

## Quadrupolar XMCD at the Fe K-edge in Fe Phthalocyanine film on Au: an insight into the magnetic ground state

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The observation of an anomalous quadrupolar signal in x-ray magnetic circular dichroism (XMCD) at the Fe K-edge of iron phthalocyanine (FePc) films is reported. All ground states previously suggested for FePc are incompatible with the experimental data. Based on *ab initio* molecular orbital multiplet calculations of the isolated FePc molecule, we propose a new model for the magnetic ground state of the FePc film, which explains the XMCD data and reproduces the observed values of the orbital moments in the perpendicular and planar direction. The computed ground state corresponds to a spin triplet including  ${}^3A_{2g}$ ,  ${}^3E_g^2$ , and  ${}^3E_g^1$  states.

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As building blocks in innovative spintronics and nanodevices, organic magnetic molecules are subjects of special research interest. Among these, Fe phthalocyanine (FePc) molecules are promising candidates due to their strong magnetic anisotropy [1] and the possibility of switching the easy axis of magnetization from planar to perpendicular by the application of a small external electric field through the magnetoelectric effect [2]. It is therefore of extreme importance to have a model of the magnetic ground state of the molecule, an objective which has been elusive for decades (see Refs. 3–6 and references therein).

In an isolated molecule, the Crystal Field (CF) on the Fe site, with approximate  $D_{4h}$  symmetry, splits the Fe  $3d$  states into three orbital singlets ( $d_{xy}$ ,  $d_{z^2}$ ,  $d_{x^2-y^2}$ ) and a doublet ( $d_{xz}$ ,  $d_{yz}$ ), which yield the basis for the formation of molecular orbitals (MO) of the corresponding symmetry. One can ignore the antibonding orbital of  $x^2 - y^2$  symmetry as the electronic density points toward the four nearest neighbors, the N ligands, and therefore it lies at too high of an energy. Out of the four remaining states one can construct four spin-triplets:  ${}^3E_g^1 = (d_{xy}^2 d_{xz}^1 d_{yz}^2 d_{z^2}^1)$ ,  ${}^3E_g^2 = (d_{xy}^2 d_{xz}^2 d_{yz}^1 d_{z^2}^1)$ ,  ${}^3A_{2g} = (d_{xy}^2 d_{xz}^1 d_{yz}^1 d_{z^2}^2)$  and  ${}^3B_{2g} = (d_{xy}^1 d_{xz}^2 d_{yz}^2 d_{z^2}^1)$ , where  ${}^3E_g^{1,2}$  are orbitally degenerate. Which one is the ground state in the molecule is still being questioned, and this uncertainty affects any model one can construct out of these building blocks for a molecule in an epitaxial film.

In this letter we provide new experimental evidence for the magnetic state of FePc films, through x-ray magnetic dichroism (XMCD) at the Fe K-edge where an anomalous quadrupolar contribution is observed.

The ground states suggested previously are among the four triplet states listed above. None of them can account for the observed angular dependence of the quadrupolar XMCD. Supported by *ab initio* molecular orbital multiplet calculations, we construct a new, minimal model for the magnetic and orbital structure of the FePc ground state that is compatible with the experimental data.

The thin film sample in this work was prepared by organic molecular beam epitaxy technique (details can be found in Refs. [7, 8]). The FePc molecules on the film lie parallel to the Au/sapphire substrate and stacked in chains (see inset in Fig. 1 and Ref. [9]). The thickness of the FePc film of the investigated sample was 133 nm.

X-ray absorption (XAS), and XMCD measurements at the Fe K (7110.9 eV) edge on the FePc thin film samples were performed at the ESRF ID12 beamline. The APPLE-II undulator and a Si(111) double-crystal monochromator were used to collect the spectra. The energy resolution around the Fe-K edge energy region was about  $\Delta E/E = 2 \times 10^{-4}$ . The spectra were recorded by a fluorescence detector in backscattering geometry.

