

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/257032169>

Features of metal atom 2p excitations and electronic structure of 3d-metal phthalocyanines studied by X-ray absorption and resonant photoemission

ARTICLE *in* APPLIED SURFACE SCIENCE · FEBRUARY 2013

Impact Factor: 2.71 · DOI: 10.1016/j.apsusc.2012.08.095

CITATIONS

2

READS

15

6 AUTHORS, INCLUDING:



K.A. Simonov

Uppsala University

11 PUBLICATIONS 87 CITATIONS

SEE PROFILE



M. Brzhezinskaya

Helmholtz-Zentrum Berlin

86 PUBLICATIONS 434 CITATIONS

SEE PROFILE



Alexei Preobrajenski

Lund University

89 PUBLICATIONS 1,677 CITATIONS

SEE PROFILE



Alexander Yu Klyushin

Fritz Haber Institute of the Max Planck Soci...

9 PUBLICATIONS 43 CITATIONS

SEE PROFILE



Features of metal atom 2p excitations and electronic structure of 3d-metal phthalocyanines studied by X-ray absorption and resonant photoemission

K.A. Simonov^{a,*}, A.S. Vinogradov^a, M.M. Brzhezinskaya^{a,b,1}, A.B. Preobrajenski^c, A.V. Generalov^a, A.Yu. Klyushin^a

^a V. A. Fock Institute of Physics, St.-Petersburg State University, 198504 St.-Petersburg, Russia

^b BESSY, 12489 Berlin, Germany

^c MAX-lab, Lund University, Box 118, 22100 Lund, Sweden

ARTICLE INFO

Article history:

Available online 1 September 2012

Keywords:

Phthalocyanine

NEXAFS

Resonant photoemission

Exchange interaction

ABSTRACT

The metal atom 2p core excitations in 3d-metal phthalocyanines (MPc's, M = Ni, Co, Fe) have been studied via a combination of near edge X-ray absorption fine structure (NEXAFS) and resonant photoemission (ResPE) spectroscopy. On the basis of comparison of the corresponding spectra of NiPc, CoPc and FePc it has been shown that the presence of a partly filled molecular orbital (MO) dramatically affects the formation and decay processes of the M 2p core excitation in CoPc and, to a greater extent, in FePc due to the significant 3d–3d exchange interaction. It has been found that the low-lying unoccupied electronic states of NiPc, CoPc and FePc are strongly localized within the MN₄ quasi-molecule and have nearly pure 3d character. Moreover, mainly 3d metallic character of the high-lying occupied MOs of NiPc, CoPc and FePc has been proved.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The 3d-metal phthalocyanines are very stable planar complexes that show various interesting properties and have extensive applications in the areas of catalysis, pigments, semiconductors and sensors [1]. It is known that the occupied and empty 3d electron states of the metal atom are essentially responsible for the unique properties of MPc's. Thus it is evident that a detailed investigation of the 3d-derived states, located near the Fermi level, is required for the optimal utilization of these properties.

Such information can be obtained with high-resolution X-ray absorption (XA) spectroscopy. In particular, the central metal 2p (M 2p) XA spectra are of great interest because they probe directly unoccupied electronic states with the 3d character [2]. Thereby, the M 2p XA spectral profile, ideally, reflects the energy distribution of the empty 3d-derived states. However, this is only true for the compounds with fully unoccupied 3d-derived valence states. In the case of partly occupied states, M 2p XA spectra can be additionally complicated by the final-state multiplet effects, such as the screened Coulomb/exchange interaction of the 3d electrons with each other and, to a lesser degree, with 2p core hole. Therefore studying the role of multielectron effects in the formation of M 2p core

excitations have fundamental significance for compounds containing 3d-elements[3].

A combination of XA spectroscopy and resonant photoemission (ResPE) is particularly efficient for gaining new additional information about the nature, localization, lifetime of core excitations, the role of the multielectron effects for these excitations as well as about the energy positions of 3d-derived occupied states in the valence band [4].

During the last decades, metal phthalocyanines have been extensively studied theoretically and experimentally. In particular, a systematic study of 2p absorption edges of MPc's was performed by Cook et.al. [5] in order to trace the changes in the oxidation state of metal atom in going from MPc to its oxidized or chlorinated derivatives.

