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Chemisorption and fragmentation of C_{60} on Pt(111) and Ni(110)

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The interaction between C_{60} and the Pt(111) surface has been studied by high-resolution electron-energy-loss spectroscopy, photoemission and Auger spectroscopy, and low-energy electron diffraction from 100 to 1150 K. C_{60} forms strong covalent bonds with Pt with very small charge transfer (<0.8 electrons/molecule from C_{60} to the substrate), has a low surface mobility, and decomposes at about 1050 K, leaving a multidomain graphitic surface layer. C_{60} decomposes also on Ni(110) at about 760 K, forming a carbidic carbon layer, which transforms into graphitic carbon at higher temperatures. Both surfaces act as a catalyst for the fragmentation process.

I. INTRODUCTION

The interaction between C_{60} and metal substrates is of great interest for the epitaxial growth of C_{60} and C_{60}-based compounds and for the understanding and the control of the charge-transfer mechanism between C_{60} and its environment. The charge state of the C_{60} molecule determines the electronic properties of the fullerene compounds, including superconductivity.[1]

The charge transfer and the interaction between metallic substrates and C_{60} has been measured on Au(110),[2] Au(111),[3] Ag,[4,5] Ni(110),[5] Ti, Cr, La, In,[6] Yb,[7] Rh(111),[8] Ta(110) (Ref. 9) and alkali-metal covered surfaces.[2,10] The charge transferred to the molecule has been found to vary from about one electron/molecule to about eight electron/molecule.[2,10] In order to bring out the correlations between the substrate characteristics and the nature of the C_{60}-metal bond, we extend the investigation to the surface with the highest work function, i.e., Pt(111), and we report on the geometric and electronic structure of the C_{60}/Pt(111) interface. The Pt surfaces are quite reactive towards absorbed molecules, therefore, the bonding to C_{60} is expected to be particularly strong.

Isolated C_{60} molecules are observed to fragment above about 1700 K,[11] while solid C_{60} has been found to decompose above 900 K.[12] It is interesting to investigate whether the fragmentation process is catalyzed by the substrate and to determine the maximum temperature at which C_{60} can interact with a solid surface without decomposition. Therefore, in this paper, we also report on the thermal stability of C_{60} monolayer adsorbed on reactive transition-metal surfaces like Pt(111) and Ni(110) up to about 1200 K.

II. EXPERIMENT

Thin films of C_{60} have been grown in an ultrahigh vacuum chamber (base pressure 5×10^{-11} mbar) on top of Ni(110) and Pt(111) surfaces by sublimation of pure (99%) C_{60} powder from a Ta crucible. The C_{60} powder was degassed for several hours at about 500 K before growing the sample. Sample cleanness and film thickness was determined by Auger electron spectroscopy (AES). During the whole experiment no contamination of the sample was detected by AES within our experimental accuracy (1%).

The electronic and vibrational spectra were collected by means of a Leybold Heraeus ELS 22 spectrometer. The spectra were measured in specular geometry and about 15° off the specular geometry, the incidence angle was 28°. The experimental resolution was about 20 meV for the electronic excitations and 5–7 meV for the vibrational excitations. The photoemission spectra were obtained using He I radiation (21.1 eV) and collecting the photoelectrons with a hemispherical analyzer (acceptance angle 5°) and an energy resolution of 80 meV. The surface geometry and ordering have been checked by low-energy electron diffraction (LEED). The sample temperature was measured with an accuracy of 10 K by a chromel-alumel thermocouple inserted in a small hole in the side of the substrate.

The C_{60} coverage was estimated using the Auger spectrum of 1 ML of C_{60} as the calibration point. It is well known that the interaction between the molecules is mainly van der Waals in solid C_{60}, while the first layer of C_{60} is chemisorbed on metallic substrates.[2,5,8] Consequently the first C_{60} layer on these substrates has a sublimation temperature substantially higher than that of the C_{60} molecules in the bulk ($\sim$450 K). The coverage of the one monolayer has, therefore, obtained heating a thick film of C_{60} at $T>600$ K or growing C_{60} at $T>600$ K.

