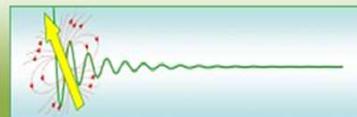


SPP 1601

New Frontiers in Sensitivity for EPR Spectroscopy:
from Biological Cells to Nano Materials



DFG Priority Programm SPP 1601

***New Frontiers in Sensitivity for EPR Spectroscopy -
From Biological Cells to Nano Materials***

Abstract Book

Hirschegg, October 4 - 8, 2016



Venue

Darmstädter Haus
Oberseitestraße 38
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Schedule

October 4, 2016

-16:30 Arrival

17:00-17:50 Overview 1

17:50-18:30 Guest 1

18:30-19:30 *Dinner*

19:30-21:00 SPP talks

October 5, 2016

7:30-8:30 *Breakfast*

8:30-9:20 Overview 2

9:20-10:00 Guest 2

10:00-10:30 SPP talk

10:30-11:00 *Coffee*

11:00-13:00 SPP talks

Posters and discussions

18:30-19:30 *Dinner*

19:30-20:00 Guest N

20:00 **SPP assembly**

October 6, 2016

7:30-8:30 *Breakfast*

8:30-9:20 Overview 3

9:20-10:00 Guest 4

10:00-10:30 SPP talk

10:30-11:00 *Coffee*

11:00-13:00 SPP talks

Posters and discussions

18:30-19:30 *Dinner*

19:30-20:10 Guest 3

20:10–21:10 SPP talks

October 7, 2016

7:30-8:30 *Breakfast*

8:30-9:20 Overview 4

9:20-10:00 Guest 5

10:00-10:30 SPP talk

10:30-11:00 *Coffee*

11:00-13:00 SPP talks

Posters and discussions

18:30-19:30 *Dinner*

19:30-20:10 Guest 6

20:10-21:10 SPP talks

October 8, 2016

7:30-9:00 *Breakfast*

Departure



Contributions

Overview lectures (45 min)

Prisner, Thomas: Advances with AWG and Optimum Control Pulses

Schiemann, Olav: New Spin Labels

Steinhoff, Heinz-Jürgen: In cell EPR

Suter, Dieter Microresonators

Guest lectures (35 min)

Blank, Aharon: A new approach for distance measurements between two spin labels in the >10 nm range

Choi, Taeyoung: Magnetic dipole-dipole sensing at atomic scale using electron spin resonance STM

Doorslaer, Sabine van: Light-induced EPR of fullerene-free blends for organic solar cells

McCracken, John: The Aromatic Amino Acid Hydroxylases: Exploring the Details of a Catalytic Cycle with EPR Spectroscopy

Stoll, Stefan: Effects of coherent rectangular and sech/tanh pump pulses in DEER experiments with up to three pump pulses.

Walsworth, Ronald: Nanoscale Magnetic Sensing Using NV-Diamond

Progress reports (25 min)

Bejenke, Isabel (AG Bennati): Electron-nuclear cross polarization in 1H and 2H ENDOR: further developments and first applications to real samples.

Deichmüller, Jacqueline AG Havenith Sensing of Light induced Magnetization by Magnetic Resonance Force Microscopy

Eng, Julien (AG Neese): Magnetic relaxation in single ion magnets.

Friedlaender, Stefan (AG Pöpl) Continuous wave single crystal electron paramagnetic resonance of cupric ions in the zn(ii) doped porous coordination polymer $\text{Cu}_{2.965}\text{Zn}_{0.035}(\text{btc})_2$.

Häberle, Matthias (AG Anders) CMOS voltage-controlled oscillators for PoC and rapid scan ESR experiments.

Hagelueken, Gregor: Actin induced activation of the T3SS effector YopO studied by EPR spectroscopy.

Harneit, Wolfgang: From EDMR to recombination spectroscopy.

Hrubesch, Florian (AG Brandt): Efficient electrical spin readout of NV- centers in diamond.

Kraffert, Felix (AG Behrends): Transient EDMR: Recent Progress and Challenges Ahead.

