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Vibrational dynamics of fullerene molecules adsorbed on metal surfaces : a synchrotron infrared study

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ABSTRACT

Infrared spectroscopy of chemisorbed C₆₀ on Ag(111), Au(110) and Cu(100) reveals that a non-IR active mode becomes active upon adsorption and that its frequency shifts proportionally with the charge transferred from the metal to the molecule by about 5cm⁻¹ per electron. The temperature dependence of the frequency and the width of this IR feature has also been followed for C₆₀/Cu(100) and was found to agree well with a weak anharmonic coupling (dephasing) to a low frequency mode which we suggest to be the frustrated translational mode of the adsorbed molecules.

Additionally the adsorption is accompanied by a broadband reflectance change which is interpreted as due to the scattering of conduction electrons of the metal surface by the adsorbate. The reflectance change allows to determine the friction coefficient of the C₆₀ molecules which results to be rather small ($\sim 2 \times 10^9$ s⁻¹ for Ag and Au, and $\sim 1.6 \times 10^9$ s⁻¹ for Cu), consistent with a marked metallic character of the adsorbed molecules.

Pre-dosing of alkali atoms onto the metal substrates drastically changes the infrared spectra recorded during subsequent C₆₀ deposition: antiabsorption bands, as well as an increase of the broadband reflectance occur and are interpreted as due to strong electron-phonon coupling with induced surface states.

Keywords: Infrared reflectance, fullerenes, synchrotron infrared, friction, surface.

1. INTRODUCTION

Electron-phonon coupling plays an important role in determining the physical properties of fullerene-based materials, its most important manifestation being the superconductivity exhibited by fullerides (A_xC₆₀, A=alkali or alkaline earth metal) at transition temperatures only exceeded by those of the cuprates. Not all of the A_xC₆₀ salts are superconductors, they can also be either semiconductors or metals and present a variety of crystallographic phases, depending on the concentration and the type of metal atoms used to form the compound.¹ Electron-phonon coupling does not only determine the transport properties of these materials it also has a strong impact on the vibrational spectra, as was first found by Fu *et al.* who discovered the giant vibrational resonances in K₆C₆₀.² Later on it became clear that the vibrational spectra of all metal fullerides³ exhibit mode-specific shifts and intensity variations associated with electron donation to the fullerene molecules from the metal atoms intercalated into the interstitial sites of the lattice. The physical origin of the effects of the charge transfer on the phonon spectrum were clarified by *ab-initio* calculations⁴ for K₆C₆₀: the excess electrons are accommodated in the lowest unoccupied (t_{1u}) orbitals of C₆₀ which have antibonding character⁵ leading to a structural relaxation of the molecule. This structural relaxation is primarily responsible for the frequency shifts, more specifically for the softening of the tangential modes. The intensity variations on the IR spectrum are instead mainly brought upon by electron-phonon coupling which plays an important role in the vibrational excitation process. A first theoretical approach to the problem was the charge-phonon model⁶ which considered the coupling of the dipole-active T_{1u} modes to the t_{1u}-t_{1g} electronic transitions. This model has subsequently been suggested to be oversimplified since couplings to many different electronic excitations have to be considered to get a consistent picture.⁴ However, the detailed understanding of the electron-phonon

coupling in the fullerides is hampered by the complicated interplay between structural, vibrational and electronic properties in these compounds.

