

Control of the growth of ordered C₆₀ films by chemical modification of Pt(111) surfaces

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Received 14 September 1998; accepted 6 December 1998

Abstract

The chemisorption of C₆₀ on Pt(111) results in strong bonding of the adsorbed molecules to the surface and immobile adsorbates, that lead to the growth of disordered C₆₀ films. We show that the Pt(111) surface can be chemically modified in a controlled manner, in order to grow ordered C₆₀ films. Modification of the Pt(111) surface was accomplished by pre-adsorbing oxygen adatoms, hydrogen adatoms, a graphite adlayer and an ordered C₆₀ adlayer. Growth of C₆₀ films on these modified surfaces was studied by Auger electron spectroscopy (AES), low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS) and UV photoelectron spectroscopy (UPS). Chemical modification of the surface inhibited charge transfer to the C₆₀ molecule in all cases, leading to weaker bonding and greater adsorbate mobility on the surface that contributed to the growth of ordered C₆₀ films. The ordering of the film can be expressed quantitatively as the intensity ratio of the dipole active T_{1u}(1) mode to the non-dipole active H_g(4) mode as determined by vibrational spectroscopy using HREELS. C₆₀ films grown on the graphite adlayer on Pt(111) were highly ordered because of the weak physisorption interactions between the adsorbate and surface. The degree of ordering upon modification of the Pt(111) surface in this study compares well to that of previous studies using different methods. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Fullerenes; Ordering; Vibrational spectroscopy; Chemisorption and physisorption; Charge transfer

1. Introduction

The growth of ordered C₆₀ films on metal and semiconductor substrates has been the objective of many recent studies [1–6]. In fact, ordering and disorder play a crucial role in both fullerene solids and fulleride intercalation compounds. For example, the electrical properties of C₆₀ and fulleride films are determined by ordering and charge transfer interactions, and it is important to control ordering in these films especially in the light of recent efforts to construct electrical devices composed of C₆₀ films [7].

The chemisorption and decomposition of C₆₀ on Pt(111) has been studied recently [8,9]. It was determined that monolayer C₆₀ is strongly bound to Pt(111) due to charge transfer of about two electrons from the surface to the C₆₀ molecule [9]. This resulted in low mobility of the C₆₀ molecules on Pt(111) at room temperature and contributed to the growth of a disordered film. It has been reported that ordering of C₆₀ on the Pt(111) could be brought about by annealing the films to 900 K [8], but we have determined that this

results in partial decomposition and graphitization of C₆₀ [9].

Apart from the use of various substrates to change the adsorbate-surface interactions [10] and high temperature annealing of the C₆₀ films to induce ordering on the surface [6,8], the presence of adsorbates on a particular surface prior to growth of C₆₀ may also be used to control the ordering and charge transfer interactions. The only experiments of this type reported so far are those studying these interactions in the presence of alkali metals [11,12], and those on H-terminated silicon surfaces [2,3]. The Pt(111) surface is quite reactive towards adsorbed hydrocarbon molecules and has also been reported to strongly interact with C₆₀ [8,9]. The Pt(111) surface enables us with the capability to form a wide array of ordered surfaces of progressively lower reactivity using various adsorbates [13,14].

The objective of this study was to chemically modify the Pt(111) surface in a controlled manner, and to investigate the growth of ordered C₆₀ films. C₆₀ films were grown and characterized on the Pt(111) surface at 300 K and 100 K, O(2 × 2)/Pt(111) surface, H-terminated Pt(111) surface, ordered graphite/Pt(111) surface and on an ordered C₆₀ adlayer/Pt(111) surface. These films were characterized by Auger electron spectroscopy (AES) for determining mono-

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layer coverage on the substrate, UV photoelectron spectroscopy (UPS) for determining the valence band electronic structure of the C₆₀ overlayers, work function measurements for probing substrate–overlayer interactions, temperature programmed desorption (TPD) to monitor the evolution of gaseous products from the reaction between C₆₀ and the adsorbates and finally high resolution electron energy loss spectroscopy (HREELS) to study the vibrational spectrum of the C₆₀ overlayers, particularly to quantify ordering and charge transfer interactions.

2. Experimental methods

Experiments were conducted in a three-level ultrahigh-vacuum chamber with a base pressure of 2×10^{-10} Torr, as has been described previously [9]. The top level was equipped with a double pass cylindrical mirror analyzer (CMA) which was used for AES, X-ray photoelectron spectroscopy (XPS) and UPS. The middle level was equipped with low energy electron diffraction (LEED) optics and a quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD) studies. The bottom level was equipped with an LK2000 spectrometer for HREELS. The Pt(111) crystal was mounted on two vertical Ta rods that were fastened to liquid nitrogen cooled copper blocks at the bottom of a differentially pumped XYZ-manipulator, with on-axis sample rotation and translation capability. The sample could be cooled to 90 K or resistively heated to 1200 K. The Pt(111) sample was cleaned by Ar⁺ ion sputtering at 5×10^{-5} Torr Ar pressure, followed by annealing to 800 K in 5×10^{-8} Torr O₂ and repeated flashing to 1200 K in vacuum. AES detected no impurities, LEED showed only sharp (1 × 1) spots and HREELS detected only a featureless background for clean Pt(111) [15].