Gerstmann, Uwe: Radio frequency STM-spectroscopy for single-molecule spin resonance

Mathies, Guinevere: Efficient cross-effect DNP with trityl-nitroxide radicals

Möser, Jannik (AG Schnegg) Combined High- and Low-Frequency Electrically Detected Magnetic Resonance.

Neugebauer, Petr: High Frequency ESR Spectroscopy in Field and Frequency Domains.

Pribitzer, Stephan (AG Jeschke) The Revival of TRIER.

Schnegg, Alexander: FD-FT THz-EPR for Magneto-Structural Correlations in Integer and Half-Integer High Spin Transition Metal Ions.

Schöps, Philipp (AG Prisner) Pushing SIFTER towards new application

Shiddiq, Muhandis (AG Suter) Microresonators for High-Frequency Optically-Detected Magnetic Resonance.

Sperlich, Andreas: Observation of Spin States involved in Organic Electroluminescence Based on Thermally Activated Delayed Fluorescence.

Weichselbaumer, Stefan (AG Hübl): pEPR Experiments at Millikelvin Temperatures using Adiabatic Pulses.

Zeier, Robert (AG Glaser): From modeling to optimization in multi-spin systems.

Poster presentation

Assafa, Tufa Enver (AG Bordignon): Orthogonally spin labelling Bcl-2 proteins for in-organelle and in-cell EPR.

Auth, Michael (AG Sperlich): Ambipolar Charge Transfer In Single-Wall Carbon Nanotube Based Bulk-Heterojunctions.

Berndhäuser, Andreas (AG Schiemann): In-cell measurement of the Trityl-Iron distance in CYP101 via RIDME.

Bloos, Dominik (AG Slagern): Application of High Frequency Microwave Spectroscopy on Electron Transport of Solid State Materials.

Bondarenko, Elena (AG Steinhoff) Modular bio-orthogonal site-directed spin labeling for EPR spectroscopy in vivo and in vitro.

Bunzmann, Nikolai (AG Sperlich): Investigation of spin states in organic light emitting diodes based on thermally activated delayed fluorescence via multi-frequency ELDMR and EDMR techniques.

Gerstmann, Uwe: NV centers in SiC polytypes: identification, modeling and basic properties

Godt, Adelheid: Gd(III) and Mn(II) complexes and molecular rulers for testing and development of EPR techniques.

Jeschke, Gunnar: Optimization of shaped pulses for EPR- Dos and Don'ts.

Kallies, Wolfgang (AG Glaser): Optimum Control Pulses – Convergence and Applications.

Kern, Michal (AG Slagern): Integration of molecular quantum bits with semiconductor spintronics.

Kultaeva, Anastasiia (AG Pöppl): EPR Study of the Isostructural Elastic Layer-Structured Metal-Organic Framework (ELM-11).

Masaaki Saito (AG Neese): Linear-scaling electronic structure methods which can be applicable to large, real-life molecules in the domain-based local pair-natural orbital (DLPNO) framework.

Ronneburg, Hendrik (AG Risse): Current efforts to set up an EDMR experiment working under ultra-high vacuum (UHV) conditions to investigate defects on semiconductor surfaces.

Schnegg, Alexander: FD-FT THz-EPR with Improved Versatility and Spectral Range.

Prisner, Thomas

Some questions and remarks regarding AWG pulses

Thomas F. Prisner, Institute of Physical and Theoretical Chemistry and Center of Biomolecular Magnetic Resonance, Goethe University Frankfurt

In this talk I want to address and discuss some important aspects that fast phase, amplitude and frequency modulated pulses offer in the field of EPR spectroscopy. The availability to modulate microwave pulses on the sub-nanosecond time scale by arbitrary waveform generators open up new avenues for pulse sequences and experiments in all fields of pulsed EPR, ranging from Fourier-transform EPR to hyperfine- and dipolar spectroscopy. Of course such pulses also challenges traditional concepts of spectrometer design and thinking and need improved microwave technology to achieve its full power. General basics, requirements and limitations will be discussed and a rather personal vision on the potential of these new tools for EPR will be given.

