Uppsala University

This is an accepted version of a paper published in *Journal of Chemical Physics*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the published paper:

Brena, B., Puglia, C., de Simone, M., Coreno, M., Tarafder, K. et al. (2011)
"Valence-band electronic structure of iron phthalocyanine: An experimental and theoretical photoelectron spectroscopy study"
Journal of Chemical Physics, 134(7): 074312

URL: <http://dx.doi.org/10.1063/1.3554212>

Access to the published version may require subscription.

Permanent link to this version:

<http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-148939>

<http://uu.diva-portal.org>

Valence-Band Electronic Structure of Iron Phthalocyanine: an Experimental and Theoretical Photo-Electron Spectroscopy Study

Barbara Brena,^{1, a)} Carla Puglia,¹ Monica de Simone,² Marcello Coreno,³ Kartick Tarafder,¹ Vitaly Feyer,⁴ Rudra Banerjee,⁵ Emmanuelle Göthelid,¹ Biplab Sanyal,¹ Peter M. Oppeneer,¹ and Olle Eriksson¹

¹⁾*Department of Physics and Astronomy, Uppsala University, BOX 516, SE-75120 Uppsala, Sweden*

²⁾*CNR-IOM Laboratorio TASC, ss.14 Km. 163,5 Basovizza, 34149 Trieste, Italy*

³⁾*CNR-IMIP, Montelibretti, c/o Laboratorio Elettra, Basovizza, 34149 Trieste, Italy*

⁴⁾*Sincrotrone Trieste SCpA, ss.14, Km.163,5 Basovizza, 34149 Trieste, Italy*

⁵⁾*S. N. Bose National Center for Basic Sciences, Block JD, Sector-III, Salt Lake City, Kolkata-98, West Bengal, India*

(Dated: October 2010; Revised 6 August 2012)

^{a)}Electronic mail: Barbara.Brena@fysik.uu.se

ABSTRACT

The electronic structure of iron phthalocyanine (FePc) in the valence region was examined within a joint theoretical-experimental collaboration. Particular emphasis was placed on the determination of the energy position of the Fe 3d levels in proximity of the highest occupied molecular orbital (HOMO). Photoelectron spectroscopy measurements were performed on FePc in gas phase at several photon energies in the interval between 21 and 150 eV. Significant variations of the relative intensities were observed, indicating a different elemental and atomic orbital composition of the highest lying spectral features. The electronic structure of a single FePc molecule was first computed by quantum chemical calculations by means of Density Functional Theory (DFT). The hybrid B3LYP and the semi local PBE of the generalized gradient approximation (GGA) type, exchange-correlation functionals were used. The DFT/B3LYP calculations find that the HOMO is a doubly occupied π -type orbital formed by the carbon 2p electrons, and the HOMO-1 is a mixing of carbon 2p and iron 3d electrons. In contrast, the DFT/PBE calculations find an iron 3d contribution in the HOMO. The experimental photoelectron spectra of the valence band taken at different energies were simulated by means of the Gelius model, taking into account the atomic subshell photoionization cross sections. Moreover, calculations of the electronic structure of FePc using the GGA+U method were performed, where the strong correlations of the Fe 3d electronic states were incorporated through the Hubbard model. Through a comparison with our quantum chemical calculations we find that the best agreement with the experimental results is obtained for a U_{eff} value of 5 eV.

I. INTRODUCTION

Organic molecules such as Metal Phthalocyanines (Mpc's) have attracted enormous attention as building blocks for innovative materials and devices. Due to their structural similarity to the active sites of hemoglobin and chlorophyll, they are intensively studied as biomimetic catalysts¹. Moreover, their electronic properties set them as promising candidates for optical and electronic devices for gas sensing², solar cells³ and field effect transistors⁴, among many others. The magnetic properties of some of these molecules, like the FePc studied in this work, are also interesting for molecular spintronics studies as prototypes of small molecular

magnets⁵. The Pc's are aromatic macrocycles with high thermal and chemical stability. They have a porphyrin like structure in which the azabridge carbons are substituted by nitrogens, surrounded by four benzene rings. A metal atom or two hydrogens are located in the center of the macrocycles, determining the electronic, optical and magnetic properties of the molecule. A sketch of the FePc molecule is shown in Fig. 1.