AES data were obtained using an incident beam energy of $E_p = 3$ keV and at a resolution of 0.6% of the kinetic energy, with the incident electron beam current reduced to 1 μA to minimize electron beam damage of C₆₀. He(I) (21.2 eV) UPS spectra were obtained using a high pressure discharge lamp and spectra were acquired at an analyzer resolution of 300 meV. The energy axis of all the UPS-spectra presented in this paper were referenced to the Fermi level of the Pt(111) crystal ($E_F = 0.0$ eV BE). Based on this, we obtain a work function of 5.8 eV for clean Pt(111) which compares well with that reported earlier [8]. Work function measurements were made by measuring the onset of secondary electron emission using the UPS spectra. We estimate an accuracy of ± 0.2 eV for the value of $\phi_{\text{Pt(111)}}$ and estimate that $\Delta\phi$ values can be measured to at least ± 0.05 eV. The HREELS spectra were recorded in the specular direction with an angle of 60° from the surface normal and at a primary beam energy of 4.5 eV. The overall energy resolution of the spectrometer was about 6 meV (50 cm^{-1}), and the count rates at the elas-

tic peak were about 100 kHz for clean Pt(111). The spectra were normalized to the intensity of the elastic peak.

C₆₀ (99.9% purity, MER Corp.) was evaporated from a Ta boat on the various surfaces at a substrate temperature of 300 K. A thermocouple spotwelded on the boat was used to determine the temperature of the boat during the evaporation of C₆₀, and all depositions were carried out at a fixed boat temperature so that the surface coverages of carbon were reproducible. The absence of substantial hydrocarbon impurities from C₆₀ deposition was confirmed by the absence of any detectable C–H stretching mode in HREELS. AES studies of the deposition of C₆₀ on clean Pt(111) [9] and on each of the modified Pt(111) surfaces were used to determine the monolayer formation conditions, and we assigned monolayer coverage to the first ‘break point’ in the uptake curve. An upper limit for the C₆₀ coverage in the monolayer on Pt(111) would be given by a hcp monolayer with 1.15×10^{14} molecules/cm² or $\theta(\text{C}_{60}) = 0.1$ relative to the Pt(111) surface atom density.

The surfaces used in this study were prepared as follows.

- The O(2 × 2)/Pt(111) surface was prepared by dissociatively adsorbing 10 l O₂ on Pt(111) at 300 K, followed by annealing to 600 K to obtain an ordered (2 × 2) overlayer structure in LEED. The coverage was calibrated by TPD to be 0.25 ML oxygen.
- Two hydrogen precovered Pt(111) surfaces were prepared. The first by dissociatively adsorbing H₂ on Pt(111) at 300 K to give $\theta_{\text{H}} = 0.4$ ML and the second by exposing 300 l H₂ on Pt(111) at 100 K to obtain $\theta_{\text{H}} = 0.8$ ML.
- The graphite adlayer was grown on Pt(111) by annealing the crystal to 700 K in 40 l ethylene followed by annealing to 800–900 K to obtain ordered graphitic domains in LEED [16,17].
- The ordered C₆₀ adlayer on Pt(111) [8,9] was prepared by annealing multilayer C₆₀ films to 900–950 K to obtain a LEED pattern corresponding to two hexagonal domains rotated by $29 \pm 3^\circ$. This ordered C₆₀ adlayer is composed of polymerized C₆₀ along with some graphitic domains [9].

In all the above cases, TPD was used to check on reaction of the adsorbates with C₆₀. Upon heating 1 ML C₆₀ on the O(2 × 2)/Pt(111) surface to 700 K, we find that oxygen adatoms induce polymerization of C₆₀ [18].

3. Results

3.1. Growth of C₆₀ on Pt(111) and oxygen and hydrogen-precovered Pt(111) surfaces

HREELS spectra of monolayer and multilayer C₆₀ films grown on clean Pt(111) at 300 K are shown in Fig. 1. The C₆₀ mode assignments were made based on those in the literature [3,6]. Multilayer C₆₀ films show dipole active

