

2p x-ray absorption of iron-phthalocyanine

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Abstract. 3d transition metal ions, like Fe(II) in a planar organic environment are subject to the details of the ligand coordination. In this study the 3d orbital splitting in planar D_{4h} symmetry is investigated for Fe(II) using the charge transfer multiplet program. By variation of the 10Dq, Ds and Dt crystal field parameters, the 3d orbitals split differently giving rise to different spin multiplicity. The relative occupations of the 3d orbitals yield a range of ground states. Experimental x-ray absorption spectra of FePc powder are compared with theoretical simulations, resulting in the spin ground state of the Fe(II) ion being 3E .

1. Introduction

The interest in 3d-transition metal ions in a planar organic environment, for example in metallo-phthalocyanines (MPc's) has two main reasons: their numerous technological applications [1], such as chemical sensors [2; 3], use in optoelectronic devices [4] and solar cells [5] and their similarity to the biological molecules chlorophyll and haemoglobin. Haemoglobin in particular, is a close relative of iron(II) phthalocyanine (FePc). Over decades phthalocyanines have been extensively investigated by various experimental techniques [6; 7]. Their catalytic properties have been studied for some time, in particular for redox catalysis such as in fuel cell applications [8]. FePc and CoPc may have interesting applications as spin crossover materials which are useful in magnetization control [9; 10]. Theoretical studies of the electronic structure of phthalocyanines include density functional theory [11; 12] and (multi-configuration) Hartree-Fock based calculations [13; 14].

The electronic structure and especially the spin state of transition-metal complexes such as MPc's are controlled by the number and nature of the ligands. In particular, 3d-transition metal ions adopt a variety of electronic structures, including high-spin, low-spin and in some cases intermediate-spin states. For example, the Fe(II) [Fe(tp)(ImH)₂] heme compound has a characteristic low-spin iron L edge [15]. Furthermore, each spin state could have different electronic configurations and different arrangements of 3d-orbitals. Although several theoretical and experimental studies have been performed on the electronic ground state of the FePc, there is no agreement in these studies with

regard to the electronic ground state symmetry. The ground state of the FePc-molecule has been reported as 3E_g [6; 16], ${}^3B_{2g}$ [17] and ${}^3A_{2g}$ [18]. On the basis of bulk magnetic susceptibility [6] and single crystal magnetic anisotropy measurements [17] the conclusion was that the iron(II) ion in FePc is in the S=1 state and that the ground state seems to be an orbital singlet. Stillman and Thomson found evidence for the S=1 state of Fe(II) phthalocyanine in solution [18]. Filoti et al. used Mössbauer spectroscopy on α -FePc and demonstrated that α -FePc has the 3E_g spin ground state that gives rise to an orbital-degenerate ground state and as a consequence an expectation value for the average orbital moment L_z of approximately minus one [19]. DFT calculations have produced similarly varying predictions of ${}^3A_{2g}$ [20] and ${}^3B_{2g}$ or 3E_g [14]. Reynolds et al. state that FePc has the 3E_g (or less likely ${}^3B_{2g}$) ground state [14]. Liao et al. have investigated the electronic structure of a group of metal phthalocyanines. They found that FePc has the ${}^3A_{2g}$ ground state, but report that their calculated energies of ${}^3B_{2g}$ and 3E_g states were very close [20]. The general consensus is that FePc has an S=1 intermediate-spin ground state, but within the triplet ground states all possibilities are found in the various studies.

In this study, Fe(II) phase diagrams are created as a function of 10Dq, Ds and Dt. Using the information in these phase diagrams, some representative X-ray absorption spectra (XAS) of different ground states are simulated. The Fe $L_{2,3}$ edge XAS, x-ray magnetic circular dichroism (XMCD) spectra of a FePc powder sample has been measured. Simulated spectra of different ground states will be compared with the experimental spectrum, yielding the optimized ground state(s) for FePc.

2. Theoretical section

The details of the ligand coordination give rise to different 3d orbital splitting in the planar D_{4h} environment, usually approximated with crystal field parameters. Calculations were performed using the charge transfer multiplet model [21]. This approach includes both electronic Coulomb interactions and spin-orbit coupling for each sub-shell. To simulate the spectra, the Slater-Condon parameters are first reduced to 80% of their Hartree-Fock calculated values to account for the overestimation of electron-electron repulsion in *ab initio* Hartree-Fock calculations of the free ion. XAS can then be calculated from the sum of all possible transitions for an electron excited from the 2p core level into an unoccupied 3d level. In the crystal field limit the ground state is approximated by a single electronic configuration $3d^n$, where n is the number of valence 3d electrons split in energy by electron repulsion and a crystal field potential in D_{4h} symmetry defined by the parameters 10Dq, Ds and Dt for D_{4h} symmetry.

