs_xC_{60}, $x = 1$ and 4, grown on Au(110) are annealed to beyond 800 K, strong desorption of fullerene molecules and/or Cs atoms occurs. The resulting film displays both Auger and photoemission signatures associated with a monolayer C_{60} film on 1-ML Cs. Further annealing to 900 K and beyond leads to a sharp decrease in the Auger signals from carbon and cesium relative to that of the substrate, and an increase in the intensity of Au photoemission features. The ratios between Auger C and Cs peaks, and the nature of the photoemission spectrum (indicating that the molecular charge state remains ≈ -3) point to a stoichiometric desorption of Cs and C_{60} at $T > 900$ K. The desorption behavior of the Cs and C_{60} suggests that the substrate may form chemical bonds with *both* the Cs adatoms and fullerene molecules which stabilize this composition; otherwise one would expect that the stoichiometric evaporation of A_4C_{60}, which distillation experiments,[75] as previously mentioned, indicate is the most stable bulk composition.

It is worth noting that for C_{60} monolayers deposited on Au(110) with Cs precoverages even as low as 0.25 ML (in which the CsC_{60} ratio is 0.91 ± 0.09), the dominant features in vibrational and electron-energy-loss spectra could be attributed to C_{60} in the -3 oxidation state. If one considers the vibrational spectra, one would expect the relative intensity of the $T_{1u}(4)$ mode to increase with charge transfer, while that of the $T_{1u}(1)$ mode should decrease. Therefore, if there is a mixture of fullerene oxidation states one should observe that the spectrum is dominated by molecules in the -1 oxidation state at low loss energies, and those in the -3 oxidation state at higher losses. Such an interpretation of the spectra suggests that fullerene molecules on the 0.25-ML Cs-precovered Au(110) surface acquire all the charge available from the Cs adatoms as well as charge from the gold substrate. At monolayer Cs coverages, in which the Cs:C_{60} ratio is approximately 4:1, we observe a fullerene oxidation state of ≈ -3, rather than -4, or higher, indicating that there is a competition between charge flow from Cs to Au and Cs to C_{60} as the alkali coverage increases.

VI. C_{60} MONOLAYERS ON 1.4-ML Cs/Au(110)

Let us now turn to Cs precoverages of about 1.4 ± 0.1 ML. Adsorption of a monolayer of C_{60} on Au(110) precovered with this amount of Cs leads to an electronic excitation spectrum, Fig. 1, markedly different from those observed at either higher or lower Cs coverages. Moreover, the features in this spectrum cannot be reproduced by a simple superposition of the higher- and lower-coverage spectra. In fact, the main feature of this spectrum, a sharp peak at 1.07 eV, is observed to persist to Cs precoverages of around 1.8 ML, coexisting with the features seen in the spectra for C_{60} monolayers adsorbed at ≥ 2-ML Cs coverages. Similar spectra have been observed for C_{60} at intermediate K coverages, upon annealing C_{60} deposited on K multilayers,[76] and in bulk

samples of K_4C_{60} (Refs. 28, 63, and 66) produced by both dosing thin films and by vacuum distillation.

A close agreement is once again exhibited between the gross features of the monolayer C_{60} film and TEEL spectra,[28] this time for C_{60} in the -4 oxidation state—K_4C_{60}. However, one particularly important difference exists between the electronic excitation spectrum from the monolayer of C_{60} adsorbed on the 1.4-ML Cs-precovered surface and bulk K_4C_{60}; that is, the presence of a strong continuum of low-energy electronic transitions. As has been noted for a C_{60} monolayer on the 1-ML Cs/Au(110) surface, the presence of a strong low-energy-loss continuum in electronic excitation spectra is indicative of a surface that is either metallic or a small-band-gap semiconductor.

