Core-level XPS spectra of fullerene, highly oriented pyrolitic graphite, and glassy carbon

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Abstract

The C 1s spectra of fullerene C_{60}, highly oriented pyrolitic graphite (HOPG) and amorphous carbon (a-C) have been measured using X-ray photoemission. The assumed background due to the inelastic scattering of electrons of these spectra has been subtracted by the Tougaard's method. The relative intensities and the energy positions for the core-level satellites have been determined. For C_{60}, a comparison of the low energy π type shake-up satellites gives good agreement between theory and experiment. Also, the energies of these features for fullerene and glassy carbon are very similar, whereas the corresponding energies for HOPG are somewhat larger, presumably, because of the higher density of the latter. Moreover, the atomic force microscopy (AFM) study indicates that the C_{60} samples consist of a thick layer of large clusters on the Si(111) surface, which is in line with the molecular character of the XPS spectrum. Furthermore, the broad high energy satellite does not consist of a single plasmon but of many components due to collective excitations characteristic of molecules and solids. These features are discussed in the light of theoretical excitation energies.
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1. Introduction

In recent years, much attention has been focused on the different phases of carbon, not only because of the potentially interesting applications but also due to phenomena related to the basic science. The diamond-like carbon is a good coating material for tools, where a hard surface is needed, for instance. It improves the wear resistance, as well. On the other hand some fullerenes, doped with alkali and alkaline earth atoms, show promising high-temperature super-conductivity properties. Needless to say, these findings have offered a unique opportunity for spectroscopic studies [1,2]. Optical conductivity [3,4], electron energy loss measurements (EELS) [5,6] and X-ray photoemission spectroscopy (XPS) [7–9] have been used to characterize these materials. In optical conductivity and EELS measurements, a molecule remains electrically neutral in the sense that during the excitation, no electrons will be removed from an atom. This means that dipole selection rules ($\Delta L = 1$) are basically valid for these methods. It is assumed that the system consists of N electrons.

In the case of XPS, however, a photoelectron is

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escaping from the molecule and we have a $N-1$ electron system, because one electron is missing in the final state. Therefore, besides the main line, monopole transitions ($\Delta L=0$) are characteristic giving shake-up satellites for XPS [7]. In spite of these differences, the energy positions of the features in the spectra are very similar for the above spectroscopies. However, the intensities of the satellites are quite different for XPS in comparison with the other methods.

In order to extract the relative intensities for the satellites of the C 1s core-level spectra, Tougaard's background subtraction method [10] has been used to remove the effect of the inelastically scattered electrons from the XPS spectra. When comparing the experimental intensities of the low energy shake-up satellites for C_{60} with the theoretical ones, calculated by Enkvist et al. [11], good overall agreement is obtained between experiment and theory provided the universal two-parameter background subtraction method [10] is used for the experimental spectrum. One should note that the same parameters are used for HOPG and glassy carbon, as well. Also, the excitation energies of the high energy satellites are compared with the theoretical ones and the relative intensities of these features are considered.

The main line of C_{60} is symmetric and the true Voigt line shape is assumed to be valid describing the spectrum. On the other hand, HOPG and glassy carbon show asymmetric main lines and therefore the Feldkamp–Davis type line shape [12,13] has been used for these materials.

2. Experimental

The experimental system consisted of two UHV chambers, one for sample preparation and the other for ESCA spectrometer. Both chambers had base pressure in the 10^{-10} Torr range.

Glassy carbon and highly oriented pyrolitic graphite were from Goodfellow Cambridge Limited. To prepare a clean surface, a glassy carbon rod of 4 mm diameter was fractured in situ under ultra-high vacuum. A highly ordered pyrolitic graphite sample was also cleaved in the preparation chamber using a sharp blade attached to a wobble stick.

The fullerene sample was prepared using the PVD (Physical Vapour Deposition) method. A thick C_{60} film was deposited on a cleaned Si(111) surface in the preparation chamber by sublimation of the fullerene powder from a crucible. Heating was done by thermal radiation and temperature was monitored using a thermocouple in contact with the crucible. The powder and the crucible were first heated to about 600 K in order to outgas the system. During the final evaporation at 850 K, the pressure remained below 2×10^{-9} Torr. After preparation the samples were transferred under vacuum into the analysis chamber.

