PETER SUMMER SCHOOL

Book of Abstracts

Acknowledgement

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Magnetometric and Spectroscopic Investigation of Iron Extraction from Soils by Siderophore Desferrioxamine B

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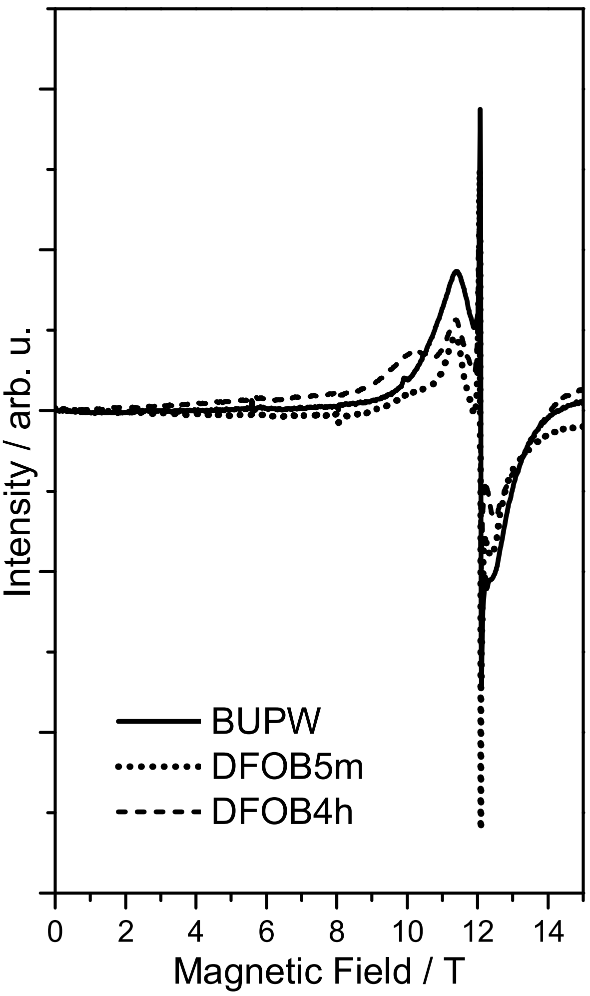
Iron plays an important role as a micronutrient in nature. In many environments, the solubility of ferric oxides and hydroxides is below the amount needed by most plants or microorganisms. To cope with this situation, organisms have developed strategies to enhance iron solubility and mobility. One of these strategies is the formation and subsequent uptake of soluble Fe(III) complexes by exudation of chelating ligands. These molecules are called siderophores and one example is desferrioxamine B (DFOB). [1]

We investigated the extraction of iron from a soil sample (BUPW) with DFOB. High-Frequency Electron Paramagnetic Resonance (HFEPR) spectroscopy and SQUID magnetometry were employed for this purpose. We showed that the formation of the complex takes places and the process and its kinetic can be monitored qualitatively by HFEPR, as can be seen in the increasing peak at 10.2 T for increasing extraction times (spectra recorded at 5 K and 340 GHz). The observations were verified by magnetometry and Mössbauer spectrometry.



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Microwave Spectroscopy of Graphene

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Graphene has a huge potential in various applications because of its unique properties. Its high mobility even at room temperature, its flexibility and its transparency makes it a promising candidate for a range of applications in beyond Moore electronics. Whereas fundamental physical investigations can be carried out on micrometer scale devices there is a demand for large area, uniform, high quality, reproducible and cost-effective graphene for a wide range of applications. In large scale high quality graphene the uniformity is substantial issue, which can differ substantially from smaller size samples. Therefore the determination of the intrinsic charge transport properties of large area graphene samples on wafer scales is an essential prerequisite for applications. Classical methods for determination of transport properties are time consuming and challenging, since contacts and gates are needed. In addition the graphene properties may be influenced.

Here we report Shubnikov-de Haas oscillations on large area quasi free standing epitaxial monolayer graphene detected by contactless microwave absorption. We compare these measurements to conventional contacted Hall bar measurements. Both simultaneous, but independent measurements of the transport properties were evaluated and compared. While the charge carrier density and the Berry phase in both measurements are the same, Hall bar measurements showed higher mobilities than microwave detected measurements. This indicates that both methods have different area sensitivities. This relatively simple and powerful tool can be used for spectroscopic characterization of the sample quality and can help in the production of large area graphene.

