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

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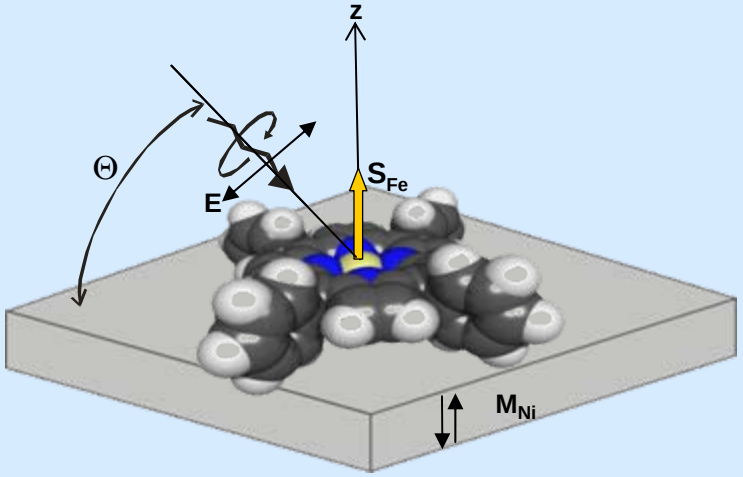
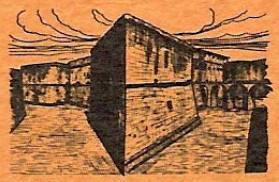


PERSPECTIVES
FOR HYPERFINE INTERACTIONS IN MAGNETICALLY ORDERED SYSTEMS
BY NMR AND OTHER METHODS

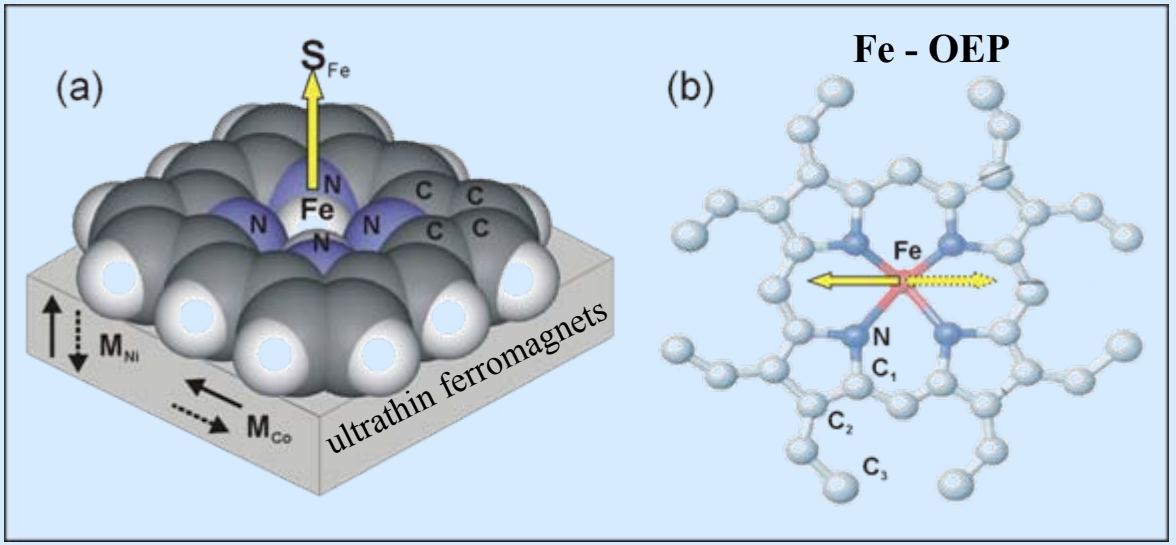
ABSTRACTS



SEPTEMBER 11 - 15, 1972 UNIVERSITA' DELL'AQUILA

L'AQUILA, ITALY

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
4. Discussion

   only very few publication cover this full range of XAFS

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

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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]
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[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

2. NEXAFS at the C and N K-edges

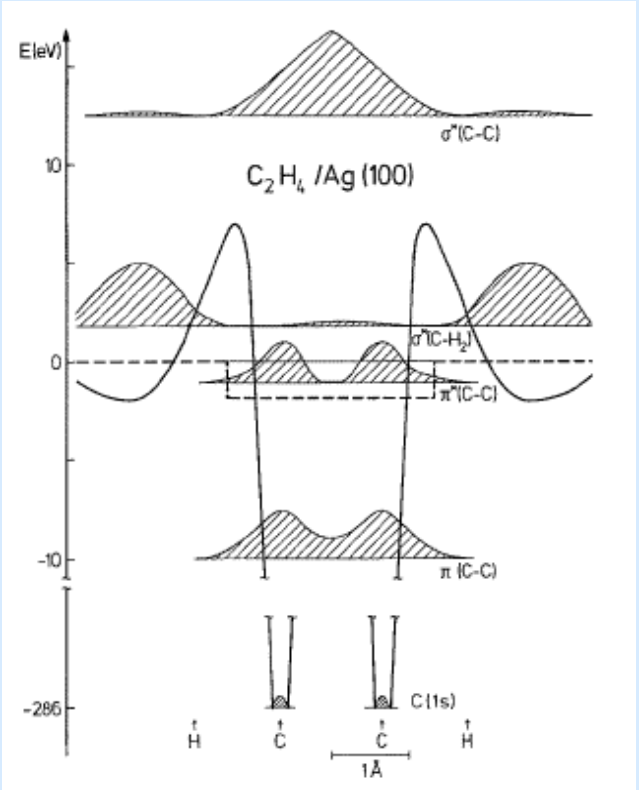
Distinguish between (I. Nenner 1986):

