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Journal of Molecular Structure 648 (2003) 183–189

Journal of
MOLECULAR
STRUCTURE

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Electronic structure of the complexes of fullerene C_{60} with polyaromatic molecules

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Received 28 October 2002; revised 6 December 2002; accepted 6 December 2002

Abstract

Electronic structure of the complexes of fullerene C_{60} with triphenylene (TP) and 9,10-diphenylantracene (DPA) has been studied by an X-ray fluorescent spectroscopy. The C Kα spectrum of a complex was shown to be almost an additive sum of the C Kα spectra measured for fullerene and organic ligand. The quantum-chemical calculation of a DPA·C_{60} structural unit using density functional theory (DFT) revealed a slight charge transfer from DPA molecule to the C_{60} cage. The intermolecular interaction in the complex was found to proceed through quit energy deep molecular orbitals.

Keywords: Fullerene C_{60} complexes; X-ray fluorescent spectra; Density functional calculation

1. Introduction

The peculiarities of chemical behaviour of fullerene molecule C_{60} are determined by a large size, high symmetry and spherical shape of the carbon cage being rich in the π-type electrons. Owing to the high polarizability, fullerene C_{60} forms a lot of molecular complexes [1,2]. A modification of these complexes by doping trough the gas phase [3], using the photoinduced charge transfer [4] or the field transistor technology [5–7] could produce the novel materials with unusual conducting and magnetic properties.

The goal of the present work is a joint X-ray spectroscopic and quantum-chemical investigation of the electronic structure of complexes C_{60} with polyaromatic molecules 9,10-diphenylantracene (DPA) and triphenylene (TP). A choice of these molecules for complexation with C_{60} is caused by their good steric compatibility to the fullerene cage. A flexibility of phenyl fragments in the DPA structure allows formation of short Van der Waals contacts with C_{60}, whereas a shape of TP molecule, consisted of four conjugated hexagons, corresponds to a fragment of C_{60}.

An X-ray emission arises as the result of electron transitions form the occupied valence levels to the previously created core holes. Due to the dipole

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0022-2860/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-2860(03)00027-9

selection rules and localization of inner electrons, X-ray fluorescent spectrum measures the local partial density of occupied states that, in turn, can be derived from a quantum-chemical calculation of a compound. A comparison between the spectrum of complex and the spectra of individual compounds involved in this complex allows estimating a change of electronic structure of fullerene and ligand in the result of their interaction.

2. Experimental details

The fullerene C_{60} of 99.9% purity was used for the synthesis of complexes. To prepare the complexes $(TP)_2C_{60}$ and DPA·C_{60} a benzene solution of fullerene C_{60} and polyaromatic hydrocarbon taken in a molar ratio of 1:2 was evaporated under argon [2,8].

C Kα spectra of C_{60}, TP, DPA, $(TP)_2C_{60}$, and DPA·C_{60} were recorded with a laboratory X-ray spectrometer. A sample was located on a copper support and cooled down to the liquid nitrogen temperature in the vacuum chamber of the X-ray tube operating with copper anode ($U = 6$ kV, $I = 0.5$ A). The single crystal of ammonium biphthalate NH_4AP was used as an analyzing crystal. How this crystal is used to obtain the C Kα spectrum is described elsewhere [9,10]. The nonlinear reflection efficiency of NH_4AP crystal-analyzer allows reliable measurement of Kα emission of carbon in the energy region of 285–275 eV. Determination of X-ray band energy was accurate to ±0.15 eV with spectral resolution of ~0.5 eV.