Effect of ligand exchange on magnetic anisotropy in pentacoordinate Co(II) field induced SIMs with tri- and tetradentate alkylamine N-donor ligands

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The aim of this contribution is to report on synthesis, crystal structure and magnetic investigations of pentacoordinated Co(II) complexes with alkylamine ligands. Two structural types were studied:

a) complexes with general formula [Co(trenb)X]X‘, with tetradentate ligand trenb = tris[2-(benzylamino)ethyl]amine, and X ;X‘ = monodentate halide ligands/anions.

b) $[Co(L3)(L1)_2]$, [Co(L3)(L)X], $[Co(L3)X_2]$ compounds with tridentate ligand 1,1,4,7,7 – pentamethyldiethylenetriamine. L1 stands for monodentate pseudo halide ligand and X for monodentate halide ligand.

All prepared compounds were characterized by elemental analysis and DC and three of them by AC magnetic measurements. Magnetic data were fitted on spin Hamiltonian involving zero-field splitting term. The crystal structure was determined for prepared compounds. Non-linear relationship between Addison parameter (τ) and axial parameter of magnetic anisotropy (*D*) was suggested.

Comparative study of plasmonic antennas: EBL vs. FIB fabrication

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Plasmonic antennas are metallic nanostructures supporting localized surface plasmon resonances (LSPR) often fabricated by electron beam lithography (EBL) or by focused ion beam (FIB). EBL consists of following steps: (i) resist coating, (ii) electron beam patterning and resist developing, (iii) metal deposition, and (iv) lift-off and final cleaning. Contrariwise, FIB milling consists of two steps: (i) metal deposition and (ii) ion beam milling. The choice of preferred fabrication technique should also consider the time and potential risks of the fabrication process. FIB preparation is simple and more straightforward as no chemistry is used. For individual antennas or small series of antennas it is rather fast. EBL preparation provides generally antennas with higher quality, but the lithographic process induces potential risks of damaging the sample.

We present a comparative study of gold plasmonic disc-shaped antennas fabricated by EBL and FIB. Fabricated antennas were characterized using the transmission electron microscopy including energy dispersive X-ray spectroscopy and electron energy loss spectroscopy (EELS), and using atomic force microscopy. EELS measurements revealed LSPR in both EBL and FIB antennas. The energy of the LSPR is the same for both EBL and FIB antennas, but the LSPR peak magnitude is higher for the EBL antennas. We attribute this observation partly to better structural quality and partly to lower surface contamination of EBL antennas.

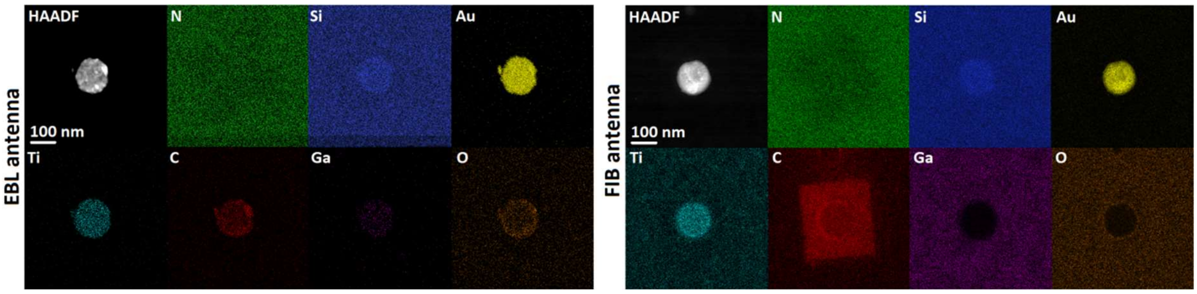

Figure 1: *HAADF micrographs and EDS elemental maps of 140-nm EBL and FIB antenna.*

Spectroscopy of Cobalt-Ferrocene Dimers Towards Nanostructured Single-Molecule Magnets

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A novel approach to electronics is based on two novel disciplines: spin electronics and molecular electronics. A fundamental connection between these two fields can be established using single-molecule magnets (SMMs) [1]. Herein, we report complex spectroscopic investigation of selected SMMs by high frequency electron spin resonance (HF-ESR), ultraviolet-visible (UV-VIS), and x-ray photoelectron (XPS).

Bulk properties of cobalt-ferrocene dimers (CFDs) with linear chemical formula: $[X_2Co(P(C_6H_5)_2C_5H_4)_2Fe$, where X = Br, Cl, and $(P(C_6H_5)_2C_5H_4)_2Fe$ = dppf] were investigated by HF-ESR and allowed us to determine that the Co^{2+} ions are in the high-spin state ($S = 3/2$) with spin Hamiltonian parameters: $g_x = 2.22$, $g_y = 2.22$, $g_z = 2.28$ and zero-field splitting terms: $D = -11.2\ \mathrm{cm}^{-1}$ and $E/D = 0.09$, representing suitable bulk magnetic properties for applications as SMMs [2].

