Quadrupolar XMCD at the Fe *K*-edge in Fe phthalocyanine film on Au: 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 model for the magnetic ground state of the FePc film that explains the XMCD data and reproduces the observed values of the orbital moments in the perpendicular and planar directions.

As building blocks in innovative spintronics and nanodevices, organic magnetic molecules are subjects of special research interest. Among these, the Fe phthalocyanine (FePc) molecule is a promising candidate as new ideas and methods can be applied due to its simple, beautiful, and robust planar structure. Moreover its spin moment can be chemically manipulated by oxidation [1] and Li doping [2] while its strong magnetic anisotropy [3] can be switched from planar to perpendicular by the application of a small external electric field through the magnetoelectric effect [4]. 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. [5–7]).

In an isolated molecule, the crystal field (CF) on the Fe site, with approximate D_{4h} symmetry, splits the Fe 3*d* 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 (MOs) of the corresponding symmetry. Ignoring the antibonding orbital of $x^2 - y^2$ symmetry lying at too high energy [5], 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.

Density functional theory (DFT) calculations have shown that the above configurations are very close in energy so that the theoretically predicted ground state of the FePc molecule/film depends on computational details such as the exchange correlation potential and the way self-consistency is achieved (e.g., constrained DFT) [5]. Measurements of the x-ray magnetic dichroism (XMCD) at Fe L_{23} absorption edge showed a large, unquenched orbital moment [3]. While accounting for the magnetic anisotropy of the films, the crucial question of the ground electronic configuration could not be answered from these data. However these findings prompted the investigation of the Fe *K*-edge XMCD, since this signal is known to be sensitive only to the orbital moment [8].

In this Rapid Communication, we show that this unique experimental information, together with a detailed theoretical analysis based on molecular orbital multiplet calculations, allows us to determine the electronic ground state configuration of the film. Indeed, the measured Fe *K*-edge XMCD shows an anomalously large quadrupolar (E2) pre-edge signal, which is fully incompatible with any of the pure configurations listed above and other ground states proposed earlier. Instead, it implies a large configuration mixing between ^3E_g and $^3A_{2g}$ multiplets, whose relative amplitude can be estimated from the data, providing a consistent model for the magnetic and orbital ground state of the FePc film. As a by-product, the new state predicts a further planar anisotropy of the orbital moment that breaks the equivalence of the *x* and *y* directions in the plane and might have a bearing in future studies on spintronics. This type of electronic configuration is very hard to achieve, if not impossible, in the various DFT schemes, which may explain why the electronic ground state has been elusive so far.

The thin film sample in this work was prepared by organic molecular beam epitaxy technique (details can be found in Refs. [9,10]). The FePc molecules on the film lie parallel to the Au/sapphire substrate and stacked in chains (see inset in Fig. 1 and Ref. [11]). 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.

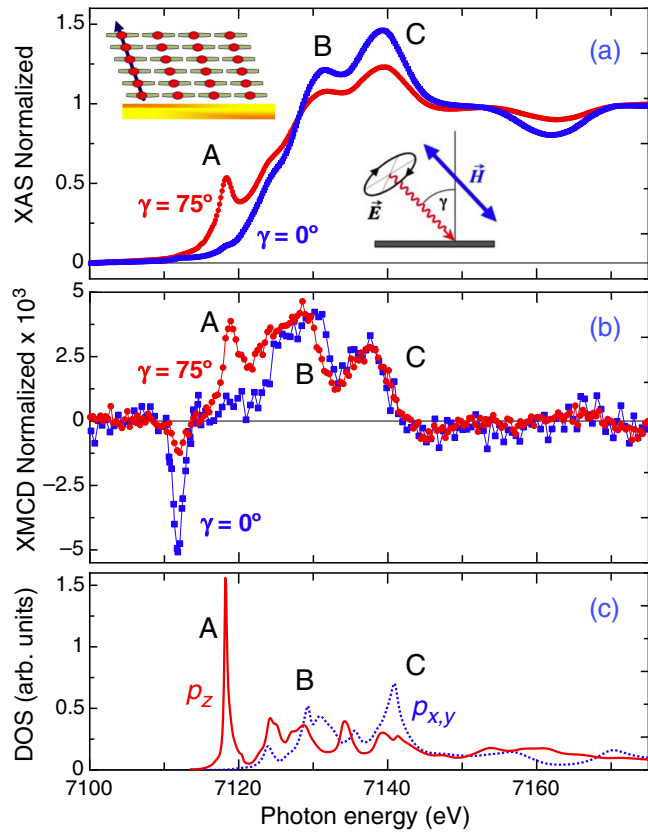The XMCD signal was obtained by differences of XAS spectra measured at $T = 7$ K with opposite helicities of the

FIG. 1. (Color online) (a) Normalized circularly polarized XAS spectra at the Fe K-edge on FePc film at $T = 7$ K and $\mu_0 H = 6$ T for incidence angles $\gamma = 0°$ and $75°$. 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 $\mu_0 H = 6$ T, parallel or antiparallel to the helicity of the beam for every γ. (c) Calculated density of states of p_z (full line) and $p_{x,y}$ symmetry (dashed line).

