Magnetic switching of Fe-porphyrin molecules adsorbed on surfaces: An XAFS and XMCD study

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Outline

1. Introduction
2. NEXAFS at the C and N K-edges
3. NEXAFS and XMCD at the Fe L_{3,2}-edges
   
   *3d^n-energy scheme and magnetism of the Fe-ion*
   
   *L-edge spectra*

   only very few publication cover this full range of XAFS

4. THz-ESR on SMM

Magnetic switching of Fe-porphyrin molecules adsorbed on surfaces

switching will change the conductance?
1. Introduction

Supramolecular control of the magnetic anisotropy in two-dimensional high-spin Fe arrays at a metal interface

Pietro Gambardella, 1, 3, *, Sebastien Stepnowski, 1, 4, Alexandre Dmitriev, 4, 5, Jan Hendelka, 4, Frank M. E. de Groot, 1, 6, Magali Lingenfelder, 6, Subhra Sen Gupta, 7, D. P. Sarma, 7, Peter Bencskó, 7, Harald Brune, 7, Stefan Stanesco, 8, and Janis V. Baran

PRL 101, 116602 (2008)

Visualizing the Spin of Individual Cobalt-Phthalocyanine Molecules

C. Iacovita, 1 M. V. Rastei, 1 B. W. Heinrich, 1 T. Brunme, 2 J. Kortus, 2 L. Limot, 1, * and J. P. Bucher 1

1 Institut de Physique et Chimie des Matériaux de Strasbourg UMR 7504, Université Louis Pasteur, F-67034 Strasbourg, France
2 Institut für Theoretische Physik, TU Bergakademie Freiberg, D-09599 Freiberg, Germany

Nano-architectures by covalent assembly of molecular building blocks

Leonhard Grill, 1, Matthew Dyre, 1, Leif Laffrentz, 1, Mats Persson, 2, Made V. Petersen, 3

1 Institut für Experimentelle Naturwissenschaften, Freie Universität Berlin, Arndtsweg 20, 14195 Berlin, Germany
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3 Institut für Chemie, Humboldt Universität zu Berlin, Bunsenstrasse 11, 12489 Berlin, Germany

Molecular Magnets

How a nightmare turns into a vision

Heiko Wende

Nature Materials, March 2009

Nano-architectures by covalent assembly of molecular building blocks

Leonhard Grill, 1, Matthew Dyre, 1, Leif Laffrentz, 1, Mats Persson, 2, Made V. Petersen, 3

1 Institut für Experimentelle Naturwissenschaften, Freie Universität Berlin, Arndtsweg 20, 14195 Berlin, Germany
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Nature Materials, March 2009

How a nightmare turns into a vision

Heiko Wende

Two independent studies demonstrate how control over magnetic molecules on surfaces may lead to new spintronics applications.
Acknowledgement to Heiko Wende and the other coauthors.
There is plenty of research in bulk metalorganic powder, solution, i.e. random orientation of the molecules.

- Hocking et al. JACS 2007, the Stanford-Utrecht group
- See also Electron Spin Resonance in *Iron Porphyrins* Vol. 2

**Here**

NEXAFS at the C and N K-edges
NEXAFS and XMCD at the Fe L$_{3,2}$-edge
THz-ESR on SMM
2. NEXAFS at the C and N K-edges

Distinguish between (I. Nenner 1986):

1) Excitation in an unoccupied bound state,
   => discrete resonance, relax back to the ground state.

2) The core electron is ejected in the continuum
   => centrifugal barrier, scattering theory (MSM)

eff. spherical well potential → analytical solution
D. Bovenschen, Diplom Thesis 2009 University Duisburg-Essen; $V_0 a^2 = 7.3 eV \text{Å}^2$, Schwinger’s theorem 1947
Klaus,

This one is for you!
Thanks for being a good friend and collaborator all these years.
I've learned so much from our discussions and friendly arguments, and I hope they will continue.

Joachim Stöhr
Almaden
July 20, 1992
Klaus,
This one is for you!
Thanks for being a good friend and collaborator all these years.
I've learned so much.