The XPS measurements were done in a PHI 5400 ESCA spectrometer using monochromatized Al Kα radiation at 300 W. The analyzed area was about 1.5 mm in diameter and the take-off angle between the photoelectrons and the sample surface was 60°. The energy scale of the instrument was calibrated using the Ag $3d_{5/2}$ line at binding energy 368.3 eV. For narrow scans, the analyser pass energy was set at 17.9 eV. The resulting energy resolution was estimated to be 0.7 eV taken from the full width at half maximum (FWHM) of the Ag $3d_{5/2}$ line of a sputtered silver sample.

The duration of the measurement for each carbon spectrum extended to about 24 h in order to obtain good statistics. The surface cleanliness was checked by XPS survey scans taken before and after the actual measurements. The only detected impurity was oxygen which in all cases remained less than 1%. The thickness of the C_{60} film on Si(111) was estimated with XPS to be more than 70 Å using the overlayer method [14] and the electron inelastic mean free path for carbon [15].

Although the Shirley method has been widely used for background removal of the XPS spectra, the Tougaard method is now employed to consider the relative intensities of the satellites. The measured spectra were first corrected for the analyser transmission function varying with energy as $E^{-0.5}$ [16]. Tougaard's universal background subtraction method, containing only two roughly material independent parameters $B=2990$ eV^2 and $C=1643$ eV^2 [10], has been used for the C 1s XPS spectra. The results are shown in Fig. 1 for glassy carbon, HOPG and C_{60} using the same parameter values for each spectrum.

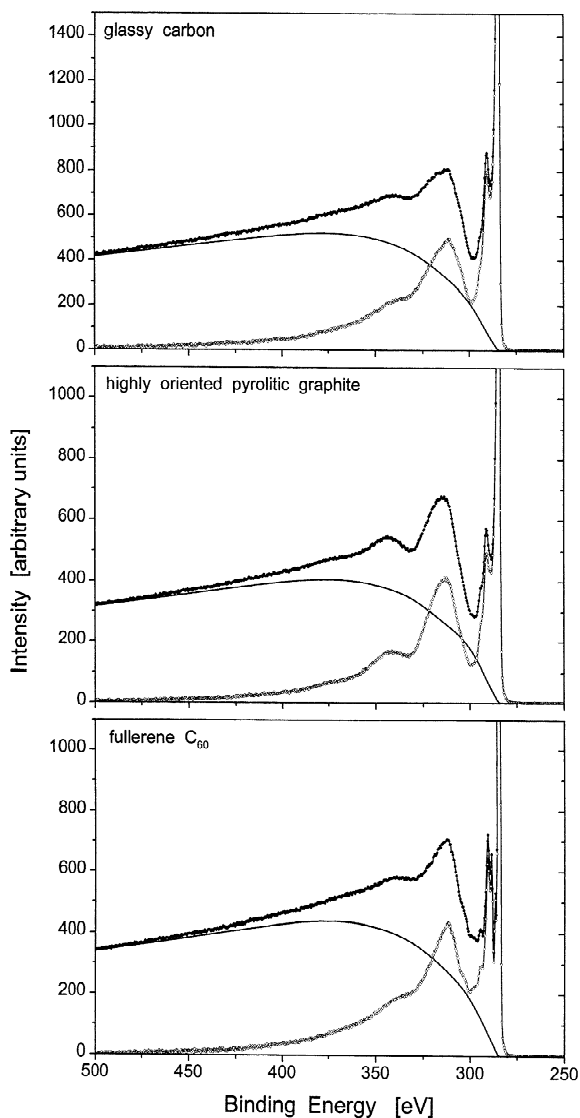The same layer of fullerenes on Si(111) were

Fig. 1. The XPS spectra of C_{60}, HOPG and glassy carbon showing the satellite structure of the C 1s line before (solid circles) and after (open circles) Tougaard's background subtraction.

further analyzed in air with the atomic force microscope (Park Scientific Instruments) at room temperature. The cantilever was covered with gold and the tip was used in contact-AFM mode. Fig. 2 reveals that the fullerite consists of large clusters, the typical size being roughly $80 \times 50 \times 4$ nm^3 and it is not a film of C_{60} molecules having a specific surface orienta-

tion. The shape of these features is comparable with those observed earlier by scanning tunnelling microscopy (STM) by Wragg et al. [17] and by AFM [18–20].