3. Calculation

The quantum-chemical calculations of C_{60}, TP, and DPA molecules were performed using a density functional theory (DFT) by B3LYP method involved into *Jaguar* package [11]. The 6-31G** bases set was utilized. The geometry of the molecules was relaxed by analytic method to the gradient value of $5\cdot10^{-5}$ Hartree/Bohr. The molecules C_{60} and $C_{18}H_{12}$ (TP) were optimized in the I_h and D_{3h} symmetry, respectively. The molecule $C_{26}H_{18}$ (DPA) was found to have three conformers belonging to the D_{2h}, D_2, and C_{2h} point group of symmetry and distinguishing by an orientation of the phenyl rings respective to the anthracene fragment. The D_2 conformer, in which the phenyl rings are located in the different planes angled by 76° and 104° respective to the anthracene fragment, has the lowest energy. Both phenyl rings of D_{2h} and C_{2h} conformers are positioned in the same plane, which are set at angle of 90° and 78° to the anthracene fragment. The total energy for DPA molecule having the D_{2h} and C_{2h} symmetry is higher by $1.14\cdot10^{-3}$ and $7.7\cdot10^{-3}$ kJ/mol than that for the D_2 conformer. The DFT optimized structures of TP molecule and C_{2h} conformer of DPA are shown in Fig. 1.

The quantum-chemical estimation of the electron interactions between C_{60} and considered polyaromatic molecules was performed for DPA·C_{60} only because a twinning of $(TP)_2C_{60}$ crystal prohibited to determine its structure. The atomic coordinates for calculation of DPA·C_{60} structural unit were taken from Ref. [8].

The theoretical C Kα spectra were plotted by the results of calculations of the compounds. As the X-ray emission process involves valence (j) and inner (i) levels, the X-ray transition energy is calculated as a difference between corresponding eigenvalues:

$$E_{ji} = \varepsilon_j - \varepsilon_i \quad (1)$$

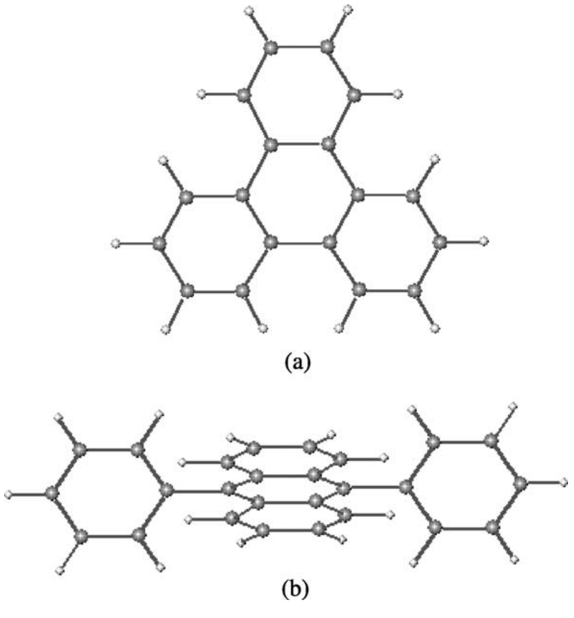

Fig. 1. DFT optimized molecular structure of $C_{18}H_{12}$ (TP)—(a) and $C_{26}H_{18}$ (DPA) belonging to the C_{2h} symmetry—(b).

Owing to the localization of carbon 1 s electrons, the X-ray transition was suggested to proceed within the same atom with an intensity calculated by:

$$I_{ji} = \sum_{A} \sum_{m} \sum_{n} |C^{A}_{im} \cdot C^{A}_{jn}|^{2}, \qquad (2)$$

where A denotes a carbon atom, C_{im} and C_{jn} are the coefficients with which 1s-atomic orbitals (AO) and 2p-AOs participate in the construction of *i*th inner or *j*th valence molecular orbital (MO). Intensities so obtained were normalized by the maximal value and broadened by the convolution with Lorentzian functions of 0.7 eV half width at half maximum. To compare the theoretical spectrum with the experimental one, the calculated X-ray transition energies were increased by 9.3 eV. This correction corresponds to the raising of the electron transition energy when compound is ionized.