Schiemann, Olav

New Spin Labels

Steinhoff, Heinz-Jürgen

Site-directed spin labeling EPR spectroscopy in vivo

H.-J. Steinhoff

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Paramagnetic labeling in combination with NMR- and EPR spectroscopy offers many approaches for studying the conformation and dynamics of biomolecular complexes in vitro and in vivo. Site-directed spin labeling (SDSL) EPR spectroscopy has emerged as a powerful technique and has been mainly based on site-directed cysteine exchange mutagenesis followed by in vitro modification with a cysteine specific spin label. Since a general versatile solution for SDSL in living cells remains to be established, EPR spectroscopy of spin labeled biomolecules in vivo has utilized the artificial integration of in vitro-labeled proteins or nucleic acids into cells by microinjection, by osmotic shock, by electroporation, or by incubation. First successful attempts of in cell SDSL have been reported. The talk will review challenges and state-of-the-art approaches of in cell SDSL EPR.

Suter, Dieter

Planar microresonators for EPR of small samples

Most types of electron spin resonance rely on resonant structures for converting microwave signals to oscillating magnetic fields that drive the relevant transitions. In the case of inductive detection, the same structures convert the precessing magnetization into an oscillating voltage signal that can be detected. The efficiency of the excitation and the detection sensitivity can therefore be significantly enhanced by designing microwave resonators that are optimised for the specific samples. In particular, in the case of small samples, the sensitivity is increased significantly if the size of the resonator is comparable to the size of the sample. It is thus essential to use sub-wavelength structures whose size can be adjusted over a wide range of sample sizes and EPR frequencies. Manufacturing of the resonators relies on lithographic techniques, which can be adapted to sample sizes of less than 1 μm . This review introduces the design principles and discusses loss mechanisms and optimization criteria. It also summarizes some specific implementations and applications to various types of samples.

Blank, Aharon

A new approach for distance measurements between two spin labels in the >10 nm range

Aharon Blank, Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa, 3200003, Israel

ESR spectroscopy can be efficiently used to acquire the distance between two spin labels placed on a macromolecule by measuring their mutual dipolar interaction frequency, as long as the distance is not larger than ~10 nm. Any hope to significantly increase this figure is hampered by the fact that all available spin labels have coherence time (T_2), which is limited to the microseconds range, proving limited window during which the dipolar interaction frequency can be measured. Due to the inverse cubic dependence of the dipolar frequency over the labels' separation distance, evaluating much larger distances, e.g. 20 nm, would require to have T_2 that is ~200 microsecond, clearly beyond any hope. Here we propose a new approach for greatly enhancing the maximum available measured distance by relying on another type of dipole interaction mediated mechanism called spin diffusion. It operates and can be evaluated during the spin lattice relaxation time, T_1 (commonly in the ms range), rather than only during T_2 . Up until recently the observation of spin diffusion in electron spin system was considered experimentally impractical. However, recent developments in our lab enabled its direct measurements by pulsed ESR employing intense short magnetic field gradients, opening the door for subsequent utilization of these capabilities. The presentation will present the subject of spin diffusion, shows how it can be directly measured, and theoretically discuss how interspin distance, even in the range of 20- 30nm, could be accurately extracted from the spin diffusing measurements.

Choi, Taeyoung

Magnetic dipole-dipole sensing at atomic scale using electron spin resonance STM

Magnetometry having both high magnetic field sensitivity (energy resolution) and nanoscale spatial resolution has been of great interest and an important goal for applications in diverse fields covering physics, chemistry, material science, and biomedical science. The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy.

Here, we successfully combine electron spin resonance (ESR) and STM, coherently driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)) [1]. A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10 μ eV) while the ESR linewidth is in the range of only a few MHz (~10 neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions.

When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show $r^{-3.024 \pm 0.026}$ distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-angstrom and one hundredth of Bohr magneton precision [2].

Our ESR-STM may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism.

We gratefully acknowledge financial support from the IBM and Office of Naval Research.

