Analysis of the nitrogen K-edge x-ray absorption spectra of Zn-porphyrin/C\textsubscript{70}-fulleren complex for solar cells

S A Suchkova\textsuperscript{1}, C Castellarin Cudia\textsuperscript{2}, A Soldatov\textsuperscript{1}

\textsuperscript{1} Southern Federal University, Sorge str. 5, 344090 Rostov-on-Don, Russia
\textsuperscript{2} Sincrotrone Trieste S.C.p.A, s.s. 14 km 163.5 in Area Science Park, 34012 Trieste, Italy

E-mail: suchkova_sv@inbox.ru

Abstract. The atomic structure models of Zn-porphyrin/C\textsubscript{70} multilayer for solar cells were examined. The local atomic structure of the Zn-porphyrin/C\textsubscript{70} complex was refined with the use of previously published results [1]. Since near-edge spectral region (XANES) is sensitive to the three-dimensional atomic geometry, the theoretical analysis of the experimental XANES was performed on the basis of finite difference method (FDMnes 2008 program code). Some electronic properties of the complex were obtained from the DFT calculations performed by means of Amsterdam Density Functional program package.

1. Introduction

Up-to-date organic photovoltaic cells are composed of organic thin films and their application requires a clear understanding of the peculiar physics driving the electronic behaviour. In artificial photosynthetic models such as Gratzel cell porphyrins in combination with fullerenes are among the most frequently employed building blocks as electron donors and sensitizers as well as of their electron affinity nature (p-type for porphyrins and n-type for fullerenes). Particularly interesting is the D/A dye formed by free-base (metallo)porphyrines directly attached to fullerenes. The atomic structure of the adsorbed molecules and their arrangement are responsible for the physical and chemical properties of the organic film.

Zn-porphyrin/C\textsubscript{70} double layer was obtained and studied by experimental XAS measurements [1]. It was shown that the molecules of Zn-porphyrin and fullerene tend to form a self-assembled structure, where porphyrin molecule is tilted with respect to the fullerene [1]. But the detailed investigation of the orientation of these molecules was not performed. Thus in present work the orientation of the Zn-porphyrin molecule and fullerene and some electronic properties of this complex was studied more precisely.

One of the most effective methods for investigating the local atomic structure of compounds analyzed is the X-ray absorption spectroscopy (XAS). The X-ray Absorption Near Edge Structure (XANES) Spectroscopy is known as effective tool to provide full information about local geometry including not only bond length, but also the bond angles [2,3] instead of the Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy that gives information about the coordination numbers and bond length around the absorbing atom. The experimental N K-edge XANES of chloro-hemin have been analyzed on the basis of full-potential calculations of XANES (FDMNES 2008).
The investigation of electronic properties was performed using density functional theory (DFT) approach. Actually the DFT calculations are successfully used to study the electronic properties of coordination compounds [4].

2. Experiment and method of calculation

Zn-porphyrin/C70 double layer was obtained by sublimation and deposition on the clean Si(111) substrate in UHV at room temperature with the use of a resistively heated Ta evaporator. XAS measurements of the N K-edge were performed in the UHV experimental chambers-base pressure 10−10 mbar of the SuperESCA and ALOISA beamlines at the Elettra Synchrotron facility.

Quantum chemical calculations were carried out with the Amsterdam density functional (ADF2008) program package [5]. The density functional used was based on the Vosko–Wilk–Nusair (VWN) local spin-density potential plus Becke’s (B) gradient correction for exchange and Perdew’s (P) gradient correlation for correlation. It has been shown that this VWN–B–P functional can provide accurate bond energies for both main group and transition metal systems [6].

The Zn-porphyrin and fullerene C70 structures were obtained from the Cambridge Crystallographic Data Centre base. Then the calculations of N K-edge XANES spectra have been performed with the full-potential FDMNES 2008 code [7], which runs within the real space cluster approach and uses the finite difference method (FDM) to solve Schrödinger equation.