The XMCD signal was obtained by differences of XAS spectra measured at  $T = 7$  K with opposite helicities of the incoming photons at a fixed magnetic field of 6 Tesla applied along the beam direction, and orienting the field in two opposite directions. The field is intense enough to reach saturation of the FePc system [1]. To avoid experimental artifacts, the four combinations of field direction and circular polarization were recorded at each incidence angle  $\gamma$ . In all cases, the polarization rate was well above

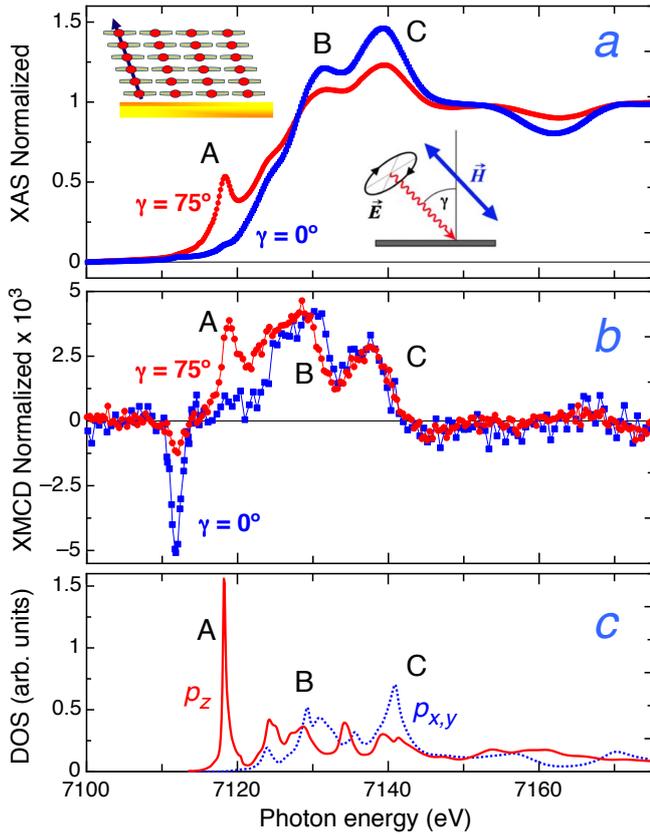


FIG. 1: a) (Color online) Normalized circularly polarized XAS spectra at the Fe K edge on FePc film at  $T = 7\text{K}$  and  $\mu_0 H = 6\text{T}$  for incidence angles  $\gamma = 0^\circ$  and  $75^\circ$ . Upper inset: FePc chains stacked on Au/sapphire substrate. Lower inset: Schematic view of the XMCD experiment. b) Normalized XMCD spectra. The applied field was  $\mu_0 H = 6\text{T}$ , parallel or anti-parallel to the helicity of the beam for every  $\gamma$ . c) Calculated density of states of  $p_z$  (full line) and  $p_{x,y}$  symmetry (dashed line).

99%. No radiation damage of the sample was detected.

Fig. 1a shows  $\mu_C(\gamma)$ , the normalized circularly polarized XAS at the Fe K edge for two incidence angles  $\gamma = 0^\circ$  and  $75^\circ$  and Fig. 1b shows the corresponding XMCD spectra. In the dipolar region, at energies above the quadrupolar transition, the XMCD signal roughly follows the absorption (and therefore the density of states, modulo a smooth energy dependent atomic absorption) of the  $4p$  conduction band of FePc (see Fig. 1c). Peak A, observed in grazing angle XAS and XMCD is correlated with a  $p_z$  level, while peaks B and C are mostly associated to excitations to empty states within  $p_{x,y}$  band levels.

While the dipolar XMCD signal shows the expected behavior, the quadrupolar one, at photon energy 7112 eV is quite anomalous. First of all, contributions from  $3d-4p$  mixing are excluded, since the stack preserves the inversion symmetry of the isolated molecule [9]. Its in-

