



Relationship between the C KVV Auger line shape and layered structure of graphite

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Abstract

C KVV Auger electron spectra of highly oriented pyrolytic graphite (HOPG) (at different emission angles) and of quaterphenyl, fullerenes C₆₀, single- and multi-wall carbon nanotubes (MWNT) have been studied. The interpretation of HOPG spectra is based on the angular dependence of the Auger line shape and on the comparison with the related carbon compounds. The Auger spectra of HOPG at normal (S_{HOPGn}) and grazing (S_{HOPGg}) emission are quite different at the high-energy side. We interpret the difference between the two spectra in terms of different sampling depth and interlayer interaction. The normal emission spectrum is formed by the top, underlying layers and interlayer interaction. The last is the interaction between π -electrons of the first and second layers. This π -state is closer to the Fermi level than the π -state of the single layer and may be responsible for metallic conductivity. Information on this π -state found in these experiments provides a unique method for identification of the interaction between carbon atomic layers or for differentiating between the single and double layer structures of carbon atoms.

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1. Introduction

Over the past decades, the new carbon allotropes – fullerenes, nanotubes and onions, were discovered and studied by different analytical methods. These

allotropes are surface-like objects so surface sensitive methods play a great role in their studies. Surface sensitivity of Auger electron spectroscopy (AES) is often used to solve problems of chemical identification and compositional analysis in the near-surface region of solids [1]. It is qualitatively supposed that AES permits to recognize sp^2 - and sp^3 -hybridisation states by simple analysis of C KVV Auger spectra. However, to our knowledge, the adequate description

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of graphite C KVV spectra is being under consideration [2–9].

Houston et al. [2] found two discrepancies between the experimental and theoretical highly oriented pyrolytic graphite (HOPG) C KVV spectra using the self-convolution of the HOPG density of states (DOS) obtained experimentally from XES and X-ray photoelectron spectroscopy (XPS) spectra [3] and taking into account dynamical initial-state screening effects and final-state hole–hole interactions. The first one is a poor agreement between the high kinetic energy regions of the experimental and model C KVV spectra; the second one is that the model does not describe the peak near 240 eV. To overcome the first one Houston et al. [2] increased the effective electron occupancy in the valence-core excitonic state by 0.27 electrons. Concerning the second problem, the structure at 240 eV in their opinion, is due to plasmon effects.

Calliari et al. [10] used the second derivative representation of both the C KVV and valence band spectra to find correlation between them and consider the first as self-convolution of the second. They mentioned that such an approach was only suitable for energetic considerations i.e. to find Auger transition energies, while Houston's description was for the total C KVV line shape, and there was no correspondence between the numbers of valence band states and states in the C KVV Auger spectrum. Because of a large number of states to be considered in the VB, a better energy resolution is needed to get a self-consistent description of the full C KVV spectrum using DOS (derived from experimental VB spectra). It is worth noting that ionisation of the C1s core-level disturbs VB states because of the core charge changes from Z to $Z + 1$, where Z is atomic number.

Our goal is to find another interpretations of discrepancies mentioned above using new experimental data. To find the reasons of the first discrepancy, we have investigated the experimental C KVV spectra of HOPG (at different angles of emission), quaterphenyl, C60 fullerene single-wall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (MWNT). Quaterphenyl, C60 fullerene and SWNT may be considered as different approximations to HOPG and references of a pure sp^2 -state without interaction between graphene layers while a double-wall carbon nanotube as a two rolled graphene sheets

with interaction between them. From a general point of view, it is evident that SWNT can be presented as a graphite sheet upon rolling and a double-wall carbon nanotube as a two graphite sheets with interaction between them.

The inelastic mean free path (IMFP) of the C KVV Auger electrons in graphite is about two monolayers [11], so the most of the electrons are emitted from the first and second layers and by approaching to grazing emission angles it seems to be possible to record Auger spectra from the top layer only. So, in the case of graphite AES is an extremely surface sensitive method and can provide depth profiling of electronic structure within two monolayers.