FIG. 1. (Color online) Schematic Structure of FePc in the D_{4h} symmetry. The molecule is planar. The interatomic distances **a** to **h** related to the molecular structures used in this work, are given in Table I

The possibility to design MPc based materials with predetermined characteristics requires a full understanding of the electronic structure of the molecules. However, this has shown in many cases not to be a trivial task. Photoelectron spectroscopy (PES) measurements show that the valence band (VB) of several Pc's, in gas phase as well as in films, has a typical profile with a HOMO, in some cases split in two parts, and three major peaks followed by minor weaker peaks, as can be seen, for instance, for H_2Pc ⁶, FePc⁷ and TiOPc⁸. Early experimental PES studies of the VB of gas phase FePc were carried out by Berkowitz in 1979, with a hollow cathode discharge lamp⁹. He compared his results to the almost contemporary measurements performed by Battye *et al.* in 1977¹⁰. Although the resolution in these spectra does not allow to separate in all cases the HOMO and HOMO-1 peaks, they still give a strong

indication that the HOMO should predominantly have carbon π character. This conclusion was based on the comparison of the photoionization cross section effects on spectra collected at different ionization energies (He I and He II, and AlK $_{\alpha}$). The PE spectra of FePc have been studied and interpreted by means of DFT calculations, which are able in most cases to well reproduce their main features and profile^{7,11}. However, the results obtained from different DFT-based exchange correlation functionals are in disagreement when it comes to the energy localization of the metal 3d-type levels, and to their contribution to the high-lying occupied molecular orbitals. Liao and Scheiner by means of quasirelativistic DFT calculations, found Fe 3d character in the HOMO of FePc¹². Fe 3d contributions in the highest lying molecular orbitals were also predicted by ab initio calculations by Kuzmin *et al.*¹³. Different results have been obtained, instead, by Sumimoto *et al.* who studied FePc by means of B3LYP/DFT and identified the HOMO orbital as a π type molecular orbital of C 2p origin¹⁴. Among the most recent theoretical investigations there are the quantum chemical DFT studies of Marom and Kronik, who also provide a review of the recent DFT computations on FePc¹¹. In this work they analysed the changes induced on the electronic structure calculations of FePc by several different basis sets and DFT functionals. From all these works it emerges that hybrid and GGA DFT functionals give a different localization for the 3d levels of the FePc, leaving, therefore, the character of the HOMO as an open question.

To clarify this matter we have performed a systematic experimental-theoretical investigation of the photoelectron spectra of the VB of FePc. Owing to the current availability of high resolution synchrotron radiation, we have measured the valence band PES at high resolution and at several photon energies between 21 and 150 eV. In this energy window, the photoionization cross sections of the 3d levels of Fe vary considerably with respect to those of the p levels of C and N, strongly affecting the experimental spectra. Using the outcomes of the DFT/B3LYP calculation, which is the method that better describes the valence band of the molecule among those we have analysed here, and by taking into account the photon energies employed, we have simulated the experimental spectra. The comparison of the experimental and theoretical curves, allows to identify the elemental and orbital contributions to all the peaks of the VB, and clarifies the energy position of the Fe 3d levels. We have also performed first principles DFT electronic structure calculations in the GGA+U framework. This method is especially well suited to describe accurately metalorganic molecules such as

metal porphyrins or metal phthalocyanines with strong d-electron correlations, deposited on surfaces^{15,16}.

II. EXPERIMENTAL METHODS

The measurements were performed at the Gas Phase Photoemission beamline of Elettra in Trieste¹⁷, using a 150 mm hemispherical electron energy analyser, equipped with six channel electron multipliers. The electron analyzer was mounted with its axis at a forward scattering angle of 54.7° with respect to the electric vector of the linearly polarized light, and in the same plane as the beam propagation direction. In this geometry the electron analyzer is set at the (pseudo) magic angle, so measurements are almost insensitive to the photoelectron asymmetry parameter. The iron phthalocyanine was obtained commercially from Sigma Aldrich in the form of crystalline blue powder with minimum purity of 80%, and was thoroughly purified in vacuum. It was evaporated from a home-built furnace with an effusive nozzle and was checked during purification procedure, comparing periodically a PE spectrum acquired at around 21 eV with Berkowitz's spectrum⁹. The measurements were started only when the vapour could be safely considered free from impurities (mainly water and phthalonitrile). The working evaporation temperature was around $460 \pm 10^\circ\text{C}$. Valence spectra were taken at photon energies between 21 and 150 eV, using a Pass Energy of 5 eV, corresponding to an energy band pass of 100 meV. The HOMO has been calibrated at 6.38 eV according to Berkowitz⁹ comparing it to the position of the Ar $2p_{3/2,1/2}$ peak ionized at $h\nu = 110$ eV, with an overall resolution of 150 meV. PE spectra have been normalized to the photon flux and to the analyser transmission function, taking into account the acquisition time. It was not possible to normalize to the sample density, being it not possible to measure its partial pressure. Moreover, the high temperature of vaporization and its long drifting periods did not allow us to assume an almost constant density of the sample. Therefore, our data can be used to extrapolate branching ratios but not relative partial cross sections of electronic states.

