Study of $C_{60} \cdot 2S_8$ by the methods of induced electron emission

Yu. M. Shul'ga,[a*] **V. I. Rubtsov,**[a] **V. N. Vasilets,**[b] **A. S. Lobach,**[a] **N. G. Spitsyna,**[a] **and G. A. Volkov**[a]

[a]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588
[b]*Branch of the Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences,*
142432 Chernogolovka, Moscow Region, Russian Federation

It was shown by the methods of induced electron emission that a transfer of the electron density from C_{60} molecules to the eight-membered ring of sulfur is characteristic of $C_{60} \cdot 2S_8$. The value of the $(\sigma+\pi)$-plasmon energy for $C_{60} \cdot 2S_8$ is approximately 1 eV less than that for pure C_{60}. In a high vacuum, the $C_{60} \cdot 2S_8$ surface is depleted in sulfur.

Key words: induced electron emission; $C_{60} \cdot 2S_8$.

Compounds of buckminsterfullerene have attracted the considerable attention of scientists (see, for example, reviews[1—3]). However, reliable X-ray data have been obtained only for some compounds of this type. The study of such structurally characterized compounds by various physical methods is of interest from the viewpoint of the development of analytical procedures for characterization of reaction products involving fullerenes, as a rule, X-ray-amorphous.

As is known,[4—6] $C_{60} \cdot 2S_8$ is crystallized in monoclinic syngony, spatial group *C2/c*, $a = 20.90$, $b = 21.01$, $c = 10.537$ Å, $\beta = 111.29^{\circ}$, and crown-like cyclic molecules of S_8 as though filling hexagonal channels in a packing of C_{60} molecules. However, the nature of the chemical interaction between C_{60} and S_8 is still unclear.

In this report, results are presented of the study of $C_{60} \cdot 2S_8$ by the methods of induced electron emission: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and electron energy loss spectroscopy (EELS). The IR spectra of diffuse reflectance of $C_{60} \cdot 2S_8$ are also presented. The data obtained made it possible to establish the direction of the electron transfer for the formation of $C_{60} \cdot 2S_8$ and to describe the loss function and some other properties of the compound studied.

Experimental

The $C_{60} \cdot 2S_8$ compound in the form of fine-crystalline powder was prepared according to the known procedure.[6] The chemical analysis and X-ray diffractometry showed its complete identity with the $C_{60} \cdot 2S_8$ compound, whose structure has been previously described.[6]

Samples for induced electron emission were prepared by the application of a thin layer of the powder of the studied compound onto an aluminum holder, whose surface was preliminarily cleaned and then oxidized in air to form a thin (40 Å) layer of Al_2O_3. The existence of the Al_2O_3 layer prevents the probable interaction of the compound studied with aluminum metal but does not prevent the electric contact of the sample with the substrate.

Electronic spectra were measured on a PHI-551 instrument supplied with an analyzer of the type of a double-pass cylindric mirror. XP spectra were excited by Mg-Kα irradiation ($h\nu = 1253.6$ eV). The analyzer was used in the regime of retarding voltage (the energy of electrons passed through the analyzer (E_p) was 50 eV) at absolute resolution of 1.1 eV. Loss and Auger spectra were excited by an electron beam from an electron gun coaxial to the analyzer. The energy of the initial electron beam was 2 keV (for the excitation of loss spectra) or 3 keV (for the excitation of Auger spectra). The half-width of the energy distribution from the initial beam was 0.5 eV. The regime of $dN(E)/dE$ with modulation voltage $V_m = 3$ V was used for recording Auger spectra. Loss spectra were recorded in the regime of retarding voltage: $E_p = 25$ eV, absolute resolution was 0.7 eV. The pressure of residual gases in a chamber of the spectrometer during recording did not exceed $3 \cdot 10^{-10}$ Torr.

