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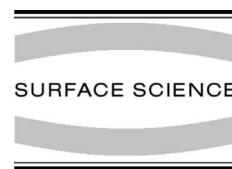
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Adsorption of fullerene and azafullerene on Cu(1 1 1) studied by electron energy loss spectroscopy

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Abstract

Fullerene and azafullerene films were studied by electron energy loss spectroscopy in reflection geometry. Compared to C_{60} , $(C_{59}N)_2$ multilayers show additional vibrational modes that are characteristic of the dimer structure. The $(C_{59}N)_2$ is semiconductor-like and giant optically allowed excitonic transitions are found in the gap in drastic contrast with C_{60} . The azafullerene monolayer on Cu(1 1 1) no longer shows the presence of dimers, indicating monomer adsorption. Similarly to C_{60} , azafullerene molecules in contact with the metal substrate receive a transferred charge between two and three electrons. However, the $C_{59}N$ appears more covalently bound to Cu because it decomposes when heated above 660 K while C_{60} only desorbs. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electron energy loss spectroscopy (EELS); Vibrations of adsorbed molecules; Fullerenes

1. Introduction

The fascinating family of C_{60} -based materials has been recently extended with the fabrication of on-ball doped molecules. The substitution of a carbon by a nitrogen atom on C_{60} leads to the creation of $C_{59}N$, also called azafullerene, which appears to be stabilised by forming dimers or by reacting with hydrogen to form $C_{59}HN$ [1,2], also called hydroazafullerene. $(C_{59}N)_2$ is stable in solution as well as in the solid state [3]. Here we re-

port on a comparison between C_{60} and $(C_{59}N)_2$ in the solid state by using electron energy loss spectroscopy (EELS) which allows the investigation of vibrational as well as electronic transitions. Both multilayer and monolayer (ML) films deposited on a Cu(1 1 1) crystal are studied.

Vibrational and electronic signatures crucially depend on the geometry/symmetry of the molecules. The icosahedral symmetry (I_h) of the C_{60} molecules implies that, among the 174 vibrational modes, only the 4 T_{1u} modes are infrared active and that the 2 A_g and the 8 H_g modes are Raman active. From the group theory point of view, dimerised $C_{59}N$ has C_{2h} symmetry and shows lower degeneracy: its 354 vibrational modes are divided in 91 A_g , 86 B_g , 87 A_u and 90 B_u , of which only three gerade and three ungerade modes are of

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intercage origin. All gerade modes are Raman active and all ungerade ones are infrared active [4].

2. Experimental set-up and samples preparation

EELS was performed in reflection geometry with a DELTA 0.5 spectrometer (Vacuum Science Instruments) capable of a resolution of 8 cm^{-1} (full width at half maximum of the elastic peak). In this experiment, the routine resolution on C_{60} was about 15 cm^{-1} . All the EELS measurements were carried out at room temperature, with the angle of incidence of the electron beam set at 75° with respect to the surface normal. The vibrational and electronic excitations spectra were recorded with primary energies of 4 and 10 eV, respectively. Below we use the usual terms of high resolution EELS (HREELS) while discussing the vibrational data and EELS for the electronic excitation measurements.

C_{60} films were deposited by sublimation of commercially available material (99.9% purity, MER Corporation) from a resistively heated Ta crucible. Epitaxial MLs of C_{60} are obtained by keeping the $\text{Cu}(111)$ substrate at about 600 K during fullerene deposition. The C_{60} multilayers are grown at room temperature on a pre-deposited C_{60} ML. $(\text{C}_{59}\text{N})_2$ was prepared and purified as described in Ref. [1]. From IR measurements a C_{60} contamination of less than 1% was deduced for this material [5]. The C_{59}N ML was produced in the same way as the C_{60} one but using a boron nitride crucible. $(\text{C}_{59}\text{N})_2$ multilayers were grown on the clean metal in order to reduce azafullerene consumption. AES and LEED were always used to verify the quality and the thickness of the (aza)fullerene films. Samples could be radiatively annealed by a filament placed behind the crystal. The temperature was measured with a K-type thermocouple in contact with the side of the crystal.