III. COMPUTATIONAL DETAILS

Unrestricted DFT calculations were carried out using the Gaussian 09 program¹⁸. The geometric structure of the FePc molecule was optimized by the hybrid B3LYP exchange-correlation functional¹⁹. A full relaxation of all the atoms was allowed, and the D_{4h} tetragonal symmetry was imposed. The cc-pVTZ (valence triple zeta plus polarization) basis set was used for Fe²⁰, and 6-31g(d,p) basis set (valence double zeta plus polarization) for the other atoms²¹. We have calculated the total and partial density of states (DOS) for the optimized molecule both with the hybrid B3LYP and with the PBE exchange-correlation functional of Perdew, Burke and Ernzerhof²² of the GGA type. The partial DOS's for each atomic orbital were calculated with the method described by Ros *et al.* in²³ for both the B3LYP and the PBE functionals. We have studied the valence region extending from about -20 eV to the HOMO of the FePc. The molecule has a triplet spin state corresponding to a total spin $S=1$, and the same optimized electronic state $^3B_{2g}$ was obtained with both B3LYP and PBE, in agreement with previous studies¹¹. The calculated energy gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) is 2.27 eV for B3LYP and 0.26 eV for PBE. To facilitate the visualization, the different elemental and orbital contributions to the calculated total DOS with the B3LYP and the PBE functionals, were convoluted with Gaussian curves of 0.5 (DOS) and 0.3 (partial DOS) eV of full width at half maximum (FWHM).

The partial DOS's obtained from B3LYP were used to simulate our experimental PE spectra taken at various photon energies, using the Gelius model²⁴. According to this method, the partial DOS's of each atomic orbital were weighed by their related theoretical subshell photoionization cross sections^{25,26}. The values of the subshell photoionization cross sections change for each element and atomic orbital as a function of the photon energy. The procedure was repeated for all the photon energies used in the experiment. To compare the simulated curves with the measured ones, we have convoluted the theoretical peaks with Gaussian curves with FWHM increasing from 0.1 eV to 1.2 eV in the region between -6.38 eV and -9.6 eV, and of 1.2 eV for the rest of the curve.

We have also computed the electronic structure of the VB by means of first principle DFT calculations on the basis of the projector augmented wave method (PAW) implemented in the Vienna *ab initio* simulation package (VASP)²⁷. Spin-polarized PBE+U calculations were

performed by explicitly including the strong Coulomb correlations between the Fe d-orbitals through the Hubbard U term, the Coulomb interaction parameter. U_{eff} is the difference between the U term and the exchange parameter $J^{28,29}$. Here the U parameter is determined by the comparison with the experimental data, and the exchange parameter J is fixed at 1 eV²⁸. The size of the simulation box employed was $21 \text{ \AA} \times 21 \text{ \AA} \times 21 \text{ \AA}$. In this way we could minimize the intermolecular interaction due to the periodic boundary conditions used in the code. The energy cut-off of 500 eV was used for the plane waves and the reciprocal space was sampled in the Γ point. The same spin state of the B3LYP calculations was reproduced, and the HOMO-LUMO gap calculated was of 1.04 eV for U_{eff} equal to 3 eV and of 1.03 eV for U_{eff} equal to 5 eV.

The atomic distances obtained for FePc in the B3LYP and in the GGA+U calculations with U_{eff} equal to 5 eV are reported in Table I, where they are compared to the experimental values measured by means of x-ray diffraction by Kirner *et al.*³⁰. The calculated distances are in good agreement with the experimental values. The FePc molecular structure optimized with the GGA+U approach did not conserve a full D_{4h} symmetry after optimization, and the values reported in Table I are averaged over their corresponding segments throughout the whole molecule.

