

MA 23: Spin Effects in Molecules at Surfaces (jointly with DS,O)

Time: Wednesday 9:30–12:15

Location: H23

MA 23.1 Wed 9:30 H23

Weak Coupling Kondo Effect in a Purely Organic Molecule: Universal Temperature and Magnetic Field Dependence —

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The Kondo effect is one of the most intriguing any-particle phenomenon in solid-state physics due to the simplicity of the underlying model: the scattering of itinerant electrons at a localized spin.[1] It has been intensely studied on the single atomic and molecular level by scanning tunneling spectroscopy (STS) in the last two decades; however a quantitative comparison with theoretical predictions remained challenging due to orbital degeneracies and a spin quantum number higher than $\frac{1}{2}$. Here, we present STS measurements on an purely organic radical coupled to the conduction electrons of a Au(111) surface. The observed zero bias anomaly is due to a spin $\frac{1}{2}$ Kondo screening in the weak coupling limit. We can describe the temperature and magnetic field dependence of the spectral features practically parameter free by perturbation theory allowing quantitative tests on more complex theoretical models.

[1] A. C. Hewson, 1997: The Kondo Problem to Heavy Fermions, Cambridge University Press

MA 23.2 Wed 9:45 H23

Density Functional Investigation of a Phthalocyanine Based Spin Transfer Material —

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Interfaces were found to be of outstanding importance for electronic and spin transfer purposes especially in molecular spintronics [1]. Recently it has been demonstrated that an organic interface purely made from metal phthalocyanines namely manganese phthalocyanine (MnPc) and perfluorinated cobalt phthalocyanine (F₁₆CoPc) exhibits a charge and spintransfer at the interface between both molecules [2]. In this talk we present a systematic theoretical investigation of the phthalocyanine based dimer MnPc^{δ+}/F₁₆CoPc^{δ-} within density functional theory framework. For all considered stackings a charge transfer from MnPc to F₁₆CoPc is observed which outlines this behavior as an intrinsic property of the molecular pair. In addition a ferromagnetic coupling ($S = 2$) of the molecular magnetic moments within the dimer is always observed due to 90° superexchange and direct exchange contributions. The comparison of the calculated absorption spectra of the geometrical arrangements to the experimentally recorded electron energy-loss spectrum strongly indicates the β -geometry to be preferred over all others. Only for this geometry an experimentally observed excitation around 0.6 eV is reproduced by the calculation.

[1] S. Sanvito, Nature Physics **6**, 562, (2010).

[2] S. Lindner *et al.*, Phys. Rev. Lett. **109**, 027601, (2012).

MA 23.3 Wed 10:00 H23

Superexchange-mediated ferromagnetic coupling in two-dimensional Ni-TCNQ networks on metal surfaces —

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We investigate the magnetic coupling of Ni centers embedded in two-dimensional metal-coordination networks self-assembled from 7,7,8,8-Tetracyanoquinodimethane (TCNQ) molecules on Ag(100) and Au(111) surfaces. X-ray magnetic circular dichroism (XMCD) measurements show that single Ni adatom impurities assume a spin-quenched configuration on both surfaces, while Ni atoms coordinating to TCNQ ligands recover their magnetic moment and exhibit ferromagnetic coupling. The valence state and the ferromagnetic coupling strength of the Ni coordination centers depend crucially on the underlying substrate due to the different charge state of the TCNQ ligands on the two surfaces. The results suggest a superexchange coupling

mechanism via the TCNQ ligands.

MA 23.4 Wed 10:15 H23

Interface magnetism of the phenalenyl based molecular dimer adsorbed on a ferromagnetic surface —

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Molecular based magnetic units represent a very exciting avenue in designing and building future data storage, sensing and computing multifunctional devices. The density functional theory (DFT) provides a framework that reliably describes the electronic properties of molecules adsorbed on magnetic surfaces which are an essential prerequisite for the design an understanding of the functionality of hybrid organic molecular spintronic devices. We will present *ab initio* studies performed to understand the interaction of a phenalenyl (PLY) based molecular dimer with a ferromagnetic Co surface. Charge transfer and hybridization between the atomic p_z orbitals of the PLY with the d -orbitals of the Co atoms create new hybrid metal-organic interface states [1,2] that lead to a large interfacial magnetoresistance near room temperature as measured in experiments [3]. Furthermore, our studies demonstrate the decisive role played by the van der Waals interactions in correctly describing the interaction between aromatic PLY dimers and metallic surfaces.