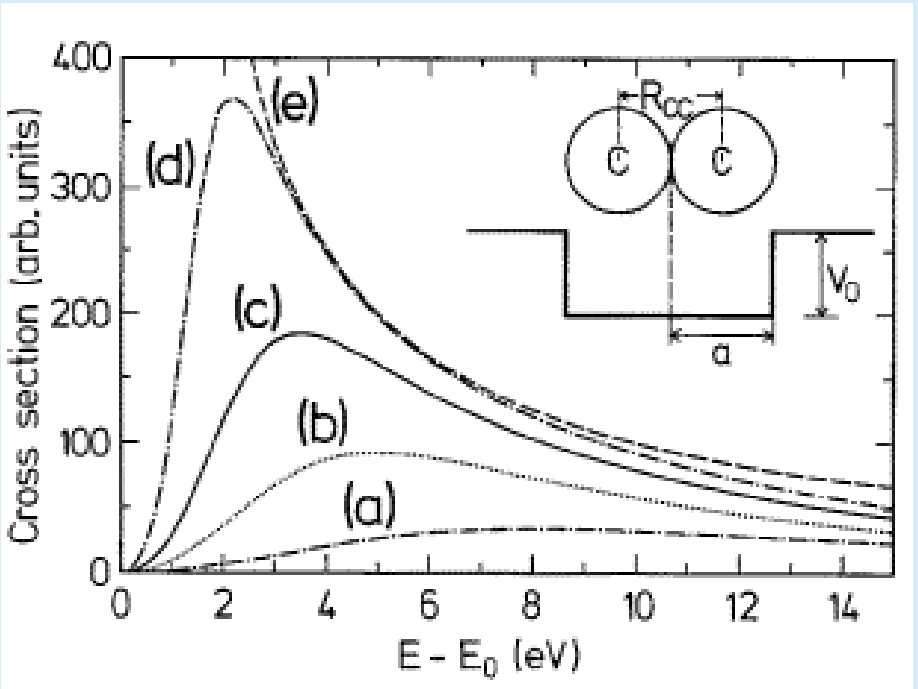
1) Excitation in an unoccupied bound state,

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

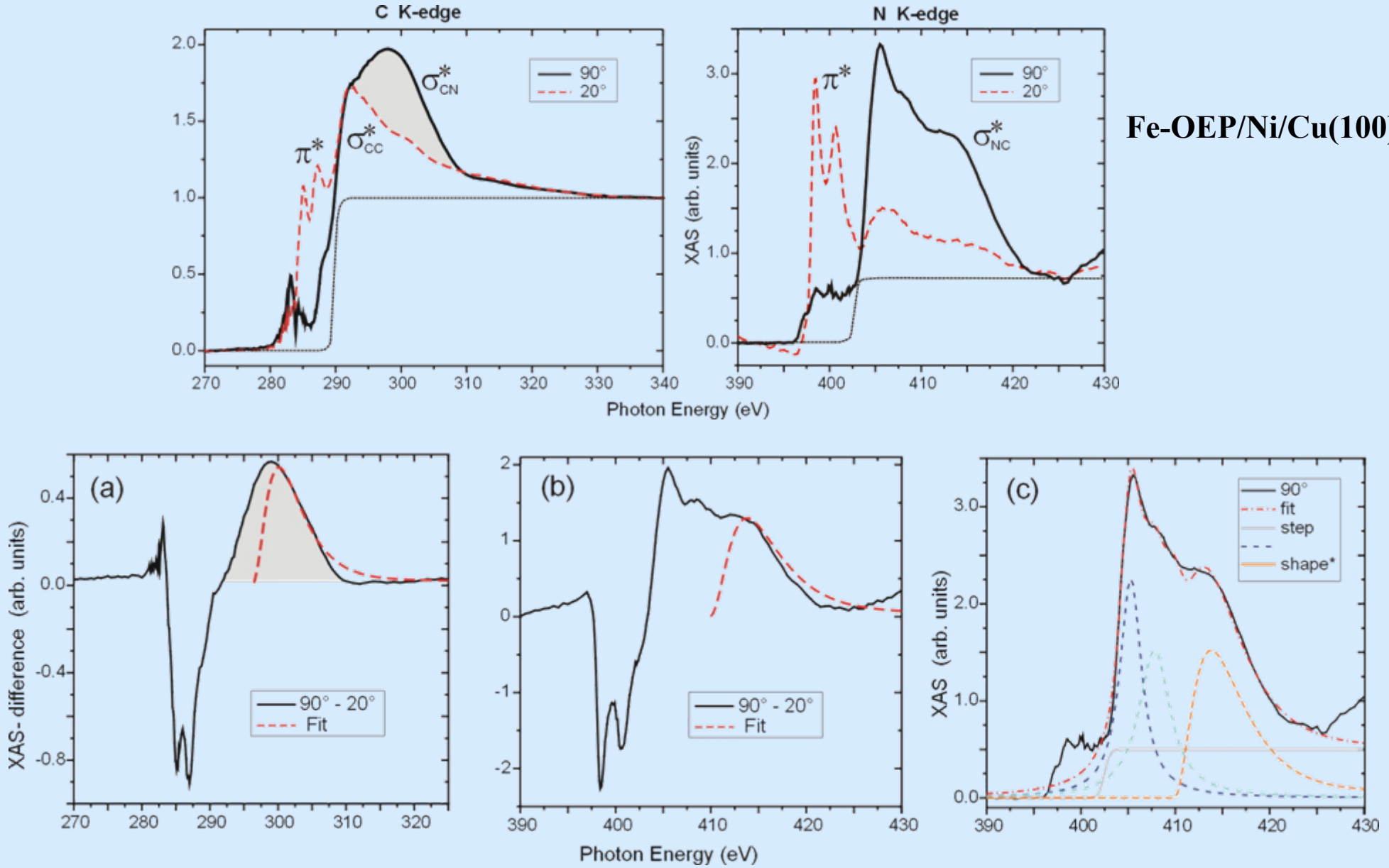
2) The core electron is ejected in the continuum