Segment	a	b	c	d
Experiment	1.927	1.378	1.322	1.450
DFT/B3LYP (D_{4h})	1.947	1.381	1.322	1.456
GGA+U ($U_{eff}=5 \text{ eV}$)	1.958	1.380	1.327	1.457
Segment	e	f	g	h
Experiment	1.392	1.395	1.390	1.394
DFT/B3LYP (D_{4h})	1.405	1.396	1.394	1.409
GGA+U ($U_{eff}=5 \text{ eV}$)	1.410	1.3969	1.396	1.409

TABLE I. Intramolecular distances in $\text{\AA}$ between the atoms indicated in Fig. 1. The experimental values are taken from³⁰, and the B3LYP and GGA+U, with U_{eff} equal to 5 eV, calculations are referred to this work. The distances related to the GGA+U calculation are averaged over the whole molecule.

IV. RESULTS

In Fig. 2 we compare the total DOS's of the VB computed by Gaussian 09 with the B3LYP and with the PBE functionals. Below the total DOS, we show the partial DOS's of carbon and nitrogen 2s and 2p, and of iron 3d, which are the atomic orbitals that predominantly contribute to the molecular orbitals in the VB. The theoretical curves are compared, as a reference, to our experimental spectrum collected at 110 eV. This is the same photon energy that we had used in a previous work to measure the polarization dependence of the VB PES of a film of FePc on Si(100)⁷. The energy scale of the curves is aligned to the experimental scale, so that the experimental HOMO and the theoretical HOMO are set at the same energy of -6.38 eV. To facilitate the discussion, we have named the main spectroscopical features A to G according to⁷. Peak A is formed by two subpeaks, A₁, the HOMO, and A₂. The intensity ratio and the composition of these two peaks will be largely discussed below. Peak B is composed by three sub-peaks, B₁, B₂ and B₃. Peak C is a low intensity but clearly visible feature, located between the peaks B and D. Peak D and peak E are formed each by two distinct contributions, D₁, D₂, E₁ and E₂. Finally it is possible to further distinguish two minor features, namely peaks F and G.

A first observation about the total DOS's computed with the hybrid B3LYP and with the PBE functionals, is that both methods are able to capture the overall structure of the VB. The major peaks from A₁ to G are clearly present in both calculations, and peaks F and G are well resolved. The DOS obtained with the PBE functional, however, is contracted in energy with respect to the B3LYP DOS, leading to evident differences in the energy positions of the respective peaks. The rigid contraction of the energy positions of the Kohn-Sham orbitals calculated by PBE has been observed before for organic molecules³¹. It's origin might be due to a reduced orbital interaction in PBE, which does not work with an orbital dependent potential and an average distribution of electrons over orbitals is favored. This effect is in large part released by hybrid functionals, like B3LYP, where the exchange correlation term is improved by including the exact exchange. The Hartree-Fock exchange interaction leads to a stronger orbital dependence causing larger splitting of the orbitals. From the comparison displayed in Fig. 2 we conclude that the energies of the peaks calculated with B3LYP are closer to the experimental photoemission peaks than the PBE ones. From Fig. 2, and bearing in mind the energy scale discrepancy, one can also see that the partial

FIG. 2. (Color online) DFT calculations of the total and partial DOS of FePc. The results given for B3LYP and for PBE. The partial DOS related to the C and N 2s and 2p, and Fe 3d states are shown. The measured spectrum collected at a photon energy of 110 eV is shown. In the inset, the Fe 3d theoretical DOS computed by B3LYP and PBE are displayed together with the measured spectrum.

DOS's calculated with the B3LYP and with the PBE functionals provide nonetheless similar descriptions with respect to the N and C contributions. The partial DOS's of the 2s and 2p electrons of C and N are in fact very similar for both functionals for all the peaks from A₁ to G. The theory predicts in both cases that the lower energy part of the VB, included between the peaks A₁/HOMO to the E₂, i.e. between -6.38 eV and about -15.5 eV for B3LYP, or -14.5 for PBE, is populated by molecular orbitals formed for the major part by a mixing of C and N 2p states. At the higher binding energies of peaks F and G, the contributions of C and N 2s electrons become more important. B3LYP and PBE provide different shapes for peak B. In fact peak B as well as A₁, are strongly influenced by the location of the Fe 3d levels. In the inset of Fig. 2, only the Fe 3d partial DOS's calculated with both methods are plotted, and compared to the photoemission experiment. The overall profile of the Fe 3d components is very similar in both cases, but in the PBE calculations it is shifted towards lower binding energies compared to the B3LYP. The most intense Fe 3d levels are located between A₂ and