In going from ZnPc to FePc the metal atom electron configuration varies from [Ar]3d¹⁰ to [Ar]3d⁶. In particular, interesting effects in the M 2p spectral profile can be expected in the series NiPc([Ar]3d⁸)–CoPc([Ar]3d⁷)–FePc([Ar]3d⁶). According to theoretical calculations [6,7] NiPc is a closed shell system with the total spin in the ground state $S=0$, while, CoPc and FePc are the open shell ones and their ground state is characterized by the total spin $S=1/2$ and $S=1$ respectively. Therefore for CoPc the Co 2p electron excited to the lowest unoccupied molecular orbital (LUMO) will interact with the 3d electron in the partly filled MO. In turn, for FePc the role of the electron–electron interaction should increase, which also has to affect the character of formation and decay of the Fe 2p excitations.

* Corresponding author. Tel.: +7 8124284352; fax: +7 8124287240.

E-mail address: konstantinsimonov1988@gmail.com (K.A. Simonov).

¹ Currently at ALBA Synchrotron Light Source, Barcelona, Spain.

In this work we apply NEXAFS and ResPE spectroscopy at the M 2p edges (i) to analyze effects of the MO's occupancy and 3d-3d electron interaction on the formation and decay of the M 2p excitations by comparing the corresponding spectra for NiPc, CoPc and FePc (ii) to get new information about the electronic structure of NiPc, CoPc and FePc, namely about the nature and properties of occupied and unoccupied states.

2. Experimental details

All measurements were performed using linearly polarized radiation at Russian–German beamline (RGLB, BESSY II, Berlin) [8]. The MPC samples were thin (30–50 nm) polycrystalline films prepared *in situ* from thoroughly dehydrated powders by thermal evaporation from a Knudsen cell. The thickness of the films was controlled by a quartz crystal monitor. The reference samples of metallic Ni, Co and Fe were also prepared *in situ* by thermal evaporation.

The NEXAFS spectra of these samples were obtained in the total electron yield mode by recording a sample current. The photon-energy resolution was set to 280 meV at the Ni 2p_{3/2} edge (~850 eV), 250 meV at the Co 2p_{3/2} edge (~780 eV) and 210 meV at the Fe 2p_{3/2} edge (~710 eV). The photon energy was calibrated using the known energy position of the first narrow peak in the Ne 1s absorption spectrum (Ne 1s → 3p; 867.13 eV [9]) and in the F 1s absorption spectrum of solid K₂TiF₆ (F 1s → t_{2g}; 683.9 eV [10]). All NEXAFS spectra were normalized to the incident photon flux.

Valence-band and core-level (not presented in this work) PE spectra for NiPc, CoPc and FePc were collected in the angle-integrated mode with a Phoibos 150 electron analyzer. The total energy resolution was about 580 meV and 520 meV for the Res PE spectra at the Ni 2p_{3/2} and Co 2p_{3/2} edges, respectively and 450 meV at the Fe 2p_{3/2} edge. The energy scale was aligned by measuring the 4f_{7/2} PE lines of the reference gold or platinum foils.

All NEXAFS and PE spectra were acquired at room temperature, with basic pressure of 2×10^{-10} mbar. No sample charging effects were observed during the absorption and photoelectron measurements.

3. Results and discussion

The M 2p absorption spectra recorded for NiPc, CoPc and FePc are compared in Fig. 1. The corresponding spectra of pure metals are also presented in this figure (green dashed lines). For convenience of the following comparison the energy scales of all spectra are aligned to the same position of the main absorption band A (vertical red dotted line) in the M 2p spectra of metals. It should be noted that our M 2p spectra in the number of absorption structures and their energy positions are in good agreement with those obtained previously [5]. In the present paper we will consider the main changes in the absorption structures only for the most intensive 2p_{3/2} absorption components. Examining the series of M 2p_{3/2} absorption spectra, one can see that the spectra of MPC's undergo drastic changes upon consistent substitution of the metal atom in the series NiPc–CoPc–FePc. Indeed, the Co 2p_{3/2} spectrum is significantly different from the Ni one. The Ni 2p_{3/2} XA spectrum is dominated by the intense absorption band A accompanied by several high-energy structures B–D. In contrast, in the Co 2p_{3/2} spectrum an additional low-energy peak A* and splitting of the main resonance A into A₁ and A₂ components are evident. In going to the Fe 2p_{3/2} spectrum the complexity of the absorption structure is increasing even further: the appearance of the new low-energy components \tilde{A}^* , \tilde{A}_1 and \tilde{A}_2 leads to a merging of all absorption resonances into one broad structured band. On the contrary, the M 2p_{3/2} absorption spectra of all pure metals are similar in the overall spectral shape. They are characterized by the dominant absorption band