FIG. 2. (Color online) (a) Quadrupolar absorption for both helicities at ($\gamma = 0°$). The average quadrupolar absorption for $\gamma = 75°$ is shown for comparison. (b) Intensity of the quadrupolar XMCD signal at the Fe K-edge on FePc film for incidence angles $\gamma = 0°$, $30°$, and $75°$. (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 various incidence angles.

incoming photons at a fixed magnetic field of 6 T 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 [3]. In all cases, the polarization rate was well above 99%. No radiation damage of the sample was detected.

We distinguish between dipolar (E1) and quadrupolar (E2) contributions of the XAS (XMCD) signal corresponding to the Fe $1s$ to $4p$ and the $1s$ to $3d$ transitions, respectively. It is known that the integrated XMCD signal at the K-edge is related to the ground-state expectation value of the orbital moment for E1 transitions and a combination of its powers for E2 transitions [8]. Figure 1(a) shows $\mu_C(\gamma)$, the normalized circularly polarized XAS at the Fe K-edge for two incidence angles $\gamma = 0°$ and $75°$ anomalous. First Fig. 1(b) shows instead the corresponding XMCD spectra. In the dipolar region, at energies above 7115 eV, 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. 1(c)] [12]. Peak A, observed in grazing-angle XAS and XMCD, is correlated with
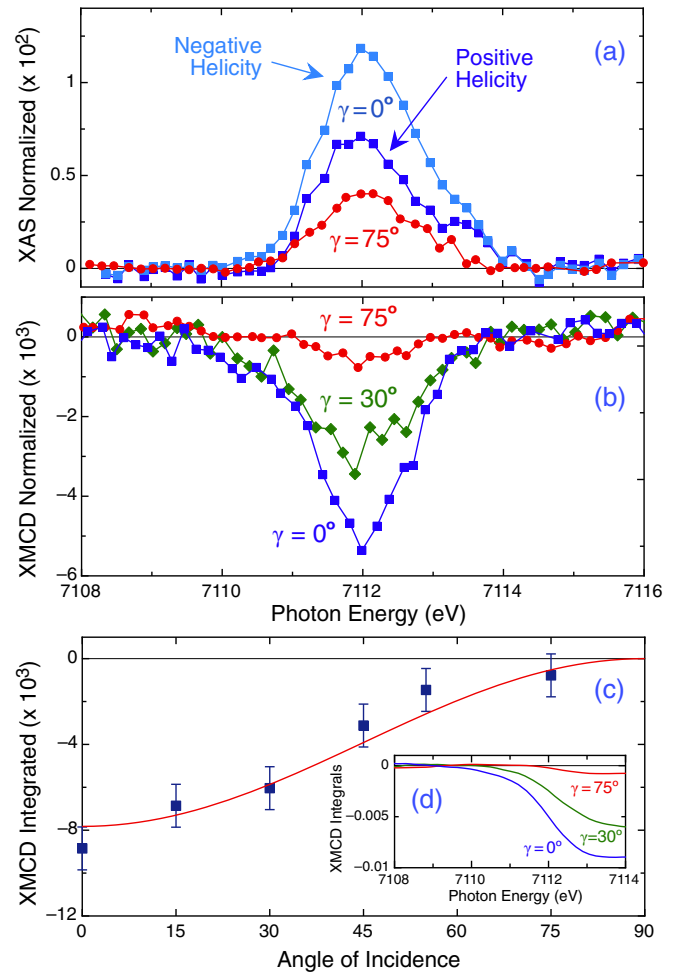
a p_z level, while peaks B and C are mostly associated with excitations to empty states within $p_{x,y}$ band levels.