D_2 according to B3LYP, and between A_1 and D_1 according to PBE. The main disagreement between the two DFT descriptions of the electronic structure is therefore related to the energy position of the Fe 3d levels, and it gives two very different results particularly for A_1 . The B3LYP finds that the HOMO, A_1 , is a π orbital originated from C 2p orbitals with an a_{1u} symmetry. The Fe 3d orbitals are located in the A_2 peak which is thus mainly a mixing of C 2p and Fe 3d contributions that build a e_g type orbital. The B3LYP method also predicts a Fe 3d contribution to the next feature at lower energy, which corresponds with the position of peak B_1 , that appears as a shoulder in the composite B feature. In the PBE calculation, instead, we obtain Fe 3d components of similar intensities in both A_1 and A_2 peaks, where they mix with the C 2p orbitals. Here e_g orbitals contribute to the peak A_1 . The same results for the molecular orbitals were obtained in [11,14](#).

FIG. 3. (Color online) **A**: Experimental and **B** simulated PE spectra of the VB of FePc. The spectra collected from 21 to 150 eV photon energy are shown.

In Fig. 3 the experimental measurements are shown as well as the theoretical simulations computed at the corresponding photon energies, according to the Gelius model. The simulated spectra are based on the partial DOS's computed by B3LYP. The elemental and orbital origin of the molecular orbitals predicted by B3LYP, with particular attention to the

A_1 and A_2 features, is confirmed by the results of the measurements, as will be discussed below.

In panel A of Fig. 3, the experimental PE spectra of the VB taken at photon energies of 21, 31, 50, 60, 70, 80, 90, 110, 130 and 150 eV are plotted. Both the experimental and theoretical spectra are displayed by imposing a constant intensity for peak B_2 . Peak B_2 was chosen as a fixed reference because it is the highest feature in almost all spectra and, according to our calculations, it is formed by a single contribution of C 2p electrons, and in extremely modest contributions by N 2p electrons. Moving from 21 eV to 150 eV of photon energy, the experimental spectra undergo evident intensity modifications, but the energy positions of the peaks remain constant. The relative intensities of the peaks A_1 and A_2 become inverted as a function of the photon energy. At low energies, and especially at 21 and 31 eV, A_1 has much higher intensity than A_2 . As the photon energy increases, the intensity of A_2 increases drastically, overcoming A_1 's at a photon energy of 70 eV. At a photon energy of 150 eV, A_1 is merely a shoulder at the base of the A_2 peak. Peak B_1 also augments in intensity with increasing photon energy in a way analogous to the peak A_2 . In fact the intensity ratio between the peaks A_2 and B_1 appears to remain almost constant as the photon energy varies, indicating a similar elemental and orbital composition for the two peaks. The intensity of the peak A_1 , instead, overcomes that of the peaks B_2 and B_3 above 90 eV photon energy. The D and E peaks are predominant at 21 and 31 eV, and have much less intensity at higher photon energies.

In Fig. 3, panel B, the PES simulations are displayed. The energy scale of the theoretical curves is aligned with the experimental one. The overall profiles of the simulated spectra are very similar to the experimental data, and undergo the same kind of modifications. At photon energies of 21 and 31 eV, the peaks B, D and E have clearly higher intensity than the peaks A. As observed in the experimental data, the intensity ratio between these peaks gets inverted at higher photon energies. The relative intensities of the theoretical peaks A_1 and A_2 clearly follow the same trend of the experiment: the similarity with the measurements is remarkable both at the lowest and at the highest energies (21, 31, 110, 130, and 150 eV). Finally, the intensity of the computed peak B_1 increases when the photon energy increases, as happens for the peak A_2 and according to the experimental spectra.