4. Results and discussion

4.1. Complex $(TP)_2C_{60}$

The experimental C Kα spectra of C_{60}, TP, and $(TP)_2C_{60}$ and theoretical spectra calculated for the molecules C_{60} and TP are compared in Fig. 2. In the interval from 285 to 274 eV the experimental spectrum of fullerene C_{60} exhibits 4 maxima (Fig. 2(a)). The shortwave maximum A at 282.3 eV and maximum B at 281 eV arise in the result of X-ray transitions of π-like electrons. The maximum *C* at 278.3 eV and maximum *D* at 275.5 eV correspond to both σ- and π-type MOs. The more detail interpretation of the experimental C_{60} spectrum has been given in Ref. [12] by the result of PM3 calculation of fullerene molecule. The C Kα spectrum of C_{60} plotted using the result of DFT calculation has 4 maxima (Fig. 2(1)) also those relative intensity and energetic separation well agree with the experimental values. The most noticeable distinguish between the experimental spectrum of C_{60} and theoretical one is a shift of the maximum *D* of the latter spectrum toward the short-wave region.

The C Kα spectrum of TP exhibits two main maxima *D* and *C′*, which are close in the intensity and located around 275 and 277 eV, respectively, and less intense maximum *B* at 281 eV (Fig. 2(b)). Additionally, a shoulder C is detected at 278.3 eV on the shortwave said of the maximum *C′*. All these spectral features are definitely observed in the theoretical spectrum of TP molecule (Fig. 2(2)). The good correspondence between calculated and measured intensity and energy position of the detected features demonstrates the high level of used quantum-chemical approach and allows to interpret the C Kα spectrum of TP from the analysis of computational

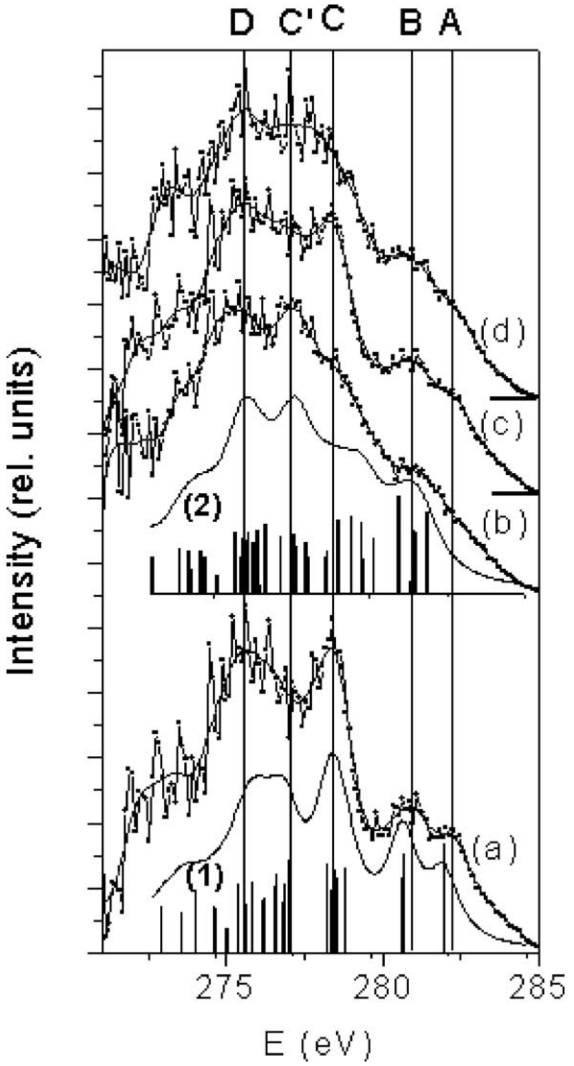

Fig. 2. C Kα spectra measured for solid C_{60}—(a), TP—(b), $(TP)_2C_{60}$—(d), and spectral profile (c) obtained by summing of the intensities for spectra (b) and (a) in ratio 1:0.6. The theoretical spectra (1) and (2) were calculated for molecules C_{60} and TP belonging to the I_h and D_{3h} symmetry, respectively.

results. The high-energy maximum *B* corresponds to the weakly bonding MOs of π-type. The shoulder *C* arises in the result of X-ray transition from the π-bonding orbitals and weekly bonding MOs of σ-type. The maxima C' and *D* correspond to MOs provided the σ-bonding between carbon atoms of aromatic rings and the formation of C–H bonds.

