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

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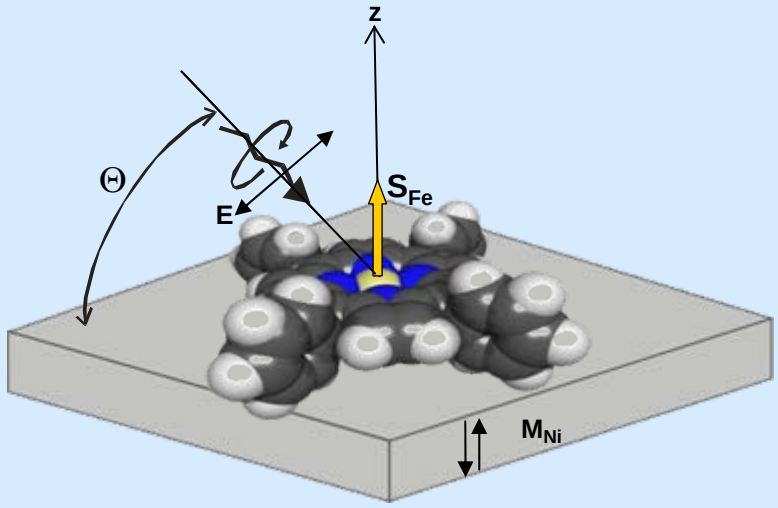
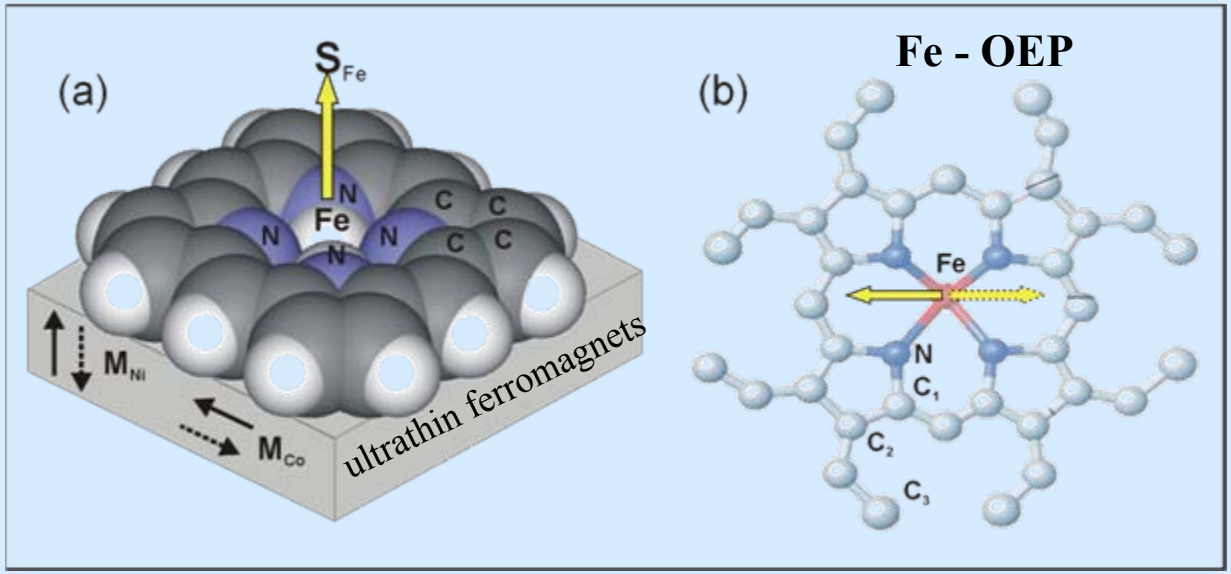


Magnetic switching of Fe-porphyrin molecules adsorbed on surfaces



switching will change the conductance ?

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

1. Introduction

ARTICLES Nature Materials **6**,516 (2007)

Substrate-induced magnetic ordering and switching of iron porphyrin molecules

H. WENDE[1*†‡], M. BERNIEN[1], J. LUO[1], C. SORG[1], N. PONPANDIAN[1], J. KURDE[1], J. MIGUEL[1], M. PIANTEK[1], X. XU[1], PH. ECKHOLD[1], W. KUCH[1], K. BABERSCHKE[1], P. M. PANCHMATIA[2†], B. SANYAL[2], P. M. OPPENEER[2] AND O. ERIKSSON[2]

PHYSICAL REVIEW B 76, 214406 (2007)

Fe-porphyrin monolayers on ferromagnetic substrates: Electronic structure and magnetic coupling strength

M. Bernien, X. Xu,* J. Miguel, M. Piantek, Ph. Eckhold, J. Luo, J. Kurde, W. Kuch, and K. Baberschke
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H. Wende† and P. Srivastava‡
Fachbereich Physik, Experimentalphysik-AG Wende, Universität Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany

PRL **102,** 047202 (2009) PHYSICAL REVIEW LETTERS week ending 30 JANUARY 2009

Tailoring the Nature of Magnetic Coupling of Fe-Porphyrin Molecules to Ferromagnetic Substrates

M. Bernien,[1,*] J. Miguel,[1] C. Weis,[2] Md. E. Ali,[3] J. Kurde,[1] B. Krumme,[2] P. M. Panchmatia,[3,†] B. Sanyal,[3] M. Piantek,[1] P. Srivastava,[2,‡] K. Baberschke,[1] P. M. Oppeneer,[3] O. Eriksson,[3] W. Kuch,[1] and H. Wende[2]
[1]*Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*
[2]*Fachbereich Physik, Experimentalphysik–AG Wende and Center for Nanointegration Duisburg-Essen (CeNIDE), Universität Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany*
[3]*Department of Physics and Materials Science, Uppsala University, Box 530, S-751 21 Uppsala, Sweden*

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.

- Penner-Hahn, Hodgson in ***Iron Porphyrins*** Vol. 3, 1989
- Goulon et al. ***The Porphyrin Handbook*** **,** 2000
- Hocking et al. JACS 2007, the Stanford-Utrecht group
- See also **E**lectron **S**pin **R**esonance 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

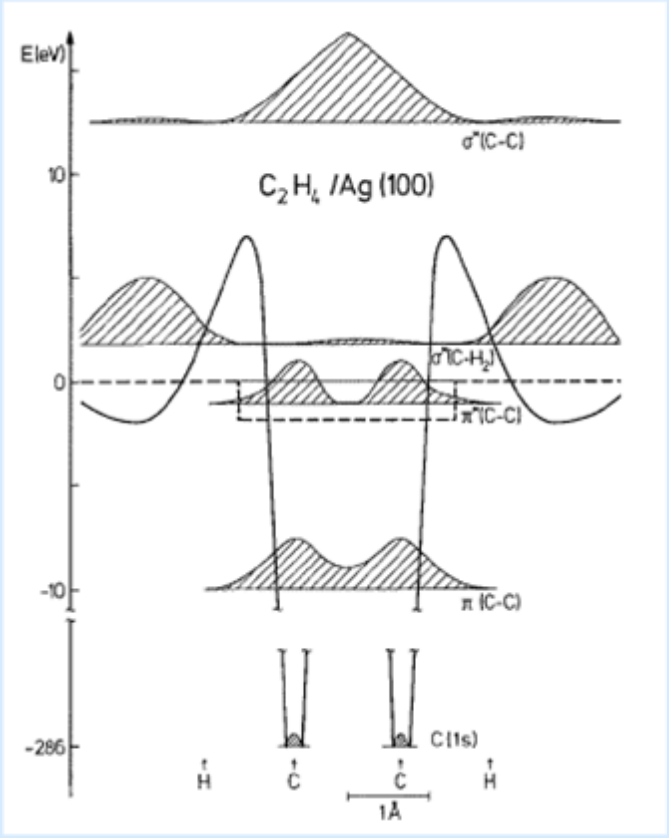
Distinguish between (I. Nenner 1986):