2. Experimental

The X-ray photoelectron spectroscopy and X-ray-excited AES (XAES) data were obtained using a MK II VG Scientific spectrometer. Photoelectron and Auger processes were excited using an Al $K\alpha$ source with photon energy of 1486.6 eV, and the vacuum in the analytical chamber was maintained at 5×10^{-10} Torr. Spectra were collected in the constant analyser pass energy (fixed analyser transmission, FAT) mode, with pass energy of 20 eV for XPS and 50 eV for XAES analysis. The energy resolution determined as full width at half-maximum of the Au 4f7/2 photoelectron line is 1.1 eV. The C 1s XPS spectra were acquired with a 0.1 eV step size; a 0.25 eV step size was used for C KVV XAES spectra. The Auger spectra were recorded with an overall collecting time of 20–30 min, a signal-to-noise ratio of 100 and within an 8° angle of acceptance relative to analyser axis. The spectrometer energy scale was calibrated using Cu 2p3/2, Ag 3d5/2 and Au 4f photoelectron lines at 932.7, 368.3 and 84.0 eV, respectively [12]. The graphite samples were in a good contact with the spectrometer. For an accurate charge reference of all the samples except for HOPG the C1s binding energy was used. For the HOPG samples, a layer was peeled off in two ways, in the outer air just prior to insertion into the vacuum chamber and in vacuum inside a preparation chamber. The spectra of both samples were the same. Survey XPS spectra were measured before and after analysis. Neither oxygen nor other contaminants were observed above the noise

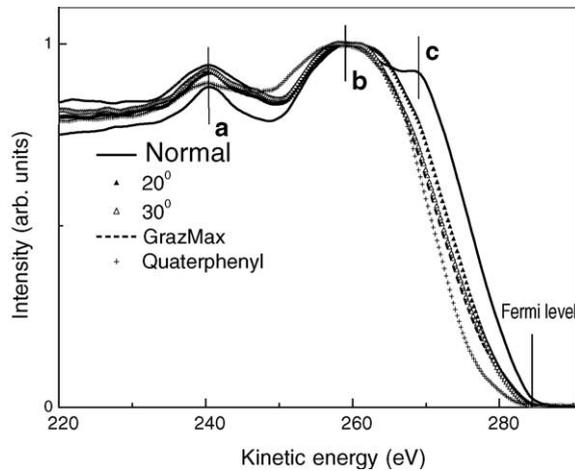


Fig. 1. The C KVV Auger spectra of the HOPG at different polar angles: (1) 0°, (2) 20°, (3) 30°, (4) 85° and (5) *p*-quaterphenyl [poly(phenylene)oligomer].

level in the spectra of all the samples including HOPG peeled off both ways.

3. Results and discussion

Fig. 1 shows dependence of the C KVV line shape on emission angle and comparison with a quaterphenyl spectrum. The spectra were normalized each to its maximum intensity. At emission angles higher than 30°, the HOPG C KVV line shape did not change except for the left part due to inelastic energy losses. As it can be seen, neither positions of the peaks **a** and **b** nor their relative intensities depend on emission angle in the HOPG spectra while there is a pronounced variation in the relative intensity of the feature **c** with increasing emission angle. The right part of S_{HOPGn} is almost parallel to that of S_{HOPGg} , which is between the S_{HOPGn} and the quaterphenyl spectra. HOPG angular-dependent C KVV spectra measured with better resolution than in our spectrometer manifest a parallel shift of the high kinetic energy part (HKEP) to lower energies [13] so the quaterphenyl spectrum may be considered as a limit case of the HOPG one at grazing incidence. This behaviour immediately suggest that the feature **c** has an origin quite different from that of the features **a** and **b**. The relative intensity of feature **c** determined as $(I_{\text{HOPGn}} - I_{\text{HOPGg}})/I_{\text{HOPGn}}$ is about 4%,

where I_{HOPGn} and I_{HOPGg} are areas under the C KVV lines after Shirley background subtraction.

There are six σ and two π energy bands in the valence band [14]. They are doubly degenerate in a single graphene sheet. We shall not separate different σ -states but shall consider two π -states denoted as π_s and π_{int} where π_s is a π -state similar to that in a single graphene sheet and π_{int} is a π -state closest to the Fermi level i.e. the upper π -band, which overlap along the Brillouin zone edges HKH and H'K'H' making graphite a semimetal [15]. Given that in the first approximation the C KVV line shape is a self-fold of VB DOS one can write

$$I_{\text{CKVV}} \sim (\sigma + \pi_s + \pi_{\text{int}}) * (\sigma + \pi_s + \pi_{\text{int}}) \\ = \sigma * \sigma + 2\sigma * \pi_s + 2\sigma * \pi_{\text{int}} + \pi_s * \pi_s + 2\pi_s * \pi_{\text{int}} \\ + \pi_{\text{int}} * \pi_{\text{int}}$$

where * denotes a self-fold procedure.