The C Kα spectrum of $(TP)_2C_{60}$ exhibits two well recognized maxima: the main maximum *D* at 275.5 eV and short-wave maximum B at 281 eV (Fig. 2(d)). To determine how the electronic structures of fullerene and organic ligand are changed with a complexing we plotted a spectral profile by summing the C Kα spectrum intensities for TP and C_{60} taken in ratio of 1:0.6. This ratio was determined from the complex stoichiometry and the numbers of carbon atoms in each molecule composing the complex. The profile obtained (Fig. 2(c)) is basically similar to the experimental C Kα spectrum of complex, hence, the bands in the $(TP)_2C_{60}$ spectrum can be attributed to the features of the electronic structure of C_{60} and TP molecules. The position of main maxima *D* and *B* almost coincides with the position of corresponding maxima in the spectra measured for C_{60} and TP. The broad maximum C' in the $(TP)_2C_{60}$ spectrum is a superposition of the maximum *C* from the fullerene spectrum and the features *C* and C' appeared in the TP spectrum. The shortwave shoulder A in the $(TP)_2C_{60}$ spectrum has an intermediate intensity compared to those for corresponding spectral features in the spectra of C_{60} and TP.

Similarity between the C Kα spectrum measured for $(TP)_2C_{60}$ and the profile obtained by summing the spectra of C_{60} and TP is indicative of very week intermolecular electron interactions in the complex. The lack of distinct interaction between π-systems of TP and C_{60} has been also determined from the optical spectroscopy measurements [2]. In the region from 220 to 1600 nm the spectrum of $(TP)_2C_{60}$ is an additive sum of the spectra measured for individual TP and C_{60} and has no extra absorption bands, which could be related with a charge transfer.

4.2. Complex DPA·C_{60}

The C Kα-spectra of C_{60}, DPA, DPA·C_{60}, and spectral profile obtained by summing of two first spectra in ratio of 1:0.43, which corresponds to the relationship between number of carbon atoms in the fullerene and that in the ligand, are presented in Fig. 3 together with the theoretical spectra calculated for C_{60} and DPA molecules and for a DPA·C_{60} unit.