While the dipolar XAS and XMCD signal shows the expected behavior as seen by the good match with the Fe-p DOS in Fig. 1(c), the angular dependence of the quadrupolar signal at 7112 eV is quite anomalous. At $\gamma = 0°$ the measured integrated intensity ratio of the quadrupolar absorption is $I_{tot}^-/I_{tot}^+ = 1.7(1)$ (see Fig. 2(a). First of all, contributions from $3d$-$4p$ mixing are excluded, since the stack preserves the inversion symmetry of the isolated molecule [11]. The XMCD intensity is maximum in normal incidence ($\gamma = 0°$) and tends to zero as $\gamma \to 90°$. Figure 2(b) shows the signal at three distinct incident angles while Fig. 2(c) 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 [8] predict a signal proportional to the angular momentum (and its powers) along the beam direction. Therefore, according to the experimental setting and

TABLE I. Eigenstates and excitation energies of the molecular orbital multiplet calculation.

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

the in-plane anisotropy of the film [3] ($\mu_z < \mu_{x,y}$) the signal in grazing incidence should be more intense than that in normal incidence, i.e., contrary to experiment.

To tackle the problem we simply calculate *ab initio* the molecular multiplets of a single FePc molecule. By a self-consistent, non-spin-polarized calculation based on the multiple scattering theory (MST) code by Johnson & Smith (JS) [13] 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 (MOs) with dominant Fe-3d 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):

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

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 (SDs) in which six out of the ten spin orbitals are occupied, corresponding to a nominal Fe^{2+} configuration. In this subspace 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.

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. The amplitude of this component is 0.9 or more in all cases, implying that all triplet states are almost pure SD. In agreement with Ref. [5], 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. [5]. 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. [6] 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_g^1, E_g^2 mix together in the new ground state. Indeed, judging from the 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 $\lvert \mathrm{GS}\rangle$ for a molecule in the stack as a spin triplet:

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

where the SD corresponding to the states $\lvert A_{2g}\rangle, \lvert E_g^1\rangle, \lvert E_g^2\rangle$ 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).

In calculating the orbital momentum averages (Ref. [16] and Sec. I of the Supplemental Material [17]), it is interesting that $\langle \mathrm{GS}\lvert L_z\rvert \mathrm{GS}\rangle$ picks up a nonzero contribution only from the combination $\beta\lvert E_g^1\rangle + i\lvert E_g^2\rangle$, $\langle \mathrm{GS}\lvert L_x\rvert \mathrm{GS}\rangle$ from $i\beta\lvert A_{2g}\rangle + \beta\lvert E_g^1\rangle$, and $\langle \mathrm{GS}\lvert L_y\rvert \mathrm{GS}\rangle$ from $\lvert A_{2g}\rangle + i\lvert E_g^2\rangle$.

In MST the charge contained in the muffin-tin sphere Ω is $\lambda_s = \alpha_s^2 \int_\Omega r^2 R_2^2(r)dr = \alpha_s^2 \overline{R_2^2}$, where $R_2(r)$ is the radial wave function for $l = 2$, and α_s the amplitude for orbital symmetry s. By using Table I in Sec. I of the Supplemental Material [17], the values of the relevant matrix elements for the orbital momentum can be evaluated: $\langle E_g^1\lvert L_z\rvert E_g^2\rangle = -i\alpha_{xz}\alpha_{yz}\overline{R_2^2}$ and $\langle A_{2g}\lvert L_x\rvert E_g^1\rangle = \langle A_{2g}\lvert L_y\rvert E_g^2\rangle = -i\sqrt{3}\alpha_{z^2}\alpha_{yz}\overline{R_2^2}$. Denoting $\lambda_{E_g} = \alpha_{xz}\alpha_{yz}\overline{R_2^2}$, and taking into account that by symmetry

$\alpha_{xz} = \alpha_{yz}$, we find

$$\langle GS|L_z|GS\rangle = \frac{\beta}{1+\beta^2}\lambda_{E_g},$$

$$\langle GS|L_x|GS\rangle = \frac{\beta^2}{1+\beta^2}\sqrt{\frac{3\lambda_{z^2}}{\lambda_{E_g}}}\lambda_{E_g}, \qquad (3)$$

$$\langle GS|L_y|GS\rangle = \frac{1}{1+\beta^2}\sqrt{\frac{3\lambda_{z^2}}{\lambda_{E_g}}}\lambda_{E_g},$$

implying that the orbital moment is roughly proportional to the charge of symmetry E_g contained in the Fe muffin-tin (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