=> 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

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

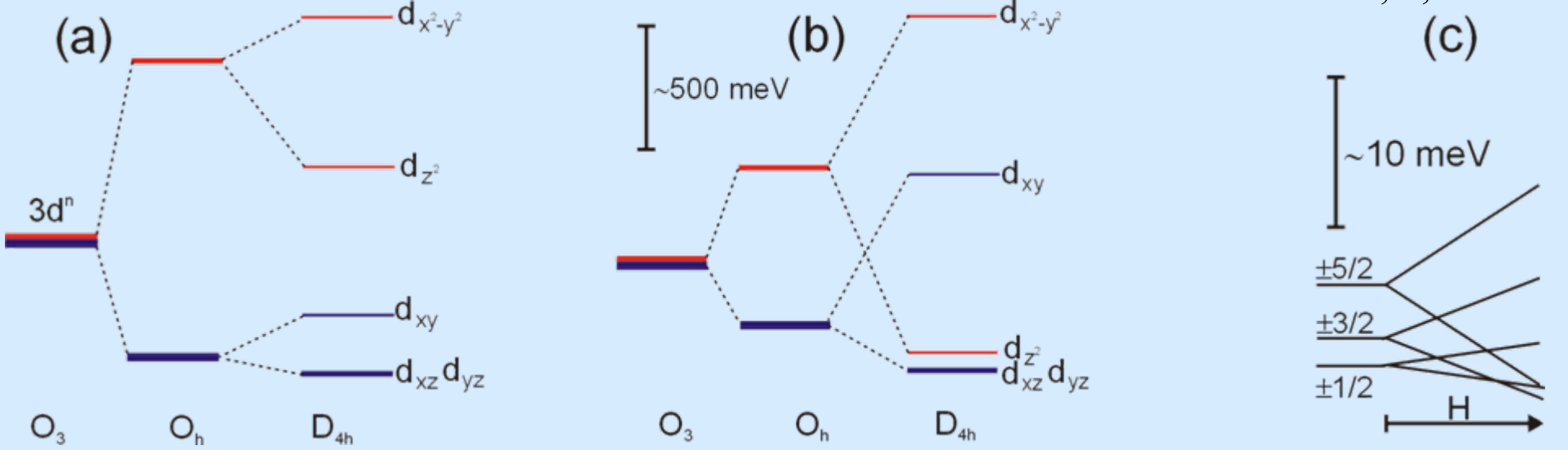
3. NEXAFS and XMCD at the Fe $L_{3,2}$-edges

$3d^n$-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:

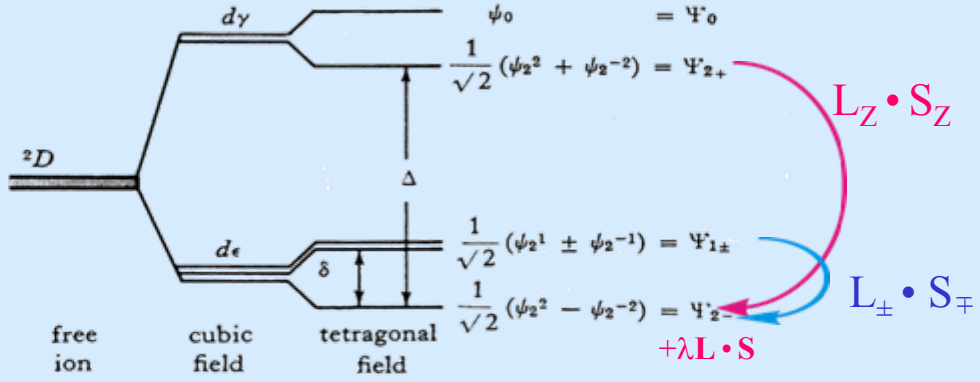


Fig. 3-4 Splitting of the ^2D term by a tetragonally distorted cubic field.