Orientation of Chemisorbed Molecules from Surface-Absorption
Fine-Structure Measurements: CO and NO on Ni(100)

J. Stöhr, K. Baberschke(✉), R. Jaeger, R. Treichler, and S. Brennan
Stanford Synchrotron Radiation Laboratory, Stanford University, Stanford, California 94305
(Received 19 March 1981)

Surface-absorption fine-structure studies for CO and NO on Ni(100) exhibit two pronounced resonances above the C, N, and O K edges. A strong polarization dependence of these resonances, which correspond to a σ→π discrete absorption and a σ→σ shape resonance, allows the precise determination of molecular orientation. Both molecules are found to be aligned along the surface normal within 10°.
Angular dependent NEXAFS ↔ flat lying porphyrin molecules on surface. In bulk usually the average over $f(\Theta)$ is measured.

- Sharp resonances below threshold:
  fine structure of $1s \rightarrow \pi^*$ transitions, angular dependence,
  similar to earlier work by Narioka et al. JCP 1995 on ZnTPP/Ag

- Broad scattering profile above threshold:
  $1s \rightarrow \infty$, $\sigma^*$-shape resonances, both at C and N edges,
  scattering-potential, -strength, direct access to bonding geometry,
  see Dehmer, Connerade, Nenner etc.

- Analysis of $\Delta \Theta$-spectra,
  ongoing work, Diplom Thesis, Bovenschen Uni- DUE 2009

- No XMCD signal at N was detected, but there will be some induced magnetism,
  see Sorg et al. @ XAFS 13 for oxygen on Fe,Co,Ni, and Amemiya et al. CO/Co/Cu(100) PRB 2001

- **Confirm a flat oriented monolayer of Fe-porphyrin on the surface**
3a. NEXAFS and XMCD at the Fe L$_{3,2}$-edges

3$d^n$-energy scheme and magnetism of the Fe-ion

Dramatic change of ligand field upon coadsorption of oxygen.
Gambardella et al. 2009,
Bernien et al. 2009

Unperturbed $e_g$, $t_{2g}$ eigenstates are no good.
“zero field splitting” $\equiv$ CEF
orbital and spin magnetic moments

The orbital moment is quenched in cubic symmetry
\[ \langle 2- | L_Z | 2- \rangle = 0, \]
but not for tetragonal symmetry
Zero field splitting:
For Cr\(^{3+}\) \(\Rightarrow S=3/2\), see FP

For Fe\(^{3+}\) \(\Rightarrow S=5/2\)

Splitting in \(E_{\pm 1/2}, E_{\pm 3/2}, E_{\pm 5/2}\)

\[ \Delta E = 2D, \quad 4D \]

Range 5 to 40 GHz, see Bittl paper
Orbital magnetism in second order perturbation theory

\[ \mathcal{H}' = \mu_B \mathbf{H} \cdot \mathbf{L} + \lambda \mathbf{L} \cdot \mathbf{S} \]

where \( \Lambda_{ij} \) is defined in relation to states \((n > 0)\) as

\[ \Lambda_{ij} = \sum_{n \neq 0} \frac{(0 \mid L_i \mid n)(n \mid L_j \mid 0)}{E_n - E_0} \]

In the principal axis system of a crystal with axial symmetry, the \( \Delta \) tensor is diagonal with \( \Lambda_{zz} = \Lambda_\parallel \) and \( \Lambda_{xx} = \Lambda_{yy} = \Lambda_\perp \). Under these conditions, \( \mathcal{H}' \) of (3-23) can be simplified, since

\[ S_x^2 + S_y^2 = S(S + 1) - S_z^2 \]

to give

\[ \mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + D[S_x^2 - \frac{1}{2}S(S + 1)] \]  

where

\[ g_\parallel = g_e (1 - \frac{\mu_\parallel}{\mu_B}) \]
\[ g_\perp = g_e (1 - \frac{\mu_\perp}{\mu_B}) \]
\[ D = \frac{\lambda^2 (\Lambda_\perp - \Lambda_\parallel)}{2} \]

Anisotropic magnetic moment (g-tensor) and magnetic anisotropy energy have the identical same origin: SOC mixes the eigenstates (l- and s-part!).

\[ g_\parallel - g_\perp = g_e \lambda (\Delta_\perp - \Delta_\parallel) \]