In accordance with HOPG VB DOS and relation between VB and Auger spectrum, the high kinetic energy part **c** should be attributed to $\pi_{\text{int}} * \pi_{\text{int}}$ and $\pi_{\text{int}} * \pi_s$ terms, and the other features to $\sigma * \sigma$, $\sigma(\pi_s + \pi_{\text{int}})$ and $\pi_s * \pi_s$ terms. It is well known that π_{int} is induced by interlayer interaction [14–18]. It is of interest, therefore, to clarify the reason for the disappearance of the HKEP at grazing emission angle, whether it is related to orientation of π -orbitals or their special space localisation.

It is widely accepted that π -orbitals of HOPG are normal to the basal plane as in benzene or quaterphenyl. But π -orbitals in benzene are localized while in HOPG they are delocalized. The shift of every other plane, in our opinion, results to off-normal orientation of some π -orbitals. We also should emphasize, that our analysis is based rather on π_{int} -state than on the total π -band because we consider HKEP.

We have some reasons to ignore main role of orientation and diffraction effects on polar angle in the C KVV line shape transformation:

- (1) There is a very small probability to observe any diffraction effects because of a large acceptance angle of the analyser. The averaging effect of the acceptance angle smears out the angular variation of the diffraction amplitude of electrons exiting from the crystal. In such cases, the intensity of

exiting electrons observed depends in a rather complex manner on the position and orientation of the specimen. It has been shown [19] that in electron-excited AES study of HOPG diffraction of Auger electrons plays a minor role in forming the angular dependence of the intensity of exiting Auger electrons. Corrugation of the surface [20] may also smear diffraction effects relative to polar angle.

- (2) The intensity ratio of C1s/C KVV is independent on emission angle although the intensity of secondary electron emission with different KE should have different dependence on emission angle if diffraction plays a great role.
- (3) If the C KVV line shape were related to anisotropy of the π -state relative to the normal one would observe change in other part of spectra due to the term $\sigma_s * \pi$, which is centred near 258 eV while all the spectra are similar in this region.
- (4) SWNT and fullerene C60 have no anisotropy of π -states because of cylindrical and spherical symmetry; however, $\pi_{\text{int}} * \pi_{\text{int}}$ and $\pi_{\text{int}} * \pi_s$ states have not been measured in their spectra.

On the other hand one can expect the C KVV line shape dependence on azimuth angle from HOPG structure. Because of the cylindrical symmetry of the analyser entrance we realize the measurement at polar angle different from normal at opposite azimuth directions. Fig. 2 shows that the spectra also differ in HKEP. The main factor of this difference is the

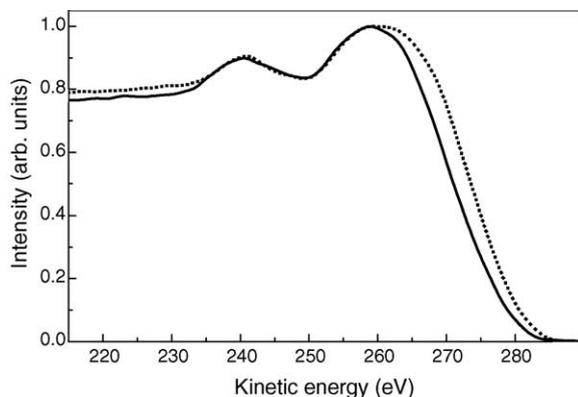


Fig. 2. The C KVV Auger spectra measured at emission angle of $\sim 45^\circ$. The difference between azimuth angles is 180° .

different sampling depth, which depends on orientation of HOPG close-packed directions.

Since the values of the C KVV IMFP and interlayer distance are comparable, there is a good chance to observe the layer structure in AES spectra and resolve the $\pi_{\text{int}} * \pi_{\text{int}}$ state. Angularly resolved XPS and AES is a well-known method of non-destructive depth profiling. [21]. However, if the effective attenuation length (EAL) is about unit cell dimension the depth profiling is rather qualitative [22]. It was estimated that the EAL could be smaller than the related IMFP by up to about 30% due to elastic-scattering effects, which could often lead to non-exponential attenuation of the AES, and XPS signal electrons with depth [23,24]. At smaller emission angles the sampling depth is larger. Fig. 3 demonstrates a simplistic picture of non-destructive depth profiling and a critical angle θ_1 when π_{int} electrons cannot leave the surface without energy losses. In our case, θ_1 is about 30° .

