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## Infrared absorption enhancement of $C_{60}$ on silver islands: Contribution of charge transfer and collective electron resonance

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Normal-incidence infrared absorption spectra of  $C_{60}$  films deposited on silver islands have been measured. The spectra exhibit bands at 1429 and 1180  $\text{cm}^{-1}$  due, respectively, to the infrared active  $T_{1u}(4)$  and  $T_{1u}(3)$  modes of  $C_{60}$  in multilayers. These bands increase in intensity rather rapidly until 20 nm thickness: the intensity increase involves an enhancement of absorption due to the excitation of the transverse collective resonance of valence electrons in the silver islands. Additionally two bands appear at 1442 and 1370  $\text{cm}^{-1}$ , both of which abruptly increase in intensity until 2 nm and saturate 10 nm thickness. These bands decrease in intensity and shift to higher wave numbers when oxygen is preadsorbed on the silver islands. The 1442  $\text{cm}^{-1}$  band is caused by the activation of the infrared inactive  $A_g(2)$  mode via electron transfer from the silver to adsorbed  $C_{60}$ , whereas the 1370  $\text{cm}^{-1}$  band is assigned to the  $T_{1u}(4)$  mode redshifted by the charge transfer. The results reveal that both the charge transfer and the collective electron resonance contribute to the IR absorption enhancement of  $C_{60}$  on silver islands.

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Free-electron-gas-model metals, e.g., silver, gold, copper, etc., have so far attracted considerable interest because of their contribution to surface enhanced Raman scattering (SERS) phenomena.<sup>1,2</sup> It is well documented that enhanced Raman scattering from molecules on these metals arises from both electromagnetic and chemical effects. In the former case, the enhancement is due to surface electric field enhanced by the collective conduction electron resonances of microscopic bumps on the surface of the metals and is relatively long ranged compared with the latter case where the enhancement is restricted to chemisorbed molecules. A phenomenon similar to SERS is the enhancement of infrared absorption which has been found to occur for molecules on silver island films.<sup>3-5</sup> The absorption enhancement observed on silver island films has two common features. First, only vibrational modes that yield a change in the dipole moment perpendicular to the metal surface are enhanced.<sup>5</sup> Second, the absorption intensity saturates at a certain distance (about 5 nm) from the metal surface.<sup>6</sup> These features have mainly been explained by the excitation of the transverse collective electron resonance of the metal islands. In support of the electromagnetic mechanism, the enhancement magnitudes depend critically on the morphology of the islands.<sup>7-11</sup>

In the present report, we present pronounced features of the enhanced infrared absorption of  $C_{60}$  deposited on silver islands in ultrahigh vacuum (UHV).  $C_{60}$  is a typical example of fullerenes<sup>12</sup> which have been studied with considerable interest. Within the scope of surface science  $C_{60}$  is an attractive molecule because of its low number of infrared and Raman active vibrations due to high degree of molecular symmetry.<sup>13</sup> Of particular interest is the possibility of electron transfer when  $C_{60}$  is in contact with metal surfaces.<sup>14-19</sup> Although a number of charge transfer experiments have been performed on  $C_{60}$  at single-crystalline metal surfaces, investigations at polycrystalline surfaces are rather limited. Goldoni and Paolucci<sup>20</sup> investigated the thermal desorption of  $C_{60}$  monolayer formed on Ag(100) and polycrystalline sil-

ver surfaces, from which they showed that the  $C_{60}$  binding nature of Ag(100) differs from that of polycrystalline silver and on the former surface  $C_{60}$  is decomposed before the complete desorption of the monolayer unlike the behavior observed on the polycrystalline surface. This indeed motivated us to investigate IR absorption enhancement behavior of  $C_{60}$  on polycrystalline silver island films. The results are presented and discussed in this report.

The silver films were deposited on chemically oxidized Si(111) surfaces at room temperature by vacuum evaporation of the metal from a Knudsen cell installed in the molecular beam epitaxy (MBE) chamber.<sup>21</sup> The Si(111) surface (originally hydrogen terminated) was oxidized in an  $\text{H}_2\text{O}:\text{H}_2\text{O}_2:\text{HCl}=5:1:1$  solution at 473 K for 1 h. The thicknesses of the silver films were evaluated by referring to the deposition rate as determined from the reflection high energy electron diffraction (RHEED) intensity oscillations during silver(111) epitaxial growth on the Si(111)-(7 $\times$ 7) surface. The morphologies of silver films similarly prepared were observed by using a field emission scanning electron microscope (FE-SEM).  $C_{60}$  was deposited from a resistively heated tantalum boat onto the silver film surface during which the mass thickness of  $C_{60}$  was monitored with a quartz oscillator. Preadsorption of atomic oxygen at the silver surface was carried out<sup>22</sup> through a surface irradiation with a UV light (254 nm) in an  $\text{O}_2$  atmosphere ( $1 \times 10^{-6}$  Torr). Infrared absorption spectra of  $C_{60}$  on the silver surface were measured at normal incidence of radiation using an FT-IR spectrometer equipped with a liquid-nitrogen-cooled HgCdTe detector. These measurements were performed in another UHV chamber of the same MBE system.<sup>21</sup>  $\text{BaF}_2$  optical windows were used to allow infrared radiation to pass through the chamber in the region above 1100  $\text{cm}^{-1}$ . All the spectra were taken at a resolution of 4  $\text{cm}^{-1}$  as the average of 500 scans and divided by the background spectrum recorded under the same conditions.