3. Results and discussion

As a result of experimental investigation [1] it was shown that the Zn-porphyrin/C70 complex has the following structure: central Zn atom is atop a double bond that belongs to the two hexagonal faces that lie under the top pentagonal face of the C70 molecule, with the four nitrogen atoms facing two hexagonal and two pentagonal faces near their centers.

To study the orientation of Zn-porphyrin and fullerene molecules in the multilayer it was decided to build some possible models of ZnP/C70 complex to perform the calculation of theoretical N-edge XANES spectra. These models and corresponding spectra are shown on the fig. 2 and 1, respectively. At the first stage of our investigation a model (a) was built, where the porphyrin molecule is tilted with the angle 33° with respect to the fullerene long axis as it was found from the experimental investigation [1]. The distance between the Zn atom and C-C bond was 2.14Å. In the next model the distance was 3Å. It is obvious that the spectra calculated for the model (b) correspond well with the experimental. In the theoretical spectra for the model (a) features C and D are absent contrary to the spectra for the model (b). Additional models (c) and (d) do not show good agreement for the simulated spectra and the experimental spectra. Therefore we conclude that the convenient geometry for the system must be depicted by the model (b).
Figure 1. The comparison of experimental N K-edge XANES polarization spectra and theoretical ones calculated for models a-d schematically depicted in the fig.2.

Table 1. Mulliken charge distribution and orbitals occupation calculated for the free Zn-porphyrin molecule (ZnP), Zn-tetra-phenyl-porphyrin(ZnTPP) and Zn-tetra-phenyl-porphyrin in ZnTPP/C_{70} complex.

|          | Free ZnTPP(ZnP) | ZnTPP in complex |
|----------|----------------|-----------------|
| 3d       | 10.0(10.0)     | 10.1            |
| 4s       | 0.59(0.58)     | 0.54            |
| 4p       | 0.80(0.79)     | 0.66            |
| Q_{Zn}   | 0.61(0.63)     | 0.74            |
| Q_{N}    | -0.45(-0.43)   | -0.537, -0.541, -0.536, -0.535 |
| Q_{C1}   | -0.03(0.08)    | 0.009, 0.013, 0.012, 0.009 |
| Q_{C2}   | 0.27(0.26)     | 0.308, 0.307, 0.308, 0.305, 0.308, 0.308, 0.307, 0.306 |

Electronic properties of the complex were obtained from the DFT calculations. The results are shown in the table 1. Mulliken charge distribution and orbital occupations are compared to the results obtained in [8]. It is shown that the formation of complex Zn-porphyrin/C_{70} causes the redistribution of charge in the porphyrin molecule and in the orbitals occupation. Also, the electron density distribution was calculated. In the fig. 4 the view of electron density distribution is shown in two different planes that pass through the atoms of the complex. It is evident from the fig.4 that in the area between the Zn atom and the side C-C bond of fullerene the redistribution of electron density is present. The HOMO and LUMO for Zn-porphyrin/C_{70} complex are given in the fig.5. It is obvious that HOMO and HOMO-1 belong to the Zn-porphyrin molecule, and LUMO and LUMO+1 belong to the fullerene molecule.
4. Conclusions
The atomic structure of the molecules in the Zn-porphyrin/C$_{70}$ double layer and their arrangement are responsible for the physical and chemical properties of the organic film. It was shown that the theoretical polarization XANES N K-edge spectra are significantly sensitive to the arrangement of molecules in the Zn-porphyrin/C$_{70}$ complex. According to this we have refined the geometry of the complex. Then the electronic properties of the refined model were obtained from the results of quantum chemical calculations that were carried out with ADF2008. It was shown that the formation of Zn-porphyrin/C$_{70}$ complex leads to the redistribution of the charge in the Zn-porphyrin molecule and changes in orbital occupation. Thus the combination of XANES technique and quantum chemical calculations allows constructing complete pattern of the formation of the Zn-porphyrin/C$_{70}$ complex.

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