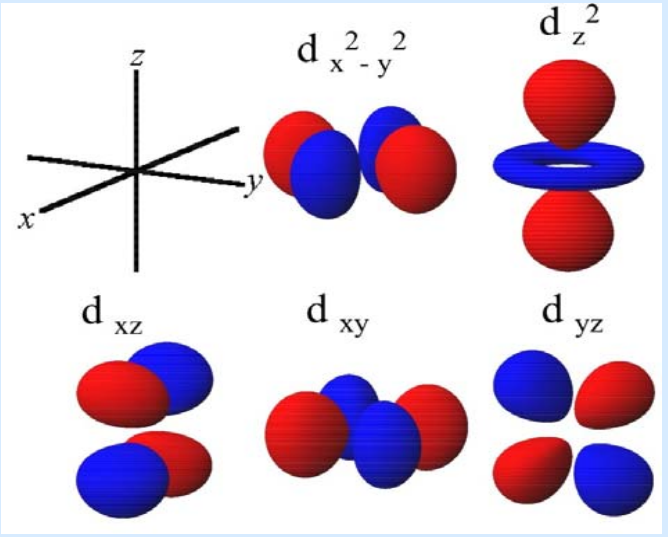
3) Berechnen Sie für den Grundzustand

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

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

Orbital magnetism in second order perturbation theory

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

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

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

+ diamagnetic terms in $H_i H_j$ (3-23)

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

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

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

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

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

where

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

G.E. Pake, p.66

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

anisotropic $\mu_L \leftrightarrow$ MAE

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

$$\updownarrow$$

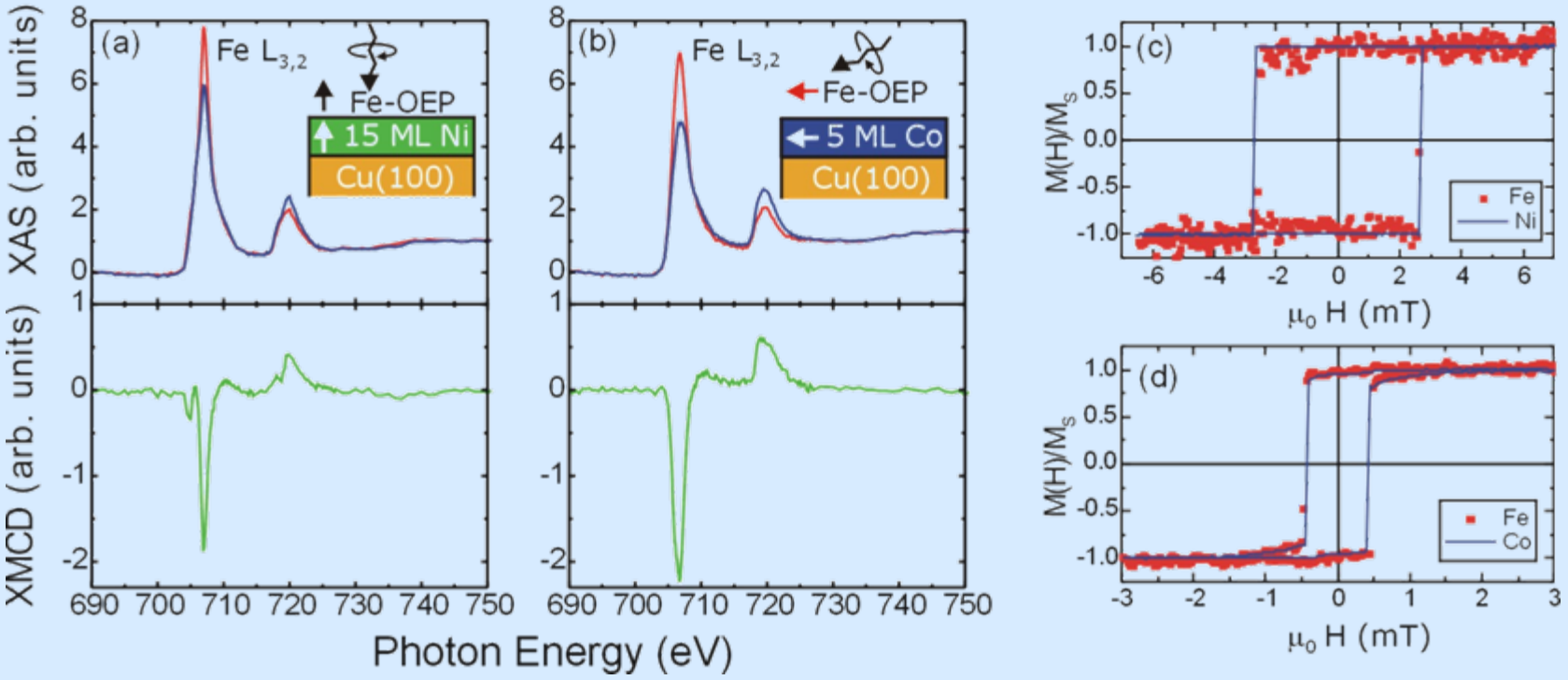
$$\text{MAE} \propto \frac{\xi_{LS}}{4\mu_B} \Delta\mu_L$$

Bruno ('89)

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

3. 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.