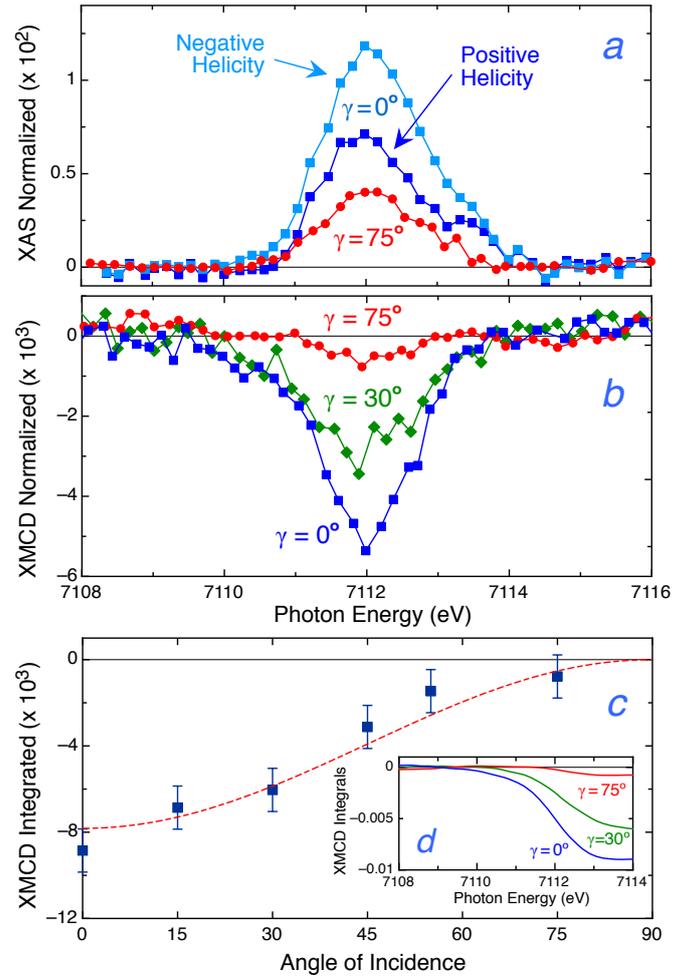


FIG. 2: a) (Color online) Quadrupolar absorption for both helicities at  $\gamma=0^\circ$ . The average quadrupolar absorption for  $\gamma=75^\circ$  is shown for comparison. b) Intensity of the quadrupolar XMCD signal at the Fe K edge on FePc film for incidence angles  $\gamma = 0^\circ, 30^\circ$  and  $75^\circ$ . c) Angular dependence of the quadrupolar integrated intensity. A fit to a  $\cos^2 \gamma$  function is shown (dashed red curve). d) integral of the quadrupolar XMCD as a function of the energy for  $\gamma = 0^\circ, 30^\circ$  and  $75^\circ$ .

tensity is maximum in normal incidence ( $\gamma = 0^\circ$ ) and tends to zero as  $\gamma \rightarrow 90^\circ$ . Fig. 2b shows the signal at three distinct incident angles while Fig. 2c gives the corresponding angular dependence of the integrated intensity. It clearly follows a  $\cos^2 \gamma$  behavior, given by the dashed red curve. This result is quite surprising, since quadrupolar sum rules at the K-edge [13] predict a signal proportional to the angular momentum (and powers of it) along the beam direction. Therefore, according to the experimental set-up and the in plane anisotropy of the film [1] ( $\mu_z < \mu_{x,y}$ ) the signal in grazing incidence should be more intense than that in normal incidence, i.e. contrary to experimental data in Fig. 2.

In the absence of an obvious selection rule dictating the observed behavior, the experiments suggest a partic-

ular structure of the ground state, which in fact can be guessed by comparing the experimental results with the forthcoming calculation. Moreover, the observed values of orbital anisotropy [1] are properly derived.

To tackle the problem we simply calculate *ab initio* the molecular multiplets of a single FePc molecule. From a self-consistent, non spin-polarized calculation based on the multiple scattering theory (MST) code by Johnson & Smith (JS) [10] we obtain the one-particle molecular orbitals to be used as a basis for a many-body hamiltonian with Coulomb interaction. We focus on the molecular orbitals (MO) with dominant Fe-3*d* contribution. We denote these MOs by their Fe-*d*-orbital character in the approximate  $D_{4h}$  point symmetry and order them according to their energy (in eV):

$$\begin{aligned} &1) d_{xy}^{\pm}(-13.34 \text{ eV}); \quad 2) d_{xz}^{\pm}(-13.02 \text{ eV}); \\ &3) d_{yz}^{\pm}(-13.02 \text{ eV}); \quad 4) d_{z^2}^{\pm}(-12.99 \text{ eV}); \\ &5) d_{x^2-y^2}^{\pm}(-10.55 \text{ eV}) \end{aligned} \quad (1)$$

This energy order agrees with many recent DFT calculations [14]. The five MOs above times a spin-function (indicated by the  $\pm$  superscript) form the single-particle basis for our multiplet calculation. We consider the space of all  $C_6^{10} = 210$  Slater determinants (SD) in which six out of the ten spin-orbitals are occupied, corresponding to a nominal  $\text{Fe}^{2+}$  configuration. In this sub-space the many-body hamiltonian containing the MO levels and the Coulomb interaction is diagonalized. The Coulomb matrix elements are calculated *ab initio* from the MO wave functions, omitting the monopole term of the multipole expansion, which is already included in the MO energies through the Hartree potential in the MST calculation. Further details of the MO multiplet calculation will be given elsewhere.