Photoemission data obtained from bulk K_4C_{60} (Ref. 77) and Cs_4C_{60} (Ref. 77 and below) indicate that the $x=4$ stoichiometry, associated with a -4 fullerene charge state, is insulating. Since the LUMO state of C_{60} is triply degenerate, a simple rigid-band filling of the C_{60}-derived bands would suggest that the -4 oxidation state of C_{60} is metallic. That A_4C_{60} compounds are insulating is generally ascribed to a splitting of the triply degenerate t_{1u} LUMO-derived band of the bulk, possibly due to the strong electron-electron correlation effects[20,78] which arise from the narrow valence-band-widths of fullerene-derived materials. Infrared reflectivity data on bulk K_4C_{60} conflict on this issue; one study[58] indicates a metallic behavior which could be modeled by a Drude term and a harmonic oscillator, while another shows an insulating behavior with a relatively small band gap.[53] It is possible that the former measurement was made on a mixed-phase sample.

Recent Raman-scattering studies[30] seem to indicate that K_4C_{60} could, in fact, be close to being a "zero-gap" semiconductor, with a gap between empty and occupied states derived from the t_{1u} band of about 50 meV. Such a gap would be so small as to be masked by the tail of the elastic peak in both electronic and vibrational excitation spectra, and therefore not detectable by the experimental techniques employed in this paper.

We may turn to photoemission to provide firmer evidence of the fullerene oxidation state for 1-ML C_{60} on the 1.4-ML Cs-precovered gold surface suggested above. A strong peak, localized 0.5 eV below E_F (Fig. 2) and originating from a partly filled LUMO-derived band, is observed on a flat background characteristic of the Cs-precovered substrate. The shape of the spectrum suggests that the contribution from C_{60} in the monolayer film has a low, or possibly zero, density of states at the Fermi level. However, the proximity of the low-binding-energy peak to the Fermi edge means that a unique subtraction of the substrate contribution weighted to the low-binding-energy region is not possible. The binding energies of the LUMO- and HOMO-derived states of the C_{60} monolayer film on 1.4-ML Cs, at 0.5 and 2.3 eV, respectively, agree well with those of a bulk Cs_4C_{60} sample, Fig. 5, which have binding energies of 0.6 and 2.2 eV.

The dimensionality of the system under consideration may also play some role in determining the electronic excitation spectrum of C_{60} in the -4 oxidation state. To explore this we contrasted the electronic excitation spectra of 1-ML C_{60} on the 1.4-ML Cs-precovered Au(110) surface with
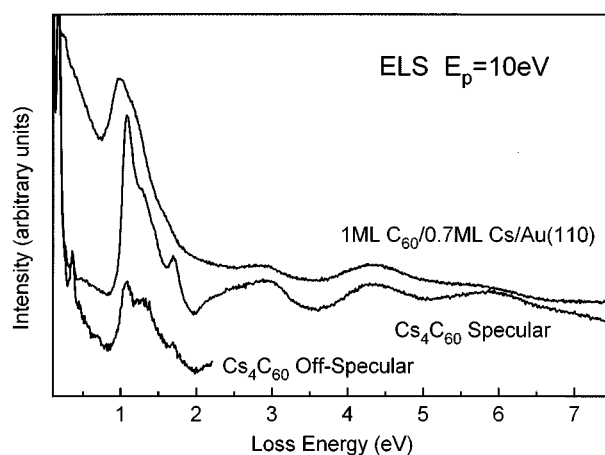

FIG. 8. Electron-energy-loss spectra from 1-ML C_{60} adsorbed on Au(110) precovered with 1.4-ML Cs compared with on-specular and off-specular spectra obtained from a bulk Cs_4C_{60} sample; see text for details.

those from a bulk Cs_4C_{60} sample, Fig. 8. The bulk sample displayed a clear LEED pattern: a distorted hexagon with spot separations corresponding to the bct (body-centered-tetragonal) (110) face of the bulk material.