In Fig. 4 the FePc DOS computed by PBE+U calculations are presented. After testing the values of U_{eff} equal to 3 and 5 eV for the Fe 3d states, we have reached, with U_{eff}

FIG. 4. (Color online) GGA+U calculations of the total and partial DOS of FePc. The results corresponding to U_{eff} equal to 3 and U_{eff} equal to 5 are shown. The measured spectrum collected at a photon energy of 110 eV is shown.

equal to 5 eV, an electronic structure analogous to the one calculated by B3LYP. As can clearly be seen in Fig. 4, the DOS obtained with U_{eff} equal to 3 eV agrees roughly with the Gaussian/PBE DOS shown in Fig. 2, and in a similar way, it locates the Fe 3d band at higher energies, where it contributes to both the A_1 and the A_2 peaks. In the calculation with U_{eff} equal to 5 eV, instead, the two higher energy peaks A_1 and A_2 are found to be composed by only C 2p, and by C 2p and Fe 3d electrons respectively, this structure being the one that best corresponds to the intensity variations observed in the measured spectra. In Fig. 4, below the total DOS, also the partial DOS of C and N 2s and 2p, and of Fe 3d atomic orbitals are shown.

V. DISCUSSION

The gradient corrected PBE and hybrid B3LYP exchange-correlation functionals give different energy positions for the Fe 3d states in the VB of FePc. As previously observed, how-

ever, these types of DFT calculations often provide a DOS profile in reasonable agreement with the experimental PE measurements. This fact hampers unfortunately the possibility to distinguish among these methods, and to identify among them a possibly more accurate electronic description. In this work we have systematically employed an effective tool to overcome this problem, which is the inclusion of the effects of the subshell cross sections in the experimental measurements and in the theoretical calculations. The variations in the shape of the VB that are observed in the experimental PES at several photon energies, Fig. 3, can be attributed to the effects of the photoionization cross sections on the molecular orbitals. If we assume the validity of the Gelius approximation, then we can expect that the spectroscopical features whose intensity varies in different ways in function of the photon energies, have a different elemental and/or atomic orbital composition.

The photon energy interval we have selected is particularly convenient in order to explore the effects of the photoionization cross sections on the valence region of materials containing C, N and Fe. For the 2p orbitals of C and N, the cross sections have their highest value close to the ionization threshold, and then decay at higher photon energies. The theoretical values of the subshell cross sections calculated by Yeh²⁵ for C and N 2p vary from about 6.1 and 9.6 Mb respectively at 20 eV photon energy, to about 0.05 and 0.2 Mb at 150 eV. For Fe 3d, instead, the cross sections have a maximum value above the ionization threshold close to 45 eV. At 20 eV the theoretical Fe 3d cross section is 4.83 Mb, it closes its maximum at 50 eV with a value of 8.6 Mb, and it decreases to about 2.3 Mb at 150 eV. This means that at 20 eV the subshell cross sections are in the same order of magnitude for C and N 2p and for Fe 3d, while at 150 eV the cross section for Fe 3d is about 50 times larger than that of C 2p and approximately 10 times larger than that of N 2p. What happens as we measure with photons of increasing energy is that the intensity of the Fe 3d levels becomes considerably more pronounced with respect to the C and N 2p and 2s levels. The intensities of the Fe 3d states are therefore greatly enhanced in the PE spectra at 150 eV in comparison to 21 eV photon energy.

The strong variations of the relative intensities of the A_1 (the HOMO) and A_2 peaks, which are observed in the measured spectra, hence, are a strong indication that they have different elemental origins. The intensity of the peak A_1 decreases with respect to that of peak A_2 as the photon energy increases. Considering the relative magnitudes of the photoionisation cross sections, it is straightforward that the peak A_2 contains a considerable

Spectral Feature (eV)	Orbital	Energy (eV)	Fe 3d (%)	C 2p (%)	N 2p (%)
A ₁	a _{1u}	-6.38	0.00	99.65	0.35
A ₁	a _{1u}	-6.39	0.00	99.80	0.20
A ₂	e _g	-7.04	72.93	21.50	5.57
B ₁	e _g	-7.70	37.22	28.03	34.75

TABLE II. Atomic orbital composition of the highest lying molecular orbitals computed by B3LYP for the peaks A₁, A₂ and B₁. The peaks A₂ and B₁ of e_g symmetry are doubly degenerate.

contribution from the Fe 3d levels, while the peak A₁ is likely to be formed mostly by C 2p contributions. This is precisely what was obtained from the B3LYP calculation, i.e. a Fe 3d component in the peak A₂, the e_g molecular orbital, but not in the peak A₁, the a_{1u} molecular orbital. The hybrid functional locates another Fe 3d peak at lower energy, which contributes to the peak B₁. This peak has an intensity behaviour analogous to A₂, showing that it too must contain a high percentage of Fe 3d contributions. The composition of the spectroscopical features in terms of percentage of atomic orbitals obtained by the B3LYP calculations for the peaks A₁, A₂ and B₁ are reported in Table II. The similarity between the experimental data and the theoretical simulations of the PE spectra that we have obtained in this work, strengthen the validity of the Gelius approximation in this context. The comparison between experiment and theory is in this case a valid tool to interpret the origin of the experimental features. And in particular we have obtained the best results with the B3LYP and the GGA+U (U_{eff}=5eV) approaches.