In this paper we contribute to this subject by investigating the electron-phonon coupling signatures in the vibrational spectra of C₆₀ deposited onto metal surfaces. There the fullerenes are chemisorbed but the degree of hybridization between C₆₀ orbitals and the substrate electronic states and the amount of charge transfer varies greatly from substrate to substrate. However, adsorbing the fullerene molecule on well defined substrates enables one to control the physical properties of the overlayer with a precision unmatched in bulk materials. Mode-specific shifts and intensity variations similar to those in fullerides have been observed in high-resolution electron energy loss^{8,9,10} and infrared¹¹ spectra of C₆₀ monolayers on bare and alkali-covered metal surfaces. Our aim here was to take advantage of intrinsic high brightness, high stability, and proportionality to the stored electron beam of synchrotron IR spectroscopy to elucidate the physical origin of these changes by recording also the IR broadband absorption on which the specific vibrational bands are superimposed. Both the vibrational bands and the broadband absorption revealed a surprisingly rich scenario for the vibrational dynamics of C₆₀ comprising both electron-phonon and purely vibrational coupling. During the adsorption on Ag(111), Au(110) and Cu(100) we found a broadband reflectance decrease typical of what Persson and Volokitin¹² were able to explain as a friction phenomenon between the adsorbate vibrations with a component of velocity oscillating parallel to the surface (such as the frustrated translations and rotations) and motion of the conduction electrons within the skin depth and driven by the external electric field brought about by the IR light (see also ref.13). At the same time a vibrational mode which is not IR-active for the isolated molecule appears and shows a temperature dependent frequency and bandwidth change characteristic of a change in adsorption state and an anharmonic coupling¹⁴ to a low frequency mode. This low frequency mode lies within the energy domain of the frustrated translation of the C₆₀. When the metal surfaces were pre-dosed with potassium we found an antiabsorption lineshape for the new IR-active mode accompanied by an increase in broadband reflectance during C₆₀ adsorption, indicating that now the coupling of the vibrational mode to induced surface state has become the process which dominates the IR spectrum.

2. EXPERIMENTAL

The IR spectra were collected with the synchrotron infrared reflection-absorption spectroscopy set-up of beamline U4IR at the National Synchrotron Light Source which is described in detail elsewhere¹⁵. The use of a synchrotron source is strictly necessary for these experiments since a thermal infrared source is subject to temperature fluctuations which cause uncertainty in the incident beam intensity. The synchrotron radiation brightness, on the other hand, is determined only by the stored current which can be accurately measured for the normalization of each of the spectra. This normalization procedure can be adopted only if another crucial requirement is fulfilled, i.e. the electron beam position in the ring remains stable during the whole experiment. At the National Synchrotron Light Source this stability is achieved by means of a global feedback system¹⁶ developed some years ago, which continues to be improved. The broadband IR-reflectance change and the absorption bands were measured during C₆₀ deposition collecting a spectrum (256 co-added scans) at a resolution of 4 cm⁻¹ over each 90 s of dosing. In order to avoid instabilities, which can result in intensity oscillations within the spectral distribution of the broadband reflectance change, we adopted a stringent procedure of data selection: 5 spectra of 256 scans each were recorded before starting the fullerene deposition; the last spectrum was ratioed to the first, and exposure to C₆₀ was initiated only if a "flat" baseline was obtained between 180 and 500 cm⁻¹ for the bolometer, or 300-3000 cm⁻¹ for the Cu:Ge detector. C₆₀ was deposited onto the metal surfaces by resistive heating of a tantalum crucible to about 700 K. The pressure in the chamber rose from 1x10⁻¹⁰ Torr to 9x10⁻¹⁰ Torr during dosing. In order to avoid an additional source of baseline drift in the spectra due to the thermal loading of the metallic substrate, a deposition rate of approximately 15 minutes per monolayer was used. The deposition time corresponding to the completion of one fullerene monolayer (ML) was calibrated by saturating the substrate kept at or slightly above (570 K) the desorption temperature of the multilayer (455 K)¹⁷ and measuring the ratio of the overlayer/substrate Auger peaks. Auger spectra were also collected after each IR experiment to check the fullerene coverage. At the beginning of each experiment, the Ag(111), Au(110) or Cu(100) single crystal was cleaned by cycles of Ar⁺ sputtering followed by annealing to restore the surface ordering, until no impurities could be detected by Auger spectroscopy and sharp LEED patterns were observed. For alkali deposition during which the pressure in the chamber never exceeded 2x10⁻¹⁰ Torr, a thoroughly outgassed K getter was used. For each exposure, the same data selection procedure was followed to make sure that no drift was present. The substrate temperature was monitored by a thermocouple inserted in a hole in the substrate and could be varied by filling the sample manipulator with liquid N₂ and by resistive heating.

3. RESULTS AND DISCUSSION

Figure 1 shows the IR spectra collected during deposition on a Cu(100) substrate held at room temperature. One clearly distinguishes only one IR band at 1440 cm^{-1} superimposed on a broadband IR reflectance change. The amplitudes of both features increase with fullerene coverage and saturate when a complete monolayer is reached. We note that with our slow deposition rate the growth at room temperature proceeds layer by layer as verified by measuring the ratio of the overlayer/substrate Auger peaks vs. deposition time (not shown). The overall reflectance shape remains unchanged.