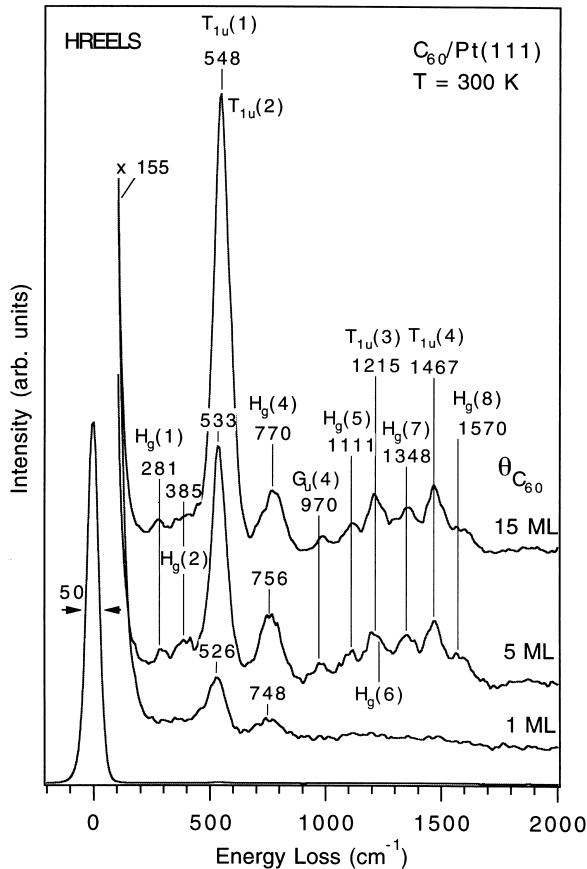


Fig. 1. HREELS studies of monolayer and multilayer coverages of C_{60} on Pt(111) at 300 K

modes $T_{1u}(1)$, $T_{1u}(3)$ and $T_{1u}(4)$ at 548, 1215 and 1467 cm^{-1} respectively, and a shoulder for the $T_{1u}(2)$ mode at 600 cm^{-1} . In addition these films show losses for various non-dipole active modes, the most prominent of them arising from the $H_g(4)$ mode at 770 cm^{-1} , the $G_u(4)$ mode at 970 cm^{-1} , $H_g(5)$ mode at 1111 cm^{-1} , $H_g(7)$ mode at 1348 cm^{-1} , and the $H_g(8)$ mode at 1570 cm^{-1} . These results suggest that multilayers of C_{60} grow as disordered films on Pt(111) at 300 K. Another feature quite clear from Fig. 1 is that the $T_{1u}(1)$ mode, which is very sensitive to charge transfer [19–22], shows a shift of about 20 cm^{-1} as the surface coverage of C_{60} increases from 1 to 15 ML. Assuming solid C_{60} properties for the 15 ML film and using the criterion described by Pichler [19], it may be concluded that about two electrons are transferred from the Pt(111) surface to the C_{60} molecule at $\theta(C_{60}) = 1$ ML [9].

In order to deactivate the Pt(111) surface and promote weaker interactions with C_{60} , oxygen and hydrogen adatoms were pre-adsorbed on Pt(111). The effects of these adsorbates on charge transfer to C_{60} and ordering of the C_{60} film were then investigated. HREELS spectra in Figs. 2 and 3 show that the charge transfer from Pt to C_{60} is arrested for both of the adsorbate precovered surfaces. Oxygen adatoms on Pt(111) have a prominent peak at 475 cm^{-1} [13] which is just visible in the submonolayer C_{60} spectrum. This peak is

gradually overwhelmed by the deposition of C_{60} beyond 1 ML. The $T_{1u}(1)$ mode of C_{60} shows no appreciable shift from the 0.5 ML spectra to that for 15 ML C_{60} spectra. This shows that there is essentially no charge transfer to C_{60} from Pt(111).

Fig. 3 shows a similar case for the H-precovered surface with no shift in the $T_{1u}(1)$ mode as the surface coverage of C_{60} changes from 5 to 15 ML. Also included in Fig. 3 is the spectrum of the C_{60} monolayer adsorbed on a Pt(111) surface precovered with $\theta_H = 0.8$ ML at 100 K. The C_{60} peaks appear unshifted but the intensities are greatly altered. The $T_{1u}(1)$ mode appears with reduced intensity, while an intense peak develops at 245 cm^{-1} and probably corresponds to the $H_g(1)$ mode. Molecular hydrogen intercalates the C_{60} lattice at low temperatures [23] and it is not known if this is responsible for the growth of the disordered monolayer C_{60} film on this surface.

Fig. 4 shows a comparison of the HREELS spectra for solid C_{60} grown on the Pt(111) and the oxygen and hydrogen modified surfaces. The intensity ratio for the $T_{1u}(1)$ mode to the $H_g(4)$ mode is enhanced for C_{60} on the modified Pt surfaces (summarized quantitatively in Table 1). Furthermore, other peaks characteristic of disordered films such as the $G_u(4)$ (985 cm^{-1}), $H_g(5)$ (1111 cm^{-1}), $H_g(7)$ (1348 cm^{-1}) and $H_g(8)$ (1570 cm^{-1}) modes are reduced for the O-precovered surface and nearly absent for the H-