SEM micrograph of a silver film [92 monolayer (ML) thick] deposited in 20 min on the oxidized Si(111) surface at

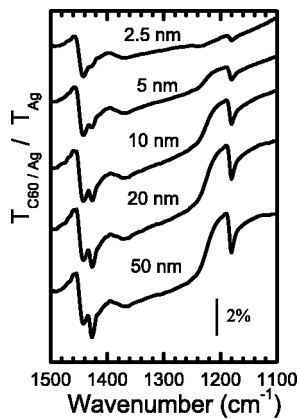


FIG. 1. Infrared transmission spectra of  $C_{60}$  as a function of  $C_{60}$  thickness on the 92 ML thick silver film deposited on chemically oxidized Si(111).

room temperature clearly showed that the film is composed of separate islands (100–200 nm in average size) with distinct channels (less than 50 nm in width) between them. The transmittance of the film in the infrared was 80% and the film allowed us to observe the  $C_{60}$  absorption with sufficient intensities.

The isolated  $C_{60}$  molecule has a structure of  $I_h$  symmetry and group theory predicts 46 distinct modes of vibrations, of which only four are infrared active ( $T_{1u}$ ) and ten are Raman active vibrations ( $A_g$  and  $H_g$ ).<sup>23–25</sup> In this report we leave the  $T_{1u}(2)$  and  $T_{1u}(1)$  modes out of consideration, since these modes appear below  $1100\text{ cm}^{-1}$ . The infrared transmission spectra of  $C_{60}$  on the chemically oxidized Si(111) surface revealed two bands at 1429 and  $1182\text{ cm}^{-1}$ : these bands were attributable to  $T_{1u}(4)$  and  $T_{1u}(3)$  modes, respectively.

Figure 1 shows the transmission spectra of  $C_{60}$  recorded as a function of  $C_{60}$  mass thickness on a 92 ML thick silver film deposited on the chemically-oxidized Si(111) surface. It should be noted that a new band appears at  $1442\text{ cm}^{-1}$  that is remarkably intense even at a thickness of 2.5 nm unlike the bands at 1429 and  $1180\text{ cm}^{-1}$  due to the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes, respectively. Additionally, another new band is observed at  $1370\text{ cm}^{-1}$  which also is already strong at the thickness of 2.5 nm. Thus, both the  $1442$  and  $1370\text{ cm}^{-1}$  bands should be attributed to  $C_{60}$  molecules in the first molecular layer on the islands, whereas the bands at 1429 and  $1180\text{ cm}^{-1}$  bear reference to multilayers. The  $1442\text{ cm}^{-1}$  band is ascribable to the infrared inactive  $A_g(2)$  mode for undisturbed  $C_{60}$ , whereas the  $1370\text{ cm}^{-1}$  band is due to a redshifted  $T_{1u}(4)$  mode.<sup>18,19</sup> Both bands arise from a charge transfer at the silver surface, as will be verified later.

The intensity of the  $A_g(2)$  mode at  $1442\text{ cm}^{-1}$  is plotted as a function of  $C_{60}$  coverage in Fig. 2, together with plots of the intensities of the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes at 1429 and  $1180\text{ cm}^{-1}$ , respectively. It can be seen in Fig. 2 that in general the  $T_{1u}(4)$  mode is more intense than the  $T_{1u}(3)$  mode, though these bands were of almost the same intensities in the normal infrared absorption spectra. This difference is due to proximity in position of the  $T_{1u}(4)$  mode to the

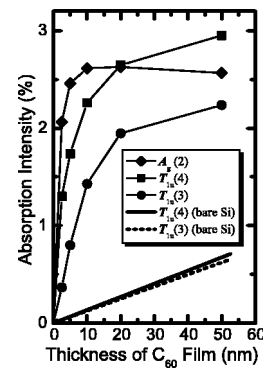


FIG. 2. Intensity variations of the  $A_g(2)$ ,  $T_{1u}(3)$ , and  $T_{1u}(4)$  modes with increasing  $C_{60}$  mass thickness. The lines are guides to the eye.