Taking into account the IMFP for the C KVV Auger electrons we can conclude that Auger electrons emitted preferentially from the top layer at grazing emission angle. It has been mentioned above that S_{HOPGg} is between S_{HOPGn} and the quaterphenyl spectra. It means, in our case, that S_{HOPGg} is not a spectrum of the top HOPG layer only as in [13] but includes the interaction between the first and second layers. Unfortunately, we could not avoid emission from the second layer because of low angular resolution and/or imperfection of the surface. Nevertheless, these results show that HOPG spectrum may be represented as a sum of two terms separated in depth, the first one is due to emission from the

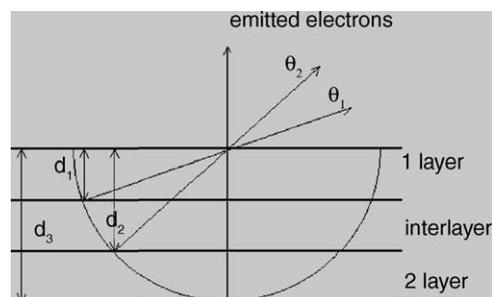


Fig. 3. A simplified picture of non-destructive depth profiling; d_1 , d_2 and d_3 are sampling depths at angles of emission θ_1 , θ_2 and normal emission, respectively. The radius of the semicircle is determined as IMFP is d_3 .

uppermost HOPG layer and the second one from the interlayer. The difference $S_{\text{HOPG}_n} - S_{\text{HOPG}_g}$ is a result of interaction between the first layer and the second one and π_{int} electrons are localized between layers. It should be emphasized that the difference spectrum $S_{\text{HOPG}_n} - S_{\text{HOPG}_g}$ is close to the Fermi level and may be related with metal type of conductivity.

It has been shown that interactions between oligophenylenes molecules in the herring bone arrangements lead to important modifications of the π -orbitals with respect to isolated molecules and dispersion of the top valence band and lowest conduction band can be taken as a measure of carrier mobility [25].

For comparison, we recorded Auger spectra of the SWNT and fullerene C60, which also could be considered as different modifications of a graphene sheet without interlayer interactions, and MWNT with the interaction between two cylindrical surfaces. There are metallic and semiconducting nanotubes and their electronic properties depend on diameter and chirality [26]. We can divide the Auger spectra into two groups of HOPG at grazing emission, fullerene C60, quaterphenyl, SWNT and HOPG at normal emission, MWNT using their similarity (see Fig. 4). The first group shows the absence of a state near the Fermi level. It means that the second group has metallic conductivity while the first has not. Fig. 5 shows that one cannot exclude interaction between π -orbitals in SWNT, fullerene C60. The shift between the quaterphenyl spectrum and any of their spectra, at

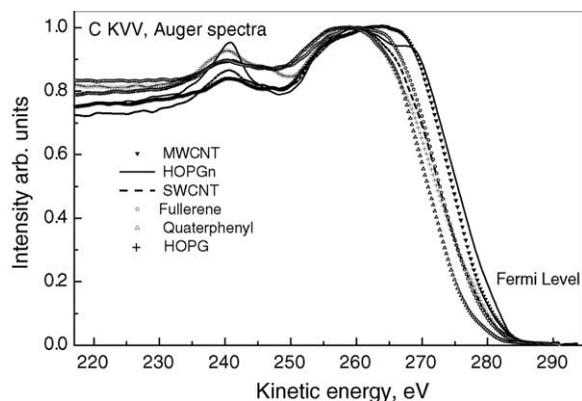


Fig. 4. Auger spectra of HOPG at normal emission, MWNT, SWNT, fullerene C60, quaterphenyl and HOPG at emission angle of 5° .