[1] S. Baumann*, W. Paul*, T. Choi, C.P. Lutz, A. Ardavan, A.J. Heinrich, *Science* **350**, 417 (2015)

[2] T. Choi et al., *manuscript in preparation*

Doorslaer, Sabine van

Light-induced EPR of fullerene-free blends for organic solar cells

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Over the last decade, the power conversion efficiencies of bulk heterojunction organic solar cells have increased steadily, demonstrating their great potential for future photovoltaic applications. One of the big challenges is to find alternative small acceptor molecules that can be used to circumvent the problems of the widely used fullerene acceptors that are expensive and have poor absorption properties and limited chemical versatility. Multi-frequency CW and pulsed EPR is used to characterize charge transfer in blends of donor polymers (such as MDMO-PPV and P3HT) and a range of electron-accepting oligomers. DFT computations are performed to identify negative polarons created upon light illumination. These results will be compared to the differences in conversion efficiencies exhibited by the different blends.

McCracken, John

The Aromatic Amino Acid Hydroxylases: Exploring the Details of a Catalytic Cycle with EPR Spectroscopy

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The aromatic amino acid hydroxylases catalyze the hydroxylation of the side-chains of the aromatic amino acids, phenylalanine, tyrosine and tryptophan, and are essential for proper function of the liver and central nervous system. This chemistry requires the binding of the amino acid substrate, a tetrahydrobiopterin cofactor, and molecular oxygen to an Fe(II) active site. In the enzyme's resting state, the metal ion features an octahedral coordination geometry with one coordination face, consisting of the side chains of two histidines and a glutamic acid, provided by the protein, and the remaining three coordination sites occupied by water ligands. While the diverse chemistry catalyzed by non-heme iron enzymes is often attributed to the facial arrangement of these open coordination sites, the proposed catalytic mechanism for these enzymes calls for the initial binding of both substrate and the tetrahydrobiopterin cofactor as second coordination-sphere ligands. In our studies, we have used nitric oxide, NO, as a substitute for O₂ for the purpose of poisoning the high-spin Fe(II) site in an S=3/2 {FeNO}⁷ form that is amenable to X-band EPR spectroscopy. Using ²H-Electron Spin Echo Envelope Modulation (ESEEM) and ¹H – Hyperfine Sublevel Correlation (HYSCORE) methods we have been able to measure ligand hyperfine couplings from substrate, cofactor and coordinated water ligands that have provided important details regarding the catalytic mechanisms of Phenylalanine and Tyrosine Hydroxylases.

Stoll, Stefan

Effects of coherent rectangular and sech/tanh pump pulses in DEER experiments with up to three pump pulses

The recent introduction of shaped pulses to DEER spectroscopy has led to significant enhancements in sensitivity. The application of DEER has so far relied on the presence of an incoherent pump channel to average out most undesired coherent effects of the pump pulse(s) on the observer spins. However, in fully coherent EPR spectrometers that are increasingly used to generate shaped pulses, the presence of coherent pump pulses means that these effects need to be explicitly considered. We examine the effects of coherent rectangular and sech/tanh pump pulses in DEER experiments with up to three pump pulses. We show that, even in the absence of significant overlap of the observer and pump pulse excitation bandwidths, coherence transfer pathways involving both types of pulses generate spin echoes of considerable intensity. These echoes introduce artefacts, which, if not identified and removed, can easily lead to misinterpretation. We demonstrate that the observed echoes can be quantitatively modelled using simple spin quantum dynamics including instrumental transfer functions. We analyze the echo crossing artefacts and propose efficient phase cycling schemes for their suppression. This enables the use of advanced DEER experiments on fully coherent EPR spectrometers.

Walsworth, Ronald L.

Nanoscale Magnetic Sensing Using NV-Diamond

Harvard University, Department of Physics, Cambridge, MA 02138 USA

Nitrogen vacancy (NV) color centers in diamond provide an unparalleled combination of magnetic field sensitivity and spatial resolution in a room-temperature solid, with wide-ranging applications in both the physical and life sciences. NV centers can be brought into few nm proximity of magnetic field sources of interest while maintaining long NV electronic spin coherence times (~millisec), a large (~Bohr magneton) Zeeman shift of the **NV** spin states, and optical preparation and readout of the NV spin. Recent applications of NV-diamond magnetometry include magnetic imaging of living cells, single proton MRI, single protein NMR, mapping magnetic signatures in >4 billion-year-old meteorites and early-Earth rocks that inform theories of solar system and Earth formation, and magnetic sensing of single neuron action potentials. I will provide an overview of this technology and its applications.