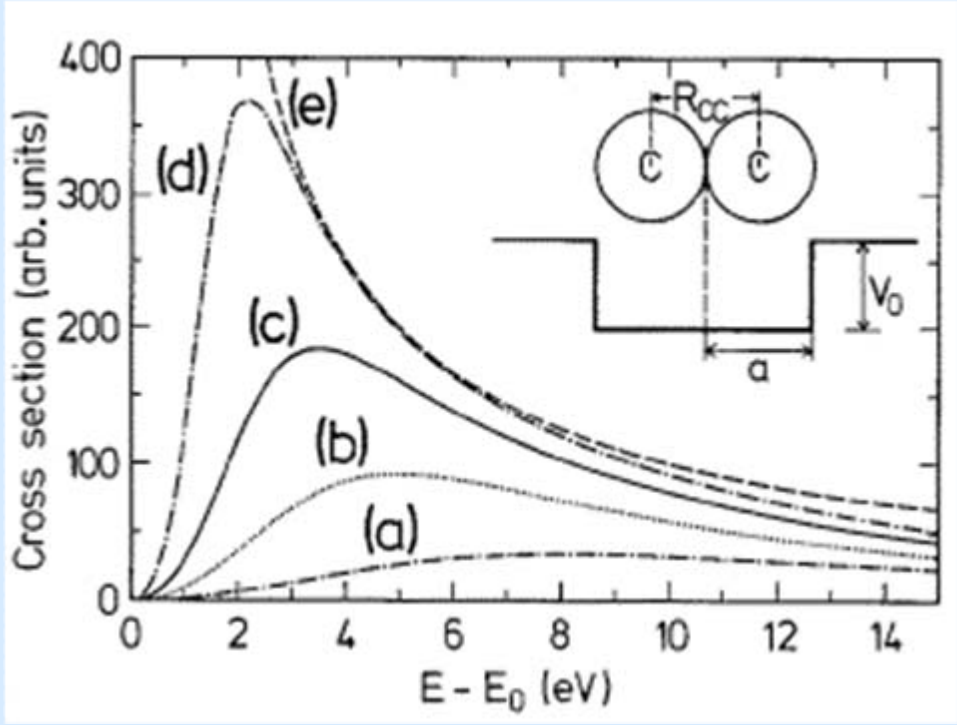
1) Excitation in an unoccupied bound state,

=> discrete resonance, relax back to the ground state.

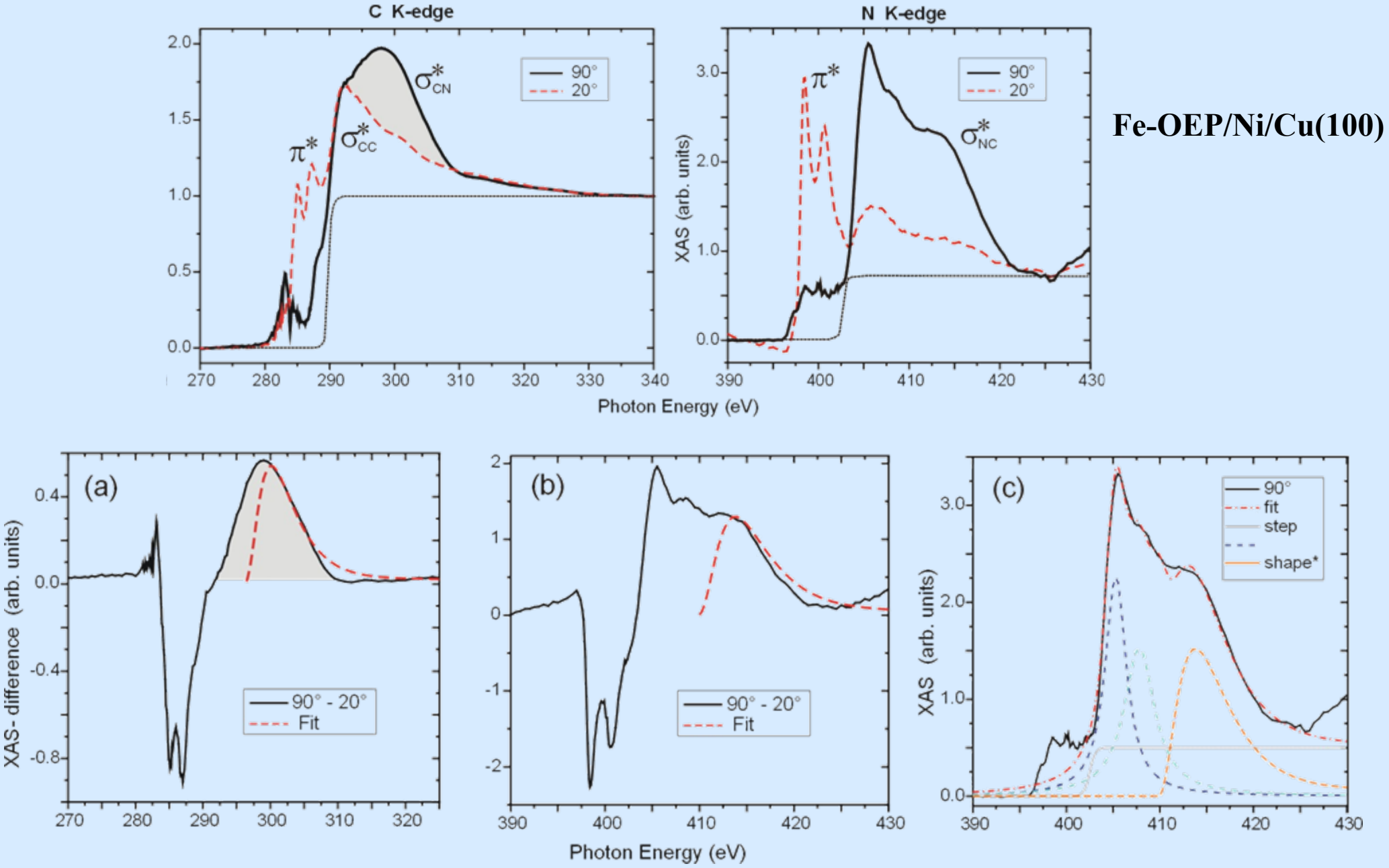
2) The core electron is ejected in the continuum

=> centrifugal barrier, scattering theory (MSM)





J. P. Connerade 1986, D. Arvanitis *et al.* Z. Physik 1989
eff. spherical well potential → analytical solution



Fe-OEP/Ni/Cu(100)

D. Bovenschen, Diplom Thesis 2009 University Duisburg-Essen; $\mathbf{V_0 a^2 = 7.3 eV Å^2}$, 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

VOLUME 47, NUMBER 5 PHYSICAL REVIEW LETTERS 3 AUGUST 1981

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

J. Stöhr, K. Baberschke,[a] R. Jaeger, R. Treichler,[b] 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 $\sigma \rightarrow \pi$ discrete absorption and a $\sigma \rightarrow \sigma$ 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(Θ) is measured.

• Sharp resonances below threshold:
fine structure of 1s → π* transitions, angular dependence,
similar to earlier work by Narioka et al. JCP 1995 on ZnTPP/Ag

•Broad scattering profile above threshold:

1s ⟶ ∞ , σ* -shape resonances, both at C and N edges,
scattering-potential, -strength, direct access to bonding geometry,
see Dehmer, Connerade, Nenner etc.

•Analysis of ΔΘ-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

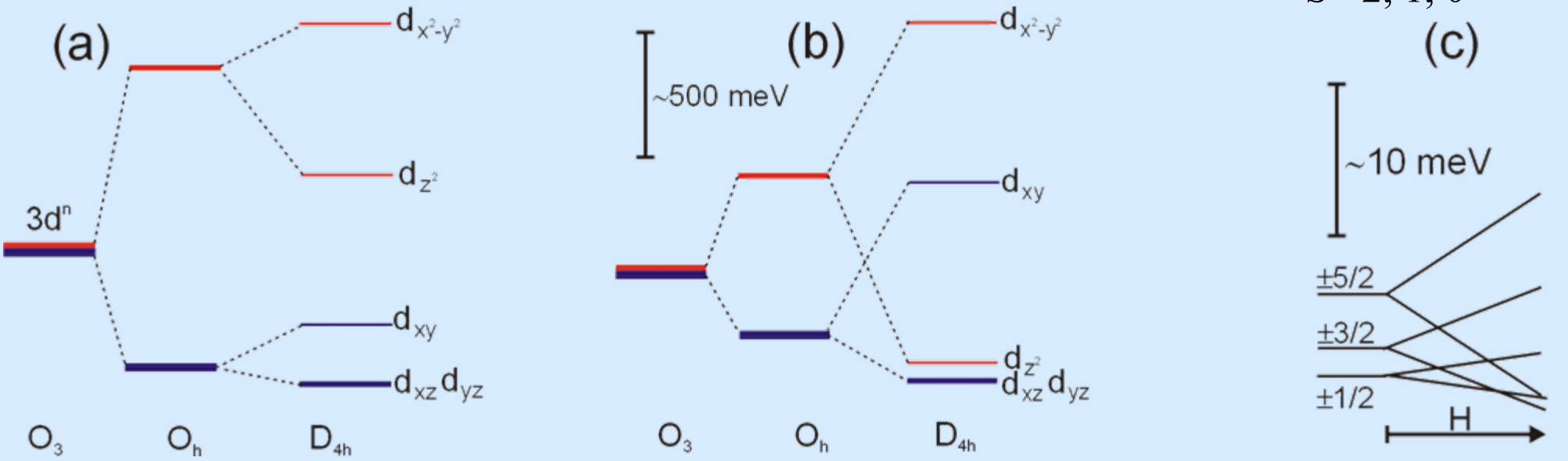
3a. NEXAFS and XMCD at the Fe $L_{3,2}$-edges