3. Results and discussion

3.1. Vibrational excitations

Fig. 1 shows a comparison between the HREELS spectra, collected in specular geometry, of a

multilayer film of C_{60} (lower spectrum) and of $(\text{C}_{59}\text{N})_2$ (spectrum in the centre), both deposited on $\text{Cu}(111)$.

The thickness of the C_{60} film is about eight MLs and its spectrum agrees well with HREELS data of C_{60} multilayers grown on $\text{Si}(100)\text{-H}(2 \times 1)$ [6] or $\text{Ag}(111)$ [7]. The four dominant modes are located at 527, 576, 1179 and 1425 cm^{-1} and exhibit a clear dipolar character as verified by comparison with the spectrum recorded in off-specular geometry (not shown). Obviously, the four peaks correspond

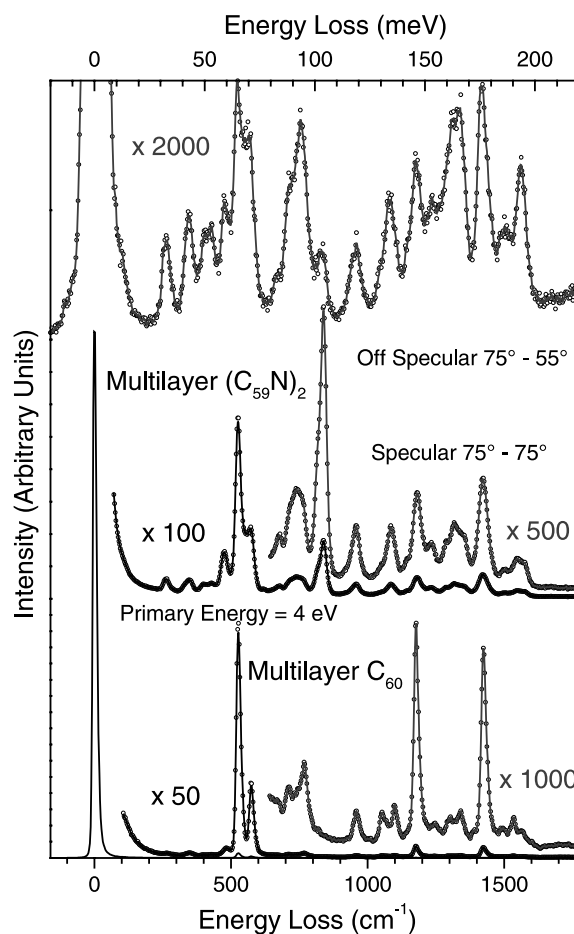


Fig. 1. HREELS spectra of C_{60} (bottom) and $(\text{C}_{59}\text{N})_2$ (centre) multilayers deposited on $\text{Cu}(111)$ recorded with a resolution of 16 and 20 cm^{-1} . Both spectra are measured in specular geometry: $75^\circ\text{--}75^\circ$ with respect to the normal of the sample surface. The top spectrum corresponds to the $(\text{C}_{59}\text{N})_2$ multilayer measured in off-specular geometry: $75^\circ\text{--}55^\circ$. In all cases the primary energy is 4 eV.

to the four infrared active modes of C_{60} of T_{1u} symmetry [8]. All smaller peaks visible in the spectrum arise mainly from the impact scattering mechanism through which also Raman active and optically forbidden modes can be excited.