The comparison to the PBE/GGA ab initio periodic calculations is a very important benchmark in order to continue our spectroscopical theoretical studies of organic molecules adsorbed on surfaces or assembled in films, which we have started by considering the FeP¹⁵ and recently the CoPc molecule³¹. For such extended systems, a periodic approach is fundamental in order to properly describe the electronic band structures of the materials, and to understand their properties and the adsorption process³². The experimental spectrum was used as a reference to calibrate the choice of the Coulomb U parameter in the GGA+U calculations. The periodic GGA+U calculations give analogous results to the PBE cluster calculations when it comes to the energy localization of the Fe 3d states. Depending on the

value of U used in the calculations, the Fe 3d levels shift towards higher binding energies. For a value of U_{eff} equal to 5 eV, we can see that the metal d band is part of the peak A_2 but not of A_1 , as in B3LYP and in agreement to the experimental findings.

VI. CONCLUSIONS

We have measured PE spectra of the VB of FePc molecules in gas phase, at varying photon energy. The changes observed in the spectra as a function of the incident radiation can be attributed to effects of the photoionization cross sections. The DOS in the VB was calculated by means of quantum chemical and plane wave DFT+U calculations. Both the hybrid B3LYP and the gradient corrected PBE functionals were used in the former approach. The consideration of the influence of the cross sections in the experimental measurements and in the theoretical simulations has allowed to determine the atomic composition of the FePc valence band. It has given the key to define the energy location of the Fe 3d states, and it has allowed to assess the results obtained with the two different density functionals considered. The B3LYP predicts for the HOMO a carbon based, π molecular orbital, and identifies the contribution of the Fe 3d states in the HOMO-1 and in the orbitals located at higher binding energies. The atomic orbital projected partial DOS's computed by the B3LYP, were used to simulate the experimental curves. The Gelius model was employed in combination with theoretical subshell photoionization cross sections. The comparison of the experimental and theoretical results show that the B3LYP provides the more accurate description of the valence band, in particular in relation to the Fe 3d states. We have also been able to calibrate our first principles, plane wave based GGA+U calculations in relation to the photoelectron spectra. This result constitutes an important benchmark for the use of GGA+U calculations in the interpretation of VB x-ray spectroscopy results. We have obtained that U_{eff} equal to 5 eV provides a correction to the energetic localization of the Fe 3d states that permits the comparison of the GGA+U results to the experimental spectrum. The determination of U_{eff} through the comparison of DFT+U method with B3LYP and experimental spectroscopy provides us a good handle to treat extended systems, e.g., 3d transition metal centered organic molecules supported on substrates with reasonable accuracy and computational resources.

ACKNOWLEDGEMENTS

We acknowledge financial support from the Swedish Research Council (VR), the Göran Gustafsson Foundation, the C. Tryggers Stiftelse, and the Uppsala University Unimolecular Centre (U3MEC). The grants for computer time from the Swedish National Infrastructure for Computing (SNIC) are acknowledged. K.T. acknowledges the Swedish International Development Cooperation Agency (SIDA). R.B. is thankful to the Swedish Institute for the scholarship and financial support. B.S. acknowledges financial support from STINT Institutional Grant for Young Researchers. O.E. acknowledges support from European Research Council (ERC).