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

Fe $^{3+,2+}$

S= 5/2, 3/2, 1/2

S= 2, 1, 0



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" ≡ CEF

orbital and spin magnetic moments

20110 Ü **Übung zur Festkörperphysik II** SS 1998

Baberschke
Farle
Bovensiepen

Ausgabe: 28.0498 Abgabe: 08.05.98

Für einen $3d^1$ Zustand mit MX_6 Liganden ist die Energieaufspaltung in tetragonaler Symmetrie wie folgt gegeben:

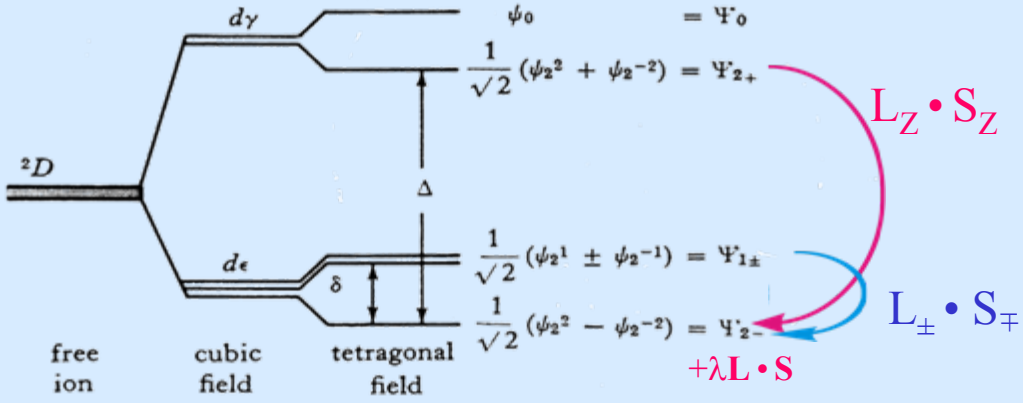


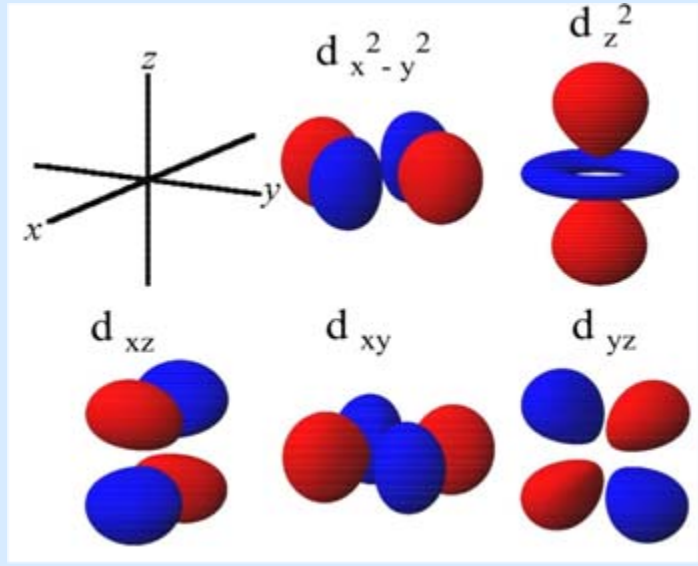
Fig. 3-4 Splitting of the ^2D term by a tetragonally distorted cubic field.

3) Berechnen Sie für den Grundzustand

$$\Psi_{2-} \equiv (2)^{-1/2}\{|2> - |-2>\} \equiv |2->$$

die Beimischung der angeregten Zustände durch $\lambda \mathbf{L}\cdot\mathbf{S}$ und beachten Sie dabei, daß auch Spinzustände einzuführen sind (zweckmäßig $\alpha|2->$ und $\beta|2->$ für Spin "up" and "down") (2 P)

4.) Gerechnen Sie für den in Ü3 gefundenen neuen Grundzustand die anisotropen g-Faktoren g_z, $g_x=g_y$ durch "Einschalten" der Zeeman Ww: $\mu_B(\mathbf{L}+g_e\mathbf{S})\mathbf{H}$ (3 P)



The orbital moment is quenched in cubic symmetry

$$\langle 2- | L_Z | 2- \rangle = 0,$$

but not for tetragonal symmetry

20110 Ü **Übung zur Festkörperphysik II** **SS 1998**

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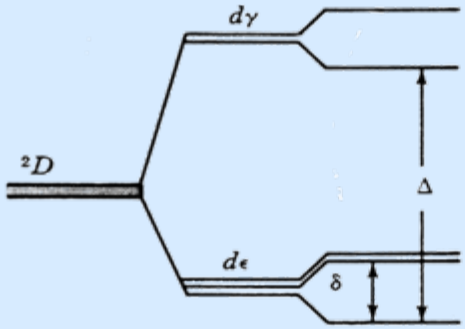


$\psi_0 = \Psi_0$

$\frac{1}{\sqrt{2}}(\psi_2^2 + \psi_2^{-2}) = \Psi_{2+}$

Fig. 3-4 Splitting of the ^2D term by a tetr

3) Berechnen Sie für den Grundzustand

$\Psi_{2-} \equiv (2)^{-1/2}\{|2> -$

die Beimischung der angeregten Zustände durc
Spinzustände einzuführen sind (zweckmäßig α|2-> und β|2-> für Spin "up" and "down")

(2 P)

4.) Gerechnen Sie für den in Ü3 gefundenen neuen Grundzustand die anisotropen g-Faktoren g_Z, g_X=g_Y durch "Einschalten" der Zeeman Ww: $\mu_B(\mathbf{L}+g_e\mathbf{S})\mathbf{H}$ (3 P)

$$\mathcal{H}_s = \beta H(g_\parallel \cos\theta S_z + g_\perp \sin\theta S_x) + D(S_z^2 - \tfrac{1}{3}S(S+1)) \quad (4.10)$$

with $S = \frac{3}{2}$; where, as above, H is applied at an angle θ to the z axis in the zx plane.

The operator S_z^2 is diagonal, so in zero magnetic field it is easy to see that the eigenvalues of Equation 4.10 are

$$E_{\pm\frac{1}{2}} = -D$$
$$E_{\pm\frac{3}{2}} = +D \quad (4.11)$$

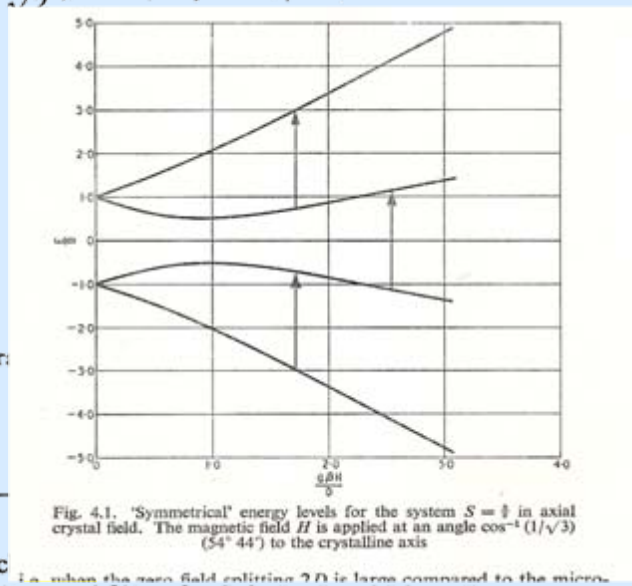


Fig. 4.1. 'Symmetrical' energy levels for the system $S = \frac{3}{2}$ in axial crystal field. The magnetic field H is applied at an angle $\cos^{-1}(1/\sqrt{3})$ (54° 44′) to the crystalline axis

Zero field splitting:

For Cr^{3+} => S=3/2, see FP

For Fe^{3+} => S=5/2

Splitting in $E_{\pm1/2}$, $E_{\pm3/2}$,$E_{\pm5/2}$

$\Delta E = 2D, 4D$

Range 5 to 40 GHz, see Bittl paper

Orbital magnetism in second order perturbation theory

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

g_{exp} $\qquad$ $B_2^0 \rightarrow K_2^0$

$$\mathcal{H} = \sum_{i,j=1}^{3} [\beta g_e(\delta_{ij} - 2\lambda\Lambda_{ij})S_i H_j - \lambda^2 \Lambda_{ij} S_i S_j]$$

$$+ \text{ diamagnetic terms in } H_i H_j \qquad (3\text{-}23)$$

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

$$\Lambda_{ij} = \sum_{n \neq 0} \frac{(0|L_i|n)(n|L_j|0)}{E_n - E_0} \qquad (3\text{-}24)$$