Figure 1: Infrared spectra in the $400\text{--}2500\text{ cm}^{-1}$ region of a Cu(100) surface collected during C_{60} deposition at room temperature. A broadband reflectance change as well as one absorption band at 1440 cm^{-1} are clearly seen.

Similar experiments were performed on Ag(111) and Au(110) and the broadband reflectance change associated with the deposition of one monolayer of C_{60} on each of the three single crystal substrates is shown in figure 2. The specific vibrational bands also visible in the spectra will be discussed later. Here we note that the broadband IR reflectivity change has a frequency dependence in good agreement with the theory which considers the electronic energy dissipation arising from the scattering of the substrate conduction electrons by the adsorbate.^{12,18} The relative motion between the sliding adsorbate and the electron "fluid" will give rise to a drag-force action on the adsorbate. So one can define an electronic friction coefficient which has been set to be equal to the inverse lifetime of the frustrated translation of the adsorbate due to creation of electron-hole pairs. The microscopic theory of the friction¹⁹ based on the Newns-Anderson model of chemisorption, expresses this electronic friction coefficient in terms of the width of the adsorbate-induced resonance state, Γ , the adsorbate-induced density of states at the Fermi level, $\rho(E_F)$, and a term which accounts for the electron transfer interaction between the adsorbate orbital and metal states. According to the diffuse scattering model, the friction coefficient can be obtained from the asymptotic "high frequency" value of the IR reflectance change

$$\Delta R_p = -\frac{4 n_a M}{c n m \cos \Theta} \frac{\eta}{F}$$

where F is a correction factor which is important at grazing incidence geometry²⁰, $F = \cos^2 \theta / (\cos^2 \theta + \omega^2 / \omega_p^2)$, and θ , m , ω_p , ω and n_a are the angle of incidence, the electron mass, the plasma frequency, the frequency of the light and the density of the adsorbate respectively. The broken lines in figure 2 are the fits of the experimental data to this theory, which were obtained using the plasma frequencies of 74560, 65760 and 87100 cm^{-1} , and the skin depths of 31.5, 35.8 and 27 nm for Ag, Au and Cu, respectively. The asymptotic limits of the reflectance change are $1 \pm 0.1\%$ for Ag(111) and Au(110) and $0.8 \pm 0.1\%$ for Cu(100). Accounting for the C_{60} mass ($720 \times 1.66 \times 10^{-27}\text{ kg}$) and the average density for one monolayer of C_{60} on noble metal surfaces ($\approx 1.15 \times 10^{-2}\text{ Å}^{-2}$), the friction coefficient is found to be $2.08 \times 10^9\text{ s}^{-1}$ for C_{60} on Ag(111) and Au(110), and $1.66 \times 10^9\text{ s}^{-1}$ for C_{60} on Cu(100).

The same scattering mechanism of the substrate conduction electrons by the adsorbate will also cause a resistance change in a metallic thin film when adsorbates are chemisorbed on the surface.^{12,15,18} Our results can therefore be compared with resistance change measurements during C_{60} deposition on copper films evaporated on sapphire substrates, where a value of 5 Å^2 for the scattering cross section of the adsorbed molecules has been found.²¹ Using the bulk parameters of copper, a friction coefficient of $9.4 \times 10^8\text{ s}^{-1}$ can be deduced, which is in fairly good agreement with the value obtained from IR

reflectance measurements, considering the differences in surface structure. Thus we can deduce that the diffuse scattering model^{12,15,18} also accounts for the shape and amplitude of the broadband IR reflectance change induced by the adsorption of large molecules like C₆₀.

Figure 2: Broadband reflectance change for 1 ML C₆₀ on Ag(111) (top left panel), on Au(110) (top right panel) and on Cu(100) (bottom panel). The broken line is a fit according to the Persson-Volokitin model¹². The dotted lines have been obtained with the plasma frequencies of 74560, 65760 and 87100 cm⁻¹ and the skin depth of 31.5, 35.8 and 27 nm for Ag, Au and Cu, respectively.