III. RESULTS AND DISCUSSION

A. Adsorption on Pt(111)

Figure 1(a) shows the LEED pattern of 1 ML of C_{60} grown on top of Pt(111) maintaining the substrate temperature at 100 K. Only weak rings around the Pt(111) spots are visible, the diameter of which corresponds to a C_{60}-C_{60} distance of about 10 Å. This value has been obtained measuring the distances of the (00) LEED spot and the nearest Pt and C_{60} spots, the ratio of which results $\sim$3.5, and considering that the Pt-Pt distance is 2.77 Å.[13] No change occurs upon heating the sample up to 770 K. Above this temperature, some weak spots become visible and a well-ordered LEED structure appears at 900 K [Fig. 1(b)]. The well-ordered structure of the C_{60} ML is also reached growing the C_{60} film

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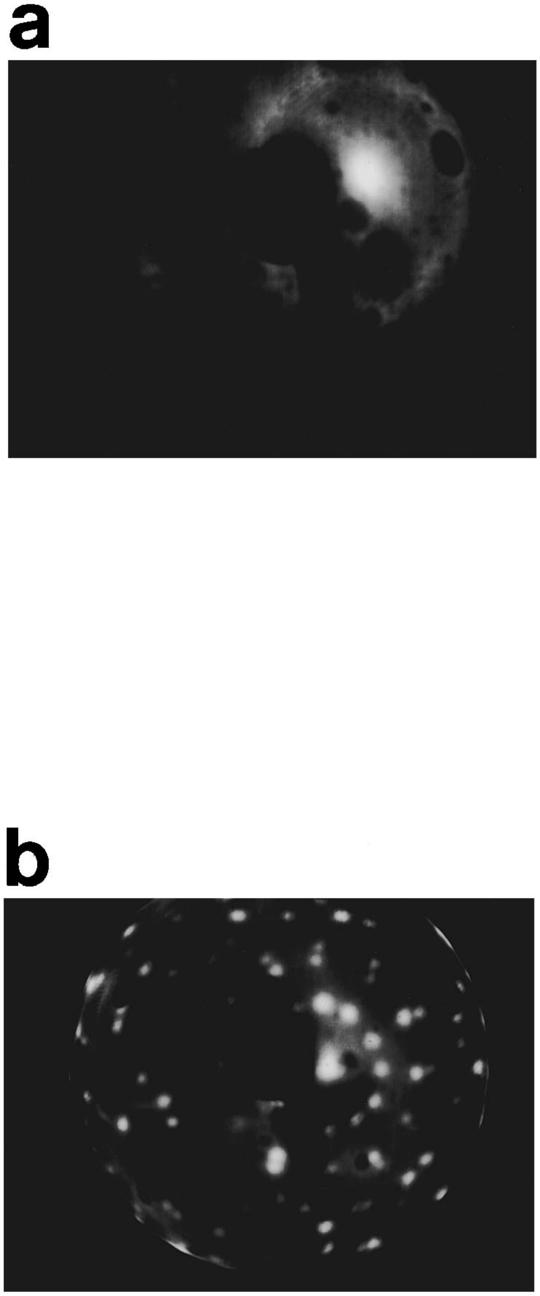

FIG. 1. (a) Diffuse ring observed in the LEED pattern of 1 ML of C_{60} on Pt(111) at $T<770$ K. The spot at the center of the ring is the (00) beam and the primary energy E_p is 20 eV. (b) LEED pattern of the well-ordered C_{60} monolayer obtained after annealing at $T>900$ K at $E_p=26$ eV.

on a Pt(111) substrate maintained at 900 K. This ordered structure is observed below ~1050 K and it disappears when the sample is annealed at 1050 K for ~1 min. After this treatment, the carbon *KVV* Auger signal decreases to a value corresponding to a C_{60} coverage of 0.9 ML. At a higher temperature ($1050<T<1150$ K), the LEED patterns consist of the Pt(111) spots and weak rings, which correspond to a lattice parameter of 2.2±0.5 Å, similar to that of graphite (2.4 Å). In this temperature range, the carbon *KVV* Auger signal is still significant, and at 1150 K the C coverage is about 60% of the low-temperature value.

The overlayer LEED pattern of Fig. 1(b) corresponds to two hexagonal domains rotated by 29°±3°, with a C_{60}-C_{60} distance of 10.0±0.3 Å [in the fcc solid C_{60}-C_{60} distance is 10.03 Å (Ref. 14)]. This pattern can be explained by the model shown in Fig. 2. In this model, commensurate structures are obtained placing the C_{60} molecules in two hexagonal domains rotated by 27.8°, with lattice vectors:

