EXPERIMENTAL AND THEORETICAL STUDY OF X-RAY K EDGES ABSORPTION SPECTRA OF CARBON AND NITROGEN IN THE PHTHALOCYANINE H₂Pc MOLECULE

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UDC 541.6:541.49

The study of the electronic structure of H₂Pc was carried out to examine the structure of the lowest unoccupied molecular orbitals (LUMO) of molecule phthalocyanine by X-ray absorption spectroscopy using quantum-chemical calculations. The theoretical calculations were performed on the stationary theory (frozen orbital approximation, Z+1 model) and time-dependent density functional theory (TDDFT). A consideration of K edges absorption spectra of carbon and nitrogen in the common scale of binding energies allows estimating the contributions of AO of all phthalocyanine atoms to the LUMO, defining the sequence of levels, the binding energies of the corresponding levels, and also the character of electronic interactions between individual atoms. It was shown that the best agreement between the experimental and theoretical pre-edge structures of the absorption spectra of nitrogen and carbon for H₂Pc is observed in the case of the application of stationary density functional theory in Z+1 model to account for an X-ray hole. In this case the 2pπ AO of the Nα(1,2) and Cα atoms make a predominant contribution to the LUMO. The 2pπ AO of the Nα (1,2) atoms mainly contribute to the boundary LUMO with the energy ~ –2.3 eV.

DOI: 10.1134/S0022476616070064

Keywords: phthalocyanine, X-ray absorption spectroscopy, stationary and time-dependent density functional theory.

INTRODUCTION

Condensed compounds involving phthalocyanine molecules (H₂Pc) relate to organic compounds. Materials based on phthalocyanine and its analogues are applied for production of photovoltaic cells for solar batteries [1, 2] and also for creating electroluminescent and organic light-emitting devices [3, 4]. It is worth noting that structurally phthalocyanines are synthetic analogues of porphyrins, wide class of biologically important organic compounds [5], which are constituents of hemoglobin, catalase enzymes, peroxidase and numerous group of cytochromes. So, molecule H₂Pc is an important model object both for the study of the electronic structure of phthalocyanines with the different structure of an inner macrocycle and for compounds with the similar structure, for example, porphyrins. Physical and chemical properties of the considered class of organic compound are controlled, primarily, by the features of the structure of high occupied molecular orbitals (HOMO) and low

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1334 0022-4766/16/5707-1334 © 2016 by Pleiades Publishing, Ltd.
unoccupied molecular orbitals (LUMO). X-ray absorption spectroscopy (XAS) is an informative method for the energy position determination of the LUMO and its atomic composition.

At present X-ray absorption spectra are widely applied for the study both the electronic structure and local structure of various compounds and materials [6]. It is conventional to separate two regions in X-ray absorption spectra: X-ray absorption of near edge spectra (XANES spectra) and Extended X-ray absorption fine structure (EXAFS spectra). XANES spectra are used for the study of the energy distribution of vacant electronic states of atoms, molecules, complexes and solids, while EXAFS spectra are informative for the study of the character of the nearest surrounding of specific atoms entering into the composition of compounds and materials. At the theoretical interpretation of the experimental XANES spectra it is used different models and approximations. One such approximation is based on the consideration of the features of the fine structure of XANES spectra as an occurrence of X-ray transitions of electrons from core atomic-like levels of the system to the lowest LUMO obtained in the result of the theoretical calculation of the ground state of the system. The corresponding approach allows the qualitative interpretation of several spectral maxima in the absorption spectrum to be carried out as an occurrence of absorption transitions of electrons from core atomic levels of the system to some LUMO. In studies of absorption spectra of atoms or molecules \((Z+1)^{N-1}\) approximation is widely used according to which X-ray absorption transitions of electrons from core atomic-like levels are realized to the LUMO of the system where the absorbing atom has the atomic number increased by one \((Z+1)\) [7]. In so doing, this model takes into account the appearance of the core electronic hole on the level from which the electron transfers to some LUMO. In this case the energies of the LUMO are calculated for the molecule in the ground state with the charge increased by one \((Z+1)\) on the atom under study. This approximation allows accounting the system relaxation associated with the appearance of the hole on the core atomic-like level of the system. The corresponding approach gives satisfactory results for molecules and complexes constructed with participation of elements of II-III periods.

The consistent approach to the interpretation of X-ray absorption spectra requires the calculation of the differences of the total energies of the initial and final states of the system, with the latter corresponding to the excitation of the core electron to one of the possible vacant levels of the system. In this case the main problem in practical realization of this approach is the adherence to condition orthogonality for the multielectron wave functions of the ground and excited states. At present time the corresponding approach is realizable for small molecules and clusters containing small number of atoms [8].

Recently the method of density functional theory (DFT) finds expanding applications in the quantum chemical modeling of the electronic structure of multi-atomic systems. The immediate account of the correlation energy and relatively low time costs led to the wide application of this method in spectroscopy of molecular systems [9-12].

At the present time all DFT applications, as applied to spectroscopic problems, are used Kohn–Sham one-electron formalism according to which the eigenfunctions \(\varphi_i\) and the corresponding orbital energies \(\varepsilon_i\) are used for the calculation of the energies and intensities of spectral transitions. Unlike Hartree–Fock one-electron equation including the exchange energy only, Kohn–Sham equations take into account both exchange and correlation through the exchange-correlation potentials. So, DFT provides the more successful description of the spectral transitions than famous Koopman’s approximation of Hartree–Fock model.

According to the modern theoretical conceptions [13] there is an analogue of Koopman’s theorem in the framework of DFT that allows Kohn–Sham orbital energies to be examined as approximate vertical ionization potentials.

At the present time the methods using Time Dependent Density Functional Theory (TDDFT) formalism actively come into use for interpretation of excited states of real chemical objects [14]. According to TDDFT the calculation of the excitation energy of the system is based on the search of the poles of the electron response function of the system at the interaction of the system with a perturbation external electromagnetic field. The eigenvalues and eigenvectors obtained in the course of the search of the poles of the response function correspond to the values of the excitation energy and transition amplitudes [15]. The satisfactory accuracy of TDDFT method used for the description of excited states is conditioned by the fact that the energies of Kohn–Sham virtual orbitals appearing in TDDFT theory correspond to a \(N\)-electron system and therefore are closer to the one-particle energies of the excited electron than in Hartree–Fock method where the energies of virtual orbitals are estimated for the system of \(N+1\) electrons.