The friction coefficients obtained for all three metal surfaces is proportional to the inverse lifetimes of the frustrated translation of the adsorbate due to creation of electron-hole pairs of the order of hundreds of picoseconds and this can be considered an independent confirmation of the metallic character of the C₆₀ monolayer, previously deduced from direct^{22,23} and inverse^{24,25} photoemission data. The values of the friction coefficient are about 6 times smaller than that found for CO adsorbed on Cu (111) films.¹⁵ Thus, the product $\Gamma\rho(E_F)$ is about 4 times higher for C₆₀ adsorbed on noble metal surfaces, compared to CO. For the CO/Cu (111) system, the $2\pi^*$ state is known to lie at ~ 3.35 eV above the Fermi level, with a width of $0.1\text{ eV} < \Gamma < 0.6\text{ eV}$.^{26,27} For C₆₀ on the three metallic substrates, the width of the LUMO (π^* character) is difficult to evaluate: direct²³ and inverse^{24,25} photoemission data show rather broad spectral features both for the occupied and the unoccupied parts of the LUMO. However, by comparison with the HOMO band, it seems plausible that most of this width is due to vibronic coupling and that the actual bandwidth amounts to less than 0.1 eV.²⁸ One therefore deduces that the adsorbate-induced $\rho(E_F)$ is much larger for C₆₀ than for CO.

Let us turn our attention now to the specific vibrational bands of the molecule: figure 3 shows the spectral region between 1250 and 1600 cm⁻¹ of the IR spectra acquired while dosing C₆₀ onto Ag(111) at room temperature. As the coverage increases, a band at 1442 cm⁻¹ appears and shifts to higher wavenumbers. Only very close to monolayer coverage (last spectrum) a second band centered at 1388 cm⁻¹ can be discerned. No additional bands are seen at lower wavenumbers. The spectra for room temperature adsorption on the other two metals are similar: a detailed inspection of the spectrum in Fig. 2

for 1 ML C₆₀ on Cu(100) shows only a weak band at 1357 cm⁻¹ and a stronger one at 1440 cm⁻¹ while for 1 ML C₆₀ on Au(110) only one strong band at 1445 cm⁻¹ can be seen. In order to better understand these features we performed another experiment in which the fullerene molecules were prevented from chemisorption onto the Cu(001) substrate by a precoverage of 1 ML of CO. The IR spectrum is shown in figure 4 corresponds to a nominal coverage of 1 ML of C₆₀. The very strong band at 2083 cm⁻¹ is the CO stretching. One can also very clearly see the first three T_{1u} modes at practi-

Figure 3: Infrared spectra in the 1250-1600 cm⁻¹ region of a Ag(111) surface collected during C₆₀ deposition at room temperature.

Figure 4: Infrared spectra in the 400-2250 cm⁻¹ region of a Cu(100) surface precovered with 1 ML CO collected during C₆₀ deposition at 90 K.

cally the same frequency as for bulk C₆₀. However, in the spectral region of the T_{1u}(4) of bulk C₆₀ two bands are seen at 1431 cm⁻¹ and 1445 cm⁻¹, respectively but it is the former which is more intense. The breaking of symmetry due to the presence of the surface induces, therefore the appearance of a new infrared active mode, as already seen previously for C₆₀ adsorption on H-terminated Si(111)²⁹ and at the surface of C₆₀ and fulleride crystals^{30,31}. This new mode has been attributed^{30,31} to the A_g(2) Raman mode, and this attribution has been adopted also in a combined IR and SFG study¹¹ of C₆₀/Ag. From the comparison of figures 1 and 4 one deduces that the visibility of all C₆₀-induced IR bands does not depend on instrumental sensitivity, and that in the case of chemisorbed fullerenes on metals the intensity of the T_{1u} modes is depressed while that of the A_g(2) is enhanced due to electron-phonon coupling effects similar to those observed in fullerides.^{2,31} We note that the intensity enhancement of the A_g(2) mode for C₆₀/Ag has been attributed to the dynamical charge transfer between the metallic substrate and the C₆₀ molecule³² but we believe, as shall be clear in the following, that this mechanism does not explain the phenomenon.