The transition from measured integral intensities in XP spectra to atomic concentrations was performed using the data of Skofield on photoelectric absorption cross-sections of Mg-Kα irradiation.[7] Quantitative data in the case of Auger spectra were obtained by the known procedure.[8]

The spectra measured were corrected taking into account the dependence of the emission coefficient of an analyzer on the kinetic energy. Single-loss spectra y(E) were determined solving the integral equation:[8] $N^{\text{in}}(E) - ky(E)*N^{\text{in}}(E) = ky(E)$, where the sign $*$ designates the energy convolution; $N^{\text{in}}(E)$ is the inelastic part of the measured loss spectrum normalized to the surface area under the elastic peak; k is the factor which takes into account the geometry of the experiment on electron reflectance.

The y(E) function thus obtained is proportional to the loss function averaged over scattering angles[9]

$$y(E) \sim \ln(1 + \theta^2_{\max}/\theta^2_E)\ \mathrm{Im}(1/\varepsilon(E)),$$

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2149—2152, December, 1994.

1066-5285/94/4312-2030 $12.50 © 1995 Plenum Publishing Corporation

where θ_{max} is the maximum scattering angle on electrons of the valence shell, $\theta_E = E/(2E_{pr})$, E_{pr} is the energy of the initial beam. This approach does not require special assumptions about a particular energy dependence of the differential cross section of inelastic scattering for plasmon and other channels of electron scattering, and this is one of the advantages of the method. The sequence of operations for the isolation of the $y(E)$ function from the experimental spectrum of C_{60} has been shown previously.[10]

IR spectra of the compounds studied were recorded on a Perkin Elmer-1720X IR-Fourier spectrometer with resolution of 0.5 cm^{-1}, using an attachment of diffuse reflectance (Perkin Elmer, an incident angle 38°, an angle of scattering irradiation collection 180°). A sample was prepared by mixing the studied compound with the KBr powder. For a concentration of the studied compound in the mixture less than 3 %, the diffuse reflectance (DR) spectrum coincides with the absorption spectrum of the sample,[11] which is also evidenced by the agreement of the literature data[12—14] and the obtained IR absorption spectra of pellets of fullerene with KBr and the IR DR spectrum for C_{60}. The DR procedure, unlike the traditional procedure of preparation of pellets with KBr, is not distorting, because it does not require molding, it possesses higher sensitivity (the signal/noise ratio is proportional to the square root of the substance concentration), and it allows one to compensate almost completely the spectral lines of water and other additions in KBr.

Results and Discussion

The summarized XP spectrum of $C_{60} \cdot 2S_8$ is presented in Fig. 1. In addition to C1s, S2s, and S2p peaks, O1s, Al2s, and Al2p peaks caused by uncovered regions of a substrate are detected in the spectrum. Regions with a sufficiently thick layer of $C_{60} \cdot 2S_8$ can be found by studying the sample surface by scanning Auger spectroscopy. The Auger spectra of these regions contain neither peaks of aluminum nor oxygen.

An analysis of the ratio of integral intensities of the peaks assigned to S2p and C1s showed that the sample surface is depleted in sulfur under the conditions of a high vacuum and, probably, in part due to X-ray irradiation. For example, the $[S/C_{60}]_{at}$ ratio determined from the XP spectra is equal to 11 and 5 for the freshly prepared sample and the sample after a long evacuation, respectively. A similar conclusion can also be drawn from the Auger analysis of those surface regions whose spectra do not contain peaks of aluminum and oxygen.

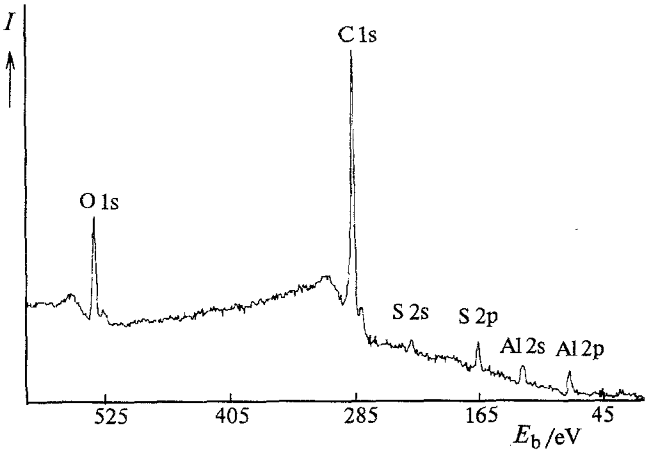

Fig. 1. Summarized XP spectrum of the studied sample.

