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Ultraviolet photoelectron spectra of C_{86} and C_{90}

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Ultraviolet photoelectron spectra of higher fullerenes, C_{86} and C_{90}, both of them having C_2 symmetry, are measured with a synchrotron radiation light source. The spectral bands above 4.5 eV are characteristic of individual fullerenes, while those below 5 eV resemble each other and are similar to other higher fullerenes. Upon the incident-photon energy change, the intensity of the bands oscillates and their peak positions shift. The bands above 5 eV of both C_2-C_{86} and C_2-C_{90} show a similar incident-photon-energy-dependent intensity oscillation.

INTRODUCTION

Thanks to high-performance liquid chromatography (HPLC), some higher fullerenes can be obtained in a macroscopic quantity, and their properties have been measured.[1–14] NMR measurements of higher fullerenes[3,5] have revealed that higher fullerenes were often a mixture of several structural isomers. Theoretical calculations[15–20] have proposed possible structures of higher fullerene isomers satisfying the isolated pentagon rule on the basis of heat of formation. These calculations also gave the electronic structure of the higher fullerene molecules. Comparison of the theoretical calculation with the ultraviolet photoelectron spectra (UPS) of higher fullerene isomers[6,7,9,12,14] is helpful for the determination of their exact structures.

In this article we report the UPS of the main isomer of C_{86} and one of the C_{90} isomers. We hope that these spectra invoke the theoretical study of the electronic structure of these fullerenes.

EXPERIMENTAL

C_{86} and C_{90} were separated and purified by a two-stage HPLC method from an extract of the solution of carbon soot prepared by an arc heating of graphite composite rods. Details of the preparation are described elsewhere.[4,21,22] Even after two-stage separation, the major HPLC fraction of C_{86} was found to consist of both the main isomer of C_2 symmetry and the minor isomers with about 4:1 abundance ratio.[21] The mixture of these C_{86} isomers was used for the photoelectron measurement. The major HPLC fraction of C_{90} contained five structural isomers of three C_2, one C_{2v}, and one C_1 symmety.[21] One of the C_2-C_{90} isomers of more than 90% concentration was used for measurement. The photoelectron spectra of our fullerene samples can be considered to reflect the precise electronic stucture of the main isomers, since the contribution from the minor isomers is negligibly small in the photoemission measurements.

Specimens for the photoelectron measurement were films deposited onto a gold-coated molybdenum disk. Deposition was carried out from a resistive heating quartz crucible in the vacuum of less than 3×10^{-9} Torr. Before deposition, heavy degassing was observed during the preheating period of the crucible, which was due to the evaporation of the solvent used in the HPLC separation. The temperature of the crucible at the sample deposition was estimated to be around 900 K from an applied wattage to the crucible and its radiation color.

The light source for the photoelectron measurements is synchrotron radiation, ultraviolet synchrotron orbital radiation, at the Institute for Molecular Science. The spectra were obtained with a photoelectron spectrometer at BL8B2 of UVSOR. Its resolution was 150 meV, and the energy calibration was carried out using the Fermi edge of gold deposited onto the sample disk before and after the measurement. The spectra were referenced to the Fermi level (E_F).

RESULTS

Figure 1 shows the photoelectron spectra of C_{86} obtained with the excitation photon energy described at the right side of each specrum. The spectral onset is 1.1 eV below the Fermi level, which is very close to that of C_{82}.[9] There are seven bands denoted by A–G in the spectra. Broken lines indicate their approximate peak positions. Band A consists of two structures, a shoulder at around 1.9 eV and a peak at 2.2 eV. Band B consists of a single peak component of which the peak position shifts with the incident-photon-energy change. The peak of band C also moves its position from 5.1 eV in the $h\nu=50$ eV spectrum to 5.3 eV in the $h\nu=40$ eV one. Bands D–G are neither sharp nor distinct so that their peak positions cannot be located exactly, but comparison among

