Magnetism and x-ray absorption spectra calculations of iron porphyrin
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Porphyrians are flat organic molecules where a magnetic transition metal atom can be inserted at the center. Due to metal-nitrogen bonding and low symmetry, transition metal porphyrins have a complex magnetic ground state which can be modified through perturbations such as crystal stacking, substrate adsorption or external fields. Therefore thin films of adsorbed porphyrin molecules are interesting for nanoscale spintronics applications. Here we report a theoretical study of the electronic and magnetic state as well as the x-ray absorption spectra of Fe-porphyrin (FeP). FeP has an intermediate (S=1) ground state, but the exact electronic configuration and orbital magnetization is still under debate and may depend on weak external perturbations. Recently angle dependent x-ray absorption (XAS) and x-ray magnetic circular dichroism (XMCD) experiments at the Fe L-edges have been performed on FeP on a Cu(100) substrate [1].

First principles calculations are not fully conclusive as for the ground state electronic configuration and cannot explain the angular dependence of the XMCD measurements. Here we report crystal field multiplet calculations of FeP. By comparing the polarization dependent XAS and XMCD spectra with the experimental data, we show that the ground state is S=1 and has mainly (xy)^2 (3z^2-r^2)^2 (xz)^1 (yz)^1 orbital character. However, spin-orbit coupling leads to a singlet state with quenched spin- and orbital moment and gives rise to the experimentally observed large in-plane magnetic anisotropy. We show that this mechanism can be explained with an analytically solvable three-orbital model. We consider the restricted space of (a=3z^2-r^2) and (e=xz,yz) orbitals with 4 electrons and S=1 states only. The Hamiltonian contains the crystal field splitting $Δ= E(e)-E(a)$ and the spin-orbit coupling $ζ L.S$.

Figure 1 shows the energy eigenvalues as a function of $x = Δ/ζ$. The states are labeled as $(J, n)$ where $J$ is the total angular momentum and $n=(-,0,+)$ is a counter. In the regime $x>−1$ the ($a^2e^2$, S=1) triplet is lowest in energy and splits into a singlet (0−) and a doublet (1−). The ground state (0−) has quenched spin and angular moment and the in-plane magnetic susceptibility (not shown) is by three orders of magnitude larger than the out-of-plane susceptibility. This explains the observed large in-plane magnetic anisotropy. The effect of metal-ligand hybridization on the magnetism is also examined.


Figure 1: Energy eigenvalues of the three-orbital model.