The lowest lying multiplet eigenstates and excitation energies are listed in Table I. Spin singlet and triplet states are denoted by SS and ST, respectively, and ‘fs’ stands for the filled core states and bonding orbitals. For the wave function, only the main component SD is given, where a hyphen indicates a missing electron. Its amplitude is 0.9 or more in all cases, implying that all triplet states are almost pure SD. In agreement with Ref. [3], we find that the ground state is an orbital singlet  $^3A_{2g}$ , followed by an orbitally degenerate state of  $^3E_g$  symmetry 0.093 eV higher. The first state of  $^3B_{2g}$  symmetry is orbitally nondegenerate and involves the excitation of a spin down orbital  $d_{xy}$  to an orbital of  $E_g$  symmetry. The calculated excitation energy of 0.82 eV is about ten times larger than that reported in Ref. [3]. The reason for this disagreement is not clear to us, but a rather large excitation energy is expected from the fact that the  $d_{xy}$  level lies by 0.32 eV below the  $d_{xz}/d_{yz}$  level.

The dots in Table I stand for three singlet and four quintet states (S=2), with excitation energies between 0.82 and 1.45 eV. The second  $B_{2g}$  is orbitally degenerate

and is mentioned here because it is suggested as a possible ground state in Ref. [4] in a parametric ligand field approach.

We now assume that, due to the perturbation of the nearest layers in the stack, the three lowest molecular states  $A_{2g}$  and  $E_{g1}$ ,  $E_{g2}$  mix together in the new ground state. Indeed, judging from the width of the band along the stack direction [15] the perturbation brought about by the neighboring molecules to the one under consideration must be of the order  $0.4 \sim 0.5$  eV.

It is then reasonable to write the ground state  $|GS\rangle$  for a molecule in the stack as a spin triplet

$$|GS\rangle = \frac{1}{\sqrt{2(1+\beta^2)}} \{ (1-i\beta)|A_{2g}\rangle + \beta|E_g^1\rangle + i|E_g^2\rangle \} \quad (2)$$

where the SD corresponding to the states  $|A_{2g}\rangle, |E_g^1\rangle, |E_g^2\rangle$  are those of Table I. The real parameter  $-1 < \beta < 1$  reduces the  $D_{4h}$  symmetry of the isolated molecule (which is restored for  $\beta = \pm 1$ ) to that of the stack (containing only space inversion).

To obtain the averages  $\langle GS|L_\alpha|GS\rangle (\alpha = x, y, z; L_\alpha = \sum_i l_\alpha^i)$  we use tables for  $l_\alpha$  acting on real spherical harmonics (RSH) with  $l = 2$  and 1 respectively on Fe and ligands (both tables, from pag. 70 of Ref. [16] are reproduced in the SM I). Note that for all MOs in (1), the contributions of the ligand atomic orbitals add up to zero by symmetry [17], such that only the action of  $l_\alpha$  on the Fe orbitals needs to be considered. It is interesting that  $\langle GS|L_z|GS\rangle$  picks up a non-zero contribution only from the combination  $\beta|E_g^1\rangle + i|E_g^2\rangle$ ,  $\langle GS|L_x|GS\rangle$  from  $i\beta|A_{2g}\rangle + \beta|E_g^1\rangle$ , and  $\langle GS|L_y|GS\rangle$  from  $|A_{2g}\rangle + i|E_g^2\rangle$ .

