Characteristic loss spectrum accompanying the C1*s* photoelectron peak of the fullerene C_{60}

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The energy of the fundamental plasmon for C_{60} has been measured in a study of the spectrum of the loss accompanying photoemission from the C1*s* level. The result is 25.7 eV.

The C_{60} modification of carbon which was recently discovered has attracted a great deal of interest because of its unique properties.[1,2] Information on this modification is accumulating rapidly. Although C_{60} is a stable molecule up to high temperatures,[3] we do not know how the properties of this material are affected by various types of radiation. More reactions involving C_{60} and superconducting materials based on it are being discovered.[2]

Characteristic loss spectroscopy is one of the most informative methods for studying the electronic structure of materials containing carbon. A few papers[4–6] have already been published with reports of studies of the loss spectra of C_{60}. The spectra were excited in those experiments through the use of monoenergetic electron beams with a high energy density, so one cannot rule out the possibility of radiation damage to the C_{60} molecules in the analysis zone.

We have now developed a method for recording loss spectra in which the excitation source is a flux of photoelectrons produced during the bombardment of a sample by monochromatic x rays.[7] In this case the total energy released in the skin layer of the sample during the recording of the spectrum is lower by two to four orders of magnitude than that during electron excitation.

In principle, the loss spectrum excited by photoelectrons might differ from the spectrum excited by external electrons, since the spectrum in the former case might include a loss arising when there is a photoelectron inside a carbon atom with a hole in the 1*s* level—the so-called internal loss.[10] This circumstance is also evidence that the loss spectra accompanying the C1*s* photoelectron peak might be a new characteristic of the fullerene C_{60}.

The x-ray photoelectron spectra were excited by Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV). The power drawn by the x-ray tube did not exceed 200 W. The visible surface area of the sample was 4 cm^2.

The C_{60} was synthesized by electric-arc evaporation of graphite in a helium atmosphere by the method of Ref. 8. The sooty material produced as a result was then subjected to an extraction process involving benzene, in a Soxhlet apparatus. The pure fullerene C_{60} was obtained in the form of a fine-crystal powder through chromatographic purification of the extract, followed by crystallization. According to data ob-

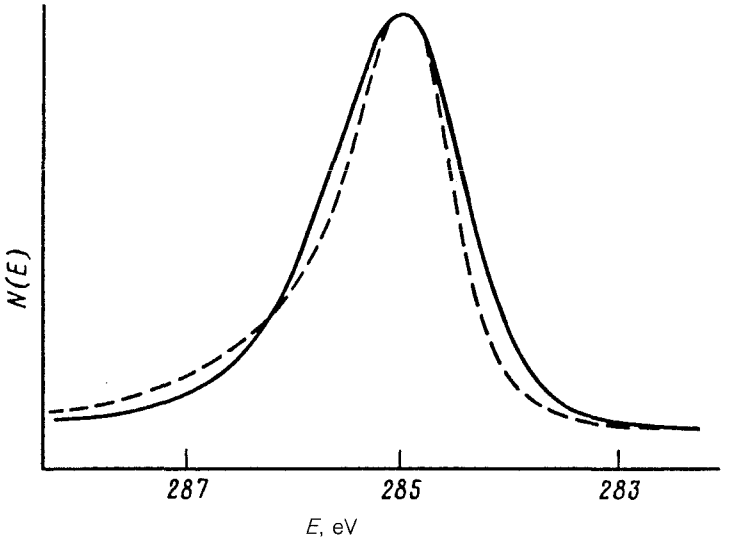

FIG. 1. The C1*s* x-ray photoelectron peaks for C_{60} (solid line) and graphite (dashed line).

tained by liquid chromatography, more than 95% of the material used to prepare the samples consisted of the basic substance.

Test samples were prepared by depositing C_{60} powder on an aluminum substrate covered with a thin ($\sim$4-nm) layer of Al_2O_3. An oxide layer of this thickness is no obstacle to the achievement of a good electrical contact between the sample and the substrate, while it does prevent a possible chemical interaction between the material of interest and the metal.

Figure 1 shows the C1*s* photoelectron peaks for C_{60} and graphite. The peaks are slightly asymmetric. The reason for the asymmetry of x-ray photoelectron peaks was discussed in the early papers on x-ray photoelectron spectroscopy (Ref. 9, for example). The width of the peak at half-maximum is 1.20 eV for graphite and 1.47 eV for C_{60}. The broadening of the C1*s* peak may be due to the larger spread in the sizes of the crystallites in the case of C_{60}.