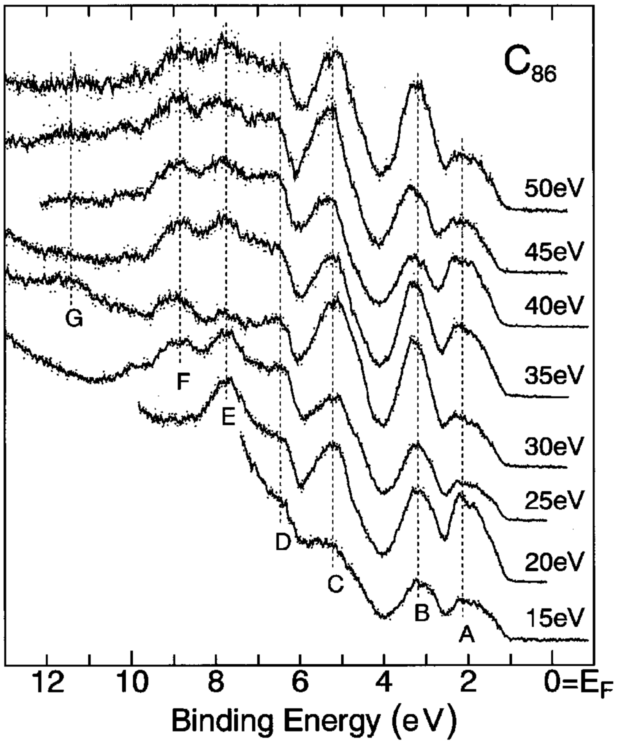

FIG. 1. The incident-photon-energy dependence of the UPS of C_2-C_{86}.

the spectra reveals that their peaks shift upon the incident-photon-energy change, as bands A–C exhibit.

The intensity of the bands oscillates when the incident-photon energy is changed. It is particularly drastic in the first two bands. The intensity of bands A–C is plotted in Fig. 2 as a function of the incident-photon energy. The intensity is normalized by the sum of the intensities of bands A–C. It seems that band A gains its intensity with a loss of the intensity of band C. Bands D–G also show intensity oscillation, though the intensity does not change drastically as the intensity of bands A–C oscillates. Band E has the highest intensity among these bands except for the $h\nu = 30$ eV spectrum. Band G is clearly observed and has the highest intensity in the $h\nu = 30$ eV spectrum.

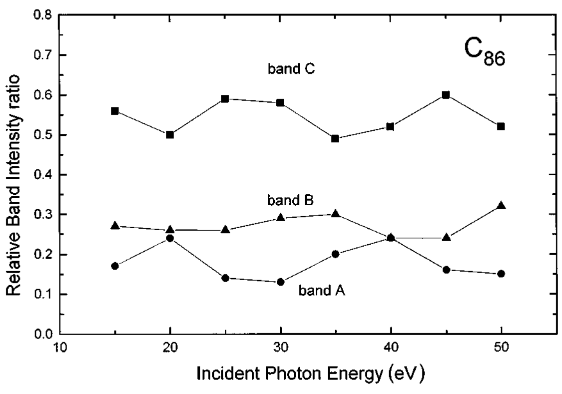

FIG. 2. The relative intensity of the bands A–C of C_2-C_{86} plotted as a function of the incident-photon energy. The intensity of each band is normalized by the sum of bands A–C.

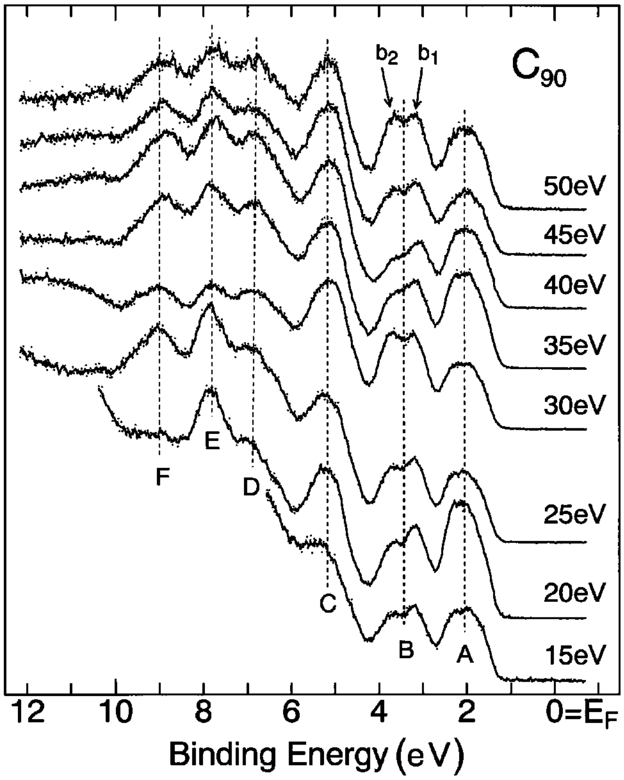

FIG. 3. The incident-photon-energy dependence of the UPS of C_2-C_{90}.