We also performed UV-VIS and XPS measurements on both bulk and nanostructured CFDs. XPS qualitative and quantitative analyses were used to evaluate reference samples consisting of bulk (dppf), $[Co(dppf)Br_2]$, and $[Co(dppf)Cl_2]$. We investigated two batches of samples, first from sublimation in UHV-deposition chamber, second from drop-cast in nitrogen atmosphere.

In conclusion, we found out that it is possible to prepare thin films of intact CFDs by drop-cast in nitrogen atmosphere and evaporation by carefully selecting an appropriate preparation environment and specific solvent in the case of wet-chemistry based methods and by controlling sublimation temperature in the case of the of the UHV-based evaporation.

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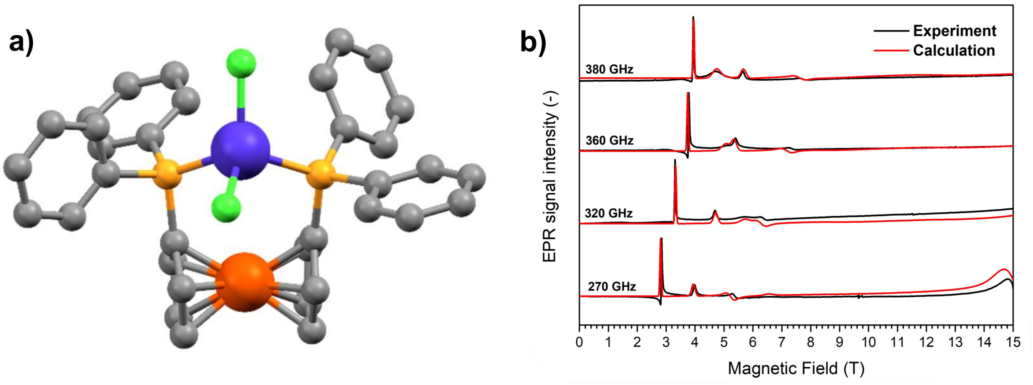

Figure 2: *a) Crystal structure of [Co(dppf)Br*$_2$*], purple: cobalt, green: bromine, orange: iron, yellow: phosphorous, b) HF-ESR spectra of the depicted SMM obtained for four frequencies at 5 K. Black lines represent experimental data and red lines are simulations based on ab initio quantum chemistry models.*

Efficiency of dynamical decoupling using constant time CPMG experiment in two different model systems

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Constant time Carr-Purcell-Meiboom-Gill (CPMG) pulse sequences were applied to two systems, ethanol doped with nitroxyl radical TEMPO and gamma-irradiated trehalose. The aim was to investigate the effect of different electron spin relaxation mechanisms in different systems on the efficiency of the preservation of the phase memory relaxation time T_m by dynamical decoupling and to test whether CPMG sequences can be used to discriminate them. In the case of ethanol, paramagnetic nitroxyl radical TEMPO was applied in the concentration range 0.2-1.1 mM. Trehalose samples were irradiated using X-ray radiation with standard dosages of 5-10 kGy. For both model systems, the measurements on glassy and crystalline type of samples were conducted to investigate impact of disorder as well. For ethanol no dependence of T_m on the concentration of paramagnetic centres and on the length of the used refocusing pulses was observed, implying nuclear spectral diffusion (NSD) as the dominant mechanism of electron spin decoherence [1]. Contrary to the observations in ethanol, no stretched exponential decay was observed when determining T_m in trehalose. In ethanol there was linear increase of T_m with number n of used refocusing pulses in the CPMG sequence. In trehalose the increase of T_m with n was not linear, the saturation effects observed for $n \geq 4$, which suggests that NSD isn't the dominant mechanism of electron spin decoherence. The impact of instantaneous diffusion (ID) in trehalose is supported by the calculation of the concentration of radicals [2]. In conclusion, the efficiency of dynamical decoupling using constant time CPMG experiment strongly depends on the dominant mechanism of electron spin decoherence, therefore it can be used to determine whether NSD or ID is the dominant mechanism of decoherence.