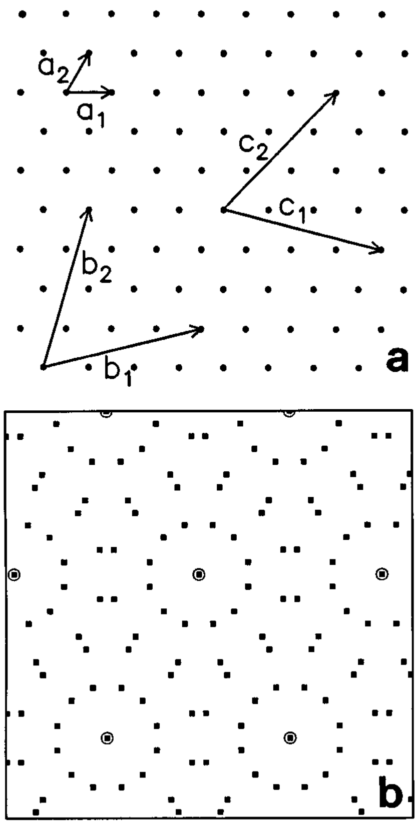

FIG. 2. (a) Proposed structures of the ordered C_{60} ML on Pt(111) and (b) computed LEED pattern. The filled squares indicate the C_{60} adsorbed molecules, the open circles the Pt substrate atoms.

$$\mathbf{b}_1=3\mathbf{a}_1+\mathbf{a}_2, \quad \mathbf{c}_1=4\mathbf{a}_1-\mathbf{a}_2,$$

$$\mathbf{b}_2=-\mathbf{a}_1+4\mathbf{a}_2, \quad \mathbf{c}_2=\mathbf{a}_1+3\mathbf{a}_2,$$

where $\mathbf{a}_i$ are the Pt(111) surface lattice vectors and $\mathbf{b}_i,\mathbf{c}_i$ are the vectors of the two overlayer domains of C_{60} molecules. The C_{60}-C_{60} distance is 10.0 Å and the simulated LEED pattern [Fig. 2(b)] is in very good agreement with our experimental data.

The stability of the C_{60} monolayer up to 1050 K indicates a strong interaction between the C_{60} molecules and the Pt(111) substrate. The molecules of the first ML sublimate at temperatures lower than 800 K on less reactive surfaces like Au(110) (Refs. 2 and 15) and GeS.[16] The disordered structure observed at temperature lower than 900 K indicates a low C_{60} mobility on Pt(111) surface and it is a further evidence of the strong interaction of the molecules with the substrate. Another indication of this strong interaction comes from the intensity of the LEED spots of the C_{60} ML, which is sensibly stronger than those of the ordered ML of C_{60} on Au(110) (Ref. 2) and Ni(110).[5] This points to a smaller Debye Waller factor, caused by a larger stiffness of the substrate

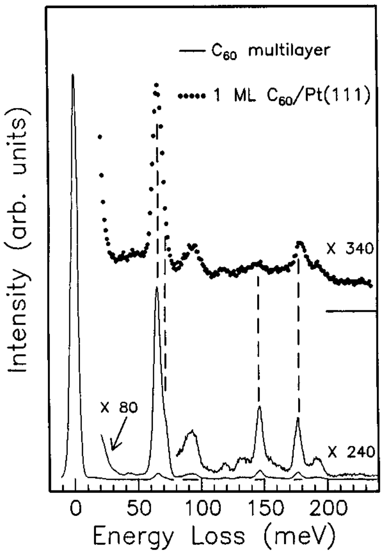

FIG. 3. Vibrational spectra of a monolayer of C_{60} on Pt(111) (dots) and of a thick C_{60} ordered film (solid line) in the specular geometry. The dashed lines indicate the energies of the T_{1u} modes.

C_{60} bond, or to a substantial displacement of the Pt atoms in contact with C_{60} from their equilibrium positions on the clean surface.

Figure 3 compares the vibrational spectra of an ordered ML of C_{60} grown on Pt(111) with that of ordered multilayer of C_{60}. The spectra have been taken in specular geometry with a primary electron energy of 5 eV. The four T_{1u} dipole active modes are indicated by dashed lines. The $T_{1u}(1)$ and $T_{1u}(4)$ modes at 66 and 178 meV are known to be sensitive to the C_{60} charge state.[17] It has been shown that these modes shift roughly linearly with the number of electrons transferred to the C_{60} molecule, in particular, the $T_{1u}(1)$ mode shifts of -1.25 meV/electron and the $T_{1u}(4)$ mode of -1.8 meV/electron.[17] A first analysis of the spectra of 1 ML of C_{60} on Pt(111) indicates that there is a decrease of the intensity of these modes, with respect to the C_{60} multilayer, but no shift is observed. A more quantitative analysis has been obtained by fitting the spectrum using the least-squares method. The spectrum has been fitted with two Gaussian peaks, plus a linear background in the energy range from 50 to 80 meV and by 6 Gaussian peaks plus a linear background in the energy range from 125 to 220 meV. The number of the Gaussian peaks has been determined by fitting the spectrum of the C_{60} multilayer. In this case, the spectrum is well resolved and the energy of each single mode is well known from the literature. The resulting energies of the four T_{1u} modes of the C_{60} ML are 65.6 ± 0.6 meV, 73.0 ± 0.6 meV, 145.3 ± 0.6 meV, and 177.7 ± 0.6 meV, respectively. These values are equal within our experimental error to those observed for the C_{60} multilayer (65.5 ± 0.6 meV, 72.0 ± 0.6 meV, 146.4 ± 0.6 meV, and 176.8 ± 0.6 meV).