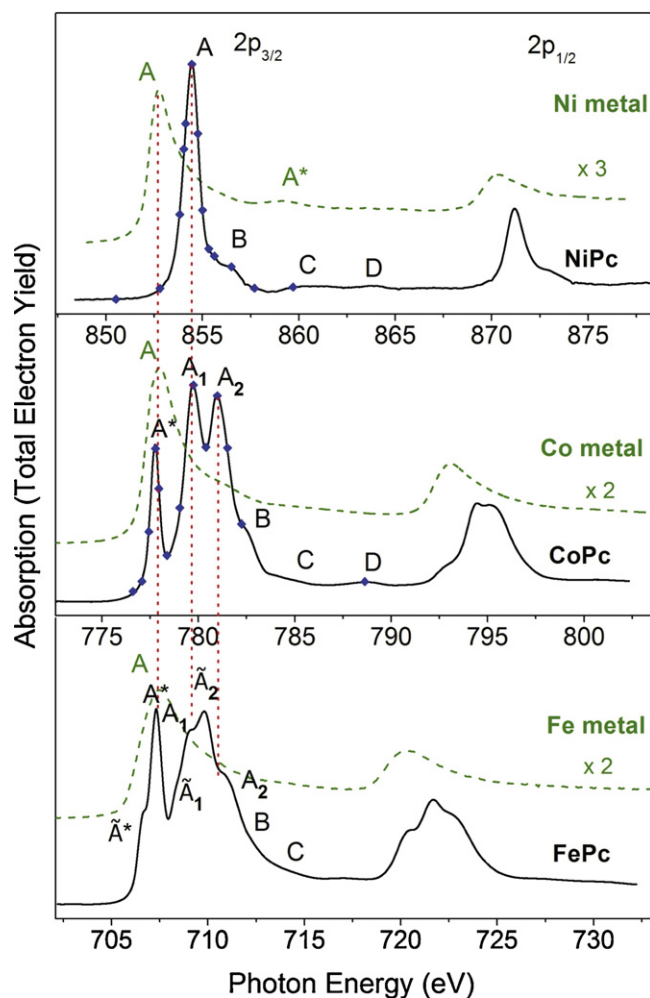


Fig. 1. Metal atom 2p absorption spectra for NiPc, CoPc and FePc (black solid lines) together with corresponding spectra of pure metals (green dashed lines). The energy scales of the spectra are aligned using the position of the main absorption resonance A in the spectra of pure metals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

A which changes only in its width and intensity with respect to the level of continuous absorption. This band corresponds to the transitions of 2p_{3/2} core electrons into unoccupied 3d-derived states of the metal conduction band [11]. Due to the strong localization of 3d states on the metal atom these transitions can be considered as almost intraatomic: $M(2p_{3/2})^4(3d)^n \rightarrow (2p_{3/2})^3(3d)^{n+1}$.

Evidently, the differences in the spectra of MPC's and pure metals are directly connected to the 3d-related features of electronic structure of complexes under investigation. An MPC molecule is composed of a central metal atom (in this case, Co, Ni or Fe) surrounded by four isoindole groups, bridged by four additional N atoms (Fig. 2). Therefore, the molecule is planar with D_{4h} symmetry. Taking into account strong spatial localization of the 2p core excitations near the absorbing atom, for further discussion it is convenient to use the so-called quasi-molecular approach [12]. In the frameworks of this approach the energy distribution of unoccupied states in the MPC molecule is believed to be determined mainly by the square-planar MN₄ quasi-molecule (here four N atoms are the nearest neighbors to M atom). Let us make some qualitative considerations in order to explain experimental data.