$A_g(2)$  mode as well as the absorption feature seemingly centered at  $1420\text{ cm}^{-1}$  which could affect our intensity evaluation. It is immediately clear from Fig. 2 that the intensities of the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes as well as the intensity of the  $A_g(2)$  mode are not proportional to  $C_{60}$  coverage. This feature is quite different from the coverage dependence of the bands due to the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes of  $C_{60}$  deposited on the chemically oxidized silicon surface which gives a straight line, as shown in Fig. 2.

It is also clear that increasing the coverage the  $A_g(2)$  mode more rapidly saturates in intensity than the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes. In contrast to the  $A_g(2)$  mode, both the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes continue to increase in intensity even though  $C_{60}$  coverage exceeds 20 nm. This intensity increase can be explained by a normal absorption of  $C_{60}$  (i.e., the linear intensity increase with coverage) deposited away from the silver surface. Taking into account the contribution of the normal absorption to the total intensity, the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes saturate at the coverage of 20 nm. However, this saturation coverage is larger than 5 nm, the value of which has been evaluated as the spatial range of the enhanced infrared absorption of other molecules on silver island films.<sup>6,26–29</sup> Further, the intensity of the  $A_g(2)$  mode saturates at a thickness of 10 nm which is approximately one order of magnitude larger than the monolayer thickness of  $C_{60}$ . The unexpectedly larger saturation coverage shown by the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes suggests that  $C_{60}$  molecules are not easily deposited in the channels surrounded by the deposited Ag islands. The molecules lying embedded in the channels away from the island surfaces do not contribute to the absorption enhancement of the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes. This aspect is specific to our method. The saturation coverage of  $C_{60}$  beyond one monolayer thickness, shown by the  $A_g(2)$  mode, is also explained similarly.

We have assigned the band at  $1442\text{ cm}^{-1}$  in Fig. 1 to the  $A_g(2)$  mode which is infrared forbidden for undisturbed  $C_{60}$ . This activation has been explained by the chemisorption which is accompanied by electron transfer from the silver metal to the lowest unoccupied molecular orbital (LUMO) of the adsorbed  $C_{60}$ .<sup>30</sup> The lower frequency shift of the  $A_g(2)$  mode from the corresponding Raman band can be explained by the chemisorption accompanied by the charge transfer at

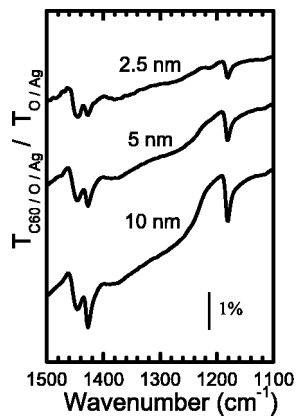


FIG. 3. The same as in Fig. 1, but the spectra observed for  $C_{60}$  on the oxygen preadsorbed silver surface. Note that the absorption scale is different from that in Fig. 1.

the silver surface. Another band at  $1370\text{ cm}^{-1}$  arising from the first monolayer may also be attributed to the charge transfer. We believe that this band corresponds to the  $T_{1u}(4)$  mode for the bulk  $C_{60}$  observed at  $1429\text{ cm}^{-1}$  in Fig. 1.

Figure 3 shows the transmission spectra of  $C_{60}$  deposited on a 92 ML thick silver film whose surface was preadsorbed by oxygen atoms. It should be noted that the absorption scale indicated in Fig. 3 is half the scale shown in Fig. 1. Although no detailed feature was elucidated on the oxygen adsorption, its effects can be clearly seen in the spectra, one of which is the decrease in intensity of the  $A_g(2)$  and as-shifted  $T_{1u}(4)$  modes due to the first molecular layer unlike the  $T_{1u}(4)$  and  $T_{1u}(3)$  modes due to overlayers. Another fact of importance is a blue shift of the  $A_g(2)$  mode to  $1446\text{ cm}^{-1}$  and of the as-shifted  $T_{1u}(4)$  mode to  $1378\text{ cm}^{-1}$ . These facts give evidence for the deactivation of the silver surface by adsorbed oxygen. In particular, the blueshift is larger for the as-shifted  $T_{1u}(4)$  mode than for the  $A_g(2)$  mode, consistent with the report by Giannozzi and Andreoni.<sup>31</sup> Another finding in Fig. 3 is that the absorption feature around at  $1420\text{ cm}^{-1}$  in Fig. 1 is washed out by the oxygen adsorption. As a consequence, the  $T_{1u}(4)$  band at  $1429\text{ cm}^{-1}$  is observed with almost the same intensity as the  $T_{1u}(3)$  band at any  $C_{60}$  coverages.