Figure 4 compares the vibrational spectra of the ordered ML of C_{60} on Pt(111) with that of the C_{60} multilayer recorded in off specular geometry. These spectra have been used to determine the dipole active modes and to verify the possible charge transfer. It has been observed that many dipole forbidden modes, like the $H_g(4)$ at 94.8 meV and $H_g(8)$ at 194.5 meV, are strongly affected by the charge state of the molecule.[5,18] The $H_g(4)$ mode shifts by -0.25 meV/electron and the $H_g(8)$ mode by -1.85 meV/electron.[18] The $H_g(4)$ mode contributes to the spectral structure at about 94 meV, since its energy is 94.8 meV. It is impossible to determine the exact position of this peak in our high-resolution electron-energy-loss (HREEL) spectrum, because of the superposition of about five modes around this energy.[19] Studies of thin films of C_{60} doped with alkali metals have shown that the structure at about 94 meV shifts linearly with the charge state. The measured shift is of 1.3 ± 0.3 meV for the electron transferred.[20] Therefore, we expect a shift of this structure if the Pt to C_{60} charge transfer occurs. A Gaussian fit of the data in the region between 80 and 110 meV shows that, even in this case, no appreciable shift takes place. The result for the C_{60} multilayer is 93.0 ± 0.6 meV, while for the C_{60} ML on Pt(111) it is 94.1 ± 0.6 meV. The shift of the $H_g(8)$ mode at 194.5 meV affects the position of the higher-energy dipole forbidden peak in the off specular spectrum and, consequently, the high-energy cutoff of the spectral structure at about 200 meV. Also, in this case, no significant shift is observed in the position of the high-energy cutoff within the experimental error (1 meV) (Ref. 21) (see inset of Fig. 4). The result for the C_{60} multilayer is 200.4 meV and for one C_{60} ML on Pt(111) is 201.1 meV.

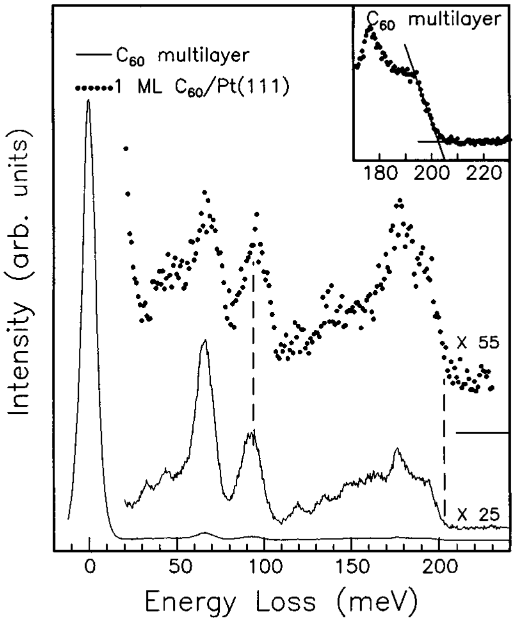

FIG. 4. Vibrational spectra of a monolayer of C_{60} on Pt(111) (dots) and of a thick C_{60} ordered film (solid line) in the off-specular geometry. The inset shows the determination of the high-energy cutoff in the C_{60} multilayer.

Although the structural analysis evidences a strong interaction between the C_{60} molecules and the Pt(111) surface, the observed shifts of the vibrational modes are within our experimental error. All the shifts are positive, and therefore, they indicate a charge transfer from the C_{60} molecules to the substrate. The upper limit is about 0.8 electron/molecule. Therefore, we conclude that the bond between C_{60} and the Pt(111) surface is mainly covalent.[22]

A possible reason for the negligible or negative charge transfer between this substrate and the C_{60} overlayer is the large work function of this surface [5.7 eV (Ref. 22)]. This