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Integration of Molecular Quantum Bits with Semiconductor Spintronics

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Molecular nanomagnets hold great promise for quantum computing, as they have been shown to exhibit coherence times from tens of microseconds up to almost a millisecond. The molecular nature of these systems offers the possibility for extended chemical tailoring for higher coherence times or surface self-assembly.

However, local addressing of molecular qubits is very challenging and for successful device development, these qubits will need to be interfaced with inorganic and/or organic semiconductor technology. To overcome this challenge, we plan to use (spin polarized) charge carriers with various possibilities to programme/readout of the quantum state of the qubits.

To investigate the possibility of interfacing magnetic molecules with organic semiconductor technology, we are manufacturing hybrid materials made of conducting polymers and molecular qubits. We have successfully observed quantum coherence in the microsecond regime in thin films of these hybrid materials using a custom Fabry-Pérot resonator at 35 GHz. To study the interaction between mobile charge carriers and localized magnetic moments in various systems, we have developed an electrically detected magnetic resonance spectrometer at 9.5 GHz.

For observations of possible coupling between surface-deposited molecular qubits and spin-polarized charge carriers in a conducting channel, we have optimized fabrication of Mn5Ge3 ferromagnetic alloy on highly doped Ge channels.

Development of a dual source 194 GHz EPR spectrometer

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Electron paramagnetic resonance (EPR) benefits from moving to higher frequencies via improved resolution of g-tensors and a reduction of zero-field splitting effects. The hardware challenges presented by moving to higher frequencies are the low microwave irradiation powers currently available and the difficulty incorporating multiple irradiation sources. These limit the capabilities for pulsed correlation experiments that enable structural and dynamic analyses. A quasi-optical approach can minimize microwave power losses throughout the system, addressing the first challenge. This quasi-optical approach was used to implement a dual source functionality in a 194 GHz EPR spectrometer with arbitrary waveform generator capabilities for pulse shaping. A dual microwave source allows for excitation of the electron spins at multiple frequencies, enabling electron-electron double resonance (ELDOR) experiments without source hysteresis effects influencing the resulting EPR signal. ELDOR is essential to investigate the electron-electron interactions in a system. This basic set-up can also act as the basis for distance measurements between electron spins, as determined via double electron-electron resonance (DEER).

Spin dynamics of potential molecular qubits in thin films

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Spin dynamics play an important role for a potential application of paramagnetic transition metal complexes as qubits. The quantum coherence time of a qubit, which is related to how long the qubit can preserve its superposition, is directly related to the phase memory time T_m of a molecular qubit. In the case of diluted paramagnetic transition metal complexes, the limiting factor of T_m is often nuclear spin diffusion caused by protons. It is well known, that deuteration of the surrounding of the spin center increases T_m by approximately one order of magnitude. However, no quantum mechanical qualitative calculations of T_m were carried out on this kind of systems, as one would have to consider a huge bath of nuclei making the calculations very demanding. Fortunately, we were able to adopt a literature know method treating nuclear spin diffusion in the P@Si system to our molecular systems. This method preserves the quantum mechanical nature of nuclear spin diffusion without assuming a statistical model for fluctuating fields. We used this method to simulate the primary echo decay of $\mathrm{Cu(dbm)_2}$ in $\mathrm{Pd(dbm)_2}$ using the positions of the protons (and thus the dipolar couplings) obtained from the crystal structure of $\mathrm{Pd(dbm)_2}$ alone. The simulation fits perfectly in this case, as well as for $\mathrm{Cu(mnt)_2^{2-}}$ in $\mathrm{Ni(mnt)_2^{-2}}$ and other systems where nuclear spin diffusion is the main source of decoherence.

We believe that for real world applications, thin films of molecular qubits will play an important role in order to interface the qubits with our current semiconductor technology. Therefore, we started to investigate thin films of paramagnetic molecules to get a better understanding of spin dynamics in thin films. As a first step, we developed a Fabry-Pérot resonator allowing us to measure large substrates covered with nanometer thin films. Our first results on 10 nm – 100 nm films of BDPA diluted in PMMA Films on silicon show that the relaxation times are nearly independent with respect to the film thickness proving the excellent robustness of the system.