As mentioned previously, when EEL spectra are obtained in the specular geometry, the dipole-scattering mechanism[56] means that electrons couple to the dipole field of excitations localized below the sample surface. In consequence, for the experimental conditions used in this paper, the penetration depth in the specular geometry is about 15 Å for an energy loss of 1 eV. In the off-specular geometry, the sampling depth will be determined by the inelastic mean free path of the low-energy electrons incident upon the surface. For an incident beam energy of 12 eV the mean free path is estimated to be about 8 Å (Ref. 42) (or perhaps less[56]). In the off-specular geometry we can thus expect about 67% of the loss intensity to arise from the outermost layer, compared to about 40% in the specular geometry. Therefore, our spectra, both on- and off-specular, are sensitive to the *surface region* of the bulk material, although an increased sensitivity is manifested in the off-specular spectra. However, the dipole selection rules that determine the relative intensity of the observed transitions also have an important role to play when considering the difference between on- and off-specular spectra. In a spectrum taken in the specular geometry, the relative intensity of dipole-allowed loss features is enhanced with respect to dipole-forbidden losses.

While the bulk material is well ordered, displaying both a LEED pattern and specular electron beam, the monolayer film is considerably less so, having only the latter. Consequently, there is likely to be a greater relative contribution of dipole-forbidden excitations in the specular spectrum of the monolayer in comparison to the bulk material. Examination of the off-specular electronic excitation spectrum of the bulk sample shows that it agrees well with that of 1-ML C_{60}/1.4-ML Cs/Au(110), indicating that the monolayer film and the surface layer of the bulk sample are very similar. It is notable, however, that there is a significant difference between the relative intensities of various components of the first strong peak, which are centered at 1.07, 1.36, and 1.65

eV, respectively, and the background in the on- and off-specular spectra from the bulk material.

The differences between on- and off-specular electronic excitation spectra obtained from the surface of the bulk film indicate either that certain features in the loss region around 1 eV are dipole active, or that there is a difference arising from the presence of bulk and surface electronic structure. It should be stressed, however, that the differences are in intensity rather than position—a simple Gaussian fit provides the same peak positions for the excitations around 1 eV (1.07, 1.36, and 1.65 eV) in both cases. What is of particular interest is that in the off-specular spectrum the 1.36-eV peak, which has only been observed as a asymmetry of the 1.07-eV feature in both bulk-[28] and surface-sensitive[66] measurements on K_4C_{60}, is clearly resolved as a separate peak. Previous interpretations of the electronic configuration that could lead to the observed low-energy electronic excitations[28,66] rely upon the fact that only features at 0.6, ≈ 1.1, and 1.65 eV are considered. These features are then interpreted as a transition between filled and unfilled components of the C_{60} LUMO band, the LUMO to LUMO+1 transition, and a transition between the HOMO band and the unfilled part of the LUMO.[28] The extra excitation resolved at 1.36 eV does not seem to fit simply into this interpretation.

Once again, a quantitative examination of the vibrational spectra from 1-ML C_{60} on the 1.4-ML Cs-precovered Au(110) surface provides an alternative means of assessing the oxidation state of the C_{60} molecules. We a observe downward shift of the first dipole active mode of 6 meV which the same as for the lower (1 ML) Cs coverage. This softening indicates that there are an extra 4.8 ± 0.7 electrons per C_{60} molecule. However, the $T_{1u}(4)$ manifests a larger shift than that observed at 1-ML coverage, moving by 12 meV to lower frequency. Calculation of the charge transfer implied by the shift of the highest-lying dipole-active mode gives 6.5 ± 0.7 electrons provided by the surface, leading to an average value of 5.6.

The effect of the likely molecular distortion of the C_{60} molecules,[60] which is not considered in the charged-phonon model,[59] is demonstrated by a direct comparison between the position of the $T_{1u}(4)$ mode determined by fitting the HREEL spectrum of Fig. 7 and the positions of the dipole-active modes observed in IR spectra of bulk A_4C_{60} (A = K, Rb).[53] The fits to the HREEL spectra indicate a peak at a frequency of 166.0 ± 0.5 meV. From IR spectroscopy,[53] the highest-laying dipole-active mode of bulk A_4C_{60} lies at about 168 meV, in reasonable agreement with the value obtained from HREELS. A second dipole-active peak, corresponding to a split component of the $T_{1u}(4)$ mode, is found at about 164 meV (163.7 meV in K_4C_{60}, 163.9 meV in Rb_4C_{60}) in the IR measurements. While our fits also show a peak at 163.8 ± 0.5 meV, in agreement with the position of this component of the $T_{1u}(4)$ mode, it is not possible to determine conclusively that this mode in our HREEL spectra is dipole-active.