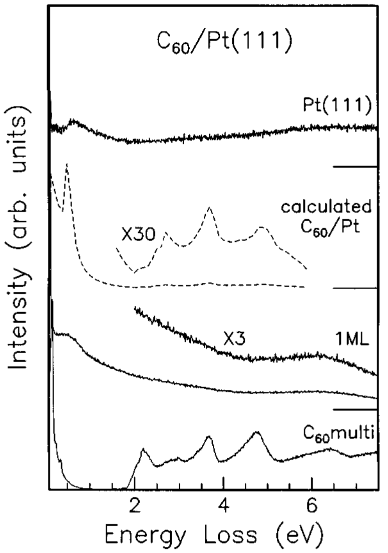

FIG. 5. EEL spectra of the electronic excitations of a thick film of C_{60}, of 1 ML of C_{60} on Pt(111) and of the clean Pt(111) surface. Also shown is the EEL spectrum of 1 ML of C_{60} on Pt computed using the two-layer model (see text).

value is substantially higher than that of other surfaces like Au(110) (5.3 eV), Ag (4.5 eV), and Ni(110) (5.0 eV),[23] where charge transfers between one and two electrons/molecule from the metal to C_{60} have been measured.

The strength of the bond between C_{60} and the substrate is also supported by the EEL spectrum of the electronic excitations. Figure 5 compares the electronic excitation spectra of a C_{60} multilayer, 1 ML of C_{60} grown on Pt(111) and the clean Pt(111) surface, in the energy range from 0.1–7.5 eV. The spectra have been measured in specular geometry with a primary electron energy of 12 eV. The C_{60} multilayer spectrum is a semiconductorlike spectrum, with an energy gap of about 2 eV and well-defined electronic transitions at about 2.2, 2.8, 3.7, and 4.4 eV.[2,24] The Pt(111) spectrum is characterized by a "surface-plasmon" peak at about 0.5 eV related to strong interband electronic transitions at 0.7 eV.[25] In the C_{60} on Pt(111) ML spectrum the typical features of the C_{60} multilayer are lost, the only feature present is a peak at about 0.5 eV. The C_{60} compounds where the molecules have a charge state lower than 6 have an EEL spectrum characterized by the plasmon of the partially filled lowest unoccupied molecular-orbital (LUMO) band at about 0.5 eV, and a sharp peak at about 1.3 eV caused by electronic transitions between the LUMO and LUMO+1 bands.[2]

The calculated EEL spectrum of C_{60} ML grown on the Pt(111) surface obtained from the two layer model[26] is shown in Fig. 5. We have used the measured dielectric function of bulk Pt (Ref. 25) and C_{60},[27] a primary beam energy of 12 eV, a scattering angle of 18° relative to the surface, and an analyzer acceptance angle of 2°. In this model, the interaction between C_{60} and the substrate is neglected. The simulated spectrum shows a strong peak at about 0.5 eV, caused by the Pt surface plasmon and the typical C_{60} structure at 2.2, 2.8, 3.7, and 4.4 eV. Therefore, it is not necessary to invoke the partial filling of the LUMO band to explain the 0.5-eV peak. The fact that the C_{60} features are not visible in the experimental spectrum indicates that a strong hybridization between the molecular orbitals and the metal states is present, causing large broadening of the molecular density of states. This effect is substantially stronger on Pt(111) than on Au(110) or Ni(110). C_{60} derived structures are still visible in the EEL spectra of 1 ML of C_{60} on these substrates, even if substantially broadened.[2,5]

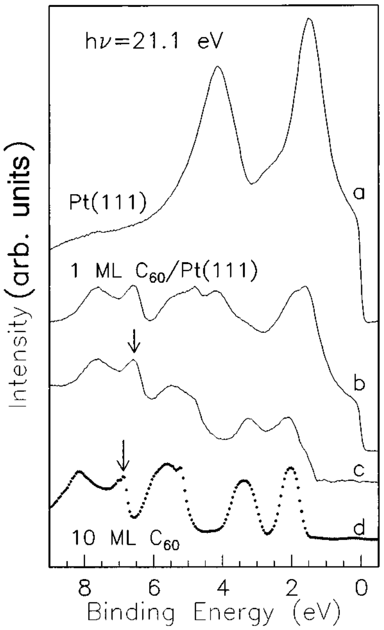

FIG. 6. Valence-band photoemission spectra of clean Pt(111) (a), 1 ML of C_{60} on Pt(111) (b), and an ordered 10-ML film of C_{60} on Pt(111) (d). The spectrum (c) is the difference between spectrum (b) and that of clean Pt(111) attenuated by a factor $Z=5$, and emphasizes the contribution of the C_{60} ML.