3. Line shape

The C 1s core-level spectrum of C_{60} shows a symmetric main line that is well described by a true Voigt function as can be seen in Fig. 3. This function is a convolution of the Lorentzian (describing the 1s hole lifetime effect) with the Gaussian containing the temperature-dependent phonon broadening and the instrumental function. The full width at half maximum (FWHM) of the Lorentzian is 0.11 eV and for the Gaussian it is 0.60 eV.

The corresponding main line of HOPG and glassy carbon is very asymmetric largely because these materials are good electric conductors. It turns out that the Feldkamp–Davis line shape convoluted with the Gaussian accurately fits the experimental spectrum shown in Fig. 3. This is a Doniach–Šunjić (DS) like line shape, in which a background due to Heaviside step function convoluted with the Lorentzian has been subtracted from the standard DS-function [21]. The intensity of the C 1s spectrum is now of the form (without the Gaussian broadening)

$$I(E) \sim I_{DS}(E) - \frac{1}{\xi_0 \pi} \left[\frac{\pi}{2} - \arctan\left(\frac{E}{\gamma}\right) \right], \qquad (1)$$

where $I_{DS}(E)$ denotes the intensity of the Doniach–Šunjić spectrum, ξ_0 is a cut-off parameter that depends on its low energy tail; 2γ is the full width at half maximum (FWHM) of the Lorentzian describing the life time of the 1s hole. The Doniach–Šunjić line shape is

$$I_{DS}(E) = \frac{\Gamma(1-\alpha)}{(E^2 + \gamma^2)^{(1-\alpha)/2}}$$
$$\times \cos\left[\frac{\pi\alpha}{2} + (1-\alpha)\arctan\left(\frac{E}{\gamma}\right) \right], \qquad (2)$$

where Γ is the gamma function and α is the singularity index, describing the asymmetry of the main line, being constant in Eq. (2). Feldkamp and Davis [12], however, assumed that index $\alpha(E)$ is not constant, but a slowly decreasing function of energy
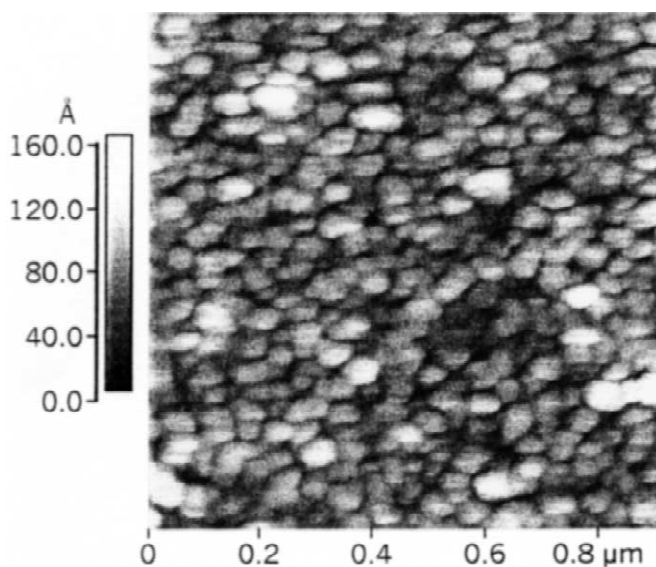
Fig. 2. AFM image of C_{60} film on the Si(111) surface. The scanning area is 1.0×1.0 μm². The depth scale of the clusters is indicated by a vertical bar.

when one is moving away from the main line to higher binding energies. It can be shown that one obtains Eq. (1) by introducing the background correction instead of varying the singularity index as a function of energy [12,13]. In the case of HOPG, the index α is 0.14 being slightly smaller than that of glassy carbon 0.19 which is in agreement with the results of Wertheim [22] and Cheung [23]. For these two materials, the Lorentzian is the same e.q. $2\gamma = 0.11$ eV and the FWHM of the Gaussian of HOPG is 0.56 eV, with the corresponding value being 0.60 eV for the latter. Recently, a surface core level shift (SCLS) of 0.12 eV for the C 1s line has been found at low temperatures, partially explaining the broad core-level spectrum of HOPG [24]. On the other hand, the inequivalent carbon sites give a contribution to the width of the corresponding line for glassy carbon [25].