Anders, Jens

CMOS voltage-controlled oscillators for PoC and rapid scan ESR experiments

Jens Anders, University of Ulm, Institute of Microelectronics

Oscillator-based spin detection has recently gained significant attention in the ESR community due to its excellent spin sensitivity in cw-ESR experiments with operating temperatures down to 4 K.^{1,2} In the talk it will be explained how a voltage-controlled oscillator (VCO), i.e. an oscillator whose oscillation frequency can be controlled by a tuning voltage V_{TUNE} , can be used to significantly simplify the experimental setup of cw-ESR experiments, enabling battery-operated true point-of-care (PoC) ESR spectroscopy. Furthermore, it will be discussed how VCOs can be used to perform frequency modulated rapid scan ESR experiments with very high repetition rates significantly beyond 1 MHz. Measured results from a prototype VCO realized in CMOS technology with an operating frequency around 14 GHz and a tuning range of approximately 1.5 GHz demonstrate the excellent performance achievable with the proposed approach. Finally, since the utilized VCOs are integrated in standard CMOS technologies, they fully benefit from speed improvements associated with technology scaling, rendering the approach scalable up to the highest commercially available ESR frequencies around 260 GHz. Results from a first G-band prototype operating around 160 GHz demonstrate this excellent scaling potential.

1. Anders et al., J. Magn. Res., 2012, 217, p. 19-26
2. Gualco et al., J. Magn. Res., 2014, 247, p. 96-103

Assafa, Tufa Enver

Orthogonally spin labelling Bcl-2 proteins for in-organelle and in-cell EPR

Tufa Assafa¹, Stephanie Bleicken¹, Sukhendu Nandi¹, Ana J. García-Sáez², Andrzej Rajca³ and Enrica Bordignon¹.

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³ Department of Chemistry, University of Nebraska, USA

There is recent interest in pushing biophysical EPR from an in-vitro to an in-vivo context. Efforts have been made to test the compatibility of spectroscopically distinct spin labels for in-cell orthogonal labelling of Bcl-2 proteins. Newly synthesized maleimido and iodacetamido gem-diethyl nitroxide spin labels[1] were tested on double cysteine mutants of T4-lysozyme. The dynamics of the new spin-labeled side chains were probed via cw-EPR and their ability to report on intramonomer distances is shown via DEER. Tests on the ability of the new nitroxide spin labels to label the Bcl-2 proteins Bax, Bid and Bcl-XL will be presented, together with corresponding activity assays: a step towards investigating the Bcl-2 interactome in the context of cell death. The first labelling tests with functionalized Gd-DOTA labels will be also presented, in order to create orthogonal spin labelling pairs in Bcl-2 proteins, increasing the information received per sample. Equivalent experiments are conducted on labelled BH3 peptides of the Bcl-2 proteins Bim and Bad. Active Bcl-2 proteins are incubated with isolated mitochondria from Sprague Dawley rat liver to compare with the data in liposomes. In a parallel effort, FLAG-tagged Bcl-2 proteins were tested for their ability to be introduced into mammalian cells by electroporation.

References

[1] Y. Wang, et al., *Org Lett* **2014**, 16, 5298.