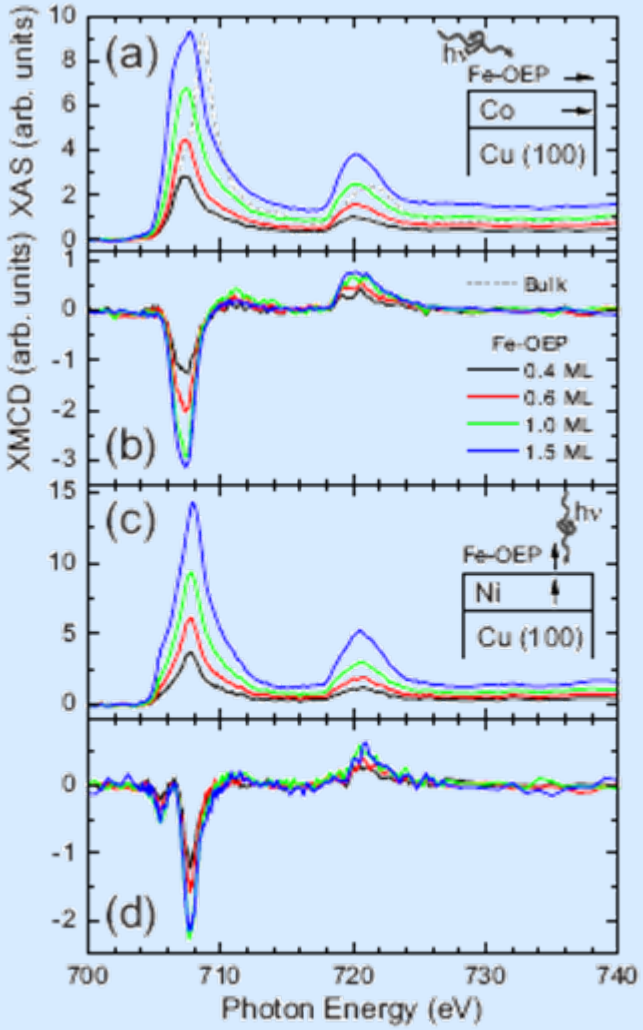


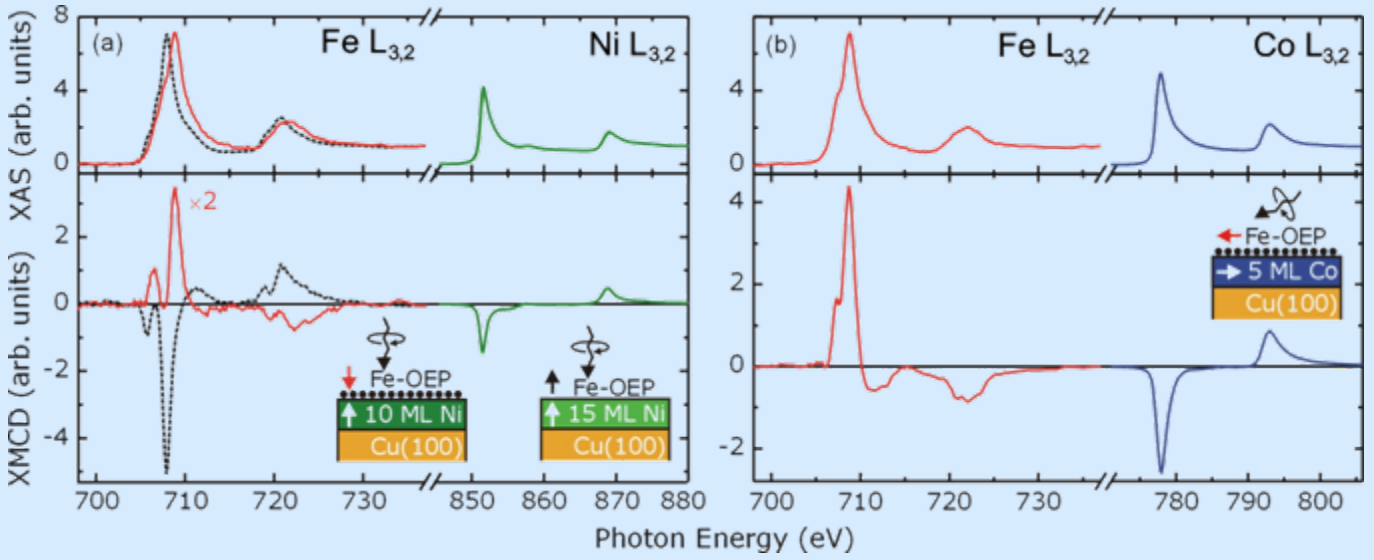
FIG. 1. (Color online) Fe-$L_{2,3}$ XAS and XMCD spectra recorded at room temperature for different coverages of Fe-porphyrin molecules [(a) and (b)] on 5 ML Co/Cu(100) and [(c) and (d)] on 15 ML Ni/Cu(100). Panel (a) includes the XAS data of Fe-OEP-Cl bulk.