Additional evidence for substantial broadening of the C_{60} electronic states and negligible charge transfer is given by the photoemission spectra reported in Fig. 6. The spectra of the clean Pt(111) surface (curve a), of one ordered ML of C_{60} on Pt(111) (curve b), and of an ordered 10-ML C_{60} film (curve d) have been angle integrated by summing spectra taken at different emission angle in order to avoid band-structure effects. The spectrum c has been obtained by subtracting the spectrum of the clean Pt surface, attenuated by a factor $Z=5$, to that of the 1-ML film and represents the overlayer contribution. The comparison of this spectrum with that of the multilayer film shows that the highest energy filled states of C_{60} at about 2 eV and 3 eV of binding energy are 80% broader in the monolayer film (about 0.9-eV full width at half height). This broadening does not depend on the attenuation factor Z, for $3<Z<7$ and indicates appreciable hybridization between the substrate states and the highest occupied molecular-orbital (HOMO). The width of the HOMO is comparable to that of C_{60} on Al(111), another case in which strong C_{60}-substrate interaction is observed without evidence for charge transfer.[28] It is substantially larger than that of C_{60} on Au(110) (Ref. 20) and Rh(111),[8] which are about 0.5 eV.

Moreover, the narrow peak at about 6.7 eV in the photoemission spectrum of 1 ML of C_{60} on Pt(111) is well resolved as in the case of the C_{60} multilayer (indicated by arrows in Fig. 6). In the photoemission spectra of 1 ML of C_{60} on metals[4,20,29] or overlayers of metals on C_{60},[4,20,29,30]

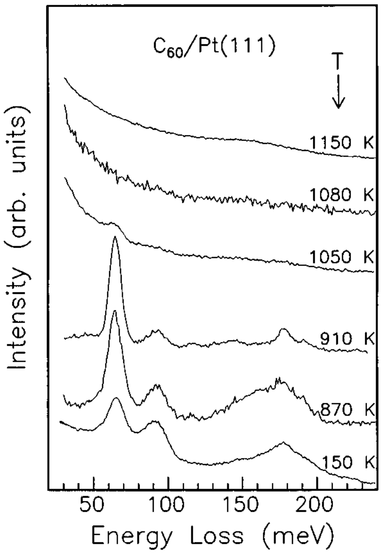

FIG. 7. Vibrational spectra of 1 ML of C_{60} on Pt(111) after annealing at different temperatures.

where a charge transfer occurs, the same peak broadens and reduces its intensity becoming visible as a shoulder of the main peak at about 8 eV. This may be a further evidence that in the case of 1 ML of C_{60} on Pt(111), the charge transfer to C_{60} is negligible.

B. C_{60} fragmentation on Pt(111)

Since LEED evidences high-temperature structural changes of the absorbed ML of C_{60}, we have analyzed the electronic and vibrational spectra of C_{60} ML on Pt(111) as a function of temperature. Figure 7 shows the evolution with the temperature of the vibrational HREEL spectrum of 1 ML grown at 100 K on top of Pt(111). Below 900 K no specularly reflected beam is present and the spectral structures are quite broad, similar to that of the off specular spectra, confirming the overlayer disorder observed by LEED. After further annealing for some minutes at about 900 K, the HREEL spectrum becomes similar to that of a well-ordered C_{60} monolayer, in agreement with LEED data. This spectrum remains unaffected after subsequent heating at $T<1050$ K. After heating the sample at 1050 K for a few seconds, a drastic change occurs in the spectrum. All of the C_{60} structures strongly decrease in intensity, broaden, and most of them almost disappear. At 1050 K, the carbon *KVV* Auger spectrum begins to decrease in intensity to a value that corresponds to a C_{60} coverage of 0.9 ML, but no substantial change in line shape is observed [Fig. 8(a)]. It is worth noting that this is the same temperature at which the ordered LEED pattern disappears (1050 K). After heating the sample for few minutes at higher temperature (1150 K), only a weak feature at about 150 meV is visible over a broad background, while the Auger signal is still significant (about 0.6 ML). This indicates that the C_{60} molecules fragment and a chaotic mixture of carbon materials are present on top of the surface. Part of the carbon atoms form disordered graphitic multidomains, as suggested by the presence of graphitelike rings in the LEED pattern.