4. Low energy satellites

On the high binding energy side of the C1s spectrum of fullerene, the nearest features to the main line consist of π type shake-up satellites. In Fig. 3, the first satellite at about 1.9 eV having an

intensity of 4.3% relative to the main line is associated with the monopole like electron transition between the HOMO–LUMO gap [7,8]. The second one at 2.9 eV possessing an intensity of 1.8% is hardly visible at all and it is not dipole allowed. The 3.8 eV (5.4%) satellite is also a monopole like feature. The next satellite having an energy of 4.8 eV as well as an intensity of 4.3% is well described by the dipole transition ($\Delta L = 1$). However, the 6.0 eV satellite with an intensity of 9.9% can only be partially explained by the dipole like $\pi \rightarrow \pi^*$ shake-up feature. It turns out that the π plasmon gives a significant contribution to this structure, too. Moreover, the previous theoretical calculation of these shake-up satellites made by Enkvist et al. gives very similar intensities for these features except in the case of the latter strongest one having an experimental intensity (9.9%) about twice as much as that of the corresponding theoretical satellite [11]. Also, the extra broadening of this satellite may be ascribed to a strong anisotropic character of the collective excitations in this energy region [26].

A small shoulder is observed at about 7.5 eV and its intensity relative to the main line has been estimated to be 3.6% as can be seen in Fig. 3. Wendin and Wästberg [27] have calculated the
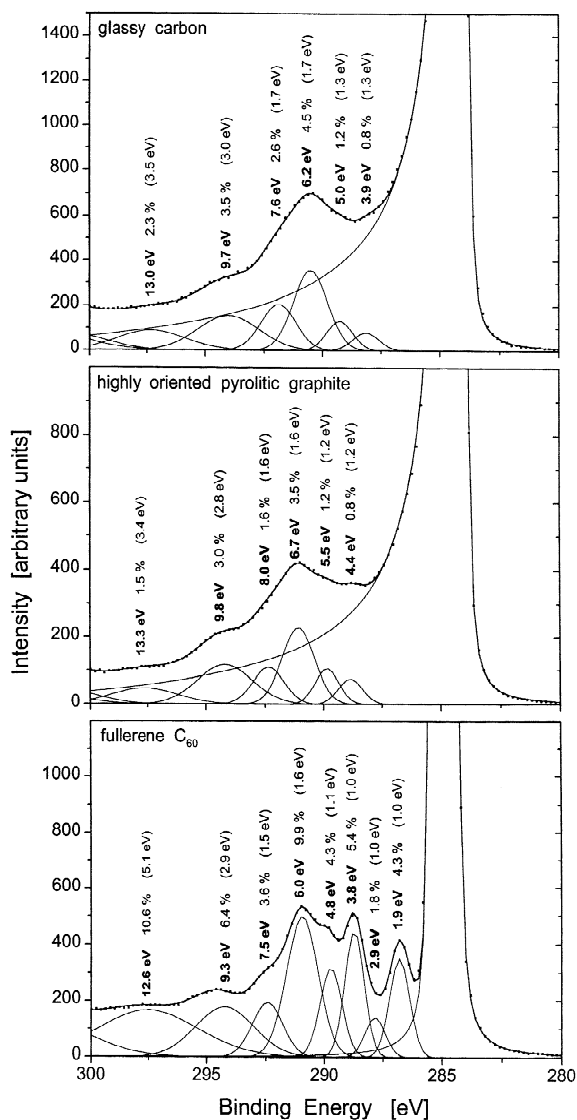
Fig. 3. The low energy satellite structure is dominated by π type shake-up features. The loss energy, relative intensity and FWHM of individual excitations are also shown.

photoabsorption cross-sections for C_{60} and they predicted a discrete feature at 7.48 eV caused by valence electron excitations having dipole character. Also, Enkvist et al. [11] find a small theoretical shake-up satellite in this energy region. The origin of the shake-up contribution to the 6.0 and 7.5 eV satellites should be similar [27].