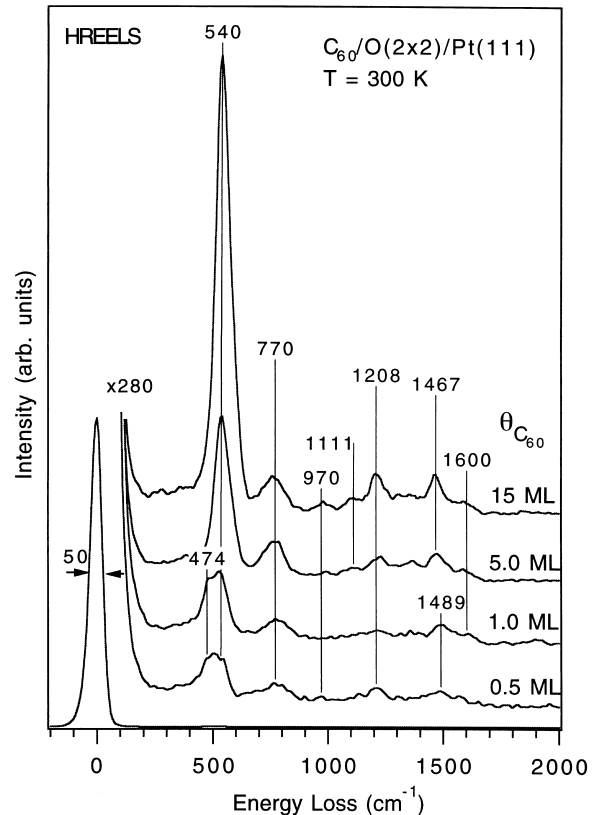


Fig. 2. HREELS spectra of C_{60} molecules deposited on $O(2 \times 2)/Pt(111)$ at 300 K.

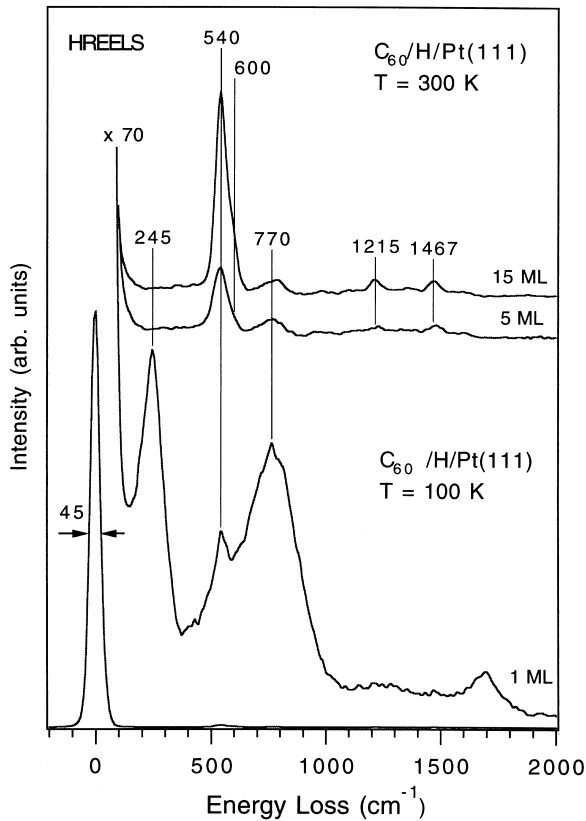


Fig. 3. HREELS spectra of C_{60} molecules deposited on H/Pt(111) at 100 K and 300 K.

precovered surface. All of these observations are indicative of a greater degree of ordering of the C_{60} films on these modified surfaces.

3.2. Growth of C_{60} on graphite precovered surfaces

The ordered graphite adlayer grown on Pt(111) using the method described in Section 2 [16,17], was used as substrate for the growth of ordered C_{60} films. STM results of Land et al. [16] showed that this graphite adlayer consists of small 20–30 Å graphite islands uniformly distributed over the surface, corresponding to a ‘single layer’ of graphite. The HREELS data of Fig. 5 show that C_{60} deposition on this graphite adlayer leads to the growth of a more ordered C_{60} film, as seen by the reduction in intensity of the $H_g(4)$ mode with respect to the $T_{1u}(1)$ mode (summarized quantitatively in Table 1), so that the former only barely rises above the background. There is no shift for the $T_{1u}(1)$ mode of the monolayer with respect to the multilayer, demonstrating that charge transfer from Pt to C_{60} is arrested by the graphite adlayer. All C_{60} desorbs by 600 K, consistent with C_{60} being bound to the graphite adlayer by only weak physisorption interactions. This again suggests that ordered C_{60} films may be obtained by inhibition of charge transfer to the C_{60} molecule for the monolayer film.

UPS studies of C_{60} deposited on the graphite adlayer on

Pt(111) are shown in Fig. 6 along with the spectra for the C_{60} monolayer deposited on clean Pt(111) at 100 and 300 K substrate temperatures. For the C_{60} monolayer on Pt(111) at 100 K, the distinct five band structure of C_{60} [24] appears clearly while for C_{60} monolayer on clean Pt(111) at 300 K, these features are broadened and shifted towards the Fermi energy. Based on the similarity of the latter results to that of polymerized C_{60} [25,26], we have suggested previously that Pt(111) induces polymerization at $T \geq 300$ K [9]. For C_{60} deposited on the graphite adlayer at 300 K, the distinct five band structure of C_{60} is seen even at 0.5 ML C_{60} coverage. This demonstrates that the graphite adlayer deactivates the Pt(111) surface and inhibits polymerization of C_{60} . The UPS spectra in Fig. 7 again confirm that all C_{60} including the monolayer is desorbed before the C_{60} sublimation temperature of 600 K, which indicates a weak physisorption interaction of C_{60} with the graphite adlayer.