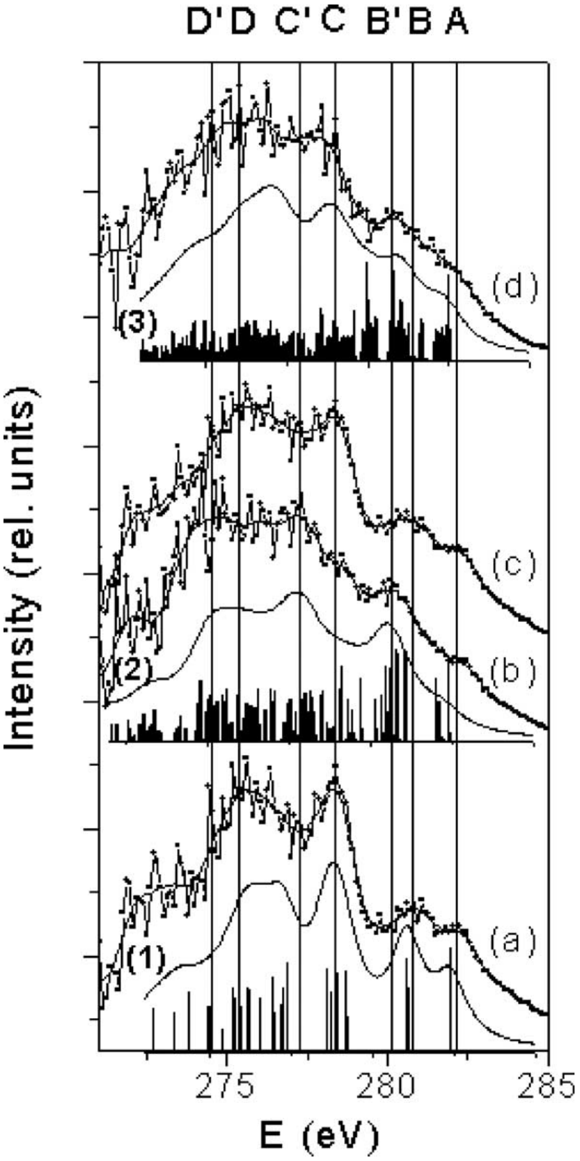

Fig. 3. C Kα spectra measured for solid C_{60}—(a), DPA—(b), DPA·C_{60}—(d), and spectral profile (c) obtained by summing of the intensities for spectra (b) and (a) in ratio 1:0.43. The theoretical spectra (1) and (2) were calculated for molecules C_{60} and DPA belonging to the I_h and C_{2h} symmetry, respectively, the spectrum (3) was plotted by the result of calculation of DPA·C_{60} structural unit.

The atomic coordinates for the structural unit were derived from the x-ray diffraction data of the DPA·C_{60} crystal [8]. The comparison of theoretical spectra plotted for three possible stable conformers of DPA molecule showed the location of phenyl rings relative to the anthracene fragment has practically no effect on the spectral shape. Taking into account this result and as the C_{2h} conformer is more close to the structure of DPA in the complex, namely its C Kα spectrum was used for the interpretation of experimental data.

Excellent correlation between spectrum calculated for the C_{2h} DPA and experimental one (Fig. 3(2, b)) in the number of spectral features, their relative position and intensity, allows interpreting the experimental results. The C Kα spectrum of DPA exhibits 4 maxima: the maximum A at 282.3 eV, maximum B' located at 280.1 eV, maximum C' at 277.3 eV, and maximum D' around 274.5 eV (Fig. 3(b)). The maximum A corresponds to the highest occupied molecular orbital (HOMO) provided weak bonding of π electrons within the anthracene fragment. A splitting of lines, which form maximum A in the theoretical spectrum (Fig. 3(2)), is caused by a difference in the 1s-level energy of carbon atoms composing the fragment. The maximum B' arises in the result of X-ray transitions of π-electrons from 6 high occupied MOs distributed in a narrow interval of 0.57 eV. Electron density from three of these MOs is localized on the phenyl rings only, one of the MOs is formed by π-electrons of carbon atoms from the anthracene fragment, and two other MOs represent the overall π-system of DPA. A shoulder C of the DPAC Kα spectrum corresponds to two π-type MOs localized on the anthracene fragment and a σ-type MO. The σ-electrons of DPA and π-electrons from two bonding MO of the anthracene fragment form the maximum C', while the maximum D$'$ is associated with σ-MOs.

The C Kα spectrum of complex DPA·C_{60} has 4 maxima A, B', C, and D (Fig. 3(d)), which are a superposition of the corresponding features of C_{60} and DPA spectra. The spectrum calculated for DPA·C_{60} unit (Fig. 3(3)) well agrees with the experimental spectrum of complex. Some distinction between the energy positions of long-wave maxima of the spectra, which is also characteristic for other studied molecules, could be due to an overestimation of electron interaction by the applied calculation method. Good correspondence between theoretical and experimental data allows interpreting the C Kα spectrum of complex. The main maximum D is attributed to the σ-systems of C_{60} and DPA, the maximum C arises in the result of x-ray transitions from high σ-orbitals and deep bonding π-type MO of the complex.