Despite the much lower degeneracy of the vibrational modes expected from symmetry considerations, we observe that for dimerised $C_{59}N$ the main features of the C_{60} HREELS spectrum are found again. In order to determine the modes of dipolar character we compare again to the spectrum recorded in off-specular geometry ($75\text{--}55^\circ$) and presented in the upper part of the Fig. 1. It shows little difference with respect to the one of C_{60} discussed above: the intensities of the modes at 477, 527, 569, 838, 1181 and 1422 cm^{-1} are strongly reduced. With reference to C_{60} , we associate the peaks at 527, 569, 1181 and 1422 cm^{-1} to the T_{1u} -derived modes and the one at 477 cm^{-1} to the A_g -derived mode, which has become infrared active due to the symmetry lowering. The dipole active mode at 838 cm^{-1} has no counterpart in the C_{60} spectrum and must therefore be characteristic of the dimerised $(C_{59}N)_2$. It agrees well with IR absorption spectroscopy which shows a mode at about 845 cm^{-1} in a region where C_{60} is silent, appearing therefore specific to $(C_{59}N)_2$ [9]. Moreover, theory predicts a vibrational band around 850 cm^{-1} that is dominated by stretching modes of C–N and C–C bonds on the pentagonal rings [9]. Raman spectroscopy [4] shows almost no activity in this frequency range.

In contrast with C_{60} , three Raman lines are observed at 82, 103 and 111 cm^{-1} which are assigned to the three gerade intermolecular vibrations of the dimer [4,10]. Despite the high resolution the corresponding ungerade vibrations cannot be observed in the spectrum recorded in specular geometry since the elastic peak is still too broad for observing such low frequency modes, especially if their oscillator strength is weak. However, in the off-specular spectrum we distinguish a shoulder at about 105 cm^{-1} on both energy loss and gain sides. A weaker shoulder is also visible at 81 cm^{-1} , but only in the energy gain region. Such shoulders are not observed in the case of C_{60} .

We also note that the $(C_{59}N)_2$ multilayer vibrational spectrum recorded in specular geometry

shows a lower contrast between dipole allowed and forbidden peaks than the one of C_{60} . Surface disorder broadens the electron beam and could account for this observation. The $(C_{59}N)_2$ film is indeed grown at room temperature and not annealed. The lower resolution obtained on the azafullerene films (20 cm^{-1}) compared to the better resolution obtained on the C_{60} ones (15 cm^{-1}) supports this explanation. However it can also be partially explained by the lower symmetry of the dimer.

Fig. 2 shows the vibrational spectra of $C_{59}N$ and C_{60} MLs adsorbed on Cu(111) before and after annealing. As deposited, both C_{60} and $C_{59}N$ MLs show a 4×4 LEED pattern which indicates that they are adsorbed with the same commensurate geometry on the Cu(111) substrate, in full agreement with previous STM studies of the $C_{60}/\text{Cu}(111)$ system [11]. The HREELS spectra are measured in the specular direction and dominated by dipolar modes as seen from comparison with the off-specular spectrum (not shown). For the C_{60} ML (Fig. 2, bottom curve) five peaks at 485, 563, 1346, 1392, and 1432 cm^{-1} are undoubtedly dipolar. Peaks of lower dipolar activities are also observed at 336, 754, 940, 1156, and 1503 cm^{-1} . The dipolar spectrum of the ML is more complex than its multilayer equivalent since the mode frequencies depend on the charge transferred from the substrate and on the environment of the fullerene molecules [12]. If dipolar cross-sections are essentially determined by the charge state of C_{60} [13], selection rules are also relaxed because of the symmetry reduction of the system. Finally, one has also to take into account electron–phonon couplings [14].

We can assign the modes of $C_{60}/\text{Cu}(111)$ by using the same arguments as previously developed for $C_{60}/\text{Ag}(111)$ in another study [7]. Surface effects are known to increase drastically the dipolar activity of the A_g modes of C_{60} [14,15] and charge transfer to C_{60} induces a softening of the first and the fourth T_{1u} modes. Consequently, as in Ref. [7], we propose the following assignment for $C_{60}/\text{Cu}(111)$: the $A_g(1)$ and $T_{1u}(1)$ modes are unresolved at 485 cm^{-1} , the $T_{1u}(2)$ is at 563 cm^{-1} and the $A_g(2)$ at 1432 cm^{-1} . The latter value shows little difference with a surface enhanced Raman