The focus is on the 3d orbital splitting of $3d^6$ Fe(II) in D_{4h} symmetry and the electronic spin (ground) states. By variation of the 10Dq, Ds and Dt crystal field parameters, different spin states can be reached for Fe(II). The relative occupations of the 3d orbitals yield a range of ground states. For some of the spin ground states representative XAS were simulated. To create sharp transitions between the spin ground states, we calculated the Fe(II) ground state phase diagrams without 3d spin-orbit coupling. The inclusion of 3d spin-orbit coupling splits the various ground states and, in addition, it mixes spin states when they are almost degenerate. The XAS calculations were performed with the inclusion of the 3d spin-orbit coupling. For each ground state we determine the relative occupation of the ten different 3d orbitals. This relative occupation is non-integer due to the effects of the electronic Coulomb interactions and spin-orbit coupling.

3. Results

In this section the results of the spin ground states of Fe(II) and the phase diagrams for different crystal field values for $3d^6$ are presented. In addition, simulated spectra of Fe L-edge XAS are compared with experimental spectra of a FePc powder sample.

3.1. Spin states of Fe(II) in D_{4h} (square planar) symmetry

If we look at $3d^6$ Fe(II), it can have a high-spin ($S=2$), low-spin ($S=0$) and an intermediate-spin state ($S=1$) depending on the coordination and the environment of the iron ion. In octahedral and tetrahedral symmetry, one only finds high-spin and low-spin Fe(II), but in square planar compounds also intermediate-spin states can be found, which could be viewed as a high-spin state with two holes in the $3d_{x^2-y^2}$ orbitals.

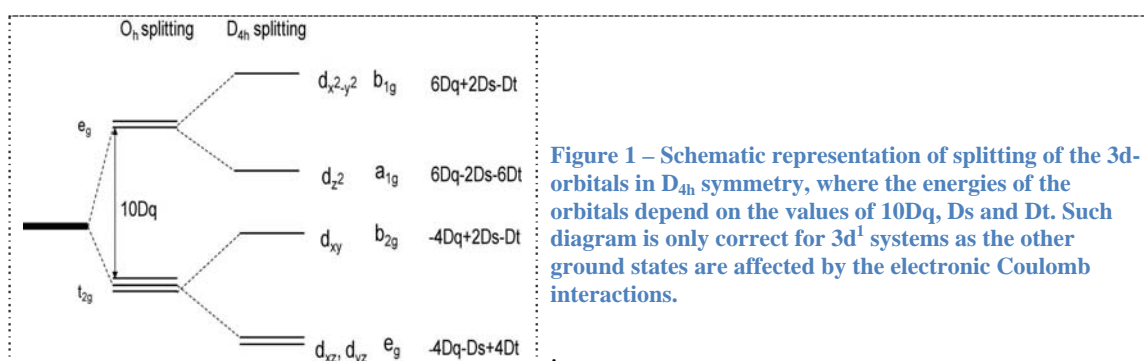


Figure 1 – Schematic representation of splitting of the 3d-orbitals in D_{4h} symmetry, where the energies of the orbitals depend on the values of $10Dq$, Ds and Dt . Such diagram is only correct for $3d^1$ systems as the other ground states are affected by the electronic Coulomb interactions.

In O_h symmetry the 3d-orbitals split in two parts (Cf. Figure 1): the $3d_{xz}, 3d_{yz}$ and $3d_{xy}$ (t_{2g}), and the $3d_{z^2}$ and $3d_{x^2-y^2}$ (e_g) orbitals, split by the cubic crystal field splitting $10Dq$. In D_{4h} symmetry the 3d-orbitals further split into four parts, respectively the $3d_{xz}, 3d_{yz}$ (e_g), $3d_{xy}$ (b_{2g}), $3d_{z^2}$ (a_{1g}) and $3d_{x^2-y^2}$ (b_{1g}) orbitals. In figure 1 the relationship between the splitting of the orbitals and the crystal field energy values $10Dq$, Ds and Dt are shown for one 3d-electron. In perfect square planar symmetry, one can derive a formal rule based on point charges that $Dt = 2/35 \cdot 10Dq$ [22]. This rule is based on the ionic limit of the point charge model; the other extreme is to describe the crystal field splitting solely based on chemical bonding using the coupling strength ratios for the four types of orbitals. The ratio for the hopping T , scale as $T(b_{1g})=3$, $T(a_{1g})=\sqrt{3} \approx 1.73$, $T(b_{2g})=1.5$ and $T(e_g)=3/\sqrt{8} \approx 1.125$ [23]. Noting that the relative energies scale with T^2 , one can derive the rule that $Dt = 2/35 \cdot 10Dq$, exactly the same rule as in the ionic limit. In addition one finds that $Ds = 19/126 \cdot 10Dq$. From these relationships one already can get an idea that the 3d-orbitals may swap places depending on the crystal field energies. This also means that the 3d-orbital occupation may differ. In table 1 the possible spin states with their relative 3d-orbital occupation numbers are shown, where these numbers have been rounded to integer values. As we will see below, the actual ground state has non-integer occupation numbers. Depending on which 3d-orbital is doubly occupied for the high-spin states there are states with the names 5A_1 , 5E and 5B_2 . If, for example, the $3d_{x^2-y^2}$ orbital (b_1) is high in energy, the intermediate-spin states are possible. Depending on which two orbitals are doubly occupied the states are named 3B_2 , 3A_2 and 3E . Also low-spin states are possible, containing only doubly occupied orbitals, yielding a 1A_1 state. By variation of the $10Dq$, Ds and Dt crystal field parameters, these different spin states can be reached for Fe(II).