It has been pointed out that for C_{60}, the energy region between 10 and 20 eV does not have discrete dipole transitions for free molecules and collective resonances are the dominating effects here [27]. This suggestion is supported by our results in Fig. 3 showing broader satellites, characteristic for plasmon like excitations, at 9.3 and 12.6 eV. In this case, one should mention that Östling et al. [28] propose a π like plasmon at 10.0 eV and a $\pi+\sigma$ resonance at 12.1 eV using a classical model. Also, Barton and Eberlein [29] predict π plasmon energies 9.96 and 13.36 eV for C_{60} molecules. Of course, the possible contribution of σ type monopole transitions to these features is also difficult to rule out [7,30].

Turning to the highly oriented pyrolitic graphite (HOPG) one can note similar shake-up satellites but having somewhat larger energies and smaller intensities relative to the main line in comparison with fullerite C_{60} as seen in Fig. 3. Although the first two low energy satellites are absent, a weak satellite having 0.8% intensity at about 4.4 eV is observed which is in line with the $\pi \rightarrow \pi^*$ transition found previously by optical methods [31]. The π type valence electrons are known to be free-electron like, which means that the collective excitations due to these electrons should have a larger energy for HOPG because of the higher density ($\rho = 2.2$ g/cm^3) of this material [32]. Indeed, in Fig. 3, the 6.7 eV satellite, having smaller intensity 3.5%, shows a ca. 0.5 eV shift to larger binding energies. Also the other low energy satellites indicate the same trend suggesting that π like plasmon excitations interact strongly with the corresponding shake-up features appearing in the same energy region [27].

This explanation becomes even more evident by considering satellite energies for amorphous (glassy) carbon in Fig. 3. In this case, the energies of the shake-up satellites are very similar to those of C_{60} having almost the same density ($\rho = 1.65$ g/cm^3) [33] in comparison with glassy carbon ($\rho = 1.4$ g/cm^3). On the other hand, the relative intensities of the satellites for amorphous carbon are quite similar to those of the highly oriented pyrolitic graphite.

5. High energy satellites

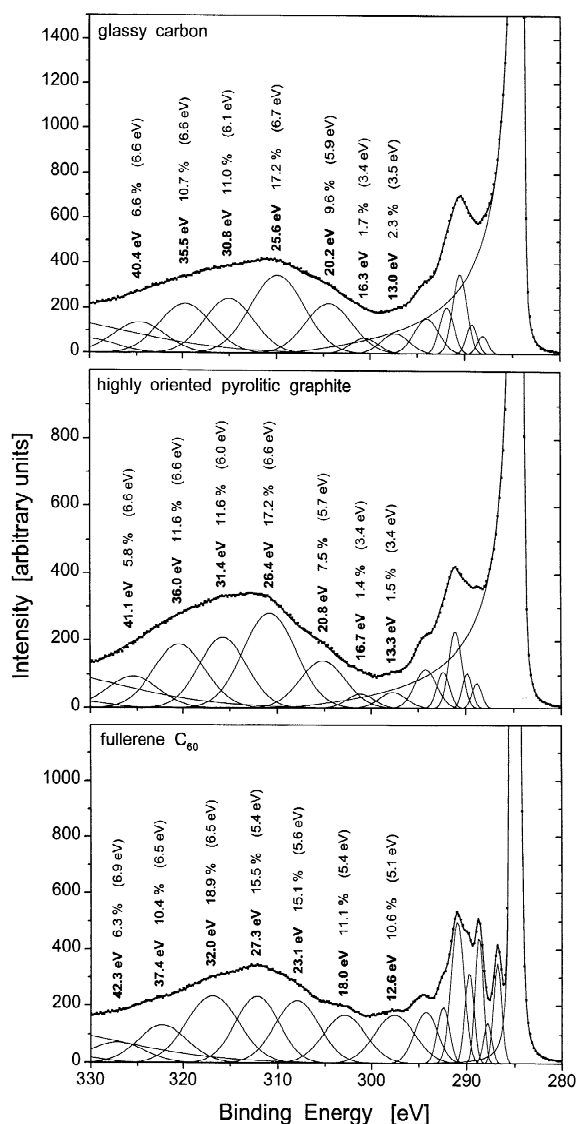The high energy satellites for C_{60} are shown in Fig. 4. The feature at about 18 eV from the main line