Figure 3 shows the incident-photon-energy dependence of the photoelectron spectra of C_{90}. The incident-photon energy is described at the right side of each spectrum. The spectral onset is 1.3 eV below the Fermi level. There are six distinct structures labeled A–F in the spectra. Broken lines indicate their approximate peak positions. Band A seems to consist of more than three peak components. While it shows one peak at 2.05 eV in the $h\nu = 40$ and 45 eV spectra, two humps emerge at 1.95 and 2.25 eV in the $h\nu = 15$, 30, and 35 eV spectra. Band B obviously consists of two peak components, b_1 and b_2. This is noteworthy, since the most spectral bands of other higher fullerenes consist of a single envelope

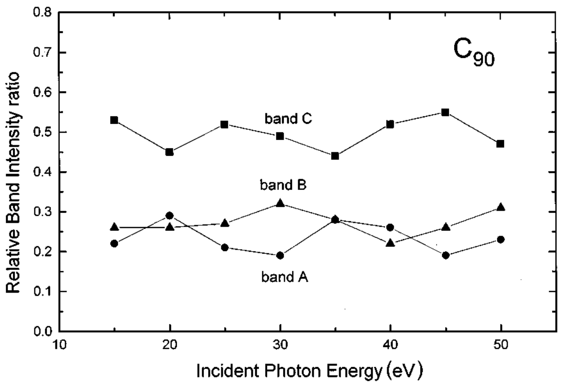

FIG. 4. The relative intensity of the bands A–C of C_2-C_{90} plotted as a function of the incident-photon energy. The intensity of each band is normalized by the sum of bands A–C.

that occasionally accompanies the shoulder structure(s). This splitting is characteristic, so that it is helpful to consider the geometry of this C_2-C_{90} isomer by the theoretical calculation. The positions of components b_1 and b_2 shift slightly upon the change of the excitation photon energy, but they remain mainly at 3.25 and 3.7 eV. The peak positions of the other bands also shift slightly upon the incident-photon-energy change.

The intensity of the bands changes with the excitation energy, as has been observed in C_{86}. The intensity of bands *A* and *B* changes drastically. Figure 4 shows the incident-photon-energy dependence of the intensity of bands *A*–*C*. The intensity of bands *A* and *B* of both C_{90} and C_{86} shows an analogous incident-photon-energy dependence: In their spectra, the intensity ratio of band *A* to *B* is almost unity at $h\nu=20$ or 40 eV, but it is much smaller than unity at $h\nu=30$ or 50 eV. Two components of band *B* also change their intensity upon the incident-photon-energy change. The intensity of b_1 is stronger than that of b_2 in most spectra except for the $h\nu=30$ eV spectrum. When the intensity of band *A* is strong, the intensity of b_1 is also strong. Band *E* has the highest intensity in all spectra except for the $h\nu=30$ eV spectrum, in which band *C* has the highest intensity and the intensities of band *D* and *F* are very close to that of band *E*.

DISCUSSION

Fullerenes are considered to be delocalized π-electron systems like conjugated polyenes. In the polyenes the band gap as well as the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is believed to decrease monotonously in accordance with the increase of the number of the carbon atoms. This presumption does not necessarily hold in higher fullerenes. The photoemission spectral onset of higher fullerenes ranges between 1.3 eV [C_{76} (Ref. 7)] and 1.0 eV [C_{96} (Ref. 14)]. In most cases, the larger the number of the carbon atoms, the smaller the onset energy. However, the onset energy of C_{90} is exceptionally large compared with those of C_{86} and C_{96}. The same relation is observed in the optical absorption spectral edge that relates to the HOMO-LUMO gap. It is about 900 nm or less in C_2-C_{90}, while it is 1050 nm in C_2-C_{86} (Ref. 4) and longer than 1100 nm in C_{96}.[23] These facts suggest either that C_{90} is unique and a magic-numbered fullerene or that the HOMO energy level of C_{90} is accidentally low so that its HOMO-LUMO gap becomes large. Systematic theoretical calculation of the electronic energy levels of these fullerenes seems to be required for further understanding.