Table 1 – The electronic ground state of Fe(II) and their occupation numbers (rounded to an integer value) of the different 3d-orbitals

S=2 and S=0 States	Occupied orbitals	S=1 State	Occupied orbitals
5E	$e^3 a_1^1 b_2^1 b_1^1$	3E_a	$e^3 a_1^1 b_2^2$
5B_2	$e^2 b_1^1 b_2^2 b_1^1$	3E_b	$e^3 a_1^2 b_2^1$
5A_1	$e^2 a_1^2 b_2^1 b_1^1$	3A_2	$e^2 a_1^2 b_2^2$
1A_1	$e^4 a_1^2$ or $e^4 b_2^2$	3B_2	$e^4 a_1^1 b_2^1$

3.2. Crystal Field Phase diagrams

We present the different ground states in two representative phase diagrams, respectively:

- (1) Figure 2 (left): D_s versus $10Dq$ for zero D_t ; D_s has a similar effect on the xy versus z orbitals (cf. Fig. 1)
- (2) Figure 2 (right): D_s equal to D_t versus $10Dq$; This creates a large difference between A_1 and E states.

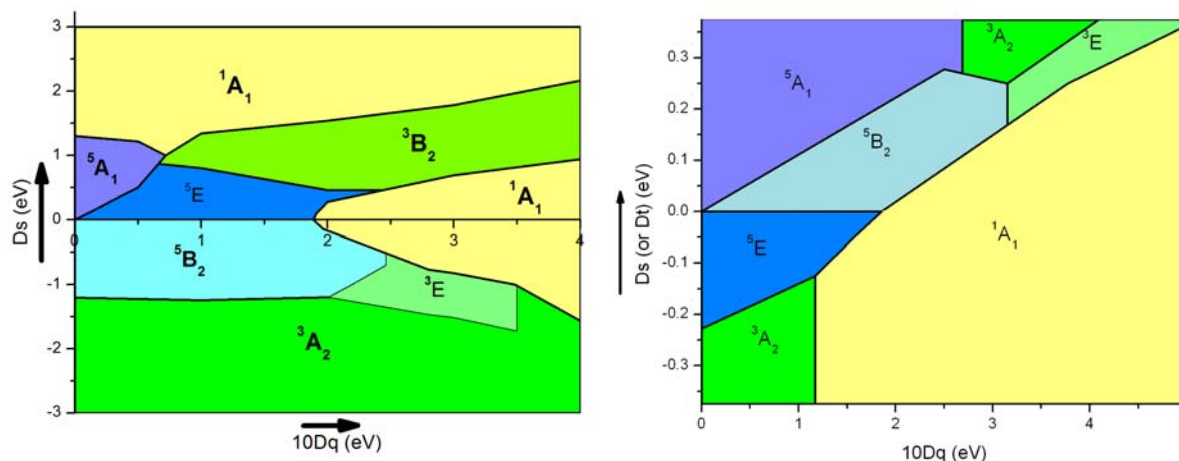


Figure 2 (left) The phase diagram of Fe(II) spin states in D_{4h} symmetry as function of D_s and $10Dq$ at fixed $D_t=0\text{eV}$; **(right)** Phase diagram of the Fe(II) spin states in D_{4h} symmetry as function of $10Dq$ and $D_t=D_s$

Figure 2 (left) shows the diagram of D_s versus $10Dq$ for zero D_t . At small $10Dq$ the 3d orbitals are closer together, leading to a diversity of high-spin ground states. For negative D_s values 5B_2 is the ground state, while 5A_1 and 5E are the ground state at positive D_s values. This is as expected, if the information of figure 1 and table 1 is qualitatively combined: the B_2 orbital becomes the lowest orbital if D_s is negative, leading to a doubly occupied b_2 orbital and to 5B_2 . For positive D_s the a_1 orbital is at much lower energy leading to 5A_1 state as ground state. When the $10Dq$ value becomes higher, the e orbital is the lowest and the 5E state becomes the ground state. At $10Dq > 2$ eV together, a high-spin low-spin transitions is observed for octahedral systems ($D_s=0$). With a D_s distortion the intermediate-spin states can become the ground state. The boundaries in the phase diagram are represented as sharp lines, which is only correct without the inclusion of the 3d spin-orbit coupling.