3.3. Growth of C_{60} on an ordered C_{60} adlayer

The final modified Pt surface used for the growth of ordered C_{60} films was that of the ordered C_{60} adlayer, which was obtained by heating C_{60} multilayers on Pt(111) to 900 K to obtain hexagonal patterns and graphitic domains in LEED as described previously [8,9]. Proceeding on the premise that the growth of C_{60} on this ordered adlayer would result in an ordered multilayer film, C_{60} was deposited on

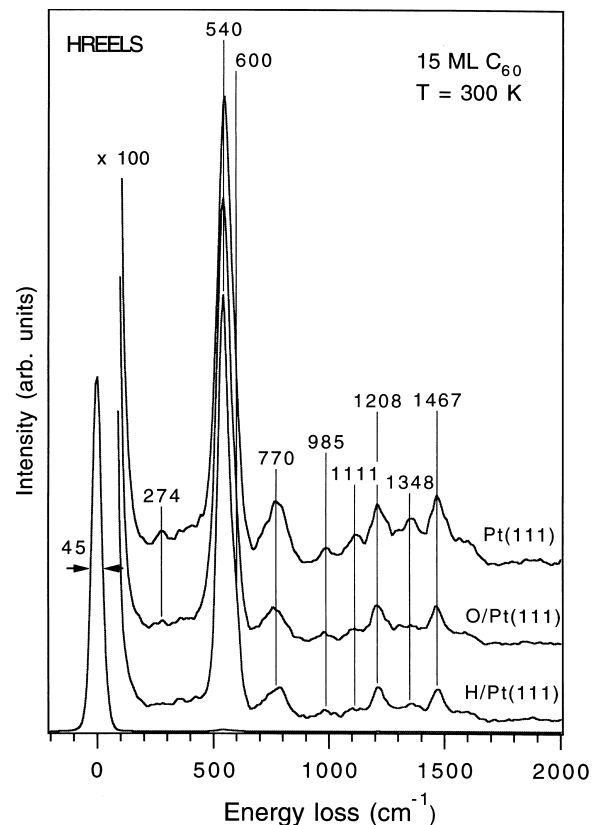


Fig. 4. HREELS spectra of 15 ML C_{60} molecules deposited on Pt(111), O(2×2)/Pt(111) and H/Pt(111) at 300 K.

Table 1

Enhancement of intensity ratio of the $T_{1u}(1)/H_g(4)$ modes for multilayer C_{60} films (10–15 ML) on the respective surfaces at 300 K, after modification. $E_p = 4.5$ eV for current study.

Surface	Intensity ratio	Reference
Pt(111)	7	this study
0.4 ML H/Pt(111)	13	this study
O(2×2)/Pt(111)	15	this study
Graphite adlayer/Pt(111)	16	this study
Ordered 1 ML C_{60} /Pt(111)	25	this study
Si(100) H(2×1)	11	[3]
Si(111) H(1×1)	13 (15) ^a	[2]
GaSe(001)	23	[6]

^a At 450 K substrate temperature.

top of this surface at 300 K. HREELS results from these studies are shown in Fig. 8. The ratio of the $T_{1u}(1)$ mode to the $H_g(4)$ mode is considerably enhanced (summarized quantitatively in Table 1) and the $T_{1u}(3)$ and $T_{1u}(4)$ modes rise up in intensity above the $H_g(4)$ mode. These point to a more highly ordered film compared to those discussed so far in this paper. Furthermore, the $T_{1u}(1)$ mode shows no appreciable shift, suggesting that the charge transfer from the substrate to C_{60} molecule is reduced.

Fig. 9 shows UPS difference spectra of the initially prepared ordered C_{60} adlayer which was used as the

substrate for the depositions described above. The HOMO peaks are clearly seen, although they are broader than those of the C_{60} monolayer on the graphite adlayer and on clean Pt(111) at 100 K. The C_{60} features of this ordered C_{60} adlayer are intact even though graphitic domains appeared in the LEED [9].

3.4. Work function measurements

The strong chemisorption interaction of the C_{60} monolayer with Pt(111) at 100 K is seen in the work function measurements shown in Fig. 10, which shows a minimum at monolayer coverage, while subsequent layers are physisorbed. For C_{60} /Pt(111) at 300 K, chemisorption extends beyond the monolayer coverage since the work function seems to decrease continuously until about 2 ML C_{60} /Pt(111). For C_{60} deposited on the graphite adlayer, work function results show a characteristic physisorption behavior that has also been verified by the HREELS and UPS warm-up studies. While HREELS results suggest charge transfer from Pt(111) to the monolayer C_{60} molecule which results in low mobility of C_{60} on the surface and contributes to the growth of a disordered film [9], the work function measurements suggest net charge transfer from C_{60} to the substrate as was also seen for C_{60} /Rh(111). However, given that results from other spectroscopic tech-