The peaks are nevertheless narrow enough that they can be regarded as elastic peaks in a study of the accompanying loss spectra, particularly in the region of loss due to the excitation of plasma oscillations of all valence electrons [the $(\sigma + \pi)$ plasmon].

Figure 2 shows the spectra in the region of the $(\sigma + \pi)$ plasmon. We see that the background can be subtracted by the method described in Ref. 7, for the example of the characteristic loss spectra of boron nitride. We see from this figure that the peak due to the fundamental plasmon in the case of C_{60} is at an energy about 1 eV lower than that for graphite. The position of this peak on the energy-loss scale is 27.0 eV for graphite and 25.7 eV for C_{60}. The measured value for graphite agrees with the energy ($\hbar\omega_p$) reported for the $(\sigma + \pi)$ plasmon in Refs. 10–12. In the C_{60} case there is also a

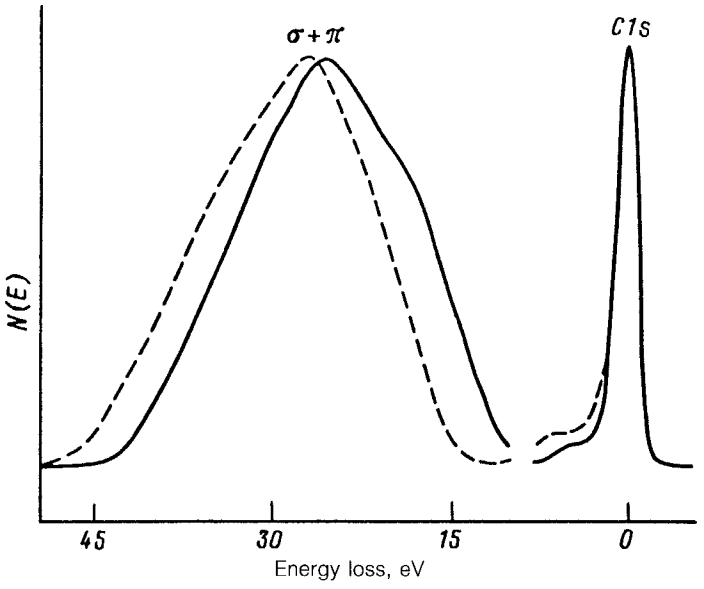

FIG. 2. Loss spectra of C_{60} (solid line) and graphite (dashed line). For clarity, the intensity of the C1*s* peak has been reduced by a factor of about 21 for C_{60} and by a factor of about 18 for graphite.

good agreement between the result of our measurements and the value of 26 eV reported in Ref. 4.

The meaning may be that bombardment by electrons in the customary method for exciting the spectra does not affect the position of the main peak in the C_{60} spectrum.

Let us use the standard formula[13]

$$\hbar\omega_p = 28.8 \left[\frac{Z \cdot \rho}{\epsilon_c \cdot A}\right]^{0.5} \text{(eV)}. \tag{1}$$

Here Z is the number of valence electrons, ρ is the mass density (in grams per cubic centimeter), A is the atomic mass, and ϵ_c is the polarizability of the core electrons, which are not involved in plasma oscillations. A decrease in $\hbar\omega_p$ thus implies a decrease in the mass density if the composition of the sample does not change.

A calculation of ρ for C_{60} from expression (1) with the help of the measured value $\hbar\omega_p = 25.7$ eV and a calibration against graphite ($\hbar\omega_p = 27.0$ eV and $\rho = 2.25$ g/cm^2) yields 2.03 g/cm^3. A corresponding calculation for diamond ($\hbar\omega_p = 33$ eV) yields $\rho = 3.4$ g/cm^3, which is not far from the value of 3.51 g/cm^3 given in handbooks.

The value found for ρ for C_{60} in this manner is substantially different from the value of 1.678 g/cm^3 found from x-ray structural data.[8] One possible explanation for this difference is that in the case of C_{60} plasma oscillations are excited only within the

electron system of one molecule, where the density of valence electrons is close to that in graphite and does not reflect the density over the entire volume of C_{60} crystallites. The difference between the conductivities of graphite (7×10^{2} S/cm) and C_{60} (3×10^{-2} S/cm at $P=200$ kbar; the energy gap is $E_g = 1.7$–1.2 eV, depending on the pressure)[14] may also be a consequence of a more pronounced localization of electrons in the case of C_{60}.

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