The position of the S2p peak is the most important parameter for the determination of the electron transfer direction in the compound studied. A bond energy of 163.7 eV is determined relative to the position of C1s to which the value of 285.0 eV is assigned. The latter value corresponds to the position of the C1s peak in the bond energy scale for pure C_{60} for the mentioned method for the sample preparation and coincides with the literature data,[15] which attest that E_b(C1s) is also equal to 285.0 eV for C_{60} films on substrates of Ti, AsGa, or SiO_2. The close value of 284.9 eV was obtained for C_{60} films on Si(111).[16] It is evident that E_b(S2p) is less than 163.7 eV for calibration over C1s < 285.0 eV, because the distance between the C1s and S2p peaks equal to 121.3 eV for $C_{60} \cdot 2S_8$ is independent of the calibration method.

The bond energy of S2p in sulfur S_8 measured in this study is equal to 164.2 eV. This value coincides with the data of works where the same calibration method is used (see, for example, Refs. 17, 18). Thus, on going from S_8 to $C_{60} \cdot 2S_8$, the E_b(S2p) value decreases by 0.4 eV. In terms of the simplest notions according to which the bond energy of the framework electrons is mainly determined by the charge on the studied atom (the effect of the extra-atomic relaxation is not taken into account),[18] one can assume that sulfur in $C_{60} \cdot 2S_8$ has a small negative charge and, therefore, fullerene has a small positive charge. Let us mention that this interpretation does not agree with the concept that C_{60} behaves as an acceptor in compounds with S_8.[6,14]

The loss functions $y(E)$ for $C_{60} \cdot 2S_8$ and C_{60} normalized to the integral intensity are presented in Fig. 2. It is seen that both of the functions have two main maxima, which are related to the excitation of plasma vibrations of all valence electrons (σ+π-plasmon, 24.0 eV for $C_{60} \cdot 2S_8$ and 25.2 eV for C_{60}) and separately of π-electrons (π-plasmon, 5.8 eV). The calculation of the energy of plasma vibrations of all valence electrons using the Drude formula ($\omega_p^2 = 4\pi ne^2/m$, n is the density of valence electrons) gives values of $\hbar\omega_p$ equal to 21.2 eV for C_{60} (ρ = 1.65 g cm^{-3}) and 20.3 eV for $C_{60} \cdot 2S_8$ (ρ = 1.89 g cm^{-3}).[6] Thus, the aforementioned shift of the main maximum at ~1 eV is well described in terms of the free electron model. However, the difference between the measured and calculated values of $\hbar\omega_p$ is as significant as in the case C_{60}.

The average density of valence electrons for $C_{60} \cdot 2S_8$ is lower than the analogous value for solid samples of C_{60}. However, the relative difference of the measured and calculated values of $\hbar\omega_p$ for the σ+π-plasmon $\delta_{rel} = 1 - \hbar\omega_p(\text{calc.})/\hbar\omega_p(\text{meas.})$ in the case of $C_{60} \cdot 2S_8$ is almost the same as in the case of C_{60} (δ_{rel} = 0.15).