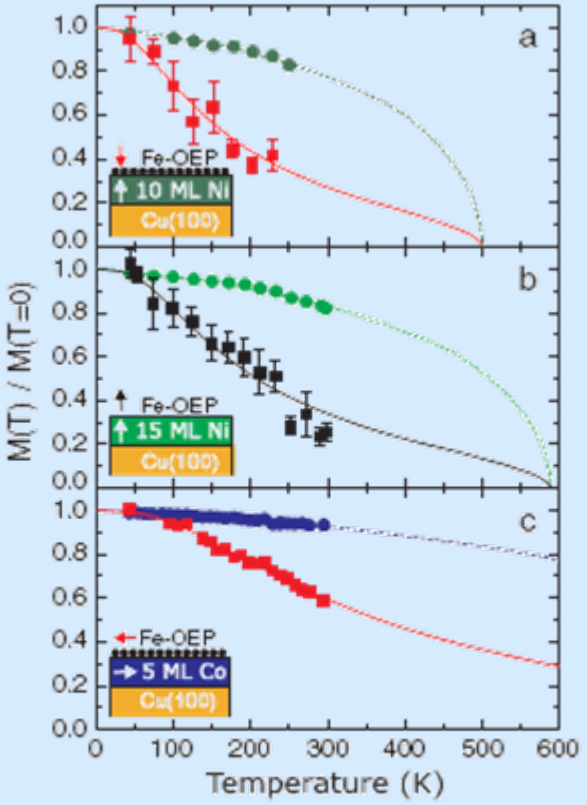
High sensitivity @ BESSY UE56-2/PGM2
1 ML of Fe-OEP ≈ 1/100 ML of Fe/Cu.

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:

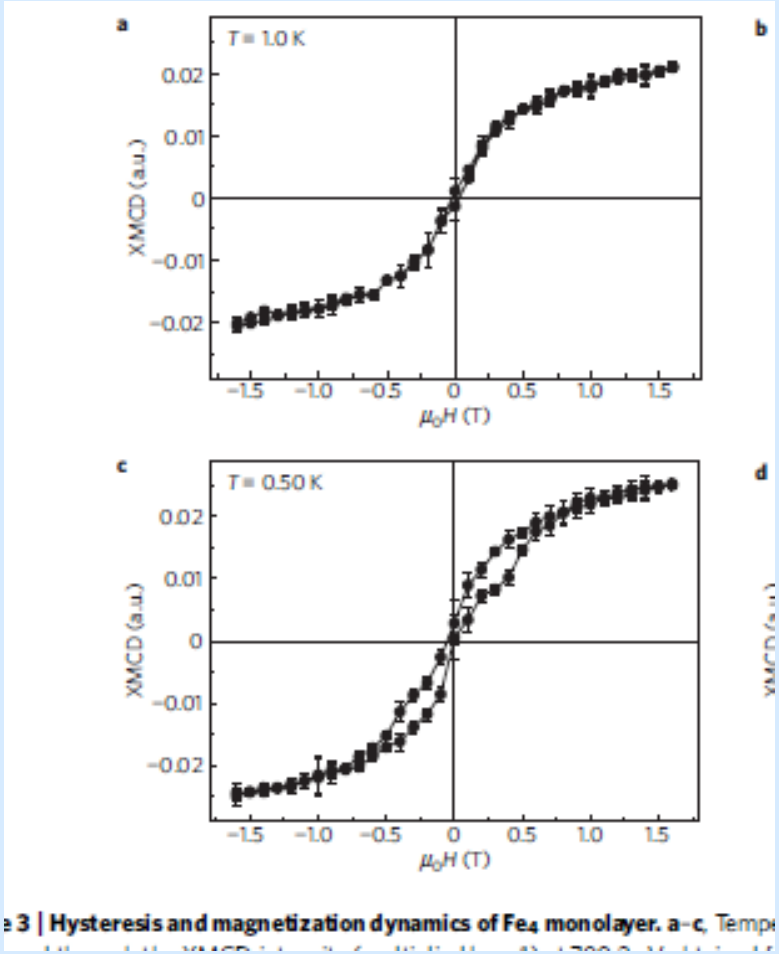
- Different Fe L_3 line shape for Ni and Co substrate. Normal (grazing) incidence is probing unoccupied Fe orbitals in plane (out of plane).
- Shift of Fe L_3 energy position $\leftrightarrow$ valence state, charge transfer