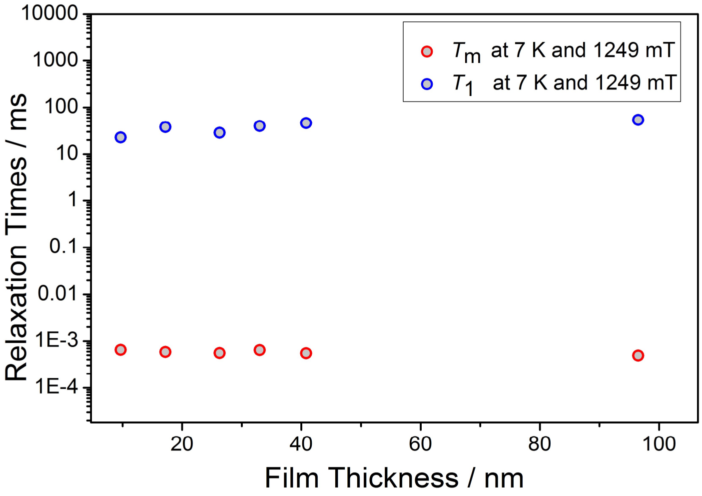

Figure 3: *Spin-Spin and Spin-Latice relaxation times of 5% BDPA in PMMA films with increasing thickness on silicon measured with our homebuilt pulsed Q-Band EPR spectrometer at 7 K using a Fabry-Pérot resonator.*

Development of Fourier Transform Infrared Spectroscopy in high magnetic field

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Far-infrared (FIR) energy region in high magnetic fields is of particular importance, since it covers the magnetic resonances such as spin resonance and cyclotron resonance. Therefore FIR spectroscopy in high magnetic fields presents an ideal experimental technique that can probe and elucidate magneto-optical properties of novel materials, such as 2D materials. This technique provides complementary information to commonly used electronic transport measurements, magnetization and thermodynamic properties measurements [1]. The FIR spectroscopy in the high magnetic field is a very important tool in the characterization of materials such as Single-Molecule Magnets (SMMs). It allows studying Electron Paramagnetic Resonance (EPR) of SMMs with very large zero-field splitting, mainly based on transition metal complexes or lanthanides, in which commonly used EPR systems do not provide experimental access to the magnetic resonance transitions. The main goal of this project is to develop the Fourier Transform Infrared (FTIR) spectroscopy in high magnetic field via magneto-optical setup (see **Figure 4)**, in which FTIR spectrometer is coupled to a superconductive magnet. This setup will allow us to broaden the spectral region to FIR, which lies adjacent to the microwave region, and thus broaden the EPR microwave range for investigations of SMMs.

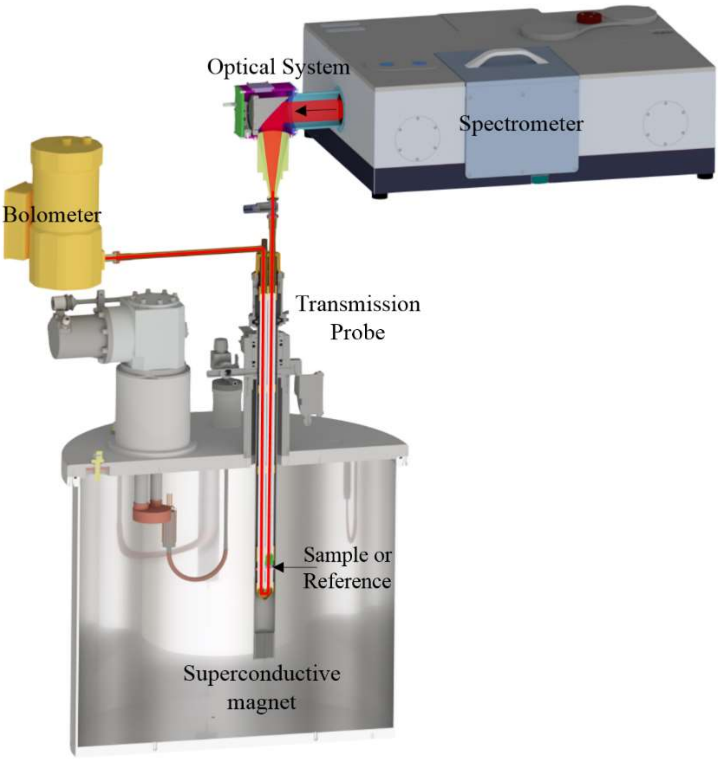

Figure 5: *The magneto-optical setup: FTIR spectrometer is coupled to a superconductive magnet.*

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The use of natural extracts as the source of antioxidants

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It is known that oxidation reactions could produce free radicals, which can lead to wrinkling, photoaging, elastosis, drying, and pigmentation of the skin [1]. Plants are sources of broad spectrum of active compounds. Some of them have antioxidant activity and are preferably used in cosmetics for improving skin care [2]. Important part of them are polyphenols and flavonoids [3].