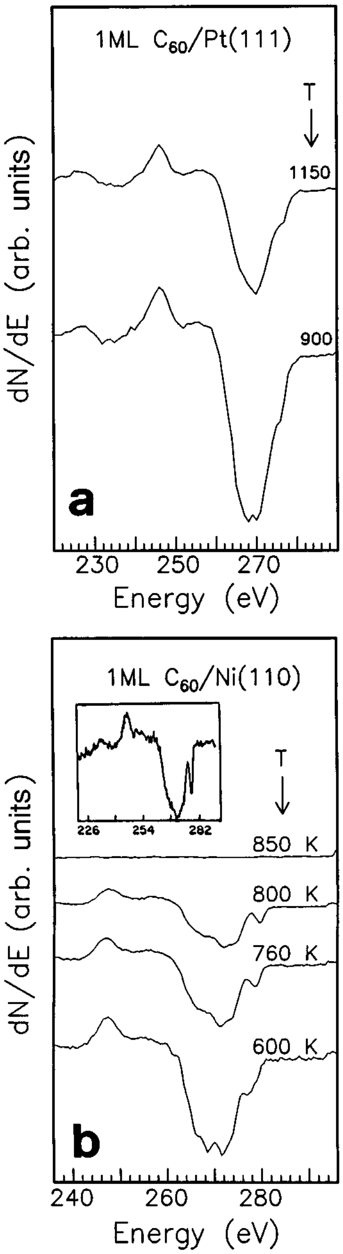

FIG. 8. Dependence of the Auger spectrum of 1 ML of C_{60} on Pt(111) (a), and on Ni(110) (b), on the annealing temperature. The inset in (b) shows the *KVV* Auger spectra of graphitic carbon on a Ni(110) surface (Ref. 31).

C. C_{60} fragmentation on Ni(110)

The C_{60} growth and interaction on Ni(110) has already been studied, showing a strong interaction and a charge transfer of 2±1 electrons/molecule. We have observed the same LEED patterns reported and discussed in Ref. 5 as a function of temperature up to 700 K. We focus our attention on the study of a well-ordered C_{60} ML on Ni(110) surface grown at 700 K. Upon heating this sample up to 760 K for a few minutes, the intensity of the *KVV* carbon Auger peak remains constant, while above this temperature, it decreases and changes shape [Fig. 8(b)]. The shape becomes very similar to that of graphitic carbon on Ni(110) [inset of Fig. 8(b)],[31] with the growth and shift of the structure at about

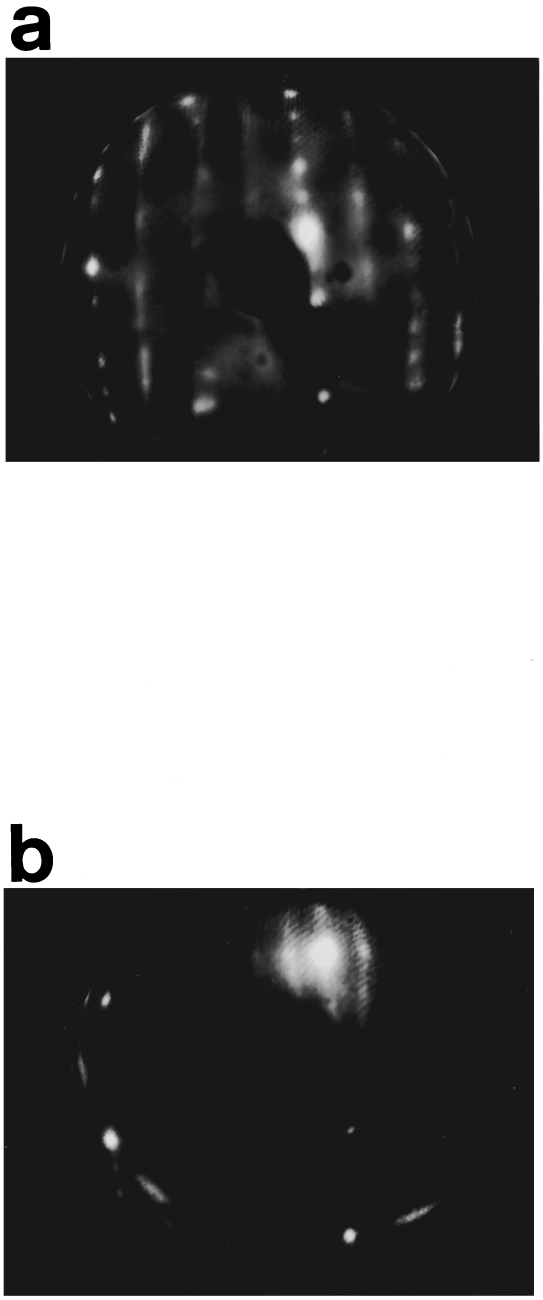

FIG. 9. (a) LEED pattern of a monolayer of C_{60} on Ni(110) after annealing at 760 K showing the carbidic (4×5) structure at $E_p=70$ eV. (b) After annealing at 800 K, graphitic rings superimposed to the (4×5) structure are visible ($E_p=64$ eV).