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

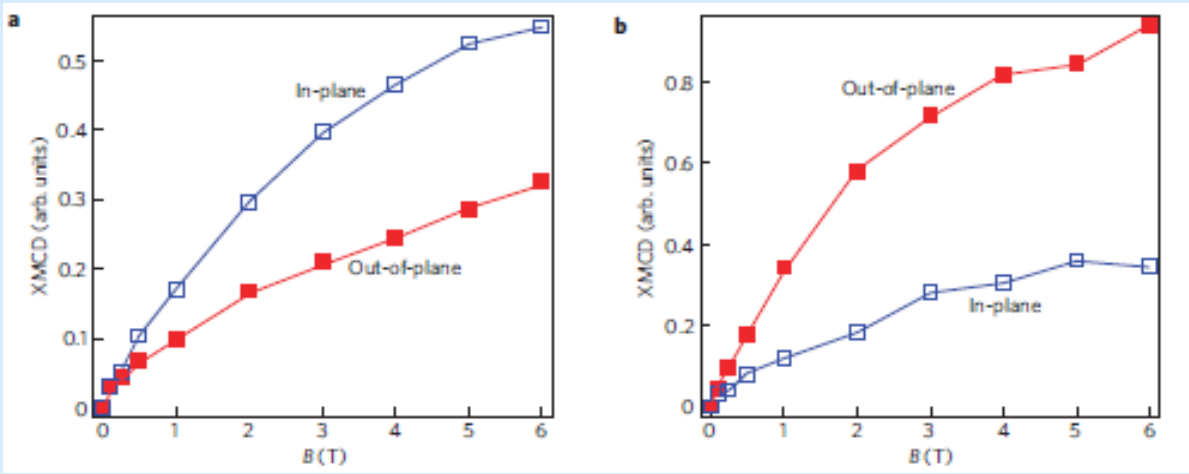
Mannini et al. @ BESSY, SLS



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

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

ELSEVIER

16 June 2000

Chemical Physics Letters 323 (2000) 329–339

CHEMICAL PHYSICS LETTERS

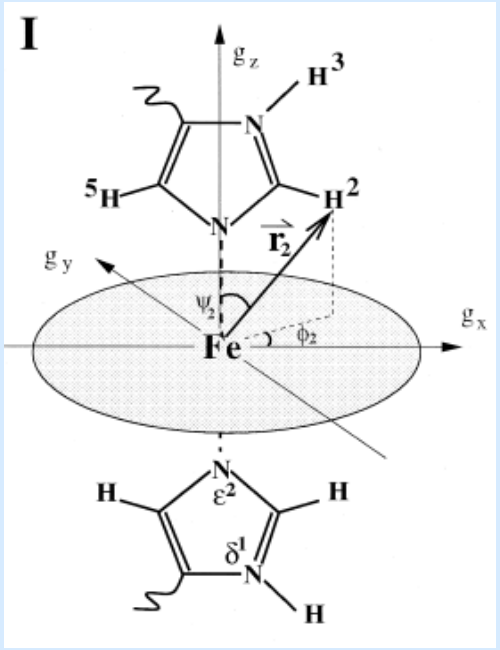
www.elsevier.nl/locate/cplett

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,*]

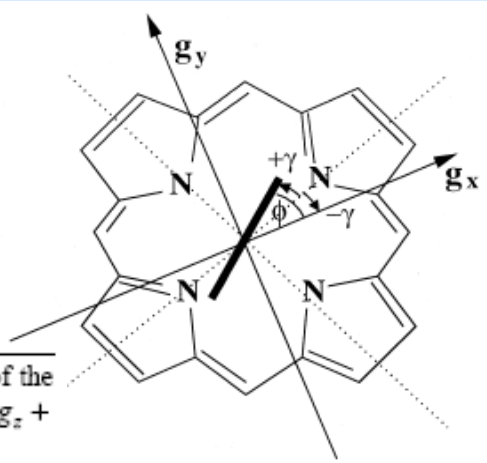
[a] *Technische Universität Berlin, Max-Volmer-Institut für Biophysikalische und Physikalische Chemie, Straße des 17. Juni 135, 10623 Berlin, Germany*

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



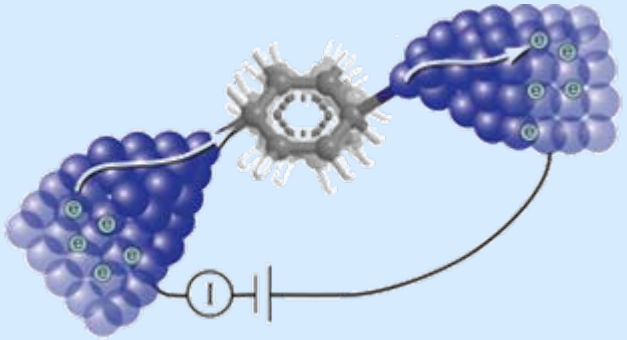
ESR gives direct access to
real ground state, wave function and g-tensor

	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 $g_z > g_y > g_x$.