In MST the charge contained in the muffin-tin (MT) sphere  $\Omega$  is  $\lambda_s = \alpha_s^2 \int_\Omega r^2 R_2^2(r) dr = \alpha_s^2 \bar{R}_2^2$ , where  $R_2(r)$  is the radial wavefunction for  $l = 2$ , and  $\alpha_s$  the amplitude for orbital symmetry  $s$ . By using Table I in SM I, the values of the relevant matrix elements for the orbital momentum can be evaluated:  $\langle E_g^1|L_z|E_g^2\rangle = -i\alpha_{xz}\alpha_{yz}\bar{R}_2^2$  and  $\langle A_{2g}|L_x|E_g^1\rangle = \langle A_{2g}|L_y|E_g^2\rangle = -i\sqrt{3}\alpha_{z^2}\alpha_{yz}\bar{R}_2^2$ . Denoting  $\lambda_{E_g} = -i\alpha_{xz}\alpha_{yz}\bar{R}_2^2$ , and taking into account that by symmetry  $\alpha_{xz} = \alpha_{yz}$ , we find:

$$\begin{aligned} \langle GS|L_z|GS\rangle &= \frac{\beta}{1+\beta^2} \lambda_{E_g}; \\ \langle GS|L_x|GS\rangle &= \frac{\beta^2}{1+\beta^2} \sqrt{\frac{3\lambda_{z^2}}{\lambda_{E_g}}} \lambda_{E_g} \\ \langle GS|L_y|GS\rangle &= \frac{1}{1+\beta^2} \sqrt{\frac{3\lambda_{z^2}}{\lambda_{E_g}}} \lambda_{E_g}, \end{aligned} \quad (3)$$

implying that the orbital moment is roughly proportional to the charge of symmetry  $E_g$  contained in the Fe MT sphere. Moreover, since  $\langle GS|L_z|GS\rangle = \mu^\perp$  and  $\frac{1}{2}(\langle GS|L_x|GS\rangle + \langle GS|L_y|GS\rangle) = \mu^\parallel$ , we find

$$\frac{\mu^\parallel}{\mu^\perp} = \frac{1+\beta^2}{2\beta} \sqrt{\frac{3\lambda_{z^2}}{\lambda_{E_g}}} = \frac{1+\beta^2}{\beta}, \quad (4)$$

TABLE I: Eigenstates and Excitation Energies of the Molecular Orbital Multiplet Calculation

Energy (eV)	Degeneracy	SD main component	symmetry
E= 0.000	3 (ST)	$ \text{fs}\dots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ - d_{z_2}^+ d_{z_2}^- \rangle$	$A_{2g}$
E= 0.093	3 (ST)	$ \text{fs}\dots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ d_{yz}^- d_{z_2}^+ \rangle$	$E_g^1$
E= 0.093	3 (ST)	$ \text{fs}\dots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ - d_{z_2}^+ \rangle$	$E_g^2$
E= 0.612	1 (SS)	$\frac{1}{\sqrt{2}}( \text{fs}\dots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ d_{z_2}^+ d_{z_2}^- \rangle -  \text{fs}\dots d_{xy}^+ d_{xy}^- - d_{xz}^- d_{yz}^+ - d_{z_2}^+ d_{z_2}^- \rangle)$	$A_{2g}$
E= 0.702	1 (SS)	$\frac{1}{\sqrt{2}}( \text{fs}\dots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- - d_{z_2}^+ d_{z_2}^- \rangle +  \text{fs}\dots d_{xy}^+ d_{xy}^- - d_{yz}^+ d_{yz}^- d_{z_2}^+ d_{z_2}^- \rangle)$	$A_{2g}$
E= 0.821	3 (ST)	$ \text{fs}\dots d_{xy}^+ - d_{xz}^+ d_{xz}^- d_{yz}^+ d_{yz}^- d_{z_2}^+ \rangle$	$B_{2g}$
E= .....	.....	.....	....
E= 1.451	3 (ST)	$ \text{fs}\dots d_{xy}^+ - d_{xz}^- d_{xz}^+ d_{yz}^+ - d_{z_2}^+ d_{z_2}^- \rangle$	$B_{2g}^1$
E= 1.451	3 (ST)	$ \text{fs}\dots d_{xy}^+ - d_{xz}^+ - d_{yz}^- d_{yz}^+ d_{z_2}^+ d_{z_2}^- \rangle$	$B_{2g}^2$

where in the last step  $\lambda_{z^2} = 0.8$  and  $\lambda_{E_g} = 0.6$ , obtained from the MO calculations, was used. Experimentally [1] we have  $\mu^\perp = 0.29 \pm 0.05$  and  $\mu^\parallel = 0.53 \pm 0.04 \mu_B$  so that  $0.5 \leq |\beta| \leq 1$ , within experimental errors.