Anisotropic \( \mu_L \) \( \leftrightarrow \) MAE

\[ D = \frac{\lambda}{g_e} \Delta g \]

MAE \( \propto \frac{\xi_{LS}}{4\mu_B} \Delta \mu_L \)

Bruno (‘89)

G.E. Pake, p.66
Magnetic Anisotropy

Anisotropy at a surface

- Free atomic spin is rotationally invariant: all spin orientations are degenerate.
- Loss of rotational symmetry breaks degeneracy of spin orientations.

\[ H = -g\mu_B \hat{B} \cdot \hat{S} + D S_z^2 \]

Magnetic field dependence varies with angle of magnetic field.

Iron magnetic moments can be flipped up and down, left and right with a small “external force” of mT, only. Wende et al. 2007
First experiments of this kind on Mn TPP /10 nm Co by Scheybal et al. Chem. Phys. Lett. 2005 @SLS
This will change the conductance thru the molecule.
High sensitivity @ BESSY UE56-2/PGM2
1 ML of Fe-OEP ≈ 1/100 ML of Fe/Cu.

T-dependent XMCD 50 – 300 K was measured for Fe and Ni/Co
and the exchange coupling determined to be
≈ 70 meV for Fe-OEP/Co and
≈ 20 meV for Fe-OEP/Ni.

See Bernien et al. PRB 2007
**Oxygen surfactant-growth** of Ni and Co ultrathin films

**Oxygen c(2x2) floats on top**  (Sorg et al. PRB 2006)

On top of this we evaporate Fe-OEP

As a result we find antiparallel alignment of $\mu_{Fe}$ and $M_{Ni,Co}$ antiferromagnetic coupling

See Bernien et al. PRL 2009

$E_{ex} \approx 37(17)$ meV for Fe-OEP/Co(Ni)

DFT calc. UU Eriksson-group
L_{3,2} NEXAFS/XANES and XMCD on oriented Fe-porphyrin contain very reach information:

Electronic:
- Different Fe L_{3} line shape for Ni and Co substrate. Normal (grazing) incidence is probing unoccupied Fe orbitals in plane (out of plane).
- Shift of Fe L_{3} energy position $\leftrightarrow$ valence state, charge transfer

Magnetic:
- Element specific magnetization
- Paramagnetic Fe moment is aligned with respect to FM film, switching, hysteresis.
- Switching also by an external field of 5T and 8 K, ongoing work at ESRF
- $f(T) \rightarrow E_{ex}$
- $f(\Theta) \rightarrow$ selective orbitals
- Sum rules $\rightarrow \mu_{\text{spin}}, \mu_{\text{orb}}, \rightarrow$ MAE  
  Caution!
4. Discussion

Mannini et al. @ BESSY, SLS

Partial saturation of an Fe$_4$SMM/Au(111) anisotropic paramagnet

Gambardezza et al. @ ESRF

Fe(TPA)$_4$ on Cu(100) O$_2$ - Fe(TPA)$_4$ change of easy axis upon O$_2$ dosage
Electron paramagnetic resonance and electron nuclear double resonance spectroscopy of a heme protein maquette

M. Fahnenschmidt a, R. Bittl a, H.K. Rau b, W. Haehnel b, W. Lubitz a,*

a Technische Universität Berlin, Max Volmer-Institut für Biophysikalische und Physikalische Chemie, Straße des 17. Juni 135, 10623 Berlin, Germany
b Albert-Ludwigs-Universität Freiburg, Institut für Biologie II / Biochemie, Schänzestraße 1, 79104 Freiburg, Germany

ESR gives direct access to real ground state, wave function and g-tensor

<table>
<thead>
<tr>
<th>Maquette</th>
<th>MOP</th>
<th>MbIm</th>
</tr>
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<tbody>
<tr>
<td>$g_1$</td>
<td>2.92 (± 0.01)</td>
<td>2.96 (± 0.01)</td>
</tr>
<tr>
<td>$g_2$</td>
<td>2.28 (± 0.01)</td>
<td>2.26 (± 0.01)</td>
</tr>
<tr>
<td>$g_3$</td>
<td>1.54 (± 0.02)</td>
<td>1.51 (± 0.02)</td>
</tr>
<tr>
<td>$V/\lambda$</td>
<td>1.95 (± 0.03)</td>
<td>1.85 (± 0.03)</td>
</tr>
<tr>
<td>$\Delta/\lambda$</td>
<td>3.27 (± 0.13)</td>
<td>3.32 (± 0.13)</td>
</tr>
<tr>
<td>$V/\Delta$</td>
<td>0.60 (± 0.02)</td>
<td>0.56 (± 0.02)</td>
</tr>
</tbody>
</table>