$<o|\mu_B \mathbf{H}\cdot\mathbf{L}|n><n|\lambda \mathbf{L}\cdot\mathbf{S}|o>$ $\qquad$ $<o|\lambda \mathbf{L}\cdot\mathbf{S}|n><n|\lambda \mathbf{L}\cdot\mathbf{S}|o>$

In the principal axis system of a crystal with axial symmetry, the $\underline{\Lambda}$ 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

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + D[S_z^2 - \tfrac{1}{3}S(S+1)] \qquad (3\text{-}25)$$

where

$$g_\parallel = g_e(1 - \lambda\Lambda_\parallel)$$
$$g_\perp = g_e(1 - \lambda\Lambda_\perp)$$
$$D = \lambda^2(\Lambda_\perp - \Lambda_\parallel) \qquad (3\text{-}26)$$

G.E. Pake, p.66

$$g_\parallel - g_\perp = g_e \lambda (\Lambda_\perp - \Lambda_\parallel)$$

anisotropic μ_L $\leftrightarrow$ MAE

$$D = \frac{\lambda}{g_e} \Delta g$$

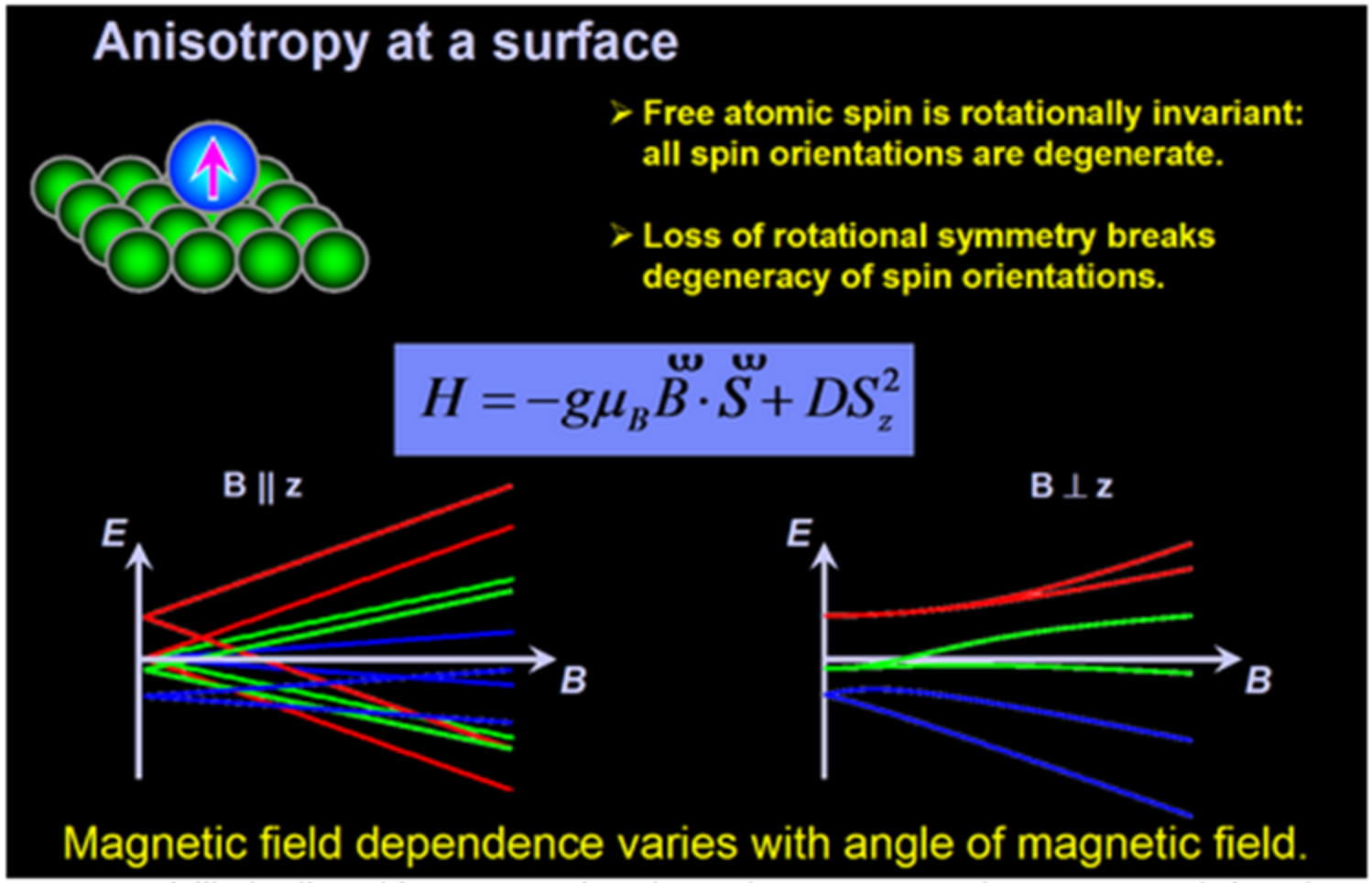
$$\updownarrow$$

$$\text{MAE} \propto \frac{\xi_{LS}}{4\mu_B} \Delta\mu_L$$

Bruno ('89)

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

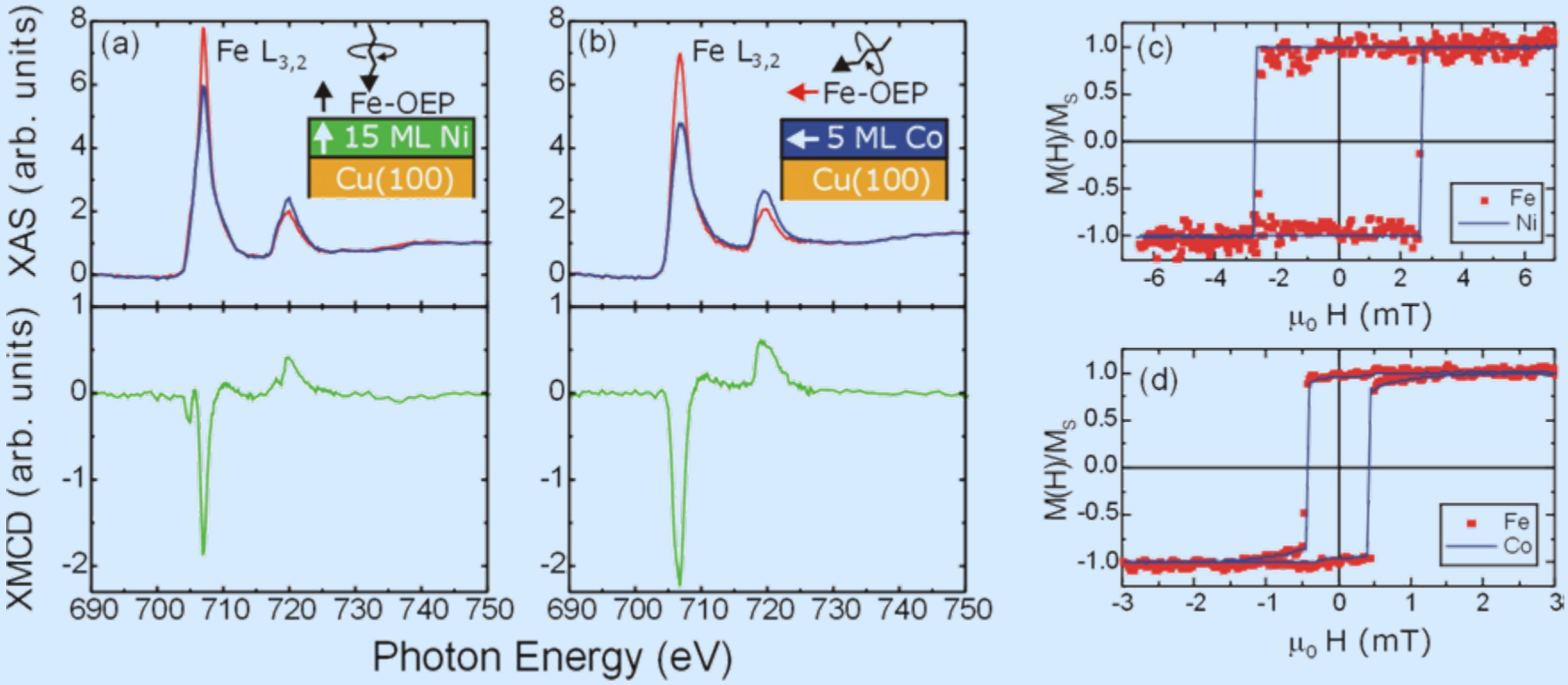
Magnetic Anisotropy



Cyrus F. Hirjibehedin, Chiung-Yuan Lin, Alexander F. Otte, Markus Ternes, Christopher P. Lutz, Barbara A. Jones, and Andreas J. Heinrich, "Large Magnetic Anisotropy of a Single Atomic Spin Embedded in a Surface Molecular Network," *Science* **317**, 1199 (2007).