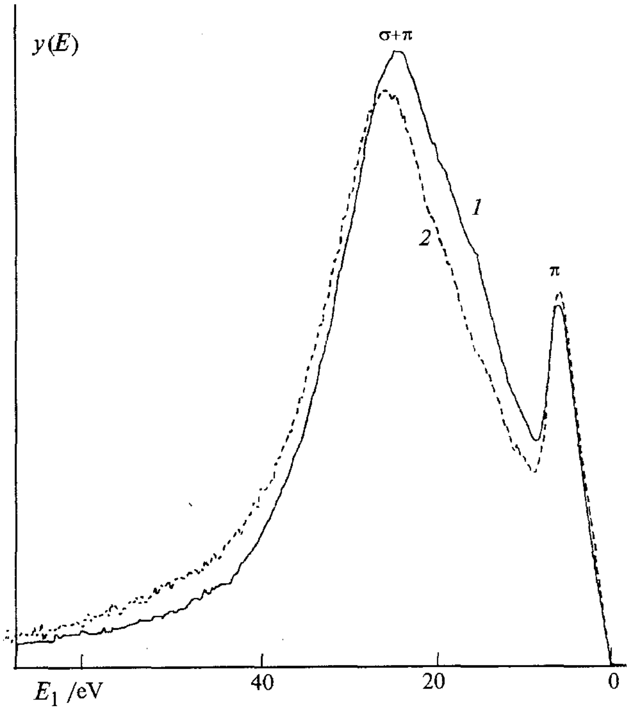

Fig. 2. Function y(*E*) (see text) for $C_{60} \cdot 2S_8$ (*1*) and C_{60} (*2*).

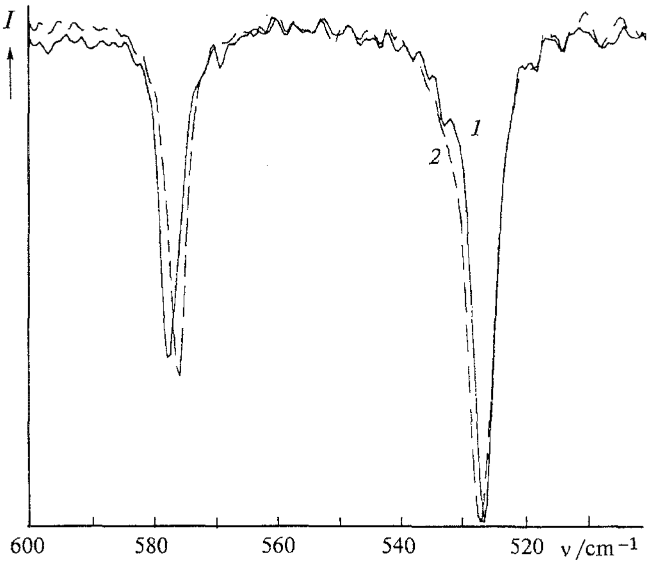

Fig. 3. IR diffuse reflectance spectra of $C_{60} \cdot 2S_8$ (*1*) and C_{60} (*2*).

It is also seen from Fig. 2 that the position of the maximum caused by the π-plasmon is the same for the compared compounds, and its peak intensity is less in the case of $C_{60} \cdot 2S_8$ than in the case of C_{60}. The coincidence of the positions of the peaks considered may be related to an increase in the relative fraction of π-electrons, which compensates a decrease in the total density of valence electrons in $C_{60} \cdot 2S_8$ compared with C_{60}. The reason for the decrease in the probability of inelastic scattering on the π-plasmon in the case of $C_{60} \cdot 2S_8$ is not clear. Perhaps in the case of the complex with sulfur, there are two π-plasmons, somewhat different in energy, which results in the broadening of the peak associated with the excitation of plasma vibrations of π-electrons and, hence, in a decrease in the observed peak intensity.

We have also measured the IR diffuse reflectance spectra of the studied sample and pure C_{60}. There are intense bands in the spectrum of C_{60}, whose positions coincide with the frequencies of pellets or films of buckminsterfullerene in the IR absorption spectra.[12–14] All intense bands characteristic of C_{60} and a low-intense band at 470 cm^{-1} characteristic of S_8 are observed in the spectrum of $C_{60} \cdot 2S_8$. The positions of the intense bands at 1430 and 1183 cm^{-1} completely coincide in the spectra of C_{60} and $C_{60} \cdot 2S_8$, and two other bands in the case of $C_{60} \cdot 2S_8$ (578 and 526.5 cm^{-1}) are arranged 1.5 cm^{-1} farther from each other than in the case of C_{60} (577 and 527 cm^{-1}) (Fig. 3).