The intensities of the $T_{1u}(2)$ and $T_{1u}(4)$ dipole-active modes of C_{60} coadsorbed with alkali metal, Fig. 7, are noticeably stronger with respect to the elastic peak than for C_{60} multilayers or C_{60} adsorbed on clean metal surfaces.[43] Furthermore the relative intensity of these modes increases with increasing C_{60} oxidation state. This in agreement both
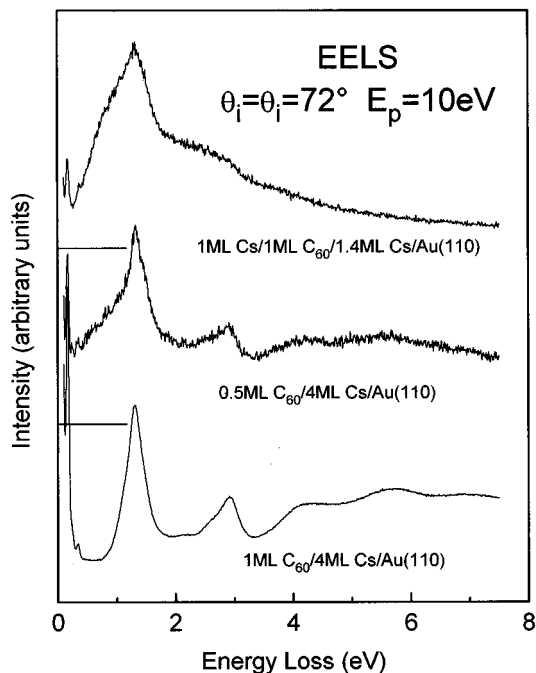

FIG. 9. Electron-energy-loss spectra, taken in the specular geometry, from 1-ML C_{60} on a 4-ML Cs-precovered Au(110) surface, 0.5-ML C_{60} on the same surface, and a sandwich structure of a Cs monolayer deposited on 1-ML C_{60} that had been grown on a 1.4-ML Cs-precovered Au(110) surface. Note the strong intensity below the peak at 1.34 eV in the latter two spectra, which corresponds to excitations associated with filling of the LUMO+1-derived states of the fullerene molecules. The spectra are normalized to the spectral intensity at 1.34 eV, and the solid lines represent the zero levels of the spectra.

with theory[59,60] and IR measurements on bulk alkali fullerides.[53,57,58] However, the dependence of the intensities of the losses in HREEL spectra upon the detailed order of the surface measured means that a *quantitative* examination of these intensity variations, as a function of the measured C_{60} charge state, is not productive.

VII. EELS OF C_{60} IN THE PRESENCE OF EXCESS Cs

It has been demonstrated[32–34] that when C_{60} molecules are adsorbed on a surface precoated with a rather thick film of potassium that significant transfer of charge into the LUMO+1 level of the C_{60} molecules can occur. This results in the transfer of more than six electrons to each fullerene molecule from the surrounding alkali atoms. The filling of the LUMO+1 is manifested in photoemission spectra by a shifting of the features associated with the -6 oxidation state to higher binding energy, and the appearance of a peak at low binding energy.[32,34] In a recent study[33] it was found that during the filling of the LUMO+1 state the C_{60} molecules are first insulating and then, at the highest coordinations studied, metallic. X-ray-absorption spectroscopy measurements showed that this ''saturated'' state did not involve complete filling of the LUMO+1 orbitals of the molecule.