[1] N. Atodiresei *et al.*, Phys. Rev. Lett. **105**, 066601 (2010).

[2] N. Atodiresei *et al.*, Phys. Rev. B **84**, 172402 (2011).

[3] K. V. Raman *et al.*, accepted for publication in Nature (2012).

MA 23.5 Wed 10:30 H23

Magnetism and molecule-surface interaction in transition metal porphyrin molecules on Cu(001) —

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We present a combined theoretical and experimental study of Fe(Co) porphyrin molecules on (O)/Cu(001) surfaces. The interaction between nonmagnetic surfaces and molecules is weak, hence the anisotropy of the molecule can be studied together with the influence of ligands and hybridization effects with the surface. Magnetic and structural properties have been investigated within DFT and angle-dependent X-ray absorption spectroscopy at the Fe $L_{2,3}$ edge. The magnetic dipole term is calculated to allow for comparison between spin moments from experiment and theory. The angle dependence of the calculated effective moments is in good agreement with the experimental findings. An intermediate spin state is obtained independent from the presence of an oxygen layer on the surface, which affects the hybridization between surface and molecule. A high-spin state can be realized by adding Cl or O ligands, which cause a stretching of the metal center-N bond.

15 min. break

MA 23.6 Wed 11:00 H23

Magnetic coupling of Cobaltocene on magnetic surfaces through a graphene layer —

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The ability to improve the current electronic devices appear to be increasingly connected with the development of the molecule-based electronics [1] and spintronics [2]. We have concentrated our study, employing state-of-the-art density functional theory calculations, on the structural and magnetic properties of the Cobaltocene (CoCp₂) adsorbed on graphene deposited on slab of Ni(111). This molecule has

been chosen because of its electronic structure rather unique among the metallocenes [3]. In several articles it has been pointed out that graphene on Nickel (111) has mainly two energetically favored adsorption modes, namely top-fcc and bridge-top [4]. We will show how the magnitude of the magnetic coupling is drastically influenced by the structural factors named above and may vary by tens of meV. We further show how this coupling could be tuned by the intercalation of a magnetic monolayer, e.g. Fe and Co, between graphene and the Ni substrate, and discuss the role of the graphene layer.

[1] X. Y. Zhu, Surf. Sci. Rep. 56, 1 (2004). [2] S. Sanvito, Chem. Soc. Rev. 40, 3336 (2011). [3] Y. Li, et al., Phys. Rev. B 83, 195443 (2011). [4] W. Zhao, et al., J. Phys. Chem. Lett. 2, 759 (2011).

MA 23.7 Wed 11:15 H23

Atomic-scale Inversion of Spin Polarisation above an Organic-Antiferromagnetic Interface — •NUALA MAI CAFFREY, PAOLO FERRIANI, and STEFAN HEINZE — Institute of Theoretical Physics and Astrophysics, Christian-Albrechts-Universität zu Kiel

The emerging field of organic spintronics aims to combine the advantages of molecular electronics such as device miniaturisation and fabrication ease with the massive potential for application inherent in spintronics. Potential devices use organic molecules to control and manipulate spin-polarised signals. Such molecules are generally contacted with non-organic materials. As such, it is vital to understand the magneto-organic interface. It has been previously found that even the simplest non-magnetic molecule is capable of inverting the spin polarisation emerging from the clean ferromagnetic surface. We consider here an antiferromagnetic surface: a monolayer of Mn on a W(110) substrate. We perform *ab-initio* calculations in order to investigate the interface between simple organic molecules, both magnetic and non-magnetic, and an antiferromagnetic surface. The molecules considered include benzene (C₆H₆), cyclooctatetraene (C₈H₈) and small transition metal - benzene complexes. Simulated spin-polarised scanning tunnelling microscopy (SP-STM) images are presented. They show that the exact magnitude and sign of the spin polarisation in the vacuum above the molecule is strongly dependent on the bonding details at the interface and due to the antiferromagnetic surface it exhibits a strong intra-molecular spatial dependence.