3b. NEXAFS and XMCD at the Fe $L_{3,2}$-edges

L-edge spectra



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.

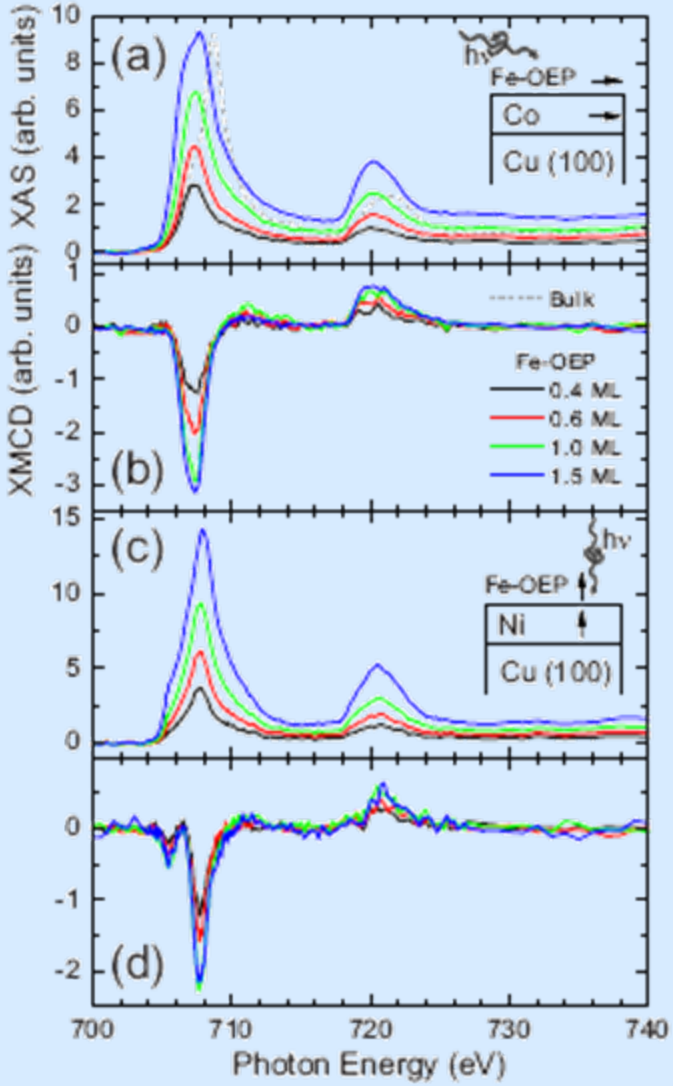


FIG. 1. (Color online) Fe-$L_{2,3}$ XAS and XMCD spectra recorded at room temperature for different coverages of Fe-porphyrin molecules [(a) and (b)] on 5 ML Co/Cu(100) and [(c) and (d)] on 15 ML Ni/Cu(100). Panel (a) includes the XAS data of Fe-OEP-Cl bulk.

High sensitivity @ BESSY UE56-2/PGM2
1 ML of Fe-OEP ≈ 1/100 ML of Fe/Cu.

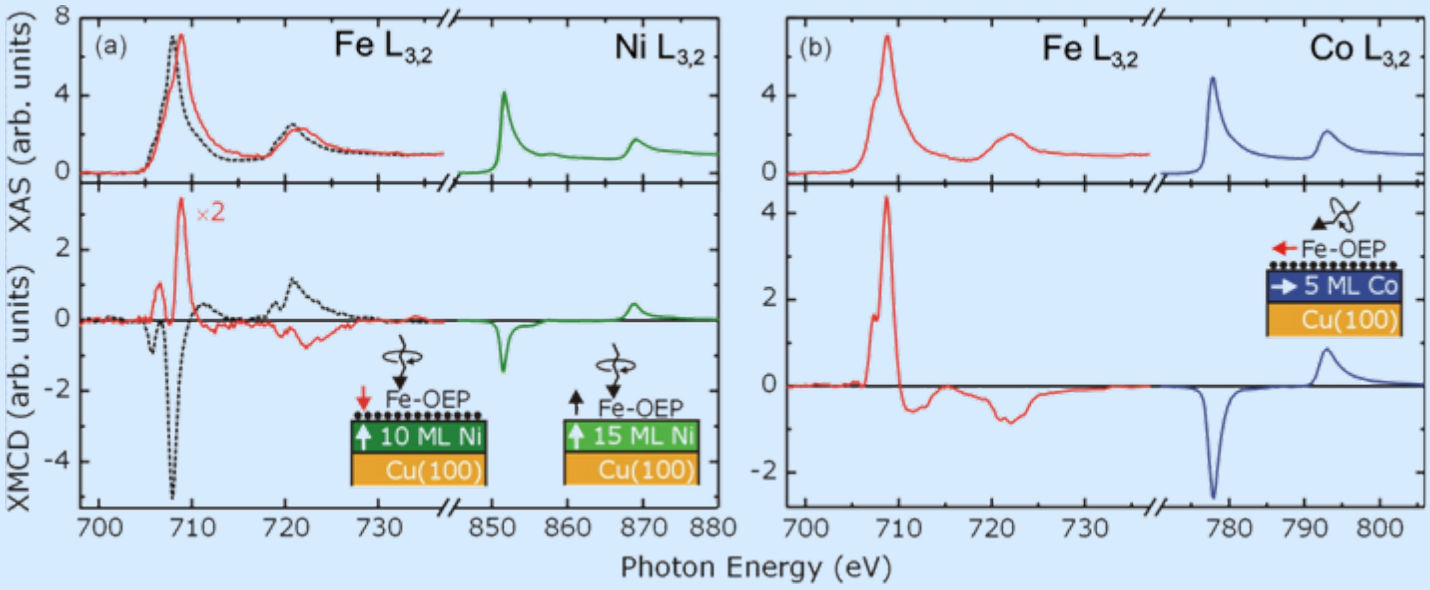
T-dependent XMCD 50 – 300 K was measured for Fe **and** Ni/Co
and the exchange coupling determined to be
≈ 70 meV for Fe-OEP/Co and
≈ 20 meV for Fe-OEP/Ni.

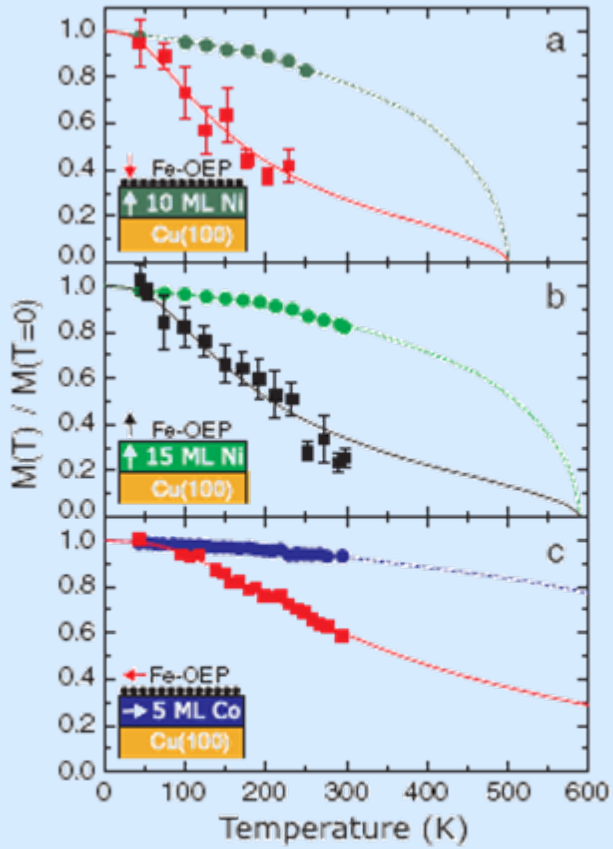
See Bernien *et al.* PRB 2007

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 μ_{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

FIG. 2 (color online). Temperature dependence of Fe XMCD (squares; full lines: fit of Brillouin-type model) and Ni or Co XMCD (circles; dashed lines: empirical curve taken from Ref. [21]) for 0.6 ML Fe-OEP on (a) O/10 ML Ni/Cu(100), (b) 15 ML Ni/Cu(100), and (c) O/5 ML Co/Cu(100).