With this hypothesis for the GS, we can calculate the quadrupolar absorption and dichroism from the Fe K-shell. In order to determine the possible final states, we need to excite a  $1s$  electron (with both spin values) up to an empty orbital state. We find

$$\begin{aligned}
|F_1\rangle &= |1s^+ \dots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ d_{yz}^- d_{z_2}^+ \rangle \\
|F_2\rangle &= |1s^+ \dots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ - d_{z_2}^+ d_{z_2}^- \rangle \\
|F_2'\rangle &= |1s^+ \dots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ - d_{z_2}^+ d_{z_2}^- d_{y^2} \rangle \\
|F_3\rangle &= |1s^+ \dots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ d_{yz}^- d_{z_2}^+ d_{z_2}^- \rangle \\
|F_3'\rangle &= |1s^\pm \dots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ d_{yz}^- d_{z_2}^+ d_{z_2}^- d_{x^2-y^2} \rangle \\
|F_4\rangle &= |1s^\pm \dots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ - d_{z_2}^+ d_{z_2}^- d_{x^2-y^2} \rangle \quad (5)
\end{aligned}$$

We assume that these states are good approximate eigenstates of the molecule in the stack, due to its strong ligand-field regime.

We shall consider first normal incidence, where a very strong quadrupolar dichroism has been observed, as shown in Figs. 1 and 2. In this case, the quadrupolar transition operator  $(\hat{\mathbf{k}} \cdot \mathbf{r})(\boldsymbol{\epsilon} \cdot \mathbf{r})$  for circular polarized light becomes  $-z(x \mp iy)/\sqrt{2}$ . Transitions to final states  $|F_2'\rangle$ ,  $|F_3'\rangle$  and  $|F_4\rangle$  are only possible from state  $|A_{2g}\rangle$  with only one of the operators  $zx, zy$  or not allowed at all. Therefore, there is no interference in the matrix elements of the transition and  $I^+ = I^-$  (no dichroism). We are left with the final state  $|F_1\rangle$  and the component  $\beta|E_g^1\rangle + i|E_g^2\rangle$  of the initial GS. The transition probability for this case, using RSH for the transition operator, is

$$\begin{aligned}
I_1^\pm &= A \frac{4\pi}{5} \frac{1}{2} \sum_{\sigma} |\langle GS|1s^\sigma|(Y_{21}^c \mp iY_{21}^s)|F_1\rangle|^2 \\
&= \frac{A}{20} \frac{R_{02}^2}{1 + \beta^2} |\beta \mp i \cdot i|^2 \lambda_{E_g} \quad (6)
\end{aligned}$$

where  $A = 4\pi^2 \hbar \omega \alpha k^2 / 3$  and the radial matrix element is  $\langle 1s|r^2|3d\rangle = \overline{R_{02}} \sqrt{\lambda_{E_g}}$ .

From eqn. (6), the dichroism is:

$$\Delta I_1 = I_1^+ - I_1^- = \frac{A}{5} \frac{R_{02}^2}{1 + \beta^2} \frac{\beta}{\lambda_{E_g}} \quad (7)$$

As shown in the SM II, the same result can be achieved by evaluating the ground state expectation value of the operator  $3L_z + 2O_{zzz}$ , introduced by Carra *et al* [13].

The previous derivation shows that a non-zero quadrupolar XMCD in normal incidence requires a common final state to which transitions are possible from two initial state components with a phase difference of  $\exp(i\pi/2)$ . For the other two transitions, showing absorption but not dichroism ( $|GS\rangle \rightarrow |F_2\rangle, |F_3\rangle$ ) we find

$$I_{2,3}^\pm = \frac{A}{5} \frac{R_{02}^2}{(1 + \beta^2)} \lambda_{E_g} (1 + \beta^2) \quad (8)$$

since transitions are only allowed from the  $|A_{2g}\rangle$  component of  $|GS\rangle$ . Therefore the area under each helicity peak in Fig. 2a is proportional to  $3(1 + \beta^2) \pm 2\beta$ , and from the measured ratio  $I_{tot}^-/I_{tot}^+ = 1.7(1)$ , we derive  $|\beta| = 0.49 \pm 0.08$ . Substituting this value in Eq. 3 one obtains  $\mu^\perp = 0.60 \pm 0.08 \mu_B$  and  $\mu^\parallel = 0.23 \pm 0.03 \mu_B$ , in excellent agreement with experimental data. This step quantitatively determines the ground state  $|GS\rangle$  of the FePc molecule in the stack [9], within our approximations.