When a *submonolayer* of C_{60} molecules (0.5 ML) is adsorbed on Au(110) precovered by 4-ML Cs, the resulting electronic excitation spectrum is somewhat different from

that observed for a complete C_{60} layer, as shown in Fig. 9. A series of excitations are now observed in what is the band-gap region of a spectrum obtained from a complete monolayer on the same Cs film (bottom curve, Fig. 9). These excitations indicate the possible presence of low-energy electronic transitions within the C_{60} molecules.

A multilayer film of Cs displays a strong peak at 2.9 eV arising from a surface plasmon, and a background at higher energies. The low-energy region of a spectrum from a Cs multilayer is rather smooth, which rules out a simple superposition of excitations from the Cs film and C_{60} as the source of the low-energy excitations of submonolayer C_{60} on multilayers of Cs. It is, however, possible that the outer layers of Cs may be perturbed due to the presence of C_{60}, resulting in low-energy excitations. These could then be suppressed upon the completion of a C_{60} monolayer due to the rather small inelastic mean free path of low-energy electrons in C_{60}. This hypothesis also appears to be incorrect, since a similar electronic excitation spectrum to that from a C_{60} submonolayer on multilayer Cs can be obtained if a single, complete, monolayer of C_{60} is sandwiched between Cs layers (1.4 ML below, 1 ML above) at 98 K, as shown in Fig. 9. Auger spectra indicate that the Cs in the sandwich structure does not diffuse below the C_{60} monolayer.

VIII. CONCLUSIONS

In conclusion, we have explored the adsorption of C_{60} on Au(110) surfaces precovered with varying quantities of Cs. The coadsorption of Cs has been demonstrated to alter radically the electronic structure and vibrational mode frequencies of the adsorbed fullerene molecules. When a single, complete, monolayer of C_{60} is adsorbed on a Cs-precovered Au(110) surface, electronic excitation and photoemission spectra indicate that, with increasing Cs dose, one obtains C_{60} oxidation states of approximately -3, -4, and -6, respectively, enabling us to ''tailor'' the charge state of molecules in a C_{60} monolayer.

The softening of the IR-active vibrational modes of the C_{60} molecules upon coadsorption with Cs support our interpretation of the photoemission and electronic excitation spectra, but serve to illustrate the important rule that molecular distortions play in determining the degree of phonon softening associated with a given fullerene oxidation state.

Comparison between measurements made on bulk $Cs_x C_{60}$ and monolayer films in which the C_{60} molecules have nominally the same oxidation state indicate that the surface layers of bulk alkali fullerides behave in a similar fashion to single monolayer films. This suggests that dimensionality effects associated with the coordination of C_{60} molecules with their nearest neighbors may not be particularly strong. However, the existence or otherwise of a difference between the electronic or vibrational excitations of C_{60} molecules in the outermost few layers of bulk alkali fullerides and those in deep the bulk itself remains an interesting open question, which does not appear to have been addressed satisfactorily in the literature. In particular, it is not clear if the differences we observe in on- and off-specular electronic excitation spectra from bulk $Cs_4 C_{60}$ arise from the dipole activity of some of the excitations or the presence of surface and bulk components.

The absence of any significant evidence for C_{60} charge states of -2 and -5 is rather interesting. This result may be attributed to (a) difficulties of preparation, for example the existence of these oxidation states over rather narrow Cs precoverage ranges; or (b) similarity between the spectra of these and the other oxidation states, preventing their detection; or (c) more fundamental reasons arising from the electronic structure of the fullerene molecules. Further measurements, for example on bulk substoichiometric bcc $Rb_x C_{60}$ with $x < 6$,[8] are required in order to resolve this important issue.

Finally, submonolayer quantities of C_{60} deposited on multilayer Cs films and sandwiches of Cs and C_{60} monolayers display low-energy excitations which fall in the band-gap region of C_{60} molecules in an oxidation state of -6. These features can be attributed to excitations involving electrons in the LUMO$+1$ band of C_{60}, occupied in the presence of excess Cs.

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