The metal 3d-derived electronic states of MPC's are usually regarded as almost purely atomic 3d components of the metal M²⁺ cation [6,7]. Therefore, the degenerate 3d orbitals of free M²⁺ cation are split by the ligand square-planar (D_{4h}) field into the e_g(d_{xz,yz}),

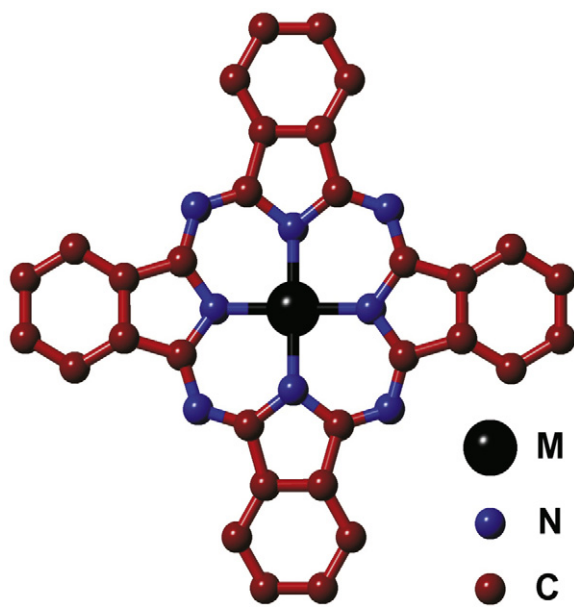


Fig. 2. Schematic view of MPc molecule (M C₃₂ H₁₆ N₈). Hydrogen atoms are not shown.

$b_{2g}(d_{xy})$, $a_{1g}(d_{z^2})$, and $b_{1g}(d_{x^2-y^2})$ components. Consequently nickel atom in the ground state formally has the electron configuration of the Ni²⁺ ion (e_g)⁴(b_{2g})²(a_{1g})²(b_{1g})⁰, while Co²⁺ ion in CoPc has the (e_g)⁴(b_{2g})²(a_{1g})¹(b_{1g})⁰ configuration. Evidently, the $3d_{a_{1g}}$ MO is partly filled in CoPc (total spin $S = 1/2$) and fully occupied for the NiPc complex ($S = 0$).

In the framework of this model, the Ni $2p_{3/2}$ spectrum for NiPc is formed by the only possible dipole-allowed transition of the Ni $2p_{3/2}$ electrons to the weakly antibonding LUMO of b_{1g} symmetry. Thus, the main resonance A in NiPc spectra is attributed to the Ni $2p_{3/2} \rightarrow 3db_{1g}$ electron transition. On the other hand, for the Co $2p_{3/2}$ spectrum of CoPc, the additional low-energy band A* can be attributed to the transition to the partly filled MO (Co $2p_{3/2} \rightarrow 3da_{1g}$). The main absorption band A in the Ni $2p_{3/2}$ spectrum has to be split in the Co $2p_{3/2}$ spectrum into a triplet and a singlet

components (A₁ and A₂ respectively) due to the 3d–3d exchange interaction between the electron excited to the $3db_{1g}$ state and the $3da_{1g}$ electron. In regard to FePc, its electron configuration in the ground state is still under discussion [13,14]. At present it is known that FePc in the ground state has a total spin $S = 1$, which corresponds to two unpaired electrons in the FePc electron configuration. According to the above discussion this should lead to the appearance of new absorption bands and splitting of the absorption transitions due to exchange interaction between the excited electron and electrons on the partly filled MOs of FePc. This suggestion is confirmed by our experimental data, which demonstrate a significant complication of the M $2p_{3/2}$ absorption spectrum in going from CoPc to FePc.

The origin of weak high-energy structures B–D in all three M $2p_{3/2}$ spectra can be associated with the covalent mixing between the valence electronic states of the central atom and N ligands within the MN₄ quasi-molecule. In other words, structures B–D in the M $2p_{3/2}$ spectra are due to the transitions to unoccupied states with the considerably hybridized M $3d\pi$ –N $2p\pi$ character [15].

PE spectra of NiPc and CoPc excited by photons of various energies in vicinity of the Ni $2p_{3/2}$ and Co $2p_{3/2}$ absorption edges (as marked by blue rhombuses in the XA spectra, Fig. 1) are shown in Fig. 3 (a) and Fig. 3 (b) respectively. The bottom curves in both figures correspond to photon energies below the Ni $2p_{3/2}$ and Co $2p_{3/2}$ excitations. Structures a–g (Fig. 3 (a)) and a'–g (Fig. 3 (b)) in these spectra are the PE signals of the valence MOs originating from the N and C 2p and 2s atomic states as well as from the Ni or Co 3d states. Examining the series of PE spectra, it is clear that some of the valence-band PE signals are significantly enhanced when the photon energy is scanned across the 2p–3d absorption resonances (band A in Ni spectrum and A*, A₁ and A₂ in Co spectrum). Three types of spectral features can be identified in the resonant spectra. The first type is characterized by the resonant enhancement of the valence-band signals a–d in consequence of the participator Auger (PA) decay process [4,16]. The second type, the nA structure, results from the normal Auger (NA) process. The last type, is related to the spectator Auger (SA) process [16]. In this case, the sA (NiPc) and sA₁, sA₂, sA₂' (CoPc) structures are shifted to higher kinetic energies (so-called spectator shift) relative to NA due to an additional screening by the spectator electron.