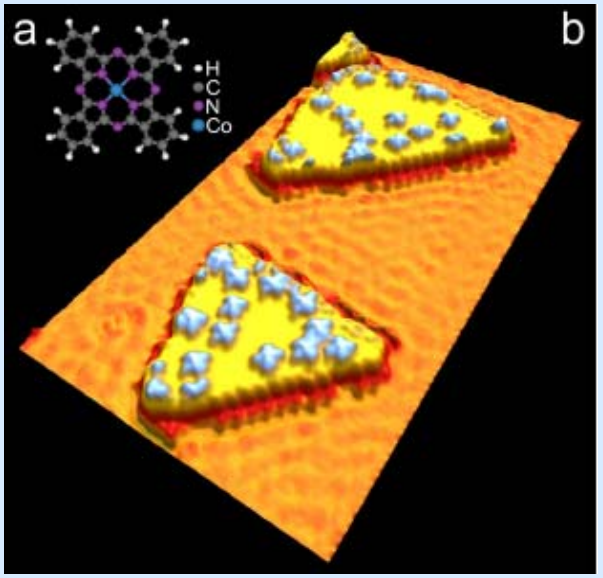
Molecular spintronics



Pt – benzene –Pt

in plane conductance,

van Ruitenbeek-group PRL 2009

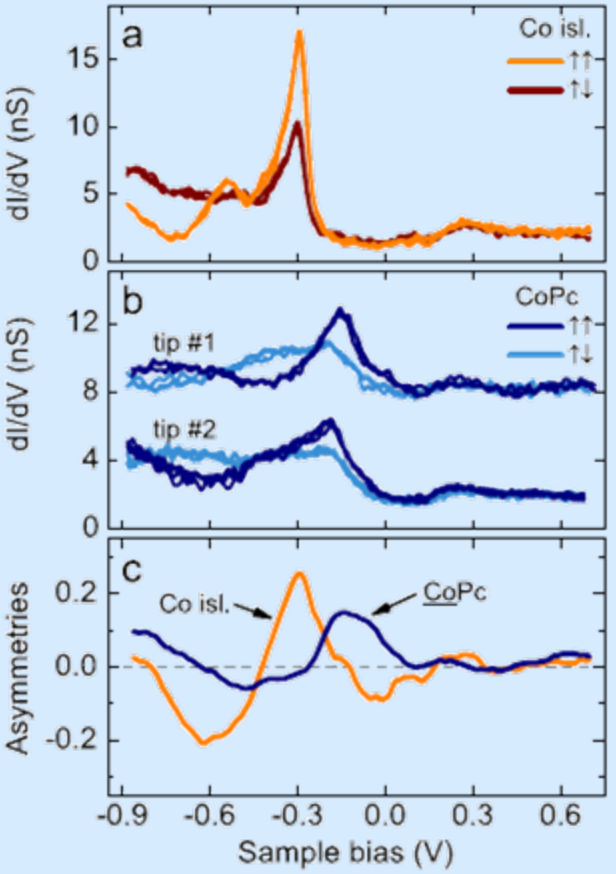


Spin-polarized STM

in CoPc on Co/Cu(111)

Bucher-group PRL 2008

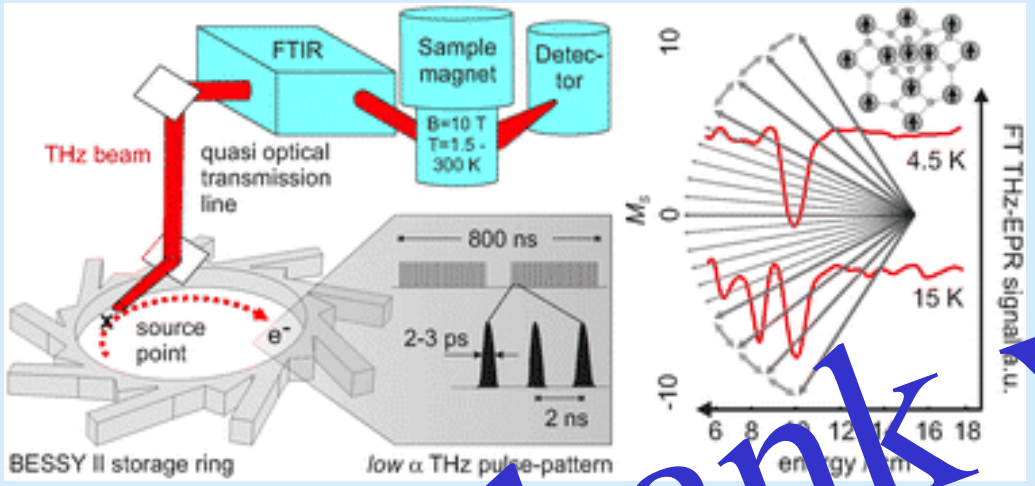
Spin dependent conductivity



Phys. Chem. Chem. Phys., 2009, online 23rd June

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

Alexander Schnegg, Jan Behrends, Klaus Lips, Robert Bittl, Karsten Holldack



Thank you !

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 ….