Bejenke, Isabel

Electron-nuclear cross polarization in ^1H and ^2H ENDOR: further developments and first applications

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Electron-nuclear cross polarization (eNCP) is a method that transfers electronic spin polarization to nuclear spins.¹ We have combined this approach with electron-nuclear double resonance (ENDOR) spectroscopy to address sensitivity issues, such as the ENDOR signal dependence on the nuclear T_{1n} , encountered in standard (Davies or Mims) ENDOR methods. CP-edited ENDOR utilizes eNCP to pre-polarize ENDOR transitions and subsequently detect this polarization via a conventional ENDOR read-out. In the last years, we demonstrated by theoretical and experimental investigations that the signal-to-noise ratio of ^1H -ENDOR can be improved significantly by our CP approach.^{2,3} Recently, the performance of CP-ENDOR as compared to standard Davies ENDOR have been demonstrated with studies on single crystals of malonic acid radical as well as on frozen solution spectra of the stable tyrosyl radical in ribonucleotide reductase.⁴ We are now expanding eNCP and CP-ENDOR to the low gamma nucleus ^2H , which is relevant in ENDOR spectroscopy for detection of H-bond interactions, as well as to further applications on real protein samples. Here we present first theoretical and experimental results on ^2H and some preliminary data on ribonucleotide reductase and YF1 protein with photo-accumulated flavin semiquinone radical. To this aims, the collaborations within the SPP1601 framework with Prof. R. Bittl (Berlin) and Prof. S. Glaser (TUM) groups are essential.

References:

1. V. Weis, M. Bennati, et al, J. Chem. Phys. 200, 113, 6795-6802.
2. R. Rizzato, I. Kaminker, S. Vega, M., Bennati, Mol Phys 2013, 111, 2809-2823.
3. R. Rizzato, M. Bennati, PCCP 2014, 16 (17), 7681-7685.
4. R. Rizzato, M. Bennati, ChemPhysChem 2015, 16 (18), 3769-3773.

Deichmüller, Jacqueline

Sensing of Light induced Magnetization by Sensing of Light induced Magnetization

Jacqueline Deichmüller¹, Arpad Rostas², Tarek Al Said², Christoph Baer³, Kerstin Oernd³, Erik Schleicher², Stefan Weber² and Martina Havenith¹

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Many functions of biological systems cannot be unraveled without the knowledge of the mechanisms on the nanometer-scale. Over the past decades an extensive effort has therefore been made pushing the limits of magnetic resonance force microscopy (MRFM) based methods to a resolution of single spins [1]. Temperature and magnetic field dependencies hamper this objective enormously. We present the implementation and first application of a novel approach called Light induced Magnetization sensed by Magnetic Resonance Force Microscopy (LIMRFM). Light induced magnetic forces, in the regime of attonewtons, are detected with the aid of a ferromagnetic nanometric cantilever. The application of light excitable paramagnetic chromophore spin samples in LIMRFM has the advantage of strong initial spin polarizations even under ambient conditions. The sample excitation into the first paramagnetic triplet state is conducted by laser irradiation from the diamagnetic ground state ($S = 0$) into the first excited state ($S = 1$). Inter system crossing of the electron into the first triplet state results in a sufficient net magnetization even at room temperature. The existence of an external magnetic field leads to a triplet sublevel splitting, while spin inversions within the triplet sublevels are initiated by a microwave magnetic field which satisfies the resonance condition. We will show first results of LIMRFM measurements of the triplet model system pentacene at room temperature. Our aim is to introduce LIMRFM as a promising tool for spin detection and to extend the existing MRFM detection schemes to new applications.

[1] D. Rugar, R. Budakian, H. J. Mamin, B. W. Chui, Nature 2004

Eng, Julien

Magnetic relaxation in single ion magnets

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(mihail.atanasov@cec.mpg.de)

Mots Clés Méthodes (2 max): Master equation, Spin Hamiltonian

Mots Clés Applications (2 max): Spin relaxation, Single Ion Magnets

Mots Clés Autres (2 max): Spin-vibronic coupling

Single ions magnets (SIM) are complexes with open d- or f- shells with high magnetic anisotropy. A magnetic field induces a net magnetic moment of the SIM which persists for some time after removal of the external magnetic field. The relaxation time of this induced magnetic moment depends on the interaction of the anisotropic spin with its environment, namely, by exchange of heat with the thermal bath via molecular and lattice vibrations. To study the relaxation of such systems, we solve the Master equation for the density matrix of the spin system interacting with a phonon bath. The Hamiltonian (H) is built as the sum: $H = H_S + H_R + H_{int}$, where H_S is the spin-Hamiltonian¹ at the equilibrium geometry, H_R describes the environment of the spin system, which includes the molecular vibrations and the phonons, as well as the coupling between them.