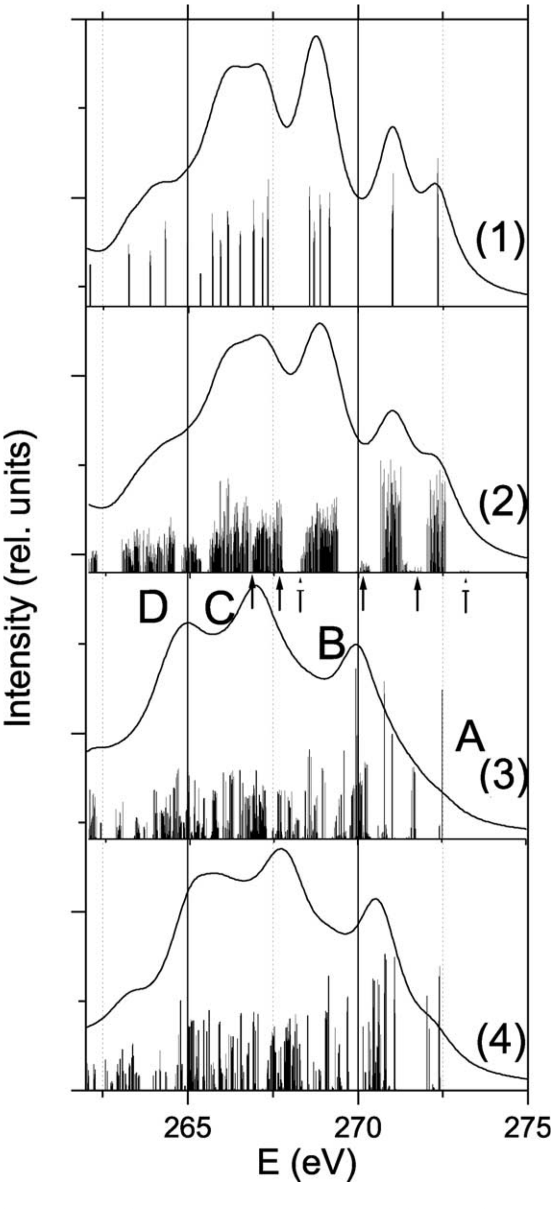

Fig. 4. Theoretical C Kα spectra calculated for C_{60} in the I_h symmetry—(1), C_{60} involved in the DPA·C_{60} unit—(2), DPA involved in the DPA·C_{60} unit—(3), and DPA in the C_{2h} symmetry—(4).

The maximum B' is formed by π-electrons only, the short-wave maximum A corresponds to the orbitals, which can be associated with HOMO of DPA molecule and five-fold degenerated HOMO of C_{60}. The spectrum of DPA·C_{60} is slightly differed from the spectral profile plotted by a summing of C_{60} spectrum and DPA spectrum (Fig. 3(c)). The spectral profile shows an enhanced intensity for the features A and C that is similar to results obtained for the complex $(TP)_2C_{60}$. The large number of lines corresponding to the X-ray transitions in the theoretical spectrum of DPA·C_{60} also indicates that the C Kα spectrum of complex is not direct sum of the spectra of individual compounds C_{60} and DPA.

To reveal the basic reasons for distinction between the spectra of C_{60} molecule or DPA molecule before and after the complex formation we compared C Kα spectrum calculated for I_h C_{60} or C_{2h} DPA and a partial spectrum, which intensities and energies were computed for the atoms belonging to fullerene cage or polyaromatic ligand of the complex (Fig. 4). The partial spectrum of C_{60} exhibits considerable increase of the lines indicated X-ray transitions relative to the spectrum of ideal molecule. There are two reasons of this effect. First, a distortion of the fullerene cage in the molecular complex causes an energy splitting both valence and core levels, which were degenerated in the icosahedral C_{60}. Second, in the result of interaction between C_{60} and DPA the additional electron transitions arise from the MOs being common for both molecules. The arrows show some of these transitions in the partial spectrum of C_{60} (Fig. 4(2)). The low intensity of the transitions is indicative of weak electron interaction between C_{60} and DPA in the complex. The increase of number of X-ray transitions in the partial spectrum of C_{60} leads to the broadening of spectral features compared to the spectrum of individual fullerene that is the most noticeable difference between two spectra.