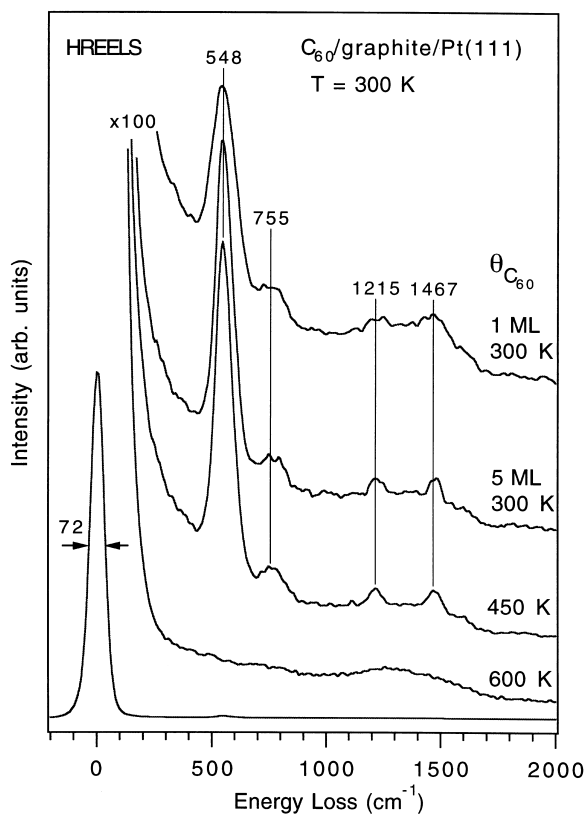


Fig. 5. HREELS spectra of C_{60} molecules deposited on single layer graphite/Pt(111) at 300 K, and then recorded after annealing at 450 K and 600 K.

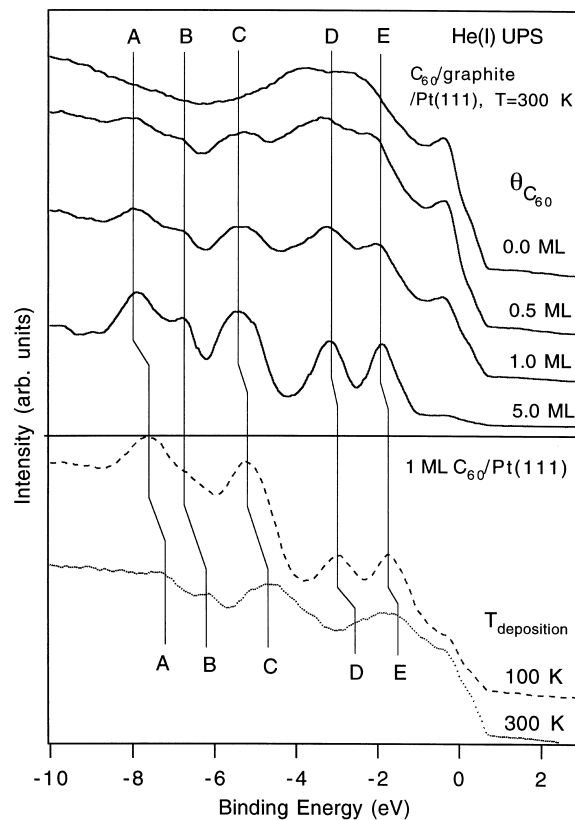


Fig. 6. He(I) UPS studies of monolayer and submonolayer coverages of C_{60} on graphite adlayer/Pt(111) at 300 K. The dots and dashed curves show UPS spectra of 1 ML C_{60} /Pt(111) at 100 K and 300 K.

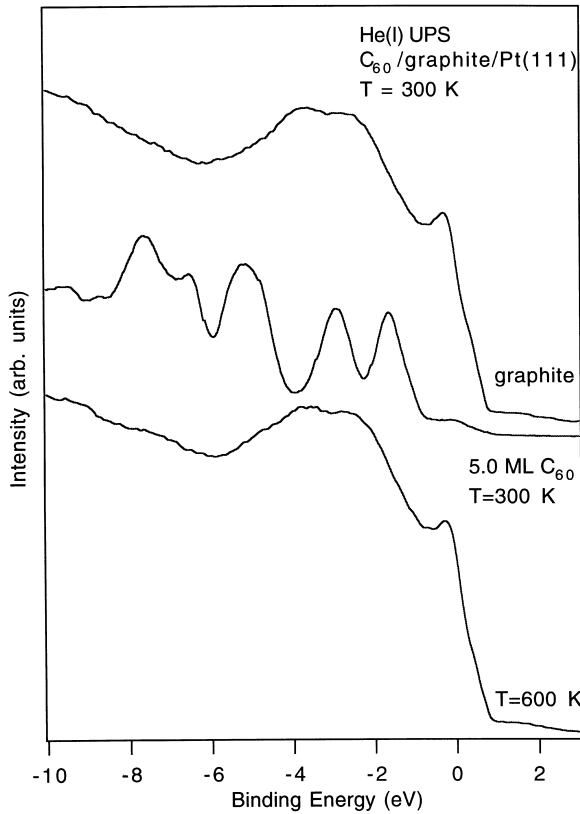


Fig. 7. He(I) UPS warm-up studies of 5 ML C_{60} on the graphite adlayer on Pt(111).

niques such as X-ray photoelectron spectroscopy (XPS) of C_{60} films are also consistent charge transfer to C_{60} , we do not choose to draw substantive conclusions about charge transfer from the work function data.

