MA 19: Molecular Magnetism I

Time: Tuesday 15:00–17:00   Location: HSZ 04

MA 19.1   Tue 15:00   HSZ 04

Molecular orientation of Er(III) cyclooctatetraene-based single-molecule magnets on Ag(100) — ●Vladyslav Romankov[1], Niéli Daffé[1], Diana Vaclavkova[1], Martin Heinrich[1], Matthias Muntwiler[1], Bernard Delley[1], Katie Harriman[2], Muralee Murugesu[2], Moritz Bernhardt[3], Maciej Korzyński[3], Christophe Copéret[3], and Jan Dreiser[1] — [1]PSI, Switzerland — [2]uOttawa, Canada — [3]ETH Zurich, Switzerland

Recently, organometallic lanthanide-(III)-based single-molecule magnets (SMMs) have shown outstanding magnetic properties up to liquid nitrogen temperature [1]. SMMs with planar ligands, like COT^{2-} (cyclooctatetraene anion) and Cp^{*-} (pentamethylcyclopentadienide), are good candidates to form ordered monolayers, but the packing and the molecule-substrate interaction play a vital role in the properties of such molecules when deposited on metal surfaces [2]. In the present work we show how two similar Er(III) SMMs, K[Er(COT)$_2$] and Cp*ErCOT, order very differently on Ag(100). In particular, X-ray linear and magnetic circular dichroism measurements show that the easy axis of K[Er(COT)$_2$] aligns parallel to the surface, while that of Cp*ErCOT SMMs is consistent with a mixed standing-lying phase. Indeed, low-temperature scanning tunneling microscopy reveals that Cp*ErCOT forms alternating rows of standing-up and lying-down molecules, while X-ray photoemission spectroscopy reveals the integrity of both the SMMs and suggests a weak molecule-surface interaction.

References: [1] F. S. Guo et al., Science, **362**, 1400, (2018); [2] C. Wäckerlin et al., Advanced Materials, **28**, 5142, (2016).

MA 19.2   Tue 15:15   HSZ 04

Machine learning based parameterization of magnetic data of single-molecule magnets — ●Zayan Ahsan Ali, Julius Mutschler, and Oliver Waldmann — Physikalisches Institut, Universität Freiburg, D-79104 Freiburg, Germany

Single molecule magnets (SMMs) have attracted a rich volume of research in the last two decades due to their potential applications in magnetic memory and quantum computing. Lanthanide-based SMMs in particular demonstrate promising magnetic retention due to large inherent anisotropies. Their magnetic properties can be parameterized by ligand-field theories involving a set of 28 parameters. Experimental data such as magnetization and susceptibility curves, however, are typically featureless for these materials. Multiple distinct parameter sets can describe the data to equal accuracy, making it a formidable task to determine the model parameters for a compound. In this work, the over-parameterization is tackled by Machine Learning (ML) applied to data simulated for a single-ion model. For dimensionality reduction, a variational autoencoder is used to determine hidden system parameters of the data, and an invertible neural network is used to relate hidden parameters with the model parameters from ligand-field theory. The effectiveness of this ML model in producing consistent sets of ligand-field parameters for novel experimental data is investigated and presented.

MA 19.3   Tue 15:30   HSZ 04

Temperature-dependent Raman spectroscopy studies of a Fe(II) spin-crossover complex — ●Lea Spieker[1], Stephan Sleziona[1], Gérald Kämmerer[1], André Maas[1], Soma Salamon[1], Senthil Kumar Kuppusamy[2], Mario Ruben[2], Uwe Bovensiepen[1], Peter Kratzer[1], Marika Schleberger[1], and Heiko Wende[1] — [1]Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen — [2]Institute of Quantum Materials and Technologies (IQMT), Karlsruhe Institute of Technology

Spin-crossover complexes with a bi-stable spin-state switching in the room temperature regime, influenced by external stimuli such as light, pressure, or temperature, are desirable for future applications, e.g., molecular switches. Combining Raman spectroscopy with optical microscopy, we investigated a Fe(II) complex showing a spin-state switching from a diamagnetic low-spin (S=0) to a paramagnetic high-spin (S=2) state in the room temperature regime ($T_{1/2} = 298$ K) with a broad thermal hysteresis of $\Delta T = 44$ K. Notable molecular bond changes during the temperature-induced spin-state switching are confirmed by Raman spectroscopy measurements combined with density functional theory calculations. In addition, optical microscopy during

heating and cooling allowed us to observe the spin-state switching on a macroscopic scale. We gratefully acknowledge the financial support by CRC 1242 Projects A05, B02, and C05 (Project-ID 278162697).

MA 19.4   Tue 15:45   HSZ 04

Spin transition of spin-crossover molecules supported by tridentate ligands deposited on HOPG — ●Jorge Torres[1], Jan Grunwald[2], Sascha Ossinger[2], Sangeeta Thakur[1], Clara W. A. Trommer[2], Marcel Walter[1], Ivar Kumberg[1], Rahil Hosseinifar[1], Evangelos Golias[1], Sebastien Hadjaj[1], Jendrik Gördes[1], Pin-Chi Liu[1], Chen Luo[3], Lalminthang Kipgen[1], Tauquir Shinwari[1], Florin Radu[3], Felix Tuczek[2], and Wolfgang Kuch[1] — [1]Freie Universität Berlin, Institut für Experimentalphysik, Berlin, Germany — [2]Christian-Albrechts-Universität zu Kiel, Institut für Anorganische Chemie, Kiel, Germany — [3]Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany

In a spin-crossover molecule (SCM) the excitation and relaxation processes can be stimulated by temperature, pressure or light. The latter is known as the light-induced excited spin-state trapping (LIESST) effect. The excitation of the high-spin (HS) and relaxation to low-spin (LS) state can exhibit single- or multi-exponential behavior. Here, we investigate the behavior of different thicknesses of the SCM [Fe{H$_2$B(pz)(pypz)}$_2$] [1] and [Fe{pypypyr}$_2$] deposited on highly oriented pyrolytic graphite (HOPG) by X-ray absorption and differential reflectance spectroscopy. The results show that the amount of molecules in the HS state as a function of temperature at constant illumination presents a sigmoidal behavior. The relaxation rates are discussed in the context of the inverse energy gap law, which is usually invoked to interpret the LIESST behaviour of Fe(II) complexes.