Fig. 4. High energy satellites are largely caused by several collective excitations. Notations are the same as in Fig. 3.

for the corresponding electron energy loss (EELS) spectrum. In addition, Davids et al. [35] suggested a giant plasmon mode at 18 eV.

The next shoulder for C_{60} can be seen in Fig. 4 having an energy of about 23.1 eV in agreement with Cohen et al. [36]. Its relative intensity is estimated to be 15.1% and the FWHM is 5.6 eV. Östling et al. [28] and Vasvári [37] obtain theoretically a collective excitation for the C_{60} molecule at about 22.0 eV and for the solid fullerene at 21.2 eV, respectively. These values are quite close to our observed energy, too. One should also mention the dressed and shifted single particle excitations at 22.5 and 23.3 eV from the main line [27] that may give some additional contribution to this feature.

The large peak (with a relative intensity of 15.5%) at about 27.3 eV for fullerite in Fig. 4 is well known and it is ascribed to the $\sigma + \pi$ plasmon (caused by all valence electrons) for solid C_{60} [3,37,28] since the corresponding feature is difficult to observe in the case of the free molecule [38–40].

The shoulder having an energy of 32.0 eV and an intensity of 18.9% relative to the main line may be largely explained by a dipole active plasmon mode that has been predicted to occur at about 33 eV by Lambin et al. [41] using a dielectric shell model. The weaker satellite (intensity 10.4%) at about 37.4 eV is more difficult to identify. However, Puska and Nieminen [42] have suggested a plasmon like excitation for the molecule to appear at about 35 eV from the main line.

Next, we shall briefly discuss the satellite structure of HOPG in Fig. 4. The hardly visible feature at about 16.7 eV having a relative intensity of 1.4% can be ascribed to the $\sigma - \pi$ transition [31,43]. The stronger 20.8 eV shoulder with an intensity of 7.5% may be due to the out-of-plane plasmon [36]. The largest satellite (relative intensity 17.2%) at about 26.4 eV from the main line is most likely caused by the in-plane $\sigma + \pi$ plasmons, all the valence electrons contributing to the excitations [36,28,3,44]. The FWHM of this peak is 6.6 eV as shown in Fig. 4 being in between those of the previously measured energy loss features having the corresponding values about 9 eV [31] and 5 eV [45]. The shoulder at about 31.4 eV relative to the main line has an intensity of 11.6%. This electron energy loss feature has been previously observed by Feely et al. [46] in the case

(having a quite large relative intensity 11.1%) can be mainly ascribed to a dipole like collective ($\sigma + \rho$) resonance which is characteristic for C_{60} molecules [34]. This is supported by the fact that Wendin and Wästberg [27] have predicted this kind of feature to appear at about 17.6 eV in their calculated photo-absorption cross-section. Also, Östling et al. [28] were able to find a $\sigma + \rho$ resonance at about 18.5 eV

of graphite and microcrystalline graphite with corresponding energies 33.3 and 30.3 eV, respectively.

The 36.0 eV satellite with the same relative intensity as the previous one has been interpreted for the electron energy loss spectra of graphite as being due to the $\sigma \rightarrow \sigma^*$ interband transition [47] or caused by the plasmon resonances perpendicular to the basal plane of the layered structure [48].

In Fig. 4, the individual components of the glassy carbon high energy satellites are slightly shifted towards the main line. This shift is roughly about 0.5 eV that to a certain extent can be ascribed to the lower density of this material in comparison with HOPG [31]. The strongest satellite, with a relative intensity of 17.2%, has an energy of 25.6 eV being in good agreement with a corresponding energy value of 25.6 ± 0.5 eV deduced from the electron energy loss spectrum of an ion-beam-thinned glassy carbon sample [49]. Nevertheless, the relative intensities of the high energy glassy carbon satellite components are very similar to those of HOPG.