4. Discussion

The growth of ordered C_{60} films at room temperatures is of great importance for many growth processes, such as for example the low temperature growth of superfulleride phases [12,27] that exhibit interesting electrical [28] and possibly superconducting properties [29]. In these cases annealing to high temperatures to form ordered films [8,9] is not an option since the phases decompose above 350 K [28]. Modification of the Pt(111) surface by methods discussed in this study play an important role in such cases, since C_{60} films of high order may be grown on Pt(111) substrates at 300 K and possibly even lower. The most apparent difference between C_{60} growth on clean Pt(111) to that on the modified Pt surfaces, is that charge transfer from substrate to the C_{60} molecule is arrested for C_{60} growth on all the modified Pt surfaces. This leads to a more ordered film in all these cases and purely physisorption interactions in the case of the graphite adlayer on Pt(111). The ordered film could result from the enhanced mobility of C_{60} on the surface due to lack of the strong binding forces that accom-

pany charge transfer. Arresting the charge transfer by modifying the surface for physisorption interactions has been used by Hebard et al. [30] to induce long-range ordering of C_{60} thin films on Si(100) and Si(111) surfaces. Recently some HREELS studies of the same have also been undertaken [2,3], and the correlation of strong chemisorption with the growth of disordered films is suggested in these studies too.

Previous results [5] showed that disordered C_{60} films exhibit a broadened angle of the dipole lobe, which results in lower intensities for the dipole active modes with respect to the Raman active modes. Specifically, the intensity ratio of the dipole active $T_{1u}(1)$ mode and the Raman active $H_g(4)$ mode was used by Lucas [5] and subsequently by Gensterblum et al. [6] for the Si(100) and GaSe(001) surfaces, Dumas et al. for the Si(111) $H(1 \times 1)$ surface and Schmidt et al. [3] for the Si(100) $H(2 \times 1)$ surface, to judge the short-range order of the C_{60} films on the different surfaces. Table 1 summarizes this ratio for C_{60} growth on Pt(111) and Pt-modified surfaces obtained from the current study. The intensity ratio is enhanced from 7 for C_{60} films on clean Pt(111) to 16 and 25 for the C_{60} films on the graphite adlayer and the ordered C_{60} adlayer, respectively. These reflect a considerable increase in ordering, such that the degree of order of C_{60} films on the modified Pt surfaces compare well with those of other substrate surfaces, as shown in Table 1.

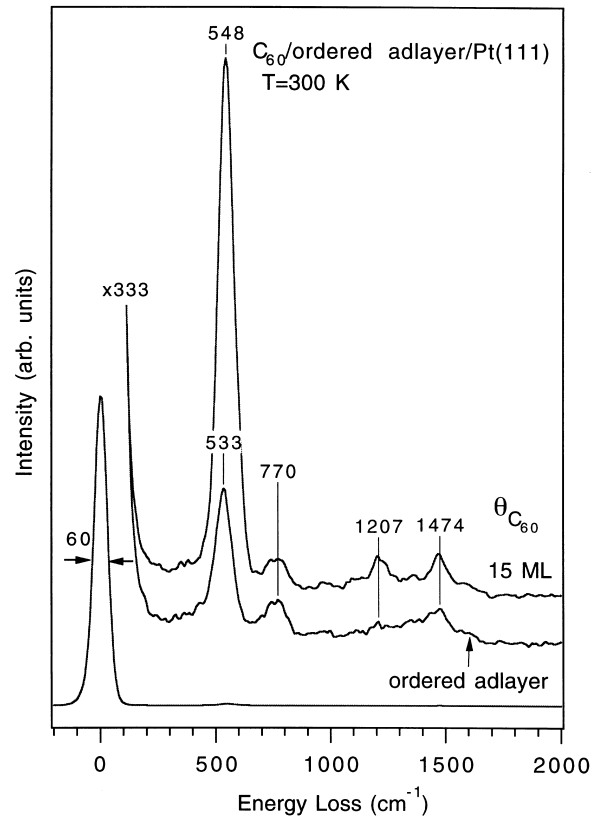


Fig. 8. HREELS spectra of ordered C_{60} adlayer on Pt(111), and 15 ML C_{60} deposited on the ordered C_{60} adlayer on Pt(111) at 300 K.