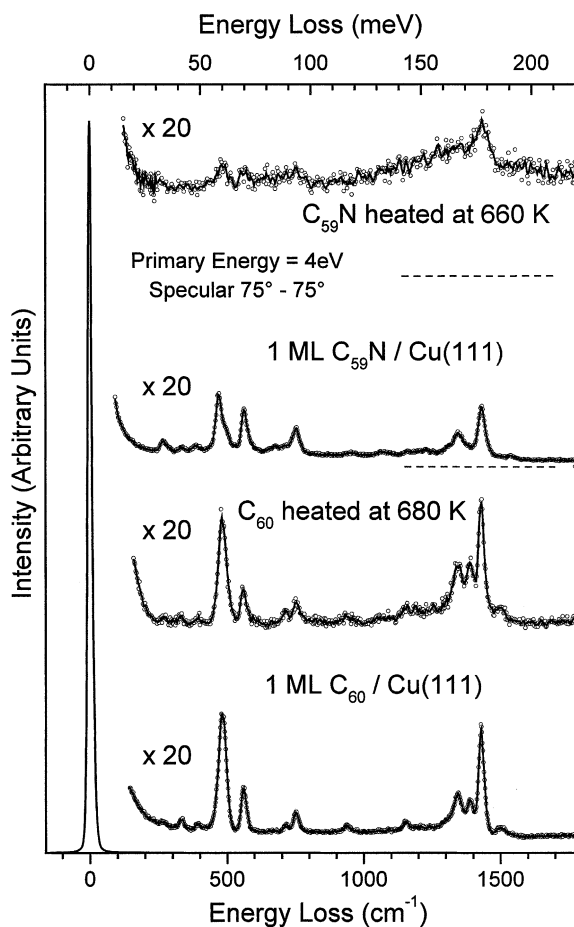


Fig. 2. HREELS spectra recorded in specular geometry (75° – 75°) and with a primary energy of 4 eV. The two lower ones correspond to 1 ML C_{60} on Cu(111) before and after annealing at about 680 K, while the two upper spectra correspond to 1 ML $C_{59}N$ on Cu(111) before and after annealing at about 660 K.

study of C_{60} deposited on Cu, where the $A_g(2)$ pentagonal pinch mode is observed at 1441 cm^{-1} [16]. This is actually not surprising due to the lower resolution of our HREELS data and to the differences between the copper surfaces. At least one of the peaks at 1346 and 1392 cm^{-1} should be related to the $T_{1u}(4)$ mode. In the case of a C_{60} ML on Ag(111), only one broad peak is observed in this region. It is not possible at this stage to present a definitive explanation. However, two hypotheses may be proposed: either a splitting of the threefold degenerate $T_{1u}(4)$ mode or the emergence of di-

polar activity of a normally not infrared mode because of surface effects.

We now turn to the $C_{59}N$ ML spectrum. The most important dipolar peaks are located at 471 (with a shoulder at 496), 561 , 752 , 1344 and 1431 cm^{-1} . By comparison with C_{60} , we attribute the peaks at 471 and 496 cm^{-1} to the $A_g(1)$ - and $T_{1u}(1)$ -derived vibrations, the one at 1344 cm^{-1} to a $T_{1u}(4)$ -derived band and, finally, we assign the one at 1431 cm^{-1} to the $A_g(2)$ -derived mode.

The $C_{59}N$ ML spectrum does not show any peak that can be associated with the intense dipolar mode observed at 838 cm^{-1} in the $(C_{59}N)_2$ multilayer film. This suggests that the monomer configuration is more stable than the dimer one when the azafullerene is adsorbed on Cu(111). Monomer adsorption has also been observed for $C_{59}N/Si(111)-(7 \times 7)$ by STM [17]. These authors infer from their images that the azafullerene sublimates as a monomer and the dimerisation on the Si surface is prevented by the formation of a molecule–substrate bond. It seems reasonable to assume that the same is true for $C_{59}N/Cu(111)$.