MA 23.8 Wed 11:30 H23

Spin Crossover in a Vacuum-Deposited Submonolayer of a Molecular Iron(II) Complex — •MATTHIAS BERNIEN¹, DENNIS WIEDEMANN², CHRISTIAN F. HERMANN¹, ALEX KRÜGER¹, DANIELA ROLF¹, WOLFGANG KROENER³, PAUL MÜLLER³, ANDREAS GROHMANN², and WOLFGANG KUCH¹ — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — ²Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany — ³Department of Physics, Universität Erlangen-Nürnberg, Erwin-Rommel-Straße 1, 91058 Erlangen, Germany

Spin-state switching of transition-metal complexes (spin crossover) is sensitive to a variety of tiny perturbations. It is often found to be suppressed for molecules directly adsorbed on solid surfaces. We present X-ray absorption spectroscopy measurements of a submonolayer of [Fe^{II}(NCS)₂L] (L: 1-{6-[1,1-di(pyridin-2-yl)ethyl]-pyridin-2-yl}-N,N-dimethylmethanamine) deposited on a highly oriented pyrolytic graphite substrate in ultrahigh vacuum. These molecules undergo a thermally induced, fully reversible, gradual spin crossover with a transition temperature of $T_{1/2} = 235(6)$ K and a transition width of

$\Delta T_{80} = 115(8)$ K. Our results show that, by using a carbon-based substrate, the spin-crossover behavior can be preserved even for molecules that are in direct contact with a solid surface.

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MA 23.9 Wed 11:45 H23

Single spin-crossover molecules triggered with a STM — •MANUEL GRUBER^{1,2}, TOSHIO MIYAMACHI¹, MARTIN BOWEN², SAMY BOUKARI², ERIC BEAUREPAIRE², and WULF WULFHEKEL¹ — ¹Physikalisches Institut, Karlsruher Institut für Technologie, Germany — ²IPCMS (UMR 7504 Uds-CNRS) and Labex NIE, Strasbourg, France

A nano-scale molecular switch can be used to store information in a single molecule. The conductance of the molecule changes when switched and can be electrically detected. Spin crossover (SCO) molecules consisting of organic ligands around a transition metal ion are known to be switchable between a high- and a low-spin state by external stimuli [1]. It is the ultimate aim to achieve combined spin and conduction switching functionality on the level of individual molecules.

Fe(1,10-phenanthroline)₂(NCS)₂ molecules, SCO complexes, were deposited on Cu(100) and CuN/Cu(100) surfaces and studied with a scanning tunneling microscope (STM) in ultra-high vacuum at 4K.

Both spin species coexist at low temperatures as deduced from spectroscopic STM data. While on bare Cu(100), the molecules cannot be switched between the two spin states, molecules on CuN can individually and reproducibly be switched between a high-spin, high-conduction state and a low-spin, low-conduction state. This difference is explained by the role of the CuN layer to decouple the molecules from the metallic surface [2].

[1] P. Gütllich et al., Chem. Soc. Rev. 29, 419 (2000). [2] T. Miyamachi et al., Nat. Commun. 3, 938 (2012).

MA 23.10 Wed 12:00 H23

Beyond the Heisenberg model: Anisotropic exchange interaction between a Cu-tetraazaporphyrin monolayer and Fe₃O₄(100) — •HANS-JOACHIM ELMERS¹, JULIA KLANKE², EVA RENTSCHLER², KATERINA MEDJANIK¹, DMYTRO KUTNYAKHOV¹, GERD SCHÖNHENSE¹, SERGEY A. KRASNIKOV³, IGOR V. SHVETS³, STEFAN SCHUPPLER⁴, PETER NAGEL⁴, and MICHAEL MERZ⁴ — ¹Institut für Physik, Johannes Gutenberg-Universität Mainz, D-55128 Mainz, Germany — ²Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz, D-55099 Mainz, Germany — ³Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) — ⁴Karlsruhe Institute of Technology, Institut für Festkörperphysik (IFP), D-76021 Karlsruhe, Germany

We investigated the Heisenberg exchange coupling between the single Cu spin of Cu-tetraazaporphyrin deposited on magnetite(100) and the ferromagnetic surface using x-ray magnetic circular dichroism (XMCD). In contrast to the common model we find an anisotropic exchange coupling depending on the orientation of the spin relative to the bonding direction. The exchange coupling is ferromagnetic for magnetization direction perpendicular to the surface and antiferromagnetic for in-plane magnetization direction. The anisotropy of the Heisenberg exchange coupling is attributed to an orbitally-dependent exchange Hamiltonian. We propose that the sign change results from the competition between ferromagnetic superexchange along Fe-N-Cu and antiferromagnetic superexchange along Fe-O-Cu with strength modified by the strong spin-orbit coupling. Funded by COMATT.