We have also studied the temperature dependence of the IR spectra as shown in figure 5. The top left panel shows the evolution of the spectral region between 1200 and 1650 cm⁻¹ when a C₆₀ monolayer deposited on Cu(100) at 90 K is heated stepwise to 375 K. While the T_{1u}(4) mode stays at constant frequency but decreases in intensity, the A_g(2) mode is seen to

shift from 1451cm^{-1} to 1440cm^{-1} and to broaden considerably. The detailed frequency behavior of the $A_g(2)$ mode is plotted in the top right panel of figure 5: if one performs repeated heating-cooling cycles between 90 K and 600 K the $A_g(2)$ mode does not shift back to the initial frequency after the first heating. This indicates that an irreversible phase tran-

Figure 5: Top left panel: Temperature dependence of the IR spectra in the region between 1200 and 1650 cm^{-1} of 1 ML $\text{C}_{60}/\text{Cu}(100)$ deposited at 90 K and heated stepwise to 375 K. Top right panel: Frequency behaviour of the $A_g(2)$ mode of 1 ML $\text{C}_{60}/\text{Cu}(100)$ during repeated heating-cooling cycles between 90 K and 600 K. Bottom panel: FWHM of the $A_g(2)$ mode of 1 ML $\text{C}_{60}/\text{Cu}(100)$ during the reversible part of heating-cooling cycles.

sition to a different adsorption state has occurred. Similar phase transitions have been observed on other metal surfaces and are a signature of the existence of activation barriers between metastable and stable adsorption geometries, sometimes accompanied by reconstruction of the substrate.³³ However, the reversible part of the frequency shift and the broadening of the $A_g(2)$ band are typical of an anharmonic coupling to a low frequency vibrational mode, also called dephasing, which becomes more and more important as the coupled mode becomes populated with increasing temperature. The theory for this mechanism is a phase relaxation exchange model¹⁴ and allows to extract the frequency, $\omega_0 \approx 45\text{--}75\text{cm}^{-1}$, of the coupled mode from the plot shown in the bottom panel of figure 5 which shows the temperature dependence of the FWHM of the $A_g(2)$ band. Given that this value of ω_0 is too low to be attributed to an internal mode of the fullerene, we suggest that it might be the frustrated translation of the C_{60} on the metal surface which couples to the $A_g(2)$ mode.

In order to gain further insight dependence of the IR spectra on charge transfer we have also studied the doping of the chemisorbed C_{60} molecules through co-adsorbed potassium as illustrated in figure 6. When K-dosing has been performed on top of a room-temperature deposited 1 ML $\text{C}_{60}/\text{Cu}(100)$ as shown in Fig. 6 top panel, the $A_g(2)$ band is seen to shift to lower frequency while its linewidth decreases. At K coverages very close to saturation decreases drastically in intensity while still redshifting while the $T_{1u}(4)$ mode suddenly increases in intensity. This behaviour is very similar to what has been observed in analogous experiments¹¹ where K was dosed on 1 ML $\text{C}_{60}/\text{Ag}(111)$. Given that highest charge transfer

obtainable by this doping procedure on Au and Ag surfaces^{8,10,11} has been found to be 6 electrons per fullerene we assume that the same is true on Cu(100). This leads us to conclude that the $A_g(2)$ shifts linearly by about 5cm^{-1} per transferred electron, while the $T_{1u}(4)$ mode shifts in a strongly non linear fashion as already observed by HREELS¹⁰ for $C_{60}+Cs/Au(110)$. Based on the linear shift of the $A_g(2)$ mode the charge transfer per fullerene molecule in 1 ML C_{60} on Au(110) and Ag(111) (see fig. 2 and 3) can be estimated to be about 1 electron while it amounts to about 2 electrons/fullerene in 1 ML C_{60} on Cu(100). These values are in very good agreement with previous estimates based on HREELS⁹ and photoemission²³ data, however they have to be considered with caution since the anharmonic coupling of the $A_g(2)$ mode to the frustrated translational mode might influence the shift differently on the different surfaces.