Let us now address the question of charge transfer to the adsorbed molecules. Photoemission spectra indicate that the orbitals of the C_{60} MLs are hybridised with the substrate bands and each molecule receives 1.8 ± 0.2 electrons when adsorbed on polycrystalline Cu [18] and between 1.5 and 2 electrons in the case of Cu(111) [19]. One can have a rough estimate of the charge transferred from the metal to the (aza)fullerenes by using the shift of the adsorbate mode frequencies with respect to their values in the bulk phase [20,21]. Frequency shifts measured by infrared [22,23] and Raman [24,25] spectroscopies for fullerides (A_xC_{60}) can be used for calibration. The softening of the $T_{1u}(1)$ -derived mode from 527 to 496 cm^{-1} indicates a charge transfer of about 3.2 electrons. Taking into account the non-linear red-shift experienced upon charge transfer, one deduces a transfer of about 3.7 electrons for the $T_{1u}(4)$ -derived mode frequency (1422 down to 1344 cm^{-1}). The small peak at 1537 cm^{-1} , that can be associated to the $H_g(8)$ band, shows a shift of 23 cm^{-1} compared with its frequency in the C_{60} multilayer films (1560 cm^{-1}). This corresponds to a charge state of 1.5 electrons. In conclusion, the

mean charge transfer is 2.8 electrons. A similar charge transfer value can be deduced from the C_{60} ML spectrum.

Even with the uncertainty affecting this value, we see that it is nevertheless near the one obtained for chemisorbed C_{60} by photoemission spectroscopy. It is reasonable to estimate a charge transfer between two and three electrons per $C_{59}N$ (C_{60}) molecule when adsorbed on Cu(111), keeping in mind that the charge transfer is probably overestimated because of molecular distortion. Charge transfer may be one of the reasons for lack of dimerisation of $C_{59}N$ on the Cu(111) surface. In fact, X-ray diffraction studies show that $K_6C_{59}N$ is isostructural with K_6C_{60} [26], indicating that the $C_{59}N$ dimer is not stable when the carbon cages are highly charged.

3.2. Electronic excitations

The energy loss spectra presenting the electronic transitions from occupied to unoccupied states and plasmon excitations of C_{60} and $(C_{59}N)_2$ multilayers in reflection geometry are presented in Fig. 3.

The low energy part of the C_{60} spectrum, in good agreement with previously published data on multilayer films [20,27], is characterised by a peak at 1.55 eV corresponding to an optically forbidden excitonic transition. The first optically allowed transitions are found at about 2 eV. The low energy part of the $(C_{59}N)_2$ spectrum is instead characterised by two excitonic transitions located at 1.55 and 1.75 eV which are optically allowed, as seen from their very strong spectral intensity. This finding agrees well with photoemission data [28], which revealed that $(C_{59}N)_2$ is a non-metallic material, and EELS experiments in transmission [29] which deduced an optical gap of 1.4 eV. Further support for the existence of a reduced optical gap in this material compared to C_{60} comes from the onset of optical absorption of azafullerene in solution at 1.58 eV [10]. Calculations show that the excitonic transitions observed on our spectrum, appear because of the dimer geometry since singly bonded dimers of pure C_{60} also show such allowed transitions but at smaller energies [30].