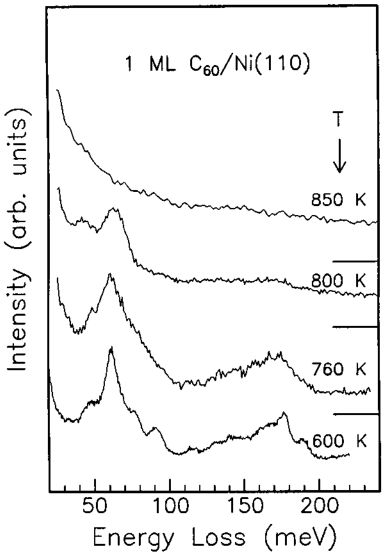

FIG. 10. Vibrational spectra of a monolayer of C_{60} on Ni(110) after annealing at different temperatures.

280 eV. The intensity of the *KVV* carbon peak decreases continuously up to 850 K, the temperature at which its signal completely disappears and the Auger spectrum of clean Ni is observed.

The LEED pattern of the ordered C_{60} ML grown on Ni(110) at 700 K is hexagonal. After heating the sample at 760 K for a few minutes, we obtain a (4×5) LEED structure, which is characteristic of atomic carbidic carbon on the Ni(110) surface [Fig. 9(a)].[32] The appearance of this pattern is connected to the decrease of the C coverage. When the sample is heated at 800 K, graphitelike rings appears superimposed to the (4×5) LEED pattern [see Fig. 9(b)]. These rings correspond to a lattice vector of 2.2 ± 0.2 Å, which is close to that of graphite (2.4 Å). At 850 K, only the LEED pattern of a well-ordered Ni(110) is observed.

From these results, we deduce that the C_{60} molecules on Ni(110) begin to fragment above 760 K, spreading atomic carbon on the surface. At about 800 K, graphitic domains are formed.

Further evidence of the C_{60} fragmentation and the formation of graphitic domains is provided by the HREEL vibrational spectra. After annealing the well-ordered C_{60} ML above 760 K, the spectrum changes in shape as shown in Fig. 10. In particular, after heating the sample at 800 K, the HREEL spectrum becomes very similar to that observed for the C_{60} on Pt(111) at 1050 K (i.e., when the LEED pattern shows the graphitelike rings). Above 850 K, no C_{60} structures are visible, and the spectrum is similar to that of the clean Ni(110) surface.

The decomposition rate in the gas phase[11] and in the solid phase of C_{60} (Ref. 12) can be described by a single Arrhenius equation with an activation energy of about 2.3 eV.[12] The time constant of this decomposition process estimated from the parameters of Ref. 12 is about 2×10^4 s at 1050 K and about 10^9 s at 760 K, i.e., several orders of magnitude longer than the time constants that we observe on Pt(111) and Ni(110), which are of the order of $10-10^2$ s. This indicates that the decomposition process is catalyzed by these surfaces. Both Pt and Ni do not form stable bulk carbides and the solubility of C in these metals at the C_{60} decomposition temperature is less than 1 at. %.[33] The peak to peak amplitude of the Auger C signal changes by less than 25% during the decomposition of C_{60} on Pt(111) between 910 and 1080 K, therefore, most of the carbon atoms remain on the surface after the fragmentation. Significant diffusion into the bulk occurs at higher temperatures. On the contrary, the C Auger intensity decreases by more than 50% during the C_{60} decomposition on Ni (720–800 K). Carbon diffusion into the bulk and C_{60} fragmentation occur simultaneously, since the temperature at which atomic C readily diffuses into Ni(110) is lower than the decomposition temperature [about 650 K

(Ref. 34)]. The temperature at which C_{60} decomposes on Ni(110) is close to that observed on Rh(111) (Ref. 8) and substantially lower than that observed on Si(100) (Ref. 35) (about 1000 K) and Si(111) (about 1250 K) (Ref. 36).

In conclusion, our data indicate that a strong covalent bond with negligible charge transfer forms between C_{60} and the Pt(111) surface. Moreover this surface, like the Ni(110) and the Rh(110) surfaces, acts as a catalyst for C_{60} decomposition. We expect that all the other transition-metal surfaces, particularly those of carbides forming metals, show a similar behavior.

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[22] A study of the vibrational spectrum of C_{60} interacting with alkali metals, noble metals, transition metals, and La (Refs. 2, 5, and 20) has shown that the shift of the vibrational modes is a function of the charge state of the molecule only, within our experimental error. The type of the chemical bonding plays a minor role.

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