REFERENCES

- ¹P. Afanasiev, D. Bouchu, E.V. Kudrik, J.-M. Millet, and A.B. Sorokin, Dalton Trans. **44**, 9828 (2009).
- ²J.A. de Saja, and M.L. Rodriguez-Méndez, Adv. Colloid Interface Sci. **116**, 1 (2005).
- ³J. He, G. Benkö, F. Korodi, T. Polivka, R. Lomoth, B. Åkermark, L. Sun, A. Hagfeldt and V. Sundström, J. Am. Chem. Soc. **124**, 4922 (2002).
- ⁴L. Zhang, H. Zhang, J.W. Ma, X.W. Zhang, X.Y. Jiang, Z.L. Zhang, Thin Solid Films **518**, 6134 (2010).
- ⁵N. Ishikawa, Functional Phthalocyanine Molecular Materials **135**, 211 (2010).
- ⁶Y. Alfredsson, B. Brena, K. Nilsson, J. Åhlund, L. Kjeldgaard, M. Nyberg, Y. Luo, N. Mårtensson, A. Sandell, and C. Puglia, J. Chem. Phys. **122**, 214723 (2005).
- ⁷J. Åhlund, K. Nilson, J. Schiessling, L. Kjeldgaard, S. Berner, N. Mårtensson, C. Puglia, B. Brena, M. Nyberg, and Y. Luo, J.Chem.Phys. **125**, 034709 (2005).
- ⁸B. Brena, P. Palmgren, K. Nilson, S. Yu, F. Hennies, B. Agnarsson, A. Onsten, M. Mansson, M. Göthelid, Surf. Sci. **603**, 3160 (1965).
- ⁹J. Berkowitz, J. Chem. Phys. **70**, 2819 (1979).
- ¹⁰F.L. Battye, A. Goldmann, and L. Kasper, Phys. Stat. Sol. B **80**, 425 (1977).
- ¹¹N. Marom, and L. Kronik, Appl. Phys. A: Mater. Sci. Process., **95**, 165 (2009).
- ¹²M.-S. Liao, and S. Scheiner, J. Chem. Phys. **114**, 9780 (2001).
- ¹³M.D. Kuzmin, R. Hayn, and V. Oison, Phys. Rev. B **79**, 024413 (2009).

- ¹⁴M. Sumimoto, Y. Kawashima, K. Hori, and H. Fujimoto, Dalton Trans. **29**, 5737 (2009).
- ¹⁵P.M. Panchmatia, B. Sanyal, and P.M. Oppeneer, Chem. Phys. **343**, 47 (2008).
- ¹⁶M. Bernien, J. Miguel, C. Weis, M.E. Ali, J. Kurde, B. Krumme, P.M. Panchmatia, B. Sanyal, M. Piantek, P. Srivastava, K. Baberschke, P.M. Oppeneer, O. Eriksson, W. Kuch, H. Wende, Phys. Rev. Lett., **102** 047202 (2009).
- ¹⁷R. R. Blyth, R. Delaunay, M. Zitnik, J. Krempasky, R. Krempaska, J. Slezak, K.C. Prince, R. Richter and M. Vondracek, R. Camilloni, L. Avaldi, M. Coreno, G. Stefani, C. Furlani, M. de Simone, S. Stranges, M.-Y. Adam, J. Electron Spectrosc. Related Phenomena **101**, 959 (1999).
- ¹⁸M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Montgomery, Jr., J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.1*, Gaussian Inc. Wallingford CT (2009).
- ¹⁹A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- ²⁰N.B. Balabanov and K.A. Peterson, J. Chem. Phys. **123**, 064107 (2005).
- ²¹V. Rassolov, J.A. Pople, M. Ratner, and T.L. Windus, J. Chem. Phys. **109**, 1223 (1998).
- ²²J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- ²³P. Ros, and G.C. Schuit, Theoret. Chim. Acta (Berl.) **4**, 1 (1996).
- ²⁴U. Gelius, J. Electron Spectrosc. Relat. Phenom. **5**, 985 (1974).
- ²⁵J.J. Yeh, *Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters*, Gordon and Breach Science Publishers, Langhorne, PE (USA), 1993.
- ²⁶<http://ulisse.elettra.trieste.it/services/elements/WebElements.html>.
- ²⁷G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

- ²⁸V. I. Anisov, F. Aryasetiawan, and A. I. Lichtenstein, *J. Phys.: Condens. Matter* **9**, 767 (1997).
- ²⁹S. L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, and A.P. Sutton, *Phys. Rev. B* **57**, 1505 (1998).
- ³⁰J.F. Kirner, W. Dow, and W.R. Scheidt, *Inorg. Chem.* **15**, 1685 (1976).
- ³¹S. Bhattacharjee, B. Brena, R. Banerjee, H. Wende, O. Eriksson, B. Sanyal, *Chem. Phys.* **377**, 96 (2010).
- ³²M.E. Ali, B. Sanyal and P.M. Oppeneer, *J. Phys. Chem. C* **113**, 14381 (2009).