[1] S. Ossinger et al., Inorg. Chem., 2020, 59, 7966-7979

15 min. break

MA 19.5   Tue 16:15   HSZ 04

Observation of exchange interaction in Iron(II) spin crossover molecules in contact with passivated ferromagnetic surface of Co/Au(111) — ●hongyan chen[1], hung-hsiang yang[1], timo frauhammer[1], haoran you[1], qing sun[2], peter nagel[3,4], stefan schuppler[3,4], ana belén gaspar[5], josé antonio real[5], and wulf wulfhekel[1,3] — [1]Physikalisches Institut, Karlsruhe Institute of Technology (KIT), Germany — [2]Laboratory for Electron Microscopy, KIT — [3]Institute for Quantum Materials and Technologies, KIT — [4]Karlsruhe Nano Micro Facility, KIT — [5]Institut de Ciència Molecular, Universitat de València, Spain

Spin crossover (SCO) complexes sensitively react on changes of the environment by a change in the spin of the central metallic ion making them ideal candidates for molecular spintronics. In particular, the composite of SCO complexes and ferromagnetic (FM) surfaces would allow spin-state switching of the molecules in combination with the magnetic exchange interaction to the magnetic substrate. Unfortunately, when depositing SCO complexes on ferromagnetic surfaces, spin-state switching is blocked by the relatively strong interaction between the adsorbed molecules and the surface. Here, the Fe(II) SCO complex with sub-monolayer (sub-ML) thickness in contact with a passivated FM film of Co on Au(111) is studied. In this case, the molecules preserve thermal spin crossover and at the same time the high-spin species show a sizable exchange interaction of more than 0.7 T with the FM Co substrate. These observations provide a feasible design strategy in fabricating SCO-FM hybrid devices.

MA 19.6   Tue 16:30   HSZ 04

Magnetic coupling of guest metallocene molecules with SURMOF-2 host matrix — ●Alexei Nefedov[1], Chun Li[1], Kai Müller[1], Anemar Bruno Kanj[1], Lars Heinke[1], Chen Luo[2], Kai Chen[2], Florin Radu[2], Evangelos Golias[3], Wolfgang Kuch[3], and Christof Wöll[1] — [1]Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany — [2]Helmholtz-Zentrum Berlin für Materialen und Energie, Berlin, Germany — [3]Freie Universität Berlin, Berlin, Germany

Metal-organic frameworks (MOFs) are crystalline and porous, molecular solids consisting of metal nodes and organic ligands. In the case of surface-anchored MOF-2 (SURMOF-2) systems the Cu^{2+} ions are

connected via carboxylate and OH groups in a zipper-like fashion. This unusual coupling of the spin-1/2 ions within the resulting 1-D chains stabilizes a low-temperature ferromagnetic (FM) phase. In this study, the magnetic properties of SURMOF-2 systems (Cu(bdc) and Cu(bpdc)) were investigated using X-ray magnetic circular dichroism both in the absorption and in the scattering geometry. Taking advantage of the element sensitivity of this technique it was established that the magnetic signal originates from Cu^{2+} ions. After loading of SURMOF-2 with metallocene molecules, the magnetic properties of the SURMOF were found to be substantially changed. In the case of nickelocene loading, a polarization effect was found resulting in ferromagnetic ordering of the guest molecules. However, the polarization effect is not observed in the case of manganocene derivatives, these molecules remained in their paramagnetic state.

MA 19.7 Tue 16:45 HSZ 04

Nickelocene molecule as an STM magnetic sensor — •Andres Pinar Sole[1], Oleksandr Stetsovych[1], Pavel Jelínek[1], Jindrich Kolorenc[1], Shaotang Song[2], Jiong Lu[2], Christian Wackerlin[3], and Ales Cahlik[4] — [1]Czech Institute of Physics — [2]University of Singapore — [3]Empa — [4]University of Zurich

Functionalization of the scanning probe of a scanning tunnelling microscopy (STM) with metallocene molecule allows performing spin-sensitive measurements on magnetic systems. Here, as a magnetic sensor, we used a nickelocene molecule (NiCp2) to probe the magnetism on 1D metallorganic chains and graphene nanoribbons (GNR).

In the first part of the work, we examined two derivatives of 1D metallorganic coordination polymers (2,5-diamino-1,4-benzoquinonediimines) on Au(111) [3] with Co or Cr atoms as metal sites respectively. Nickelocene IETS conductance spectrum deformation was observed when approaching the Nc functionalized tip to the Cr sites while no spectra changes were seen on neither Co sites nor ligand sites of the polymers.

In the second part of the work, the Nc functionalized probe was also used to measure the magnetism emerging from the unpaired electron on the edge of a wave-like graphene nanoribbon (GNR) on Au(111).

To understand the IETS from the magnetic sensor, a many-body Hubbard model was proposed. It describes the electron tunnelling through the STM tip, the nickelocene, the magnetic center, and the metallic substrate.