Finally, we shall consider quadrupolar absorption and dichroism in grazing incidence. With light incident in the  $x$  direction the transition operator is  $(xz \pm ixy)/\sqrt{2}$ . In order to take into account the random in-plane orientation ( $\phi$ ) of the molecules in the polycrystalline sample, we need to calculate the matrix element  $\langle GS|R_z(\phi)^\dagger(xz \pm ixy)R_z(\phi)|F_i\rangle = \langle GS|(xz \cos \phi - yz \sin \phi) \pm i[xy \cos 2\phi + \frac{1}{2}(x^2 - y^2) \sin 2\phi]|F_i\rangle$ . Inspection of the possible final states in (5) shows that no transition is possible involving both the real and imaginary part of the transition operator. Therefore there is absorption but not dichroism, in excellent agreement with experiment. As a consequence,  $\langle GS|3L_\alpha + 2O_{\alpha\alpha\alpha}|GS\rangle = 0$  for  $\alpha = x, y$ , as shown in SM II, Eq. (17).

We want to point out that the absence of quadrupolar dichroism in grazing incidence is mainly due to the

fact that the SD's appearing in the GS (2) all have the molecular orbital  $d_{xy}$  doubly occupied. This is reasonable, since according to (1), its orbital energy lies 0.32 eV lower than the next one.

If we relax the condition that  $d_{xy}$  be doubly occupied, we might combine the two  $E_g$  states with the state of  $B_{2g}$  symmetry to get

$$|B\rangle = \frac{1}{\sqrt{2(1+\beta^2)}}\{(1-i\beta)|B_{2g}\rangle + \beta|E_g^1\rangle + i|E_g^2\rangle\} \quad (9)$$

It would be then possible to have transitions to the final state  $|F_1\rangle = |1s^+ \dots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ d_{yz}^- d_{z^2}^+\rangle$  from state  $|E_g^1\rangle$  with operator  $xz$  and from  $|B_{2g}\rangle$  with operator  $xy$ , getting interference, and dichroism, in contradiction to the experiment. Therefore the experimental finding of the absence of quadrupolar dichroism in grazing incidence provides evidence for a double occupancy of the orbital  $d_{xy}$ , in contrast to some recent suggestions [5].

From Eqs. (7) and (3) we see that at  $\gamma = 0^\circ$  the signal is proportional to the expectation value of  $\langle L_z \rangle$ , like for a dipole transition. This can be related to the fact that in the state (2), the expectation value  $\langle O_{zzz} \rangle$  appearing in Carra's sum rule, is proportional to  $\langle L_z \rangle$ . Similarly, in the perpendicular direction  $\langle O_{\alpha\alpha\alpha} \rangle$  is proportional to  $\langle L_\alpha \rangle$  ( $\alpha = x, y$ ) (see Eqs. (13) and (16) in SM II). At an angle  $\gamma$ , in the conditions of the experiment (saturating magnetic field along the incident photon direction),  $\mu_L = \mu_\perp \cos^2 \gamma + \mu_\parallel \sin^2 \gamma$  [1]. Therefore this relation translates into  $\Delta I(\gamma) = \Delta I(0^\circ) \cos^2 \gamma + \Delta I(90^\circ) \sin^2 \gamma$ , and since  $\Delta I(90^\circ) = 0$ , we obtain the observed behavior of absence of XMCD.

Summarizing, the *ab initio* calculation of molecular multiplets in the FePc isolated molecule has allowed us to establish that only three states ( $|A_{2g}\rangle, |E_g^{1,2}\rangle$ ) are close enough in energy to be mixed by the stack perturbation. An *ansatz* on their coupling, inspired by spin-orbit interaction, but with different coefficients due to the external perturbation, has allowed us to guess the minimal structure of the magnetic ground state of the molecule in the film that explains the quadrupolar XMCD data at the Fe K-edge and reproduces the observed values of the orbital moments in the perpendicular and planar direction. In particular the angular dependence of the quadrupolar XMCD signal can only be explained with a double occupied  $d_{xy}$  molecular orbital, which implies that  $B_{2g}$  multiplets have negligible weight in the ground state.

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