$L_{3,2}$ NEXAFS/XANES and XMCD on oriented Fe-porphyrin contain very reach information:

Electronic:

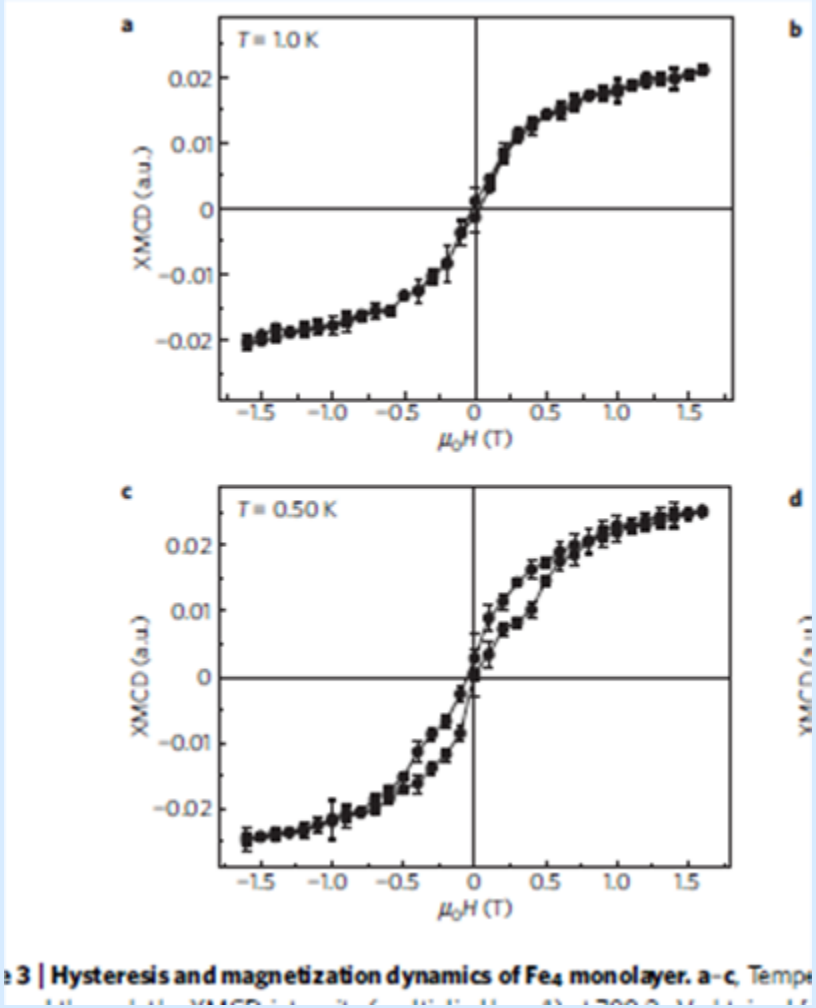
- Different Fe L_3 line shape for Ni and Co substrate. Normal (grazing) incidence is probing unoccupied Fe orbitals in plane (out of plane).
- Shift of Fe L_3 energy position $\leftrightarrow$ valence state, charge transfer

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 (Θ) $\rightarrow$ selective orbitals
- Sum rules $\rightarrow$ μ_{spin}, μ_{orb}, $\rightarrow$ MAE Caution !

4. Discussion

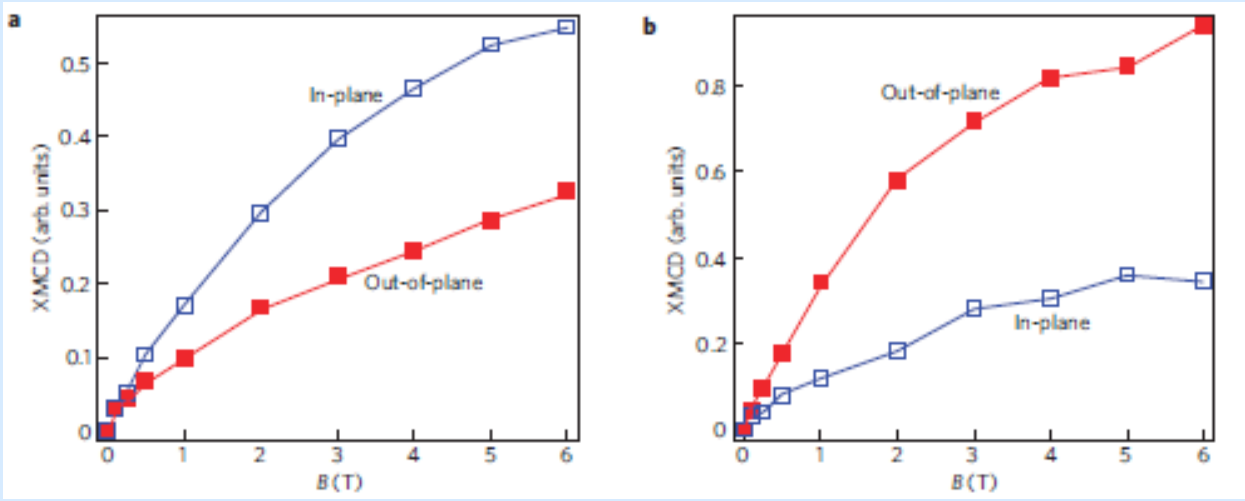
Mannini et al. @ BESSY, SLS



3 | Hysteresis and magnetization dynamics of Fe_4 monolayer. a–c, Temp

Partial saturation of an Fe_4SMM/Au(111)
anisotropic paramagnet

Gambardella et al. @ ESRF



$Fe(TPA)_4$ on Cu(100) O_2 - $Fe(TPA)_4$
change of easy axis upon O_2 dosage

16 June 2000

ELSEVIER

Chemical Physics Letters 323 (2000) 329–339

CHEMICAL PHYSICS LETTERS

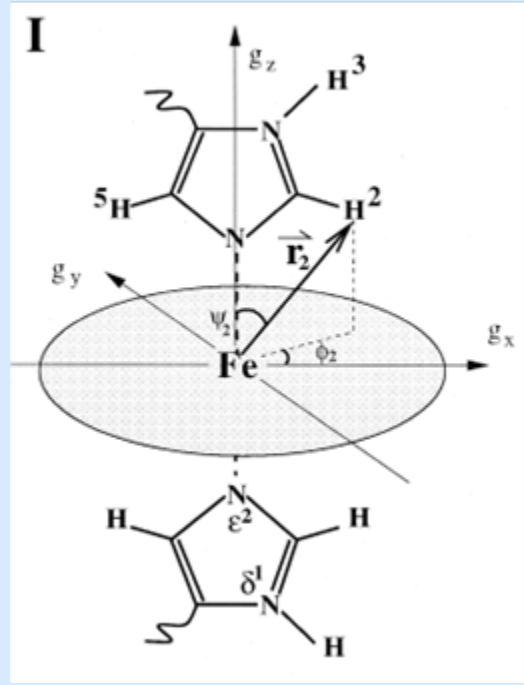
www.elsevier.nl/locate/cplett

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,*]

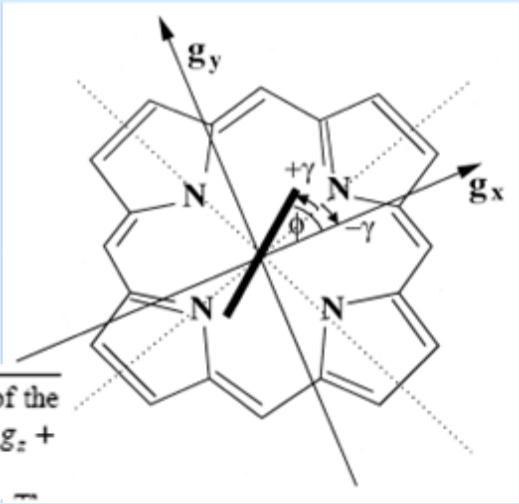
[a] Technische Universität Berlin, Max-Volmer-Institut für Biophysikalische und Physikalische Chemie, Straße des 17. Juni 135, 10623 Berlin, Germany

[b] Albert-Ludwigs-Universität Freiburg, Institut für Biologie II / Biochemie, Schänzlestraße 1, 79104 Freiburg, Germany



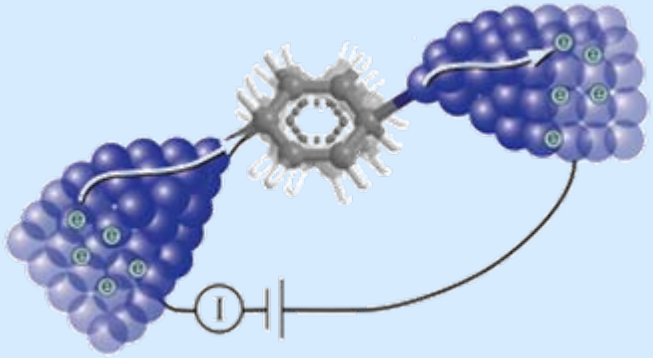
ESR gives direct access to
real ground state, wave function and g-tensor