A similar effect was observed[14] for $C_{60}S_{16} \cdot 0.5C_6H_5Cl$ and was assigned only to the shift of the band at 577 cm^{-1}.

This work was financially supported by the Russian Foundation for Basic Research, Projects Nos. 93-03-18002 and 93-03-18705.

References

1. J. S. Miller, *Adv. Mater.*, 1991, **3**, 262.
2. A. V. Eletskii and B. M. Smirnov, *Usp. Fiz. Nauk,* 1993, **163**, 33 [*Russ. Fiz. Rev.*, 1993, **163** (Engl. Transl.)].
3. V. I. Sokolov and I. V. Stankevich, *Usp. Khim.*, 1993, **62**, 455 [*Russ. Chem. Rev.*, 1993, **62** (Engl. Transl.)].
4. O. A. Dyachenko, E. B. Yagubskii, S. V. Konovalikhin, N. D. Kushch, G. V. Shilov, and N. G. Spitsyna, in *International Workshop "Fullerenes and Atomic Clusters", Book of Abstracts,* St. Petersburg, Russia, 4—9 Oct. 1993, 47.
5. G. Roth and P. Adelmann, *Appl. Phys. A*, 1993, **56**, 169.
6. L. I. Buravov, O. A. D'yachenko, S. V. Konovalikhin, N. D. Kushch, I. P. Lavrent'ev, N. G. Spitsyna, G. V. Shilov, and E. B. Yagubskii, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 262 [*Russ. Chem. Bull.*, 1994, **43**, 240 (Engl. Transl.)].
7. *Methods of Surface Analysis*, Ed. A. W. Gzanderna, Elsevier Scientific Publishing Company, Amsterdam, 1975.
8. *Handbook of Auger Electron Spectroscopy*, Physical Electronics Industries, Inc., Eden Prairie, Minnesota, 1976, 252.
9. G. M. Mikhailov and V. I. Rubtsov, *Poverkhnost',* 1987, No 7, 99 [*Surface,* 1987 (Engl. Transl.)].
10. V. I. Rubtsov and Yu. M. Shul'ga, *Zh. Eksp. Teor. Fiz.*, 1993, **103**, 2065 [*J. Exp. Theor. Phys. USSR*, 1993, **103** (Engl. Transl.)].
11. P. J. Brimmer, P. R. Griffiths, and N. J. Harrick, *Appl. Spectrosc.*, 1986, **40**, 258.

12. W. Krätschmer, K. Fostiropoulos, and D. R. Hüffman, *Chem. Phys. Lett.*, 1990, **170**, 167.
13. D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, W. G. Golden, H. Seki, C. A. Brown, and M. S. de Vries, *Chem. Phys. Lett.*, 1991, **179**, 181.
14. N. D. Kushch, I. Majchrzak, W. Ciesielski, and A. Graja, *Chem. Phys. Lett.*, 1993, **215**, 137.
15. M. B. Jost, N. Troullier, D. M. Poirier, J. L. Martins, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, *Phys. Rev.*, 1991, **B44**, 1966.
16. W. M. Tong, D. A. A. Ohlberg, H. K. You, R. S. Williams, S. J. Anz, M. M. Alvarez, R. L. Whetten, Y. Rubin, and F. N. Diederich, *J. Phys. Chem.*, 1991, **95**, 4709.
17. D. Briggs and V. A. Gibson, *Chem. Phys. Lett.*, 1974, **25**, 493.
18. T. A. Carlson, *Photoelectron and Auger Spectroscopy*, Plenum Press, New York and London, 1975.
19. K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, C. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg *ESCA, Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy*, Almqvist @ Wiksells Boktryckery AB, Uppsala, 1967, 282.

Received March 31, 1994