6. Discussion

Fullerite is a solid made of C_{60} molecules and the interaction between the molecules are due to weak van der Waals potentials. This dipole like attraction is caused by π type electrons. The σ electrons, on the other hand, are largely responsible for the interaction between atoms in a single molecule. The cohesive energy of fullerite has been estimated to be ranging between 1.5 and 2 eV per molecule [41].

Previously, the epitaxial C_{60}/GeS(001) interface has been studied and a SCLS of 0.1 eV to higher binding energy for the XPS C 1s spectrum was found [25]. This effect was interpreted as being due to the energy difference for the signal between the carbon atom at the surface and at the bottom of the first monolayer of the molecules. A similar SCLS was observed for the fullerene film on the Al(111) substrate [50]. However, in this case, the shift was explained to be caused by atoms in the first monolayer and the second monolayer of the molecules. Nevertheless, the surface effect seems to be small and it may give a possible extra broadening for the C 1s line.

Regarding the shake-up satellites of C_{60} clusters

(Fig. 3) having π-electron character, one can note very similar energy separation between these satellites and the main line as those measured from free molecules by Krummacher et al. [51] using 390 eV photon energy. Also, the gas phase spectra show only slightly larger values for the relative intensities of the low energy satellites compared with the corresponding solid state spectra measured with 1487 eV excitation energy. An exception being the 6 eV satellite where the gas phase gives a relative intensity of 5.6% whereas solid C_{60} exhibits 9.9% for the same feature. One possible reason for this deviation maybe due to Tougaard's universal background subtraction method (shown in Fig. 1) that does not take sufficiently into account the contribution of the 6 eV π-plasmon satellite to the inelastic background. The other reason might be different photon energies for the gas phase and for the solid. It has been shown that the inelastic scattering contribution to this feature is quite strong [11]. However, in reflection electron energy spectroscopy (REELS), the electron is passing the surface twice making this method more surface-sensitive than XPS would be [52,53]. This difference between the two spectroscopic methods may cause significant deviations for the background subtraction, especially for electron energies smaller than 2 keV [52].

Concerning the C 1s spectrum of C_{60}, Tougaard universal method gives a symmetric main line. On the other hand, for HOPG and glassy carbon, the main line is very asymmetric using the Feldkamp–Davis line shape, giving similar results to the previous studies [22,23]. The reason seems to be that the Tougaard background subtraction very efficiently removes the elastic electron scattering contribution from the spectra [54].

Turning to the high energy satellites of fullerene shown in Fig. 4, it is evident that the 18 eV feature can be associated with C_{60} and not with HOPG or glassy carbon, since the latter ones do not reveal any visible shoulder in this energy region. This $\pi + \sigma$ type collective excitation has also been observed by Guizzetti et al. [55] using optical methods and Hertel et al. [56] for free molecules with photoionization. This is furthermore supported by the calculation of Bulgac and Ju [57] in the gas phase, predicting a high-energy collective excitation for the EELS spectrum to occur in this energy region, as well. It has

been emphasized that for the solid, this excitation energy is shifted to lie at about 27 eV from the main line due to the dipole–dipole interaction between different fullerene molecules [28,50,37]. This suggests that our C_{60} layer contains excitations which are typical not only for fullerites but also for molecules.

In conclusion, we can say that on the basis of a comparison of our XPS spectra with the corresponding gas phase spectra and the theoretical calculations for C_{60}, Tougaard's background subtraction method seems to work very well for different phases of carbon, not only for the satellite structure but also for the C 1s main lines. Also, the high energy satellite feature consists mainly of different collective excitations appearing as shoulders. Although, the main part of the low energy satellites of fullerene can be described by π-type shake up features, the high energy satellites are largely due to $\pi + \sigma$ collective excitations of the C_{60} molecule as well as of the solid phase. Comparing the C 1s spectrum of HOPG and glassy carbon with that of fullerene, it becomes evident that an indication of the more molecular character of the latter can be ascribed to the symmetric main line and to the presence of the 18 eV satellite which is absent in the case of the former.

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