The spectra above 4.5 eV are due to π-like (pseudo-π-like) electrons. There are critical differences in the spectra of fullerenes of this energy region (E_F to 4.5 eV), which indicates that the π-electronic structure is characteristic of individual fullerenes. On the other hand, the spectral shapes below 5 eV of the higher fullerenes including C_{70} resemble each other, although there are slight deviations from one fullerene to the other in the peak positions of the corresponding bands. As the spectral region below 5 eV is mainly due to pseudo σ electrons that consist of a skeletal structure of the fullerene molecule, similarity of the spectra in this region indicates that there is hardly any difference in the σ bonding condition of the fullerenes. As the spectrum of amorphous carbon of this energy region[24] is poor in structures, the structure in the spectra below 5 eV could be used for discrimination of the cage-shaped carbon molecules.

The intensity oscillation is observed in all photoelectron spectra of fullerenes.[6,7,9,14,25,26] The difference in the symmetry, gerade or ungerade (symmetric or antisymmetric with respect to inversion), of the molecular orbitals was proposed for the reason of the intensity oscillation.[25,26] However, such a symmetry difference of the molecular orbitals cannot be the origin of the intensity oscillation in C_2-C_{86} or C_2-C_{90}, since there is no symmetric representation like gerade or ungerade in them. Further, the photoelectron spectra of C_{96}, of which symmetry is likely believed to be C_1,[14] cast doubt on this reasoning, since they also exhibit strong intensity oscillation.

Another reasoning that satisfies the experimental results is required. As the origin of the intensity oscillation seems to be a characteristic common to all fullerenes, the reasoning must be applicable to all fullerenes. The intensity of corresponding bands shows analogous incident-photon-energy dependence (Figs. 2 and 4). The same tendency is also observed in the UPS of higher fullerenes; an incident-photon energy that gives strong intensity to a specific band of one fullerene also gives strong intensity to the corresponding band of the other fullerenes, and vice versa. This suggests that the photoelectron excitation processes in all fullerenes are essentially the same: analogous incident-photon-energy-dependent cross-section and matrix elements for the photoelectron generation. From these observations we propose the photoelectron excitation process itself as one of the reasons for the incident-photon-energy-induced intensity oscillation. Another possible cause of the intensity oscillation that can be applicable to all fullerenes is the interference effect among the wave functions of outgoing photoelectrons.[27,28] The wavelength of the de Broglie wave of the photoelectrons measured in our UPS measurements ranges approximately from 0.4 to 1.2 nm, which is shorter than or close to the diameter of the fullerene cage. The photoelectrons generated from the carbon atoms situated at the bottom of the fullerene cage must travel through the cage and they are eventually scattered by the other carbon atoms. As in the case of extended x-ray-absorption fine structure, the interference effect between the outgoing photoelectrons with and without scattering might play an important role in the intensity oscillation.

The intensity oscillation seems to be responsible for the incident-photon-energy-dependent peak shift. As is clearly observed in band *B* of C_{90}, each band consists of the photoelectrons derived from several molecular orbitals. When the band is a result of superposition of the photoelectrons ejected from different molecular orbitals, the band peak top may shift its position upon the incident-photon-energy change, as far as these molecular orbitals have different incident-photon-energy-dependent cross sections. No observation of the peak shift in highly symmetric C_{60} (Ref. 26) supports this reasoning, since its degenerated molecular orbitals are expected to have the same incident-photon-energy response. Alternatively, the peak shift could be an indicator of poor symmetry in the geometry of the fullerene molecule.

SUMMARY

The ultraviolet photoelectron spectra of C_2-C_{86} and C_2-C_{90} are characteristic and different from each other in the spectral region between E_F and 4.5 eV, but they are almost identical in the region above 5 eV and resemble those of other fullerenes. This suggests that the electronic structure of pseudo σ electrons constituting the skeleton of the fullerene molecules is analogous from one fullerene to the other. The spectra of both fullerenes show strong intensity oscillations and their incident-photon-energy dependence is essentially the same. The photoelectron excitation process and/or the interference effect among the wave functions of outgoing photoelectrons could be responsible for the intensity oscillation. The peak shift seems to relate to the intensity oscillation.

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