Figure 4 summarizes the influence of the oxygen preadsorption on the absorption intensities of the  $A_g(2)$ ,  $T_{1u}(4)$ , and  $T_{1u}(3)$  bands as a function of  $C_{60}$  coverage. The  $T_{1u}(4)$  band concerns overlayers only whereas the  $T_{1u}(3)$  band could arise from the first layer also. It should be noted that the intensity of the  $A_g(2)$  band due to the first layer is about 65% decreased by the oxygen adsorption regardless of the coverage while the  $T_{1u}(3)$  band remains unchanged in intensity. Furthermore, due to the overlapping with the  $A_g(2)$  band and the absorption feature around at  $1420\text{ cm}^{-1}$  as well, the  $T_{1u}(4)$  band of  $C_{60}$  on the oxygen-free surface is evaluated to be more strongly than that on the preadsorbed surface. At any rate, oxygen preadsorption on the silver surface leads to a significant intensity reduction of the  $A_g(2)$  and  $T_{1u}(4)$  bands.

A comparison of our results with relevant IR investigations reported in the past is made in the following where we focus mainly on IR absorption intensities of  $C_{60}$  chemisorbed

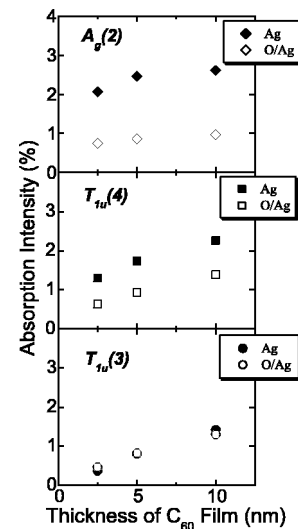


FIG. 4. Effect of oxygen preadsorption on the silver surface upon intensity of the  $A_g(2)$ ,  $T_{1u}(3)$ , and  $T_{1u}(4)$  modes of  $C_{60}$  deposited at different thicknesses.

at silver surfaces. A common finding in IR reflection absorption spectroscopic (IRRAS) studies of  $C_{60}$  adsorbed on  $Ag(111)$  (Refs. 15–17) is that the absorption intensity of the  $A_g(2)$  mode is 0.3%, whereas that observed on the polycrystalline film (Fig. 1) is larger than 2.8%, leading to approximately an order of magnitude of absorption enhancement in our case. Essentially the same magnitude of absorption enhancement (i.e., ninefold) is evaluated for the as-shifted  $T_{1u}(4)$  band observed at  $1370\text{ cm}^{-1}$  from its comparison in intensity with the corresponding band at  $1385\text{ cm}^{-1}$  observed on  $Ag(111)$  by IRRAS.<sup>17</sup> On the other hand, the saturated intensity of the  $T_{1u}(3)$  mode observed on the clean silver surface is about six times larger than the intensity of the same mode compared with the corresponding thickness on the bare silicon surface (Fig. 2). This should hold true for the  $T_{1u}(4)$  band due to the overlayers of  $C_{60}$ . These facts imply that the enhancement of the  $A_g(2)$  and as-shifted  $T_{1u}(4)$  bands was caused not only by the long-ranged electromagnetic enhancement, described before, but also by the charge transfer.

In summary, an infrared absorption study has been performed in the  $1500\text{--}1100\text{ cm}^{-1}$  region on  $C_{60}$  molecules deposited on clean and oxygen preadsorbed silver island films. As a consequence of the electron transfer from the metal to the adsorbed  $C_{60}$ , bands due to the  $A_g(2)$  and  $T_{1u}(4)$  modes are found to shift to lower frequencies. Owing to this charge transfer as well as the usual long-range electromagnetic absorption enhancement, the bands of  $C_{60}$  arising from the first layer and overlayers have been clearly distinguished. The originally infrared active  $T_{1u}(3)$  and  $T_{1u}(4)$  modes of  $C_{60}$  in the overlayers are enhanced in intensity compared with those in the absence of silver. However, the magnitude of the enhancement is about 40% less than that observed for the  $A_g(2)$  and  $T_{1u}(4)$  bands, both of which are caused by the charge transfer. Thus, we conclude that the  $A_g(2)$  and  $T_{1u}(4)$  bands are enhanced in intensity by the charge transfer in addition to the long-ranged electromagnetic enhancement.

Our absorption measurements of  $C_{60}$  on the oxygen preadsorbed silver film surface clearly reveal that the shifts of the  $A_g(2)$  and  $T_{1u}(4)$  bands to lower frequencies resulted from the charge transfer. This oxygen adsorption also causes a 65% decrease in intensity of the  $A_g(2)$  and  $T_{1u}(4)$  bands,

but the  $T_{1u}(3)$  mode remains unaffected, suggesting a little surface-sensitive mode. Thus, we demonstrate the existence of a charge transfer effect as well as the usual electromagnetic one in the infrared absorption enhancement of  $C_{60}$  on polycrystalline silver islands.

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