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

where in the last step $\lambda_{z^2} = 0.8$ and $\lambda_{E_g} = 0.6$, obtained from the MO calculations, was used. Experimentally [3] we have $\mu^\perp = 0.29 \pm 0.05$ and $\mu^\parallel = 0.53 \pm 0.04$ μ_B so that $0.5 \leqslant |\beta| \leqslant 1$ 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

$$|F_1\rangle = |1s^+ \ldots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ d_{yz}^- d_{z^2}^+\rangle,$$

$$|F_2\rangle = |1s^+ \ldots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ - d_{z^2}^+ d_{z^2}^-\rangle,$$

$$|F_2'\rangle = |1s^+ \ldots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ - d_{z^2}^+ d_{x^2-y^2}^-\rangle,$$

$$|F_3\rangle = |1s^+ \ldots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ d_{yz}^- d_{z^2}^+ d_{z^2}^-\rangle, \qquad (5)$$

$$|F_3'\rangle = |1s^\pm \ldots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ d_{yz}^- d_{z^2}^+ d_{x^2-y^2}^\mp\rangle,$$

$$|F_4\rangle = |1s^\pm \ldots d_{xy}^+ d_{xy}^- d_{xz}^+ - d_{yz}^+ - d_{z^2}^+ d_{z^2}^- d_{x^2-y^2}^\mp\rangle.$$

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 the real spherical harmonics for the transition operator, is

$$I_1^\pm = A\frac{4\pi}{5}\frac{1}{2}\sum_\sigma \left|\langle GS1s^\sigma|\left(Y_{21}^c \mp iY_{21}^s\right)|F_1\rangle\right|^2$$

$$= \frac{A}{20}\overline{R}_{02}^2 \frac{|\beta \mp i \cdot i|^2}{1+\beta^2}\lambda_{Eg}, \qquad (6)$$

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 Eq. (6), the dichroism is

$$\Delta I_1 = I_1^+ - I_1^- = \frac{A}{5}\overline{R}_{02}^2 \frac{\beta}{1+\beta^2}\lambda_{E_g}. \qquad (7)$$

This value is equal to the ground-state expectation value of the operator $3L_z + 2O_{zzz}$, introduced by Carra *et al.* [8], as shown in Sec. II of the Supplemental Material [17].

The previous derivation shows that a nonzero 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

$$I_{2,3}^\pm = \frac{A}{5}\frac{\overline{R}_{02}^2}{(1+\beta^2)}\lambda_{Eg}(1+\beta^2), \qquad (8)$$

since transitions are only allowed from the $|A_{2g}\rangle$ component of $|GS\rangle$. Therefore the area under each helicity peak in Fig. 2(a) 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 $\mu^\perp = 0.60 \pm 0.08$ μ_B and $\mu^\parallel = 0.23 \pm 0.03$ μ_B in excellent agreement with the experimental values. This step quantitatively determines the ground state $|GS\rangle$ of the FePc molecule in the stack [11], 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 (ϕ) 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 the experiment. As a consequence $\langle GS|3L_\alpha + 2O_{\alpha\alpha\alpha}|GS\rangle = 0$ for $\alpha = x,y$, as shown in Eq. (17) of Sec. II of the Supplemental Material [17].

Notice that the absence of quadrupolar dichroism in grazing incidence is mainly due to the fact that the SDs appearing in the GS (2) all have the molecular orbital d_{xy} doubly occupied. If we relax this condition, we might construct a new ground state by replacing in Eq. (2) the state $|A_{2g}\rangle$ with $|B_{2g}\rangle$. It would be then possible to have transitions to the final state $|F_1\rangle = |1s^+ \ldots d_{xy}^+ d_{xy}^- d_{xz}^+ d_{xz}^- d_{yz}^+ d_{yz}^- d_{z^2}^+\rangle$ from state $|E_g^1\rangle$ with operator xz and from $|B_{2g}\rangle$ with operator xy, getting interference, and dichroism, contrary to experiment.

From Eqs. (7) and (3) we see that at $\gamma = 0°$ 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 Sec. II of the Supplemental Material [17]). At an angle γ, in the conditions of the experiment (saturating magnetic field along the incident photon direction), $\mu_L = \mu_\perp \cos^2\gamma +$

$\mu_\parallel \sin^2 \gamma$ [3]. Therefore this relation translates into $\Delta I(\gamma) = \Delta I(0°) \cos^2 \gamma + \Delta I(90°) \sin^2 \gamma$ and since $\Delta I(90°) = 0$, we obtain the observed behavior.

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 (Eq. (2)) 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 directions. 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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[17] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.91.220401 containing the derivation of how to operate with orbital momentum operators L_α Real Spherical Harmonics (Sec. I) and the calculation of their ground state expectation values (Sec. II) in quadrupolar sum rules.