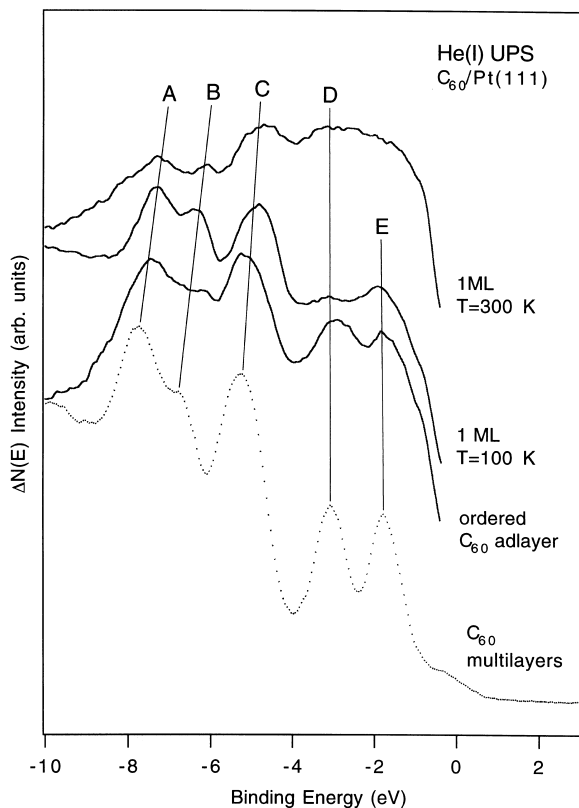


Fig. 9. He(I) UPS difference spectra of C_{60} monolayer deposited on Pt(111) at 100 K and 300 K, in comparison to that of the ordered C_{60} adlayer on Pt(111) and the He(I) UPS spectrum of C_{60} multilayers on Pt(111) at 300 K

It is of particular interest to note that the charge transfer from the substrate to C_{60} shows no systematic dependence on the surface work function. The Pt(111) surface has a higher work function than most transition and noble metal surfaces. The modified Pt surfaces presented in this study have about the same work function too (Fig. 10). Yet, charge transfer occurs from the high work function Pt(111) surface to C_{60} , but is arrested for all the modified Pt surfaces. Hunt et al. [22] have suggested that charge transfer has a greater dependence on type of surface (noble metal, transition metal, semiconductor etc.). The charge transfer of about two electrons per C_{60} molecule on the Pt(111) surface at $\theta(C_{60}) = 1$ ML, is much like that on other noble metal surfaces of Au(110) and Ag [22] and less than that for transition metal surfaces of Cr [10], Cu(110) [31] and Ni(110) [8,22].

5. Conclusions

Adsorbate C_{60} molecules are strongly bound to clean Pt(111) at 300 K due to charge transfer of about two electrons from the surface to the C_{60} molecule at $\theta(C_{60}) = 1$ ML. This results in immobile C_{60} molecules on the surface leading to the formation of a disordered film. Upon deposition of C_{60} on a Pt(111) surface modified by

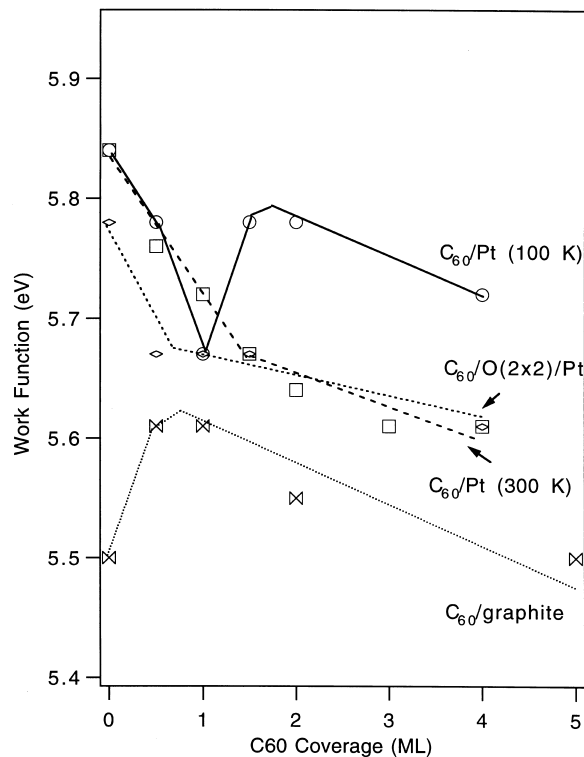


Fig. 10. Work function measurements of C_{60} deposited on Pt(111) and modified Pt surfaces as a function of C_{60} coverage.

pre-adsorbing oxygen adatoms, hydrogen adatoms, a graphite adlayer or an ordered C_{60} adlayer, the charge transfer to C_{60} is inhibited and this leads to greater mobility of the adsorbate molecules on the surface. This directly contributes to the growth of an ordered C_{60} film on the respective surfaces. The chemisorption interactions of C_{60} on Pt(111) are converted to purely physisorption interactions for C_{60} on the graphite adlayer on Pt(111).

Acknowledgements

We acknowledge support of this work by the Divisions of Chemistry and Materials Research of the National Science Foundation.

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