This work aims at extraction and preservation of chosen plant extracts into phospholipid nanoparticles to prolong their activity and stability. Extracts were characterized in terms of polyphenols and flavonoids, UV protective properties and antioxidant activity, which was evaluated spectrophotometricaly as well as with EPR. Prepared extracts were after that encapsulated into phospholipid nanoparticles.

Encapsulation efficiency of liposomes was characterized by spectrophotometry. Particle size and size distribution were observed by dynamic light scattering and colloid stability by determining zeta-potential. Safety of prepared particles with plant extracts were tested by MTT and LDH assay on human keratinocytes. Influence of functionalized particles on cell viability was evaluated. Genotoxicity was tested using SOS Chromotest.

Extracted active compounds had high antioxidant activity as well as UV protective effect. Encapsulation of active compounds into liposomes were successful. The most of prepared particles did not possess cytotoxic effect on human keratinocytes. No genotoxicity was found in tested particles.

Encapsulation of active compounds from plants into lipomas can be an interesting way how to prolong their activity. Besides UV protecting effect for natural cosmetics they can find use as preservants in cosmetics as well as in food industry.

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Dynamical effects of the intermolecular exchange interaction on the electron paramagnetic resonance of a Cu(II) coordination polymer

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Copper complexes are good model systems for studying magnetic interactions between spins inside molecules and between neighbouring molecules in coordination polymers. These materials are relevant to several fields such as molecular magnetism, catalysis, pharmaceutics, sensing, and spintronics. In this work, we investigate magnetic interactions among Cu(II) spin dimers inside and between molecular units using electron paramagnetic resonance (EPR) at 9.5 GHz (X-band) and 35 GHz (Q-band). The weak intermolecular exchange *J'* via hydrogen bonds between molecules establishes two different phases: decoupled dimeric units and long-range dynamically interacting dimeric units. Such a phase transition occurs in the crossing of EPR allowed transitions tuned by the direction of the magnetic field. Exchange couplings smaller than 1 mK can be measured selectively by EPR in oriented single crystals and we demonstrate how these dynamical effects also influence the powder spectrum in such samples. We carry on research to extend our results to samples with different ratios between the magnitude of magnetic interactions such as the intramolecular exchange coupling J_0 and the anisotropic spin-spin interaction D in the high magnetic field/ high-frequency regime.

Terahertz Magnetic Resonance Spectrometer for Electron Spin Dynamics Investigations

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During the last decades, a magnetic resonance method called High Frequency Electron Paramagnetic Resonance (HFEPR) spectroscopy experienced a boom in the fields of chemistry, biology, materials science, and physics [1], with commercially available spectrometers allowing measurements at fixed frequencies and usually up to 263 GHz.

The aim of our work is to set up and develop a general purpose state-of-the-art broadband Electron Paramagnetic Resonance spectrometer based on THz rapid frequency scans that will operate at frequencies from 80 GHz to 1100 GHz, at temperatures from 1.8 K to 300 K, and at magnetic fields up to 16 T. High spectral resolution is achieved by higher magnetic fields and higher frequencies, opening options to explore spin dynamics and other phenomena not previously accessible by current technologies.

Furthermore, we present a completely new concept of detection based on the rapid frequency sweeps that allow performing spin relaxation investigations at THz frequencies, which are currently either unexplored or undeveloped [2]. Our novel design will allow multi-frequency relaxation studies of a variety of samples ranging from bulk materials, over powdered and single crystal to air sensitive samples in liquid solutions. The new design will stimulate the development of new materials as well as lead to the development of new MRI (Magnetic Resonance Imaging) applications using HFEPR via Dynamic Nuclear Polarization (DNP) measurements.

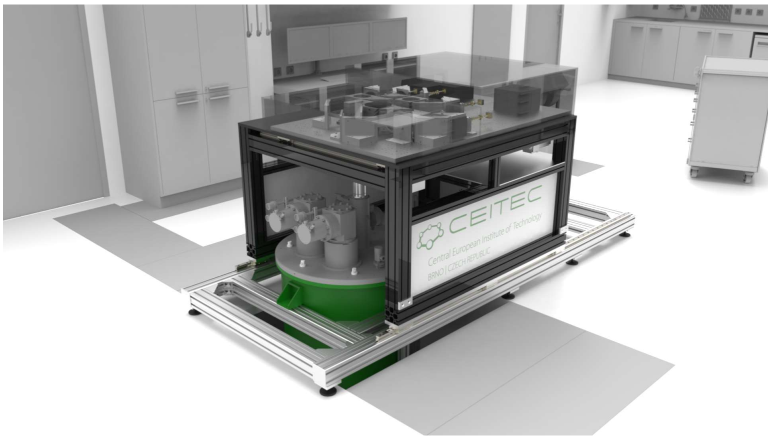

Figure 6: *Model of Electron Paramagnetic Resonance spectrometer based on THz rapid frequency scans*