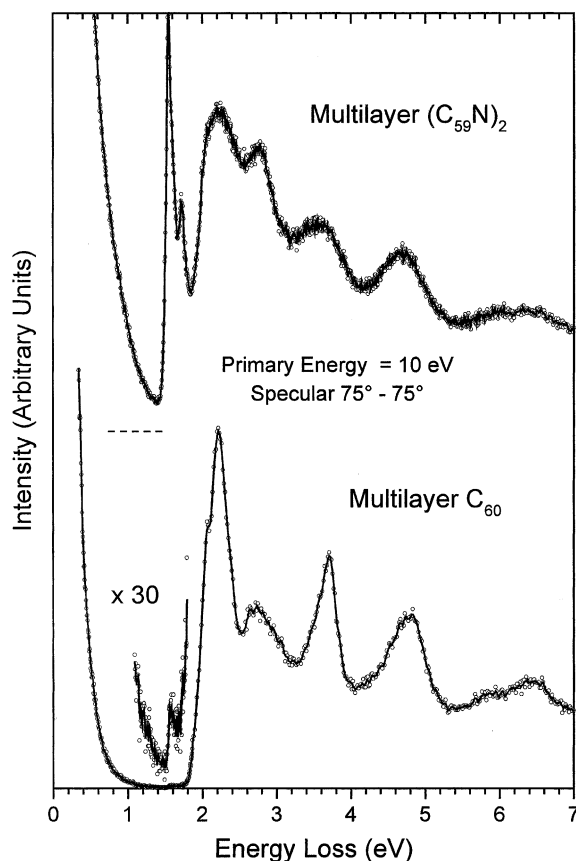


Fig. 3. EELS spectra of C_{60} (bottom) and $(C_{59}N)_2$ (top) multilayers measured in specular direction (75° – 75°) with an electron energy of 10 eV.

For the band to band transitions at higher energies, the energy loss peaks of the $(C_{59}N)_2$ film are only slightly broadened compared to C_{60} . However, we observe a weaker contrast in intensity as compared to the C_{60} spectrum. This is in line with EELS in transmission [31] where the C 1s excitation spectra show only a weak broadening in the case of the $(C_{59}N)_2$ while much broader peaks are measured in the polymer phase of o - Rb_1C_{60} due to the cycloaddition that induces a strong splitting of the energy levels.

For both C_{60} and $C_{59}N$ the EELS spectra of the ML on Cu(111), shown in Fig. 4, are very different from the multilayer spectra: the excitonic features are no longer visible and instead of a band gap there is an intense broad feature. Such a

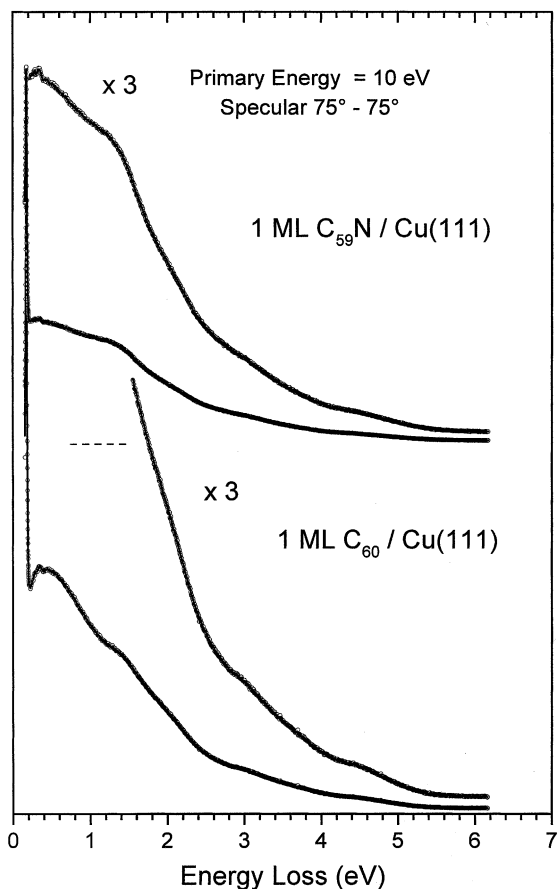


Fig. 4. EELS spectra of MLs of C_{60} (bottom) and $C_{59}N$ (top) adsorbed on Cu(111) recorded in specular geometry (75° – 75°) with an energy of 10 eV.