	Maquette	MOP	MbIm
g_1	2.92 (± 0.01)	2.97 (± 0.01)	2.96 (± 0.01)
g_2	2.28 (± 0.01)	2.27 (± 0.01)	2.26 (± 0.01)
g_3	1.54 (± 0.02)	1.51 (± 0.02)	1.51 (± 0.02)
V/λ [a]	1.95 (± 0.03)	1.84 (± 0.03)	1.85 (± 0.03)
Δ/λ	3.27 (± 0.13)	3.30 (± 0.13)	3.32 (± 0.13)
V/Δ	0.60 (± 0.02)	0.56 (± 0.02)	0.56 (± 0.02)



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

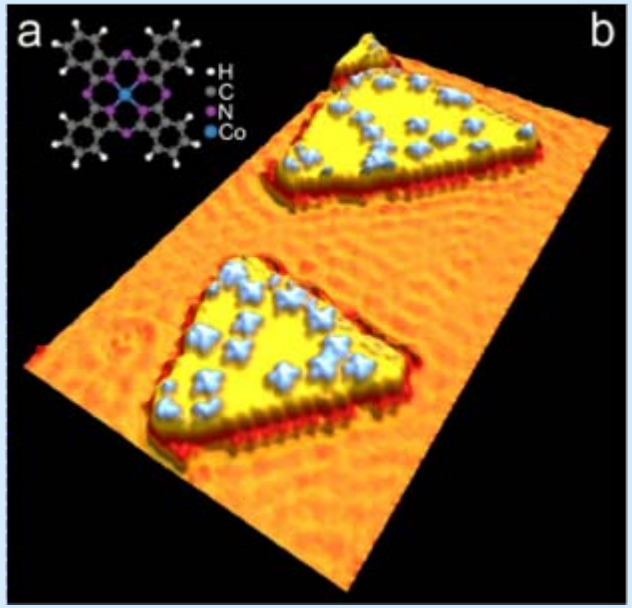
Molecular spintronics



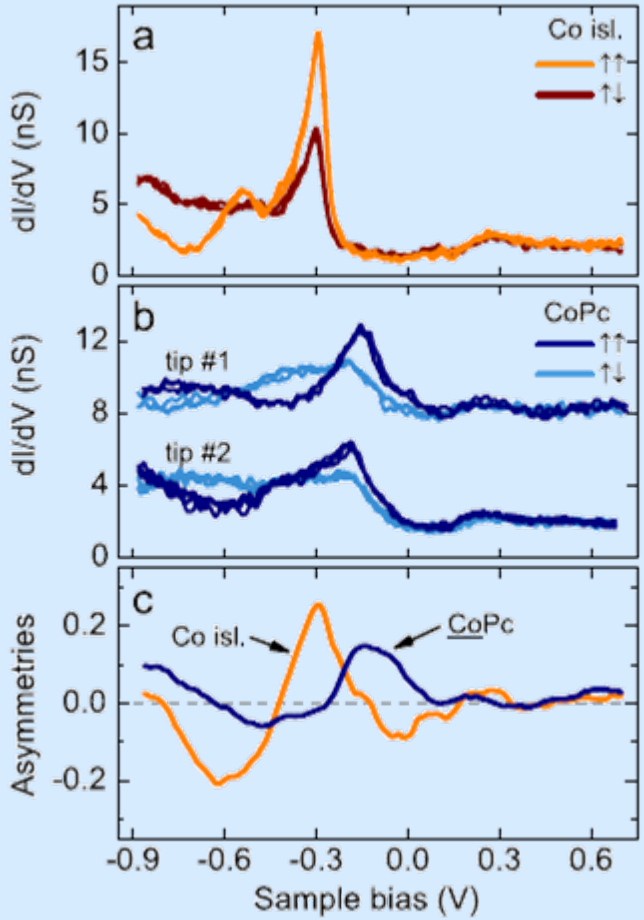
Pt – benzene –Pt

in plane conductance,

van Ruitenbeek-group PRL 2009

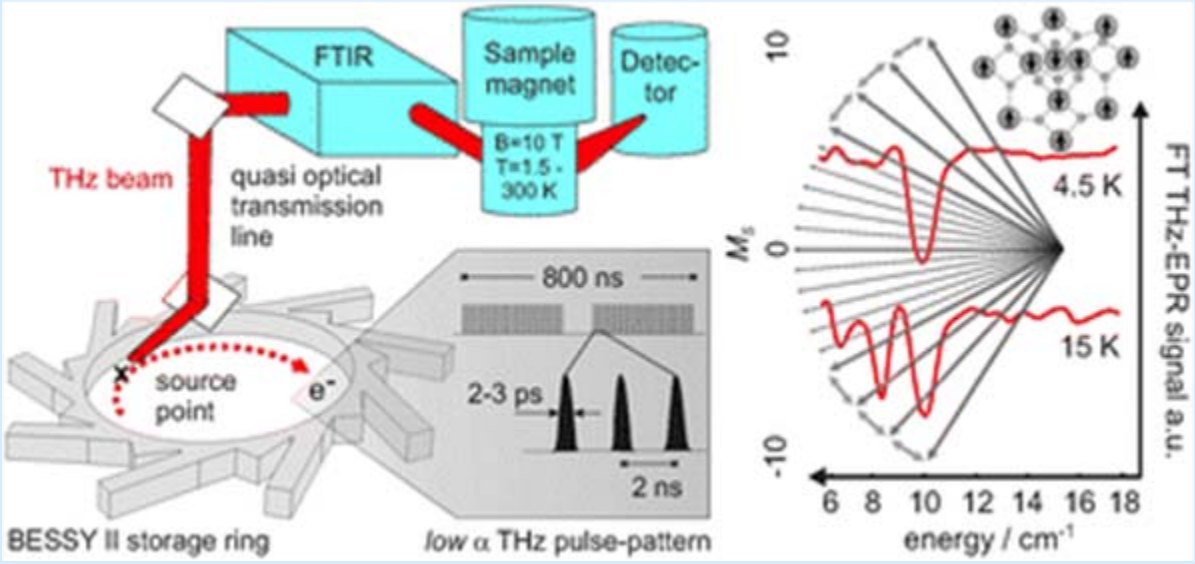


Spin-polarized STM
in CoPc on Co/Cu(111)
Bucher-group PRL 2008
Spin dependent conductivity



Alexander Schnegg et al. ***Phys. Chem. Chem. Phys.*****, 11,** 6820 (2009)

Frequency domain Fourier transform THz-EPR on single molecule magnets using coherent synchrotron radiation



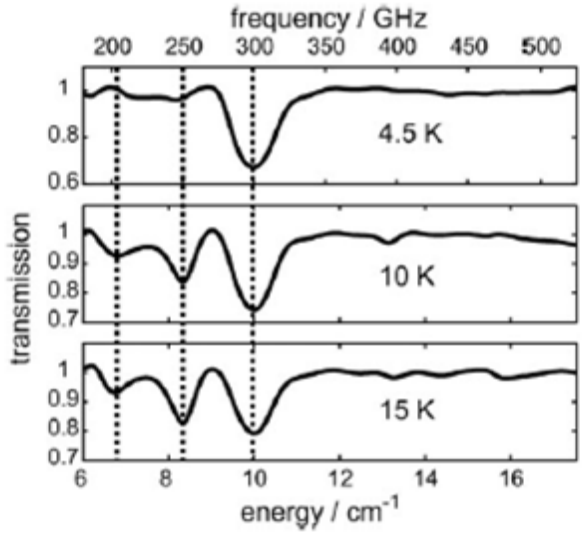
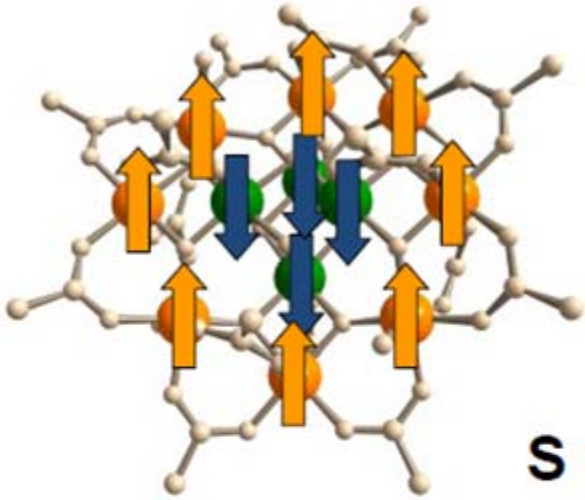


Fig. 3 FD-FT THz-EPR spectra of $Mn_{12}Ac$ obtained at T = 4.5 K, 10 K and 15 K. The spectra were obtained by dividing the spectra through a reference spectrum taken at 50 K. In the EPR spectra absorption lines resulting from $\Delta M_S = \pm 1$ EPR transitions are indicated by dotted lines. From left to right these are the $M_S = \pm 8$ to $M_S = \pm 7$ (6.9 cm^{-1}), the $M_S = \pm 9$ to $M_S = \pm 8$ (8.3 cm^{-1}) and $M_S = \pm 10$ to $M_S = \pm 9$ (10 cm^{-1}) transitions, respectively. Experimental

Frequency domain Fourier transform THz electro… FT THz-EPR) based on coherent synchrotron rad… 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 ….