The phase diagram for $10Dq$ versus the $D_t=D_s$ (figure 2, right) shows less transitions between high-spin to intermediate-spin states. The phase diagram shown here looks similar to one calculated by König et al. [24; 25]. At each point of these phase diagrams one can calculate an L edge X-ray absorption spectrum. A systematic overview of the published Fe(II) systems with a range a ground state within these phase diagrams will be published elsewhere.

3.3. X-ray absorption spectra of iron phthalocyanine

The XAS of FePc powder was measured in the total electron yield mode at beamline ID08 of the European Synchrotron Radiation Facility. The energy resolution was set to about 0.25 eV at the Fe $L_{2,3}$ edges. Figure 3 shows the experimental spectrum compared with the spectrum simulated with the CTM4XAS program with the crystal field multiplet approximation [21; 26; 27]. The used crystal field values were $10Dq=2.6$ eV, $D_s=1.08$ eV and $D_t=0.25$ eV. The spectrum was broadened with a Lorentzian of 0.2 eV (hwhm) and 0.4 eV for respectively the L_3 and L_2 edge. In addition to the L edge XAS spectrum, the XMCD spectrum was measured and will be reported with more extensive

simulations in a forthcoming publication. The unoccupied orbitals at these crystal field values are b_1 , b_1 , b_2 and e . This means an unoccupied $3d_{x^2-y^2}$ orbital and one unpaired electrons in the $3d_{xy}$ and one unpaired electron either in the $3d_{xz}$ or $3d_{yz}$ orbital. Analysis shows that this state is 98% pure. The other 2% are admixtures of other divisions over the 3d orbitals, which are mixed in due to the electronic Coulomb interactions. This ground state corresponds to a 3E electronic spin ground state, which agrees with some of the most recent allocations [19; 28]. Our crystal field values are intermediate between the configurations I and II as determined by Thole et al. [29]. These values do not correspond exactly to the ratios determined for perfect square planar symmetry, because of the influence of non-nearest neighbor atoms inside the phthalocyanine molecule and also inter-molecular interactions, which will modify the details of the chemical bonding.

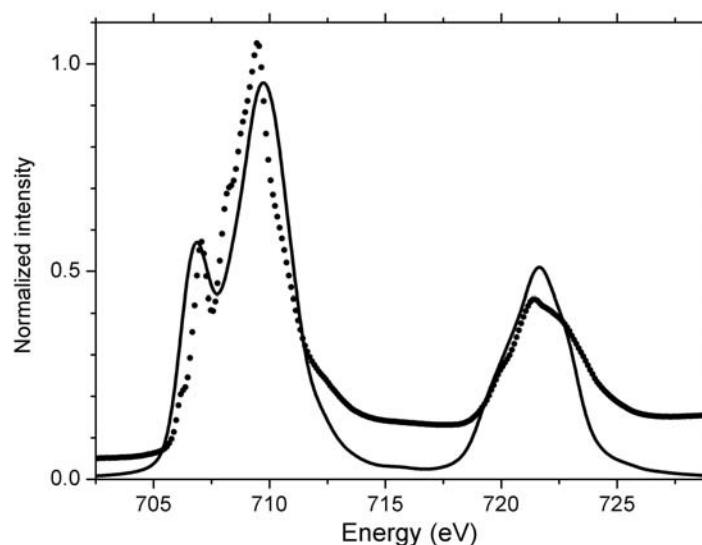


Figure 3 – Normalized experimental X-ray absorption spectrum of FePc powder at 8 K (dotted) and simulated X-ray absorption spectra of Fe(II) (black solid line).

4. Conclusions

Iron in a square planar environment can have different electronic ground states, e.g., different high-spin, intermediate-spin and low-spin states. Depending on the crystal field values, the 3d-orbital occupation differs and also the XAS spectra differ with different spin ground state. According to our fits on the experimental XAS (and MCD) spectrum, the spin ground state of FePc is 3E , which for 98% consists of a state with holes in b_1 , b_1 , b_2 and e .

Acknowledgements

P.M. and F.d.G. acknowledge financial support from the Netherlands National Science Foundation (NWO/VICI program), S.S. and P.G. acknowledge financial support from the Spanish Ministerio de Educación y Ciencia (Contract No. MAT2007-62341).

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