* The ligand field parameters $V$ (rhombic splitting) and $\Delta$ (tetragonal splitting) were calculated from the $g$-tensor values in units of the spin-orbit coupling constant $\lambda$ with Taylor's method of ligand field analysis [14]: $V/\lambda = g_x/(g_z + g_y) + g_y/(g_z - g_x)$, $\Delta/\lambda = g_x/(g_z + g_y) + g_y/(g_z - g_x) - 1/2 V/\lambda$ with $g_z > g_y > g_x$.
Molecular spintronics

Spin-polarized STM in CoPc on Co/Cu(111)
Bucher-group PRL 2008
Spin dependent conductivity

Pt – benzene – Pt
in plane conductance,
van Ruitenbeek-group PRL 2009
Frequency domain Fourier transform THz-EPR on single molecule magnets using coherent synchrotron radiation

Frequency domain Fourier transform THz electron paramagnetic resonance (FD-FT THz-EPR) based on coherent synchrotron radiation (CSR) is presented as a novel tool …. at the BESSY II storage ring … in a frequency range from 5 cm$^{-1}$ up to 40 cm$^{-1}$ … together with first measurements on the SMM Mn$_{12}$Ac where $\Delta M_S = \pm 1$ spin transition was studied …. 

Freie Universität Berlin

Stanford SSRL 3. June 2010
High Resolution THz-EPR on Mn_{12}Ac

\( S = 10 \)

**Mn_{12}Ac** \([Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_{4}]\)

- 4 Mn^{4+} ions (3d^3, S=3/2): S=6
- 8 Mn^{3+} ions (3d^4, S=2): S=16

Spins are exchange coupled to **S=10**

unpublished results:
Alexander Schnegg,
Karsten Holldack,
Helmholtz-Zentrum Berlin
für Materialien und Energie
Real Time Quantum Tunneling in Mn$_{12}$Ac

above blocking

below blocking

T = 2 K

B=-0.3 T (blue), B=0.3T (green)

T = 2.6 K, 5 min.

T = 2.6 K, 15 min.

T = 2.6 K, 30 min.

unpublished results:
Alexander Schnegg,
Karsten Holldack,
Helmholtz-Zentrum Berlin
für Materialien und Energie

Thank you
Magnetic switching of an Fe-porphyrin monolayer adsorbed on surfaces: An XAFS and XMCD study
Klaus Baberschke
Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

Metalorganic molecules like Fe-porphyrin or haemoglobin have been investigated in great detail in the past. Its importance is obvious and has been measured mostly with molecules in random orientation. Here we report on experiments of a single monolayer of Fe-porphyrin in UHV aligned flat on ferromagnetic Ni and Co films /1/. NEXAFS with linear and circular polarization is the spectroscopy of choice; it is elementspecific and measures the electronic structure as well as the magnetism at once. For the flat oriented monolayer of porphyrin molecules we have measured the angular dependence of XAFS at the C and N K-edge and XMCD at the Fe L-edges. The paramagnetic Fe-spin is aligned with respect to the ferromagnetic substrate. This altogether opens a huge field for switching the 3d-spin from parallel to perpendicular of the molecular plane, which in turn will modify the electronic transport properties and act as a single molecular switch.

We also will discuss some recent experiments at BESSY, at which synchrotron radiation was used as a THz generator for electron paramagnetic resonance (EPR) at a single molecular magnet (SMM) Mn12Ac /2/. XMCD and EPR, together, will have a great potential to investigate and understand the basics of molecular magnetism.

The work was initiated and supported by grants: BMBF 05KS4-KEB (Wende/Baberschke), Sfb 658, and Sfb 491. It has been performed mainly in collaboration with H. Wende and with the other co-authors given in /1/.