High Resolution THz-EPR on $Mn_{12}Ac$

HZB Helmholtz Zentrum Berlin

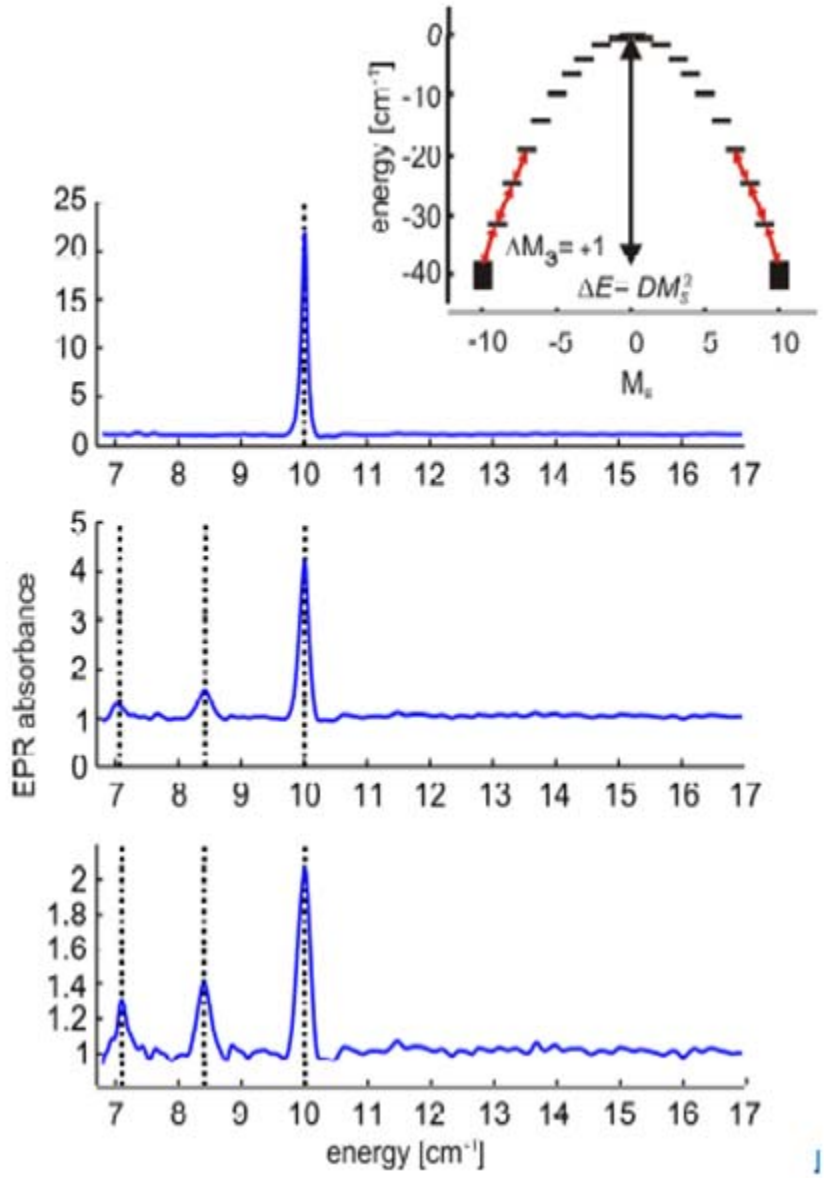


S = 10

$Mn_{12}Ac$ $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]$

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

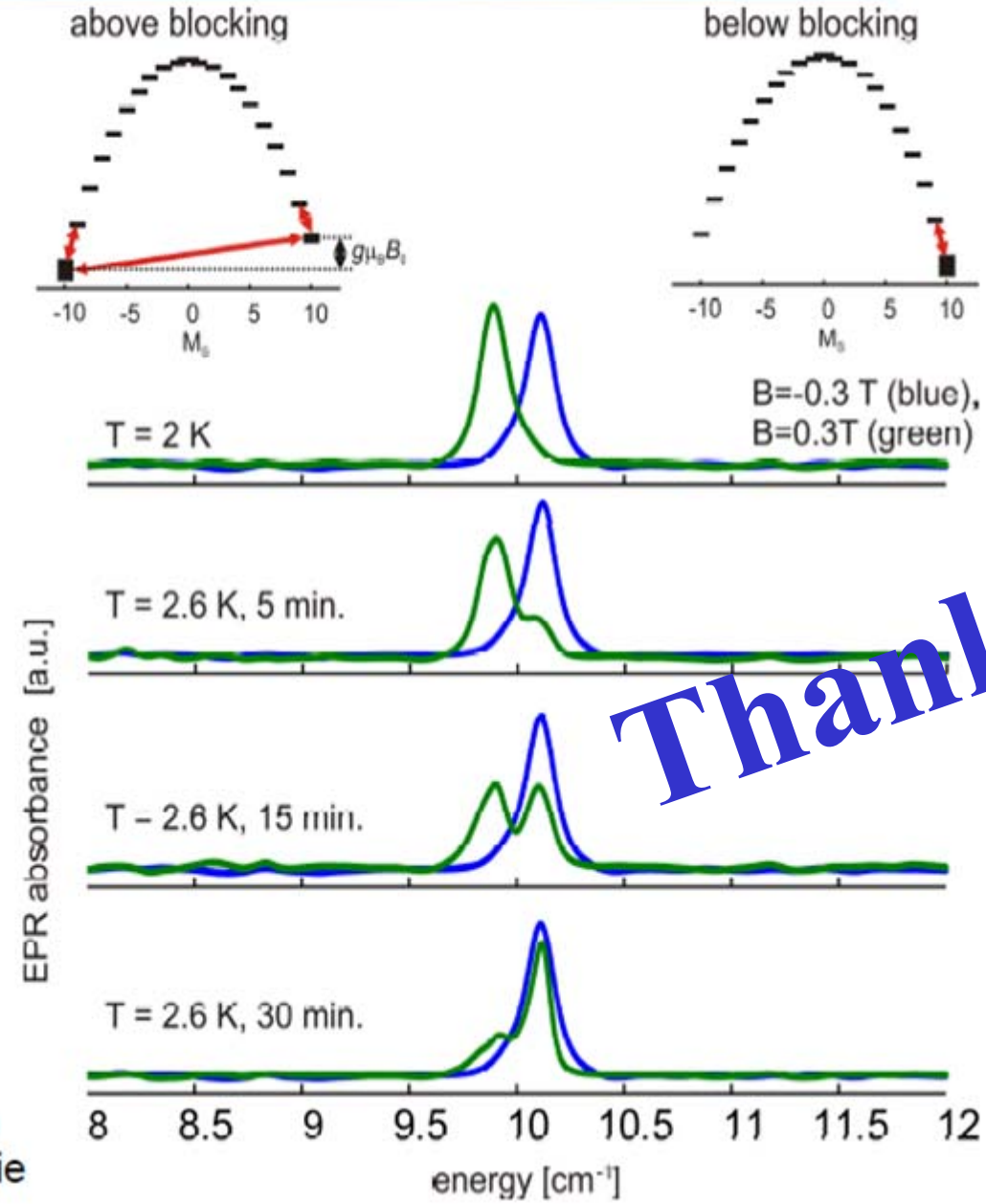
  Spins are exchange coupled to **S=10**



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

Real Time Quantum Tunneling in $Mn_{12}Ac$

HZB Helmholtz Zentrum Berlin



Thank you

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

Magnetic switching of an Fe-porphyrin monolayer adsorbed on surfaces:

An XAFS and XMCD study

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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 ori¬ented 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 radia¬tion 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/.

/1/ K. Baberschke J. Phys. Conf. Series 190, p.012012 (2009) and references therein.

/2/ A. Schnegg et al. Phys. Chem. Chem. Phys. 11, 6820 (2009)

SSRL June 3. 2010