The C Kα spectrum calculated for ligand is differed from the spectrum of free DPA by a lowering of the relative intensity of maxima *A* and *D* and a shifting of maxima *B* and *C* toward the low energy region (Fig. 4(3)). These differences are also caused by the intermolecular interactions and change of DPA geometry in the result of complexing. For example, the intensity of short-wave maximum *A* is decreased due to the more considerable energy splitting of carbon 1s-levels in the ligand. To understand this effect the HOMO of complex, which corresponds to the maximum A, was analyzed. The electron density from HOMO is almost completely localized on the DPA, although there is a slight contribution from fullerene electrons (Fig. 5(a)). In contrast to the free DPA, the HOMO of complex is formed by π-electrons belonging not only to the anthracene fragment but to the phenyl rings also. Contribution of electrons of the phenyl rings to the HOMO of complex becomes

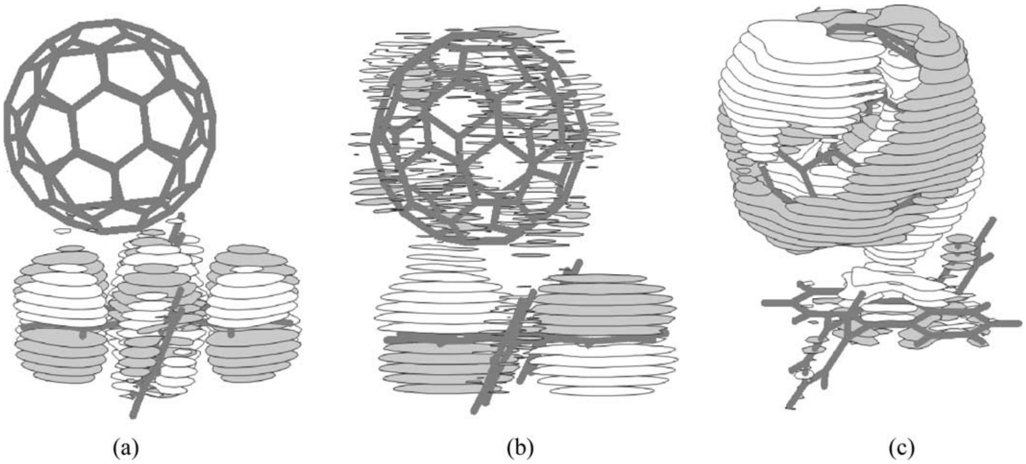

Fig. 5. Calculated distribution of electron density from HOMO of the DPA·C_{60} unit—(a) and from MOs provided the intermolecular interaction in the complex—(b, c). Various colors correspond to the different phases of wave function.

possible in the result of decrease of the rings deviation from the anthracene plane by 14° compared to that in the individual molecule.

To evaluate a charge transfer in the DPA·C_{60} complex we separately summarized the Mulliken charges on the atoms within the C_{60} cage and those on the atoms comprising the ligand. Only a slight charge transfer (~ 0.005 e) from DPA to the fullerene was revealed. Namely diffuse π-electrons provide the intermolecular interaction. The most significant overlapping proceeds through quite energy deep MOs separated by about 5 eV from the HOMO. The reason of effective overlapping is a small number of nodes in the structure of C_{60} and DPA orbitals corresponding to these energies. The examples of complex MOs provided the bonding between DPA and C_{60} are presented in Fig. 5(b) and (c). The lack of noticeable intermolecular interaction through the frontier orbitals leads to the localization of electron density from HOMO and LUMO (the lowest unoccupied MO) on the DPA and C_{60} relatively. The optical spectra measured for DPA·C_{60} complex have also indicated a pronounced interaction between π-system of DPA and C_{60} [8]. The absorption spectrum of DPA·C_{60} complex showed a presence of additional band at 630 nm, which was absent in the spectra of individual C_{60} and DPA and, therefore, could be attributed to a charge transfer from ligand to the fullerene.

5. Conclusion

Electronic structure of complexes of fullerene C_{60} with polyaromatic molecules TP and DPA was investigated by X-ray emission spectroscopy. C Kα spectrum of such type molecular complex was shown to be almost a direct sum of the spectra measured for individual compounds, which are used for complex preparation. Some observed differences in the electronic structures of fullerene C_{60} and organic molecule before and after complexing are connected with change of molecular geometry and arising of intermolecular electron interactions. The charge transfer from DPA to the fullerene cage was found by the result of DFT calculation of structural unit of the complex to proceed through the energy deep π-type MOs, which are more responsible for the effective overlapping of electronic states.

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