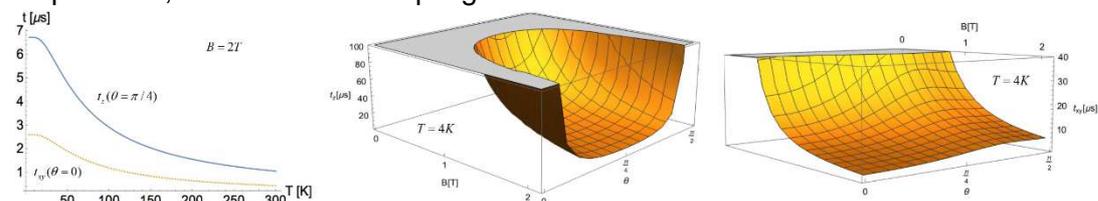


Figure 1 Application to $[\text{CuCl}_4]^{2-}$. Left: Temperature dependence of the relaxation times. Right: Orientation and intensity of the field dependence of the relaxation times.

Our method has been applied to the $[\text{CuCl}_4]^{2-}$ complex as a test-case. The g-tensor as well as the spin-vibronic coupling elements are extracted from first-principle quantum chemistry methods using the ORCA package². Solving the Master equation for this system yields relaxation time of the good magnitude but a wrong temperature dependence for low temperature ($T < 25K$)^{3,4,5} and exponential decay for higher temperatures.

1 J.H. Van Vleck, Phys. Rev., 1940, 57, 426

2 F. Neese, WIREs Comput. Mol. Sci., 2012, 2, 73

3 A.C. De Vroomen, E.E. Lijphart, N.J. Poulis, Physica, 1970, 47, 458

4 J.H. Van Vleck, J. Chem. Phys., 1939, 7, 72

5 R.D. Mattuck, M.W.P Strandberg, Phys. Rev., 1960, 119, 1204

Friedlaender, Stefan

Continuous wave single crystal electron paramagnetic resonance of cupric ions in the Zn(ii) doped porous coordination polymer Cu₂.965Zn_{0.035}(btc)

Stefan Friedländer,¹ Felix Bolling,¹ and Andreas Pöpl¹

¹ Universität Leipzig, Abteilung für Magnetische Resonanz Komplexer Quantenfestkörper, Fakultät für Physik und Geowissenschaften, Linnéstr. 5, 04103 Leipzig, Germany

In the presentation the latest dielectric resonator aided research on metal-organic framework (MOF) is presented. EPR investigations of MOF systems are often restricted to powder materials because single crystals are only available in sub-millimeter sizes. However, the elucidation of the structure of the adsorption complexes requires knowledge about the orientation of the magnetic tensors which can only be deduced from single crystal experiments.¹ We show that the use of dielectric resonators enhances the sensitivity and in that way offers the opportunity for studies of these porous, low density materials at low temperatures and non-ambient atmospheres in conventional EPR spectrometers.² Here we will present our studies of Cu(II) containing small MOF single crystals. The local paramagnetic Cu(II) ion probes were used to identify the magnetic g and A tensor orientation with respect to the crystal axes and to monitor changes at gas adsorption experiments for the first time in EPR for MOFs. DFT calculations have been conducted to interpret the measurement data; we explored that the g and A tensor orientations of the porous, low density material are tilted upon gas adsorption which is represented by a line broadening effect in the angular resolved single crystal EPR spectra.

1. Friedländer, S.; Pöpl, A. et al. Single Crystal Electron Paramagnetic Resonance with Dielectric Resonators of Mononuclear Cu²⁺ Ions in a Metal–Organic Framework Containing Cu₂ Paddle Wheel Units. *The Journal of Physical Chemistry C* 2015, 119, 19171–19179.