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Multi-frequency rapid-scan high-field EPR

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The development of the rapid scan technique was historically connected to the problem of the enhancement of the signal-to-noise ratio in Nuclear Magnetic Resonance (NMR), but it did not find wide application in NMR or EPR due to the rapid development of high power radiofrequency and microwave sources for pulse methods. However, the past decade is marked by the intense development of solid-state THz instruments, which has made it possible to perform EPR spectroscopy at very high frequencies and fields. Unfortunately, the output power of such tunable THz sources is not sufficient for the implementation of pulse methods. Consequently, the rapid scan is the only affordable technique for multi-frequency investigation of spin dynamics at THz frequencies. To our best knowledge, this EPR technique was demonstrated at frequencies up to 94 GHz only.

Here we present results of the first successful implementation of multi-frequency rapid-scan EPR in the (sub)millimetre frequency range. The experiments were performed using a home built HFEPR spectrometer operated in induction mode. The spectrometer does not require any resonator, and therefore we are able to use frequency sweeps instead of magnetic field sweeps as it was done previously in the majority of experiments. The main advantages of the frequency domain are the extremely high sweep rates (thousands of THz/s) and absence of eddy currents in the sample holder and/or resonator

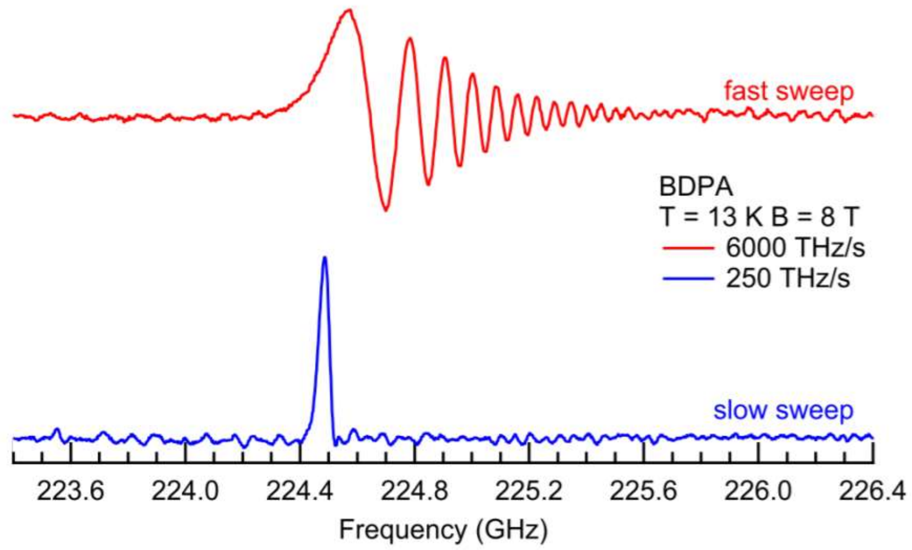

Figure 7: *Spectrum of BDPA (dissolved in toluene) at low (blue) and high (red) sweep rates*

The Static and Dynamic Electronic and Geometric Structure of Catalysts in Mesoporous Polymers

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In contrast to enzymes, organometallic catalysts often show a lack of stereoselectivity and productivity but resource depletion and an increase in environmental restrictions require optimal catalytic processes. In this project, catalysts are introduced into highly defined mesopores where we expect higher selectivities arising from the high level of order in the pores and the influence of mesopores themselves. One of the goals is to explore the cooperative effect of the support, as well as the influence of the pore size, pore polarity, tether length and rigidity of the system. In order to do so, the electronic and geometric structure of the investigated catalyst, (dppf)Fe(CO)$_3$, needs to be understood on a fundamental level. This allows the explanation of the structural changes after the introduction into the mesopores. Here, spatially-resolved EPR can be of great interest. This system was chosen because it is paramagnetic in its oxidised from, thereby allowing multiple spectroscopic methods which are well established in the group. These include EPR, MCD and SQUID magnetometry. Furthermore, Mößbauer spectroscopy will be a useful tool to investigate and characterise the iron atoms in the molecule. The collected data indicates the occurrence of two isomers of which the temperature dependent ratio was investigated via EPR spectroscopy. In a next step the catalyst is to be linked to the different mesoporous systems, consisting of polymers and covalent organic frameworks. This can be realised through click chemistry via azide groups attached to the catalyst and terminal alkine groups in the mesopores.