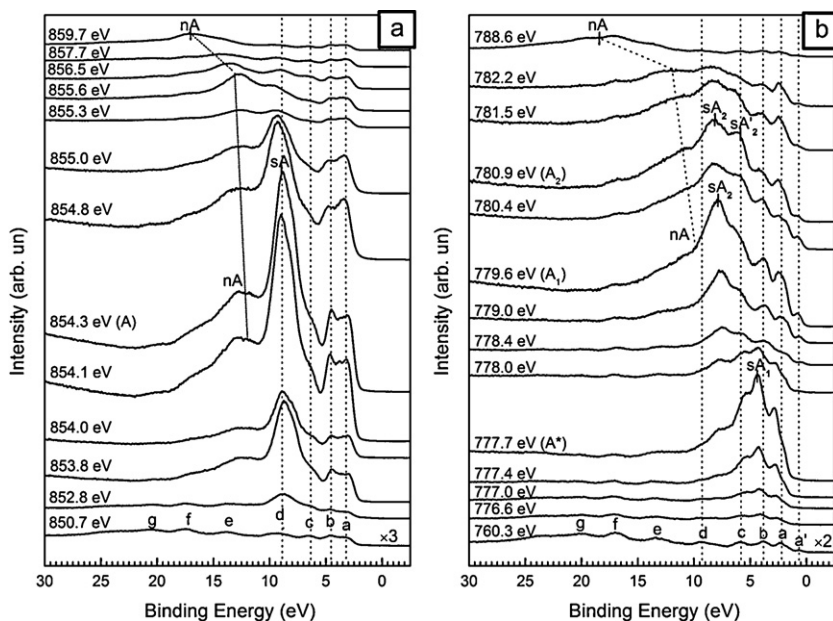


Fig. 3. ResPE spectra for (a) NiPc at the Ni $2p_{3/2}$ edge, (b) CoPc at the Co $2p_{3/2}$ edge.

The most interesting effect is the drastic increase in intensity of the upper valence band signals (mainly bands a–d) due to the interference of direct photoemission channel with the PA decay channel. This observation can be regarded as evidence for a large contribution of the Ni, Co 3d states to the corresponding occupied electronic states of the bands a–d. In addition, the strength of the PA and SA decay processes gives evidence for a strong localization of these 3d-derived states around the metal cation within the quasi-molecule. In regard to the measured ResPE spectra for FePc in vicinity of the Fe 2p_{3/2} absorption edge (not shown), the character of resonance effects is even more complex than in CoPc. But like ResPE spectra for NiPc and CoPc, ResPE spectra for FePc are characterized by a higher probability of the PA and SA processes with respect to the NA one. This means that all conclusions which were made for NiPc and CoPc are also applicable to FePc.

It is of interest that the enhancement effects are different for ResPE spectra of NiPc, CoPc and FePc (not shown). Evidently this is caused by the presence of partly filled MOs in CoPc and FePc and different role of the electron–electron correlation in formation and decay of the M 2p_{3/2} excitations.

4. Conclusions

In general, our work demonstrates the importance of taking into account multielectron effects in the analysis of XA spectra for open shell systems. To illustrate this, the NEXAFS and ResPE spectroscopy have been used for investigation of metal atom core excitations in MPC's (M = Ni, Co, Fe). A strong influence of the 3d-shell occupancy and 3d–3d exchange interaction on the formation and decay of the M 2p core excitations in MPC's has been revealed. Moreover, our data indicates that the high-lying occupied as well as the low-lying unoccupied electronic states in NiPc, CoPc and FePc are mainly 3d derived states. Moreover, the low-lying unoccupied electronic states are strongly localized within the MN₄ quasi-molecule. This work demonstrates an efficiency of NEXAFS and ResPE spectroscopy for the investigation of various polyatomic systems (molecules, complexes, clusters, nanostructures, etc.) containing 3d-elements.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (projects no. 09-02-01278, 12-02-00999) and the bilateral Program “Russian-German Laboratory at BESSY”.