strong perturbation of the fullerene response function has previously been observed for C_{60} MLs on other metallic surfaces (see Ref. [21] and references therein) and attributed to the metallic nature of the overlayer, notwithstanding the possibility that the gap in the electronic excitation spectrum, if it exists, is smaller than 100 meV and/or masked by the tail of the elastic peak. The intense low energy feature was assigned to a charge carrier plasmon degenerate with intraband transitions in the now partially filled LUMO-derived band. The similarity of our spectra with that of $C_{60}/Ag(111)$ suggests that both C_{60} and $C_{59}N$ MLs on Cu(111) are metallic and agrees with the charge transfer deduced from the vibrational spectra.

The width of the higher energy excitations has been found to be indicative of the bond between the fullerene and the substrate [12] and therefore of chemisorption. Following this trend, the barely visible and very broad peaks of the C_{60} and $C_{59}N$ MLs on Cu(111) testify to the hybridisation between (aza)fullerene and copper electronic states but do not allow to draw any conclusion on the differences in bonding to the substrate between C_{60} and $C_{59}N$. However, by studying the desorption/decomposition of the (aza)fullerene MLs, information on the covalency of the bond can be deduced.

3.3. Desorption

Dissociation of C_{60} has been reported for systems for which the metal electronic states are strongly hybridised with those of the fullerene: for example for $C_{60}/Pt(111)$ and Ni(110) [32,33] cage disruption occurs above 560 and 690 K, respectively. In the case of $C_{60}/Ag(111)$, where the bond has a more ionic character, one observes only a rapid desorption of the fullerene at 670 K [32]. The behaviour of the fullerene upon annealing seems therefore indicative of the type of bonding with the substrate.

In Fig. 2 we present the vibrational loss spectra of the C_{60} and $C_{59}N$ MLs after annealing. The MLs were slowly and progressively annealed until the Auger KLL carbon line decreased in intensity with respect to the LMM Cu line, i.e. to about 680 and 660 K for C_{60} and $C_{59}N$, respectively. After annealing the Auger spectra show that the carbon coverage on the surface has decreased by about 20% for both C_{60} and $C_{59}N$. For C_{60} , we observe that the entire shape of the vibrational signature remains unchanged. Therefore no decomposition of the carbon cages has taken place and the loss of carbon is due to molecular desorption. The behaviour of the $C_{59}N$ ML is completely different. Indeed, the top spectrum of Fig. 2 barely shows the vibrational signature characteristic of adsorbed $C_{59}N$. In addition to an important reduction of intensities of the vibrational modes, one observes an increase of the background intensity. Since no peak is found in the C–H stretch frequency range (not shown in the figure), we deduce that an

amorphous carbon film is formed. This dissociation behaviour points to a more covalent character of the $C_{59}N$ –Cu bond compared to C_{60} –Cu.

4. Conclusion

In HREELS, the dimers of $C_{59}N$ are characterised by a dipolar mode at 838 cm^{-1} and by low frequency modes seen as shoulders of the “elastic peak” in off-specular analysis. The electronic transition spectrum of $(C_{59}N)_2$ confirms that this material is semiconductor-like with the first electronic transition occurring at the same energy as for C_{60} but with a narrower optical gap. Indeed, two very intense excitons are detected on $(C_{59}N)_2$ films while only optically forbidden excitons are seen in C_{60} films.

When a ML of $C_{59}N$ is adsorbed on Cu(111), the vibrational analysis no longer shows evidence of dimers. From the analysis of the vibrational frequency shifts, the metal is expected to transfer between two and three electrons to the azafullerene and to C_{60} . The adsorption results in a broadening of the electronic excitation peaks, suggesting hybridisation with the substrate electronic states. The $C_{59}N$ is observed to decompose above about 660 K while C_{60} desorbs above about the same temperature. This suggests that the $C_{59}N$ is more covalently bound to the Cu(111) surface than C_{60} . This bond and/or the charge transfer, stabilises the monomer configuration in the ML.

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