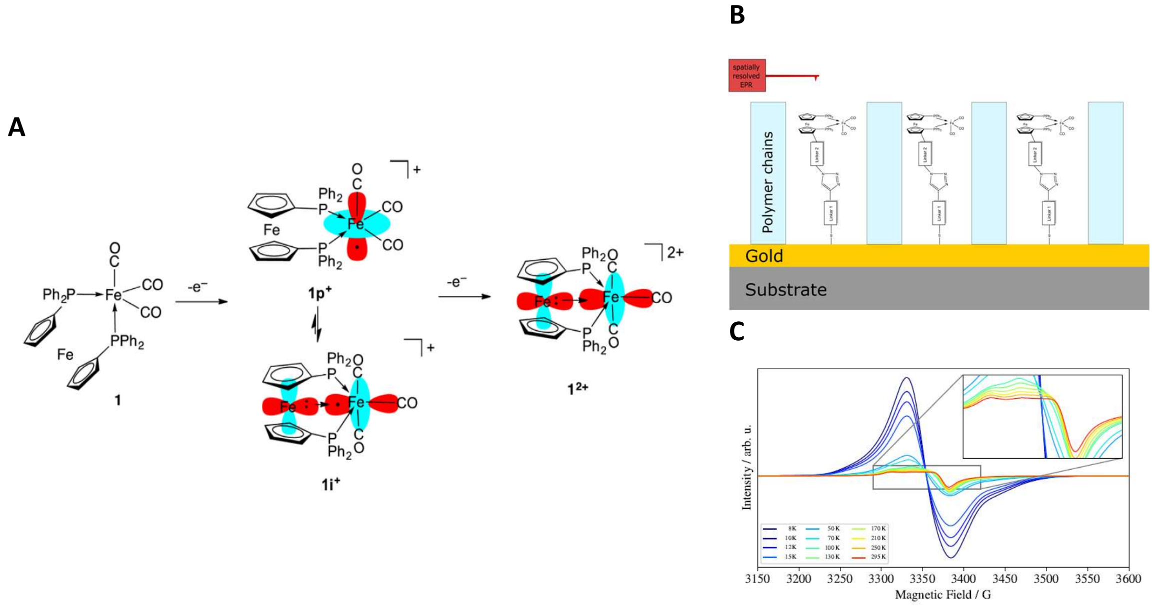

Figure 8: *A: Simplified orbital structure of the two systems for the singly oxidised and the doubly oxidised species.*[1] *B: Project idea to link the catalyst to the mesoporous structure. C: cw X-band measurement of oxidised (dppf)Fe(CO)$_3$ as a powder at different temperatures. The ratio of the two systems changes with the temperature, thereby changing the appearance of the signal.* *[1] Ringenberg, Wittkamp, Apfel, Kaim, Inorg. Chem.,* ***56****, 7501–7511 (2017)*

Impact of sulfur vacancies on electronic structure of MoS_2

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Molybdenum disulfide(MoS_2) is a novel two-dimensional layered semiconductor which has attracted substantial attention due to the unique structure and intriguing properties. MoS_2 has shown great potential in novel electronics, optoelectronics and spintronics devices [1-3]. The performance of the applications are affected significantly by the quality and defects of MoS_2 [4-5]. Sulfur vacancy is the most abundant defect in MoS_2 and it is often considered as the origin of n-type behaviour in MoS_2. However, recently some reports claimed that sulfur vacancy is irresponsible for the n-type doping of MoS_2 based on theoretical calculations [6]. The role of sulfur vacancies in MoS_2 is still unclear. Hence, we investigated the effects on the electronic structures of sulphur vacancy in MoS_2 systematically. Experimental studies were performed with high quality MoS_2 crystals grown by flux method [7]. The crystals were annealed to introduce sulfur vacancies. Angle resolved photoemission spectroscopy (ARPES) and density functional theory (DFT) calculation were used to record and calculate the electronic structure of MoS_2. A defect state close to the valence band maximum (VBM) was observed after sulfur vacancies were introduced into MoS_2. These results indicate that sulfur vacancies may cause p-type doping of MoS_2. Our result brings new possibilities and understanding to electronic structure engineering of MoS_2 by controlling the defects.

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