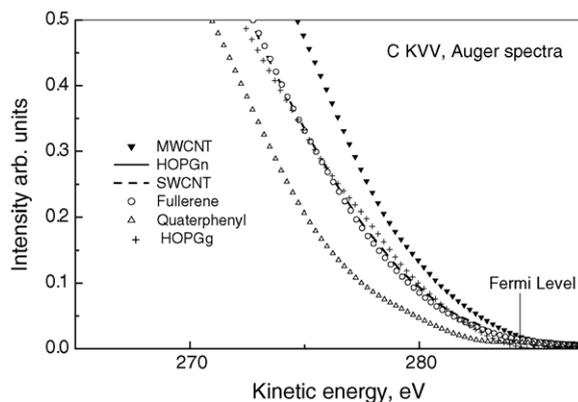


Fig. 5. Auger spectra of HOPG at normal emission, MWNT, SWNT, fullerene C60, quaterphenyl and HOPG at emission angle of 5° .

half-maximum, for example, may be a measure of such interaction.

MWNT has the regular inter-wall spacing of 3.4 \AA so its spectrum is very similar to S_{HOPG_n} (Fig. 4). However, in comparison with the HOPG, the smaller number of carbon atoms involved in interlayer interaction induces a lower intensity of HKEP in the C KVV spectrum in comparison with S_{HOPG_n} . The dependence of the C KVV peak shape may be a clear evidence for the existence of the interlayer interaction. The relative intensity of π_{int} -state is smaller than that of the π_s one so the part of the spectrum near the Fermi level is less intense than in the case of S_{HOPG_n} , while the intensity at about 270 eV is higher.

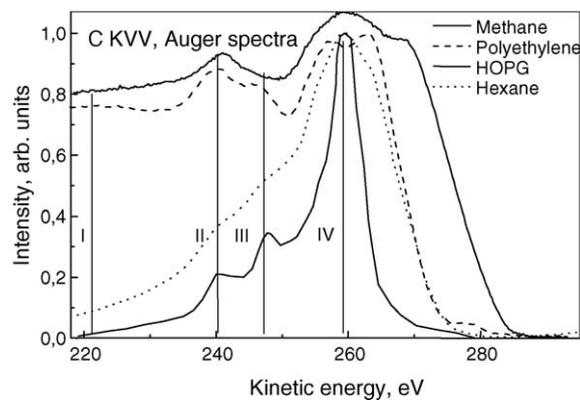


Fig. 6. Auger spectra of methane, hexane [5], polyethylene and HOPG. Feature I shows difference in electron backscattering in solid state and gas phase. Features II and III show that nature of them may be similar in methane, hexane and polyethylene.

It should be mentioned that Houston et al. included valence-core excitonic state to fit the high-energy region and “varied its electron occupancy to obtain a “best fit” with the leading edge of the experimental result” [2]. Our results show that the additional intensity in the high-energy region is related to interlayer interaction.

The high surface sensitivity of the C KVV Auger electrons has been demonstrated by using proton-induced 180° electron spectroscopy of a HOPG sample [27]. The KLL Auger spectra were recorded at normal, 80 and 84.3° emission angles. At normal emission, the spectrum has a narrow high-energy peak, which disappears at grazing emission angles of 80 and 84.3°. It also confirms our supposition that the high-energy part of the KLL Auger spectra results from the interlayer states.

The second problem mentioned above is the origin of the peak at 240 eV. Houston et al. did not interpret it adequately [2]. The theory based on self-fold of valence band DOS does not predict it. Comparison of Auger spectra of gas molecules of methane and hexane with that of solid-state polyethylene in Fig. 6 reveals peaks II and III in all the spectra [5]. Rye et al. [5] interpreted them using molecular considerations without any solid-state effects. So, one can consider this peak as a molecule-like one in polyethylene, quaterphenyl and HOPG. The 240 eV peak widths of HOPG and methane in Fig. 6 are rather similar than different.

4. Conclusions

Following Houston’s interpretation, the HOPG Auger spectrum may be represented as convolution of σ and π -state for a single layer only, while for more graphite layers additional terms, induced by interlayer interaction should be added. Electrons, related to the $\pi_{\text{int}} * \pi_{\text{int}}$ term are the closest to the Fermi level and may be responsible for metallic conductivity.

It has been shown that the C KVV Auger spectra of single-layer and multi-layer structures with sp^2 -bonds are quite different and may be used as a fingerprint of single layer and multi-layer growth modes and HKEP may be a measure of interaction between π -electrons in carbon nanotubes and fullerenes.

Information on additional π -states found in this experiment provides a promising method to explore if there is interaction between two single layers or not.

Solid-state effects should be excluded in identification of the peak at 240 eV in the HOPG Auger spectrum.

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