Figure 6: Top panel: Infrared spectra in the $1225\text{--}1550\text{ cm}^{-1}$ region collected during K dosing on top of 1 ML $C_{60}/Cu(100)$ deposited at room temperature. Bottom left panel: Infrared spectra in the $1300\text{--}1600\text{ cm}^{-1}$ region collected during room temperature C_{60} dosing on top of 1 ML K/Ag(111). Bottom right panel: Infrared spectra in the $1325\text{--}1550\text{ cm}^{-1}$ region collected during room temperature C_{60} dosing on top of 1 ML K/Au(110).

Let us now consider the potassium doping of C_{60} on Ag(111) and Au(110) which is illustrated in the bottom panels of fig.6 where we plot the evolution of the IR spectra during fullerene deposition onto the metal surfaces pre-covered by 1 ML of K. For the adsorption on gold (bottom right panel) we notice that similarly to K dosing on top of 1 ML $C_{60}/Cu(100)$ discussed above, the $A_g(2)$ band redshifts compared to the undoped monolayer. This agrees well with previous studies which find that the charge transfer for 1 ML $C_{60}/1\text{ ML K}/Au(110)$ is ~ 3 electrons per fullerene³⁴. However, a new characteristic of this system is that the shape of the $A_g(2)$ band now derivative like as for an antiabsorption line. For adsorption on K-predosed Ag(111) shown in the bottom right panel the antiabsorption line character becomes even the dominant feature in the spectrum. These features point again to strong electron-phonon coupling and resemble those observed previously for hydrogen adsorption on transition metals³⁵ issuing from the coupling of the adsorbate vibration to an adsorbate-induced electronic surface state. This coupling mechanism is characterized by an increase in broadband reflectance.³⁵ We therefore took again advantage of the possibilities of the Synchrotron radiation IR set-up to measure the broadband reflectance change

during K dosing onto the C_{60} monolayers deposited on the three metal substrates. The results are shown in figure 7. We note that these measurements are extremely demanding since one has to avoid thermal loading of the metallic substrate by the K getter source which is kept at ~ 900 K. The evolution of the broadband reflectance clearly shows an increase with potassium dosing confirming the coupling of the $A_g(2)$ mode to an electronic surface state.

Figure 7: Broadband reflectance change recorded during K dosing onto 1 ML C_{60} on Ag(111) (top left panel), on Au(110) (top right panel) and on Cu(100) (bottom panel).

4. SUMMARY

Synchrotron Infrared Studies of chemisorbed C_{60} on bare and potassium-precovered Ag(111), Au(110) and Cu(100) have revealed several new insights into electron-phonon and purely vibrational couplings in these systems. In the case of adsorption on the clean metal substrates the overall behavior of the IR reflectance change is dominated by the diffuse scattering mechanism of the conduction electrons of the metallic substrate by the adsorbate. This broadband reflectance change allows to determine the friction coefficient between the sliding adsorbate and the free conduction electrons of the metal driven by the external electric field associated with the incident IR photons. The values obtained for the friction coefficient give an independent confirmation of the metallic character of the fullerene-substrate bond and of the high density of adsorbate induced states close to the Fermi level. Superimposed on the broadband reflectance are the individual vibrational bands of the adsorbate: a non-IR active mode becomes active upon adsorption and that its frequency shifts proportionally to the charge transferred from the metal to the molecule by about 5 cm^{-1} per electron. The temperature dependence of the frequency and the width of this IR feature, attributed to the normally Raman active $A_g(2)$ mode, has also been followed for $C_{60}/\text{Cu}(100)$ and was found to agree well with a weak anharmonic coupling (dephasing) between this newly active mode and the frustrated translational mode of the adsorbed molecules. When potassium is co-adsorbed with C_{60} allowing for a

larger charge transfer to the fullerene, a new electron-phonon coupling mechanism becomes dominant in determining the shape of the IR spectra, namely the coupling of the $A_g(2)$ mode to induced surface states. This coupling manifests itself through a broadband reflectance increase and a derivative-like shape of the $A_g(2)$ band. In addition, the comparison with co-adsorption experiments of CO and C_{60} allowed to identify intensity variations of the T_{1u} infrared bands which occur both with and without co-adsorption of K similar to those observed in alkali fullerenes. Given the hybridization between C_{60} and metal substrate electronic states, these intensity variations are probably caused by the coupling to induced surface states.

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