References

- [1] C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines, Properties and Applications*, vol. 3, VCH Publishers, New York, 1993.
- [2] J.G. Chen, NEXAFS investigations of transition metal oxides, nitrides, carbides, sulfides and other interstitial compounds, *Surface Science Reports* 30 (1997) 1–152.
- [3] F. de Groot, Multiplet effects in X-ray spectroscopy, *Coordination Chemistry Reviews* 249 (2005) 31–63.
- [4] J.W. Allen, Resonant photoemission of solids with strongly correlated electrons, in: R.Z. Bachrach (Ed.), in: *Synchrotron Radiation Research. Advances in Surface and Interface Science*, vol. 1, Plenum Press, New York, 1992, pp. 253–323.
- [5] P.L. Cook, X. Liu, W. Yang, F.J. Himpsel, X-ray absorption spectroscopy of biometric dye molecules for solar cells, *Journal of Chemical Physics* 131 (2009), 194701.1–10.
- [6] A. Rosa, Metal-macrocycle interaction in phthalocyanines: density functional calculations of ground and excited states, *Inorganic Chemistry* 33 (1994) 584–595.
- [7] A. Rosa, S. Scheiner, Electronic structure and bonding in metal phthalocyanines, metal = Fe, Co, Ni, Cu, Zn, Mg, *Journal of Chemical Physics* 114 (2001) 9780–9791.
- [8] S.I. Fedoseenko, I.E. Iossifov, S.A. Gorovikov, J.-S. Schmidt, R. Follath, S.L. Molodtsov, V.K. Adamchuk, G. Kaindl, Development and present status of the Russian–German soft X-ray beamline at BESSY II, *Nuclear Instruments and Methods in Physics Research Section A* 470 (2001) 84–88.
- [9] R.N.S. Sodhi, C.E. Brion, Reference energies for inner shell electron energy-loss spectroscopy, *Journal of Electron Spectroscopy and Related Phenomena* 34 (1984) 363–372.
- [10] A.S. Vinogradov, A.Yu. Dukhnyakov, V.M. Ipatov, D.E. Onopko, A.A. Pavlychev, S.A. Titov, Fine structure X-ray absorption spectra of the (TiF₆)²⁻ radical, *Soviet Physics-Solid State* 24 (1982) 803–806.
- [11] J. Fink, Th. Müller-Heinzerling, B. Scheerer, W. Speier, F.U. Hillebrecht, J.C. Fuggle, J. Zaanen, G.A. Sawatzky, 2p absorption spectra of the 3d elements, *Physical Review B* 32 (1985) 4899–4904.
- [12] A.S. Vinogradov, S.I. Fedoseenko, S.A. Krasnikov, A.B. Preobrajenski, V.N. Sivkov, D.V. Vyalikh, S.L. Molodtsov, V.K. Adamchuk, C. Laubschat, G. Kaindl, Low-lying unoccupied electronic states in 3d transition-metal fluorides probed by NEXAFS at the F 1s threshold, *Physical Review B* 71 (2005), 045127.1–11.
- [13] A. König, F. Roth, R. Kraus, M. Knupfer, Electronic properties of potassium doped FePc from electron energy-loss spectroscopy, *Journal of Chemical Physics* 130 (2009) 214503.1–5.
- [14] P.S. Miedema, S. Stepanow, P. Gambardella, F.M.F. de Groot, 2p X-ray absorption of iron-phthalocyanine, *Journal of Physics: Conference Series* 190 (2009), 012143.1–6.
- [15] S.A. Krasnikov, A.B. Preobrajenski, N.N. Sergeeva, M.M. Brzhezinskaya, M.A. Nesterov, A.A. Cafolla, M.O. Senge, A.S. Vinogradov, Electronic structure of Ni(II) porphyrins and phthalocyanine studied by soft X-ray absorption spectroscopy, *Chemical Physics* 332 (2007) 318–324.
- [16] F.P. Larkins, Theoretical interpretation of molecular Auger spectra, *Journal of Electron Spectroscopy and Related Phenomena* 51 (1980) 115–147.