2. Friedländer, S.; Pöpl, A. et al. Dielectric Ceramic EPR Resonators for Low Temperature Spectroscopy at X-band Frequencies. *Applied Magnetic Resonance* 2015, 46, 33–48.

Gerstmann, Uwe PI

Radio frequency STM-spectroscopy for single-molecule spin resonance

Recently, a new technique of radio frequency scanning tunneling spectroscopy (rf-STs) have been introduced by Müllegger et al. [1] allowing subnanometer spatial resolution combined with single-spin sensitivity. By utilizing resonant rf current, spin transitions can be induced in single molecules directly adsorbed on Au(111) substrates. As a prototype example for such a molecular spin quantum dot, the archetypal terbium double-decker phthalocyanine molecule (TbPc₂) has been used.

At readily accessible magnetic fields (few mT) and temperatures (5 K) efficient spin transitions beyond the electromagnetic dipole selection rules (up to $\Delta J_z = \pm 12$ and $\Delta l_z = \pm 3$) can be probed. With the help of density functional theory (DFT) calculations, we show that electron tunneling via magnetic molecular orbitals is crucial for the rf-STs-based spin excitation [2]. Most of the observed high spin excitations are far away from avoided level crossings, ruling out a dominant role of quantum tunneling of magnetization. The intriguing evidence for efficient higher spin excitations in rf-STs points towards an involvement of mechanical degrees of freedom for fulfilling the fundamental angular momentum conservation [3].

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[2] Müllegger, Rauls, Tebi, Gerstmann et al., Phys.Rev. B **92**, 220418(R) (2015).

[3] Garanin, Chudnovsky, Phys.Rev. B **92**, 02441 (2015).

Hagelueken, Gregor

Actin induced activation of the T3SS effector YopO studied by EPR spectroscopy

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The bacterium *Yersinia pestis* is the causative agent of plague. Although *Yersinia* infections can be effectively treated with antibiotics, they remain a threat due to the problem of the increasing antibiotic resistance of bacteria. *Yersinia* have evolved a set of molecular tools to defend themselves against attacks by the human immune system. For example, *Yersinia* are able to avoid phagocytosis by utilizing their syringe-like type-three-secretion-system (T3SS) to inject a set of six Yop proteins (*Yersinia* outer proteins) into the attacking macrophage. Inside the macrophage, the Yop proteins interfere with several important cellular processes. As a result, the macrophage is no longer able to engulf and destroy the bacterium and instead even protects it from further attack (1). One of the Yop proteins, YopO (also known as YpkA), is subject of this study. When injected into the host cell, YopO specifically interferes with the regulation of the actin cytoskeleton in at least three different ways: 1) The C-terminus of YopO binds to Rac1, an actin cytoskeleton regulating GTPase and acts as a guanidine nucleotide dissociation inhibitor. 2) YopO binds to monomeric actin, forming a stable 1:1 complex. This interaction with actin leads to autophosphorylation and activation of the N-terminal kinase domain of YopO. 3) The bound actin molecule is then used as a bait to recruit and phosphorylate various cellular targets that are involved in cytoskeletal dynamics.(2, 3)

To investigate the actin induced activation of YopO, we have conducted PELDOR distance measurements and cw-EPR experiments on the spin labelled YopO/Actin complex. We use trilateration to follow the domain movements and found that the activation of YopO by actin is a complicated process that involves major structural rearrangements.

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Harneit, Wolfgang

From EDMR to recombination spectroscopy

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EDMR is an established tool in the magnetic resonance community, but what can it contribute to a quantitative understanding of organic solar cell operation?

We measured well-characterized fullerene-polymer organic solar cells under realistic operating conditions at room temperature. We detect a quantitative correlation of EDMR signal strengths with independently determined recombination currents in these devices, showing that there is a wealth of information to be extracted from EDMR data in a rather complicated physical situation. Using both, spectroscopic EDMR information and IV analysis, we can distinguish interfacial from bulk effects and reconstruct direct electron-hole recombination mechanisms that do not show up in EDMR due to a combination of spin and localization lifetime effects.

Furthermore, I will present first conclusive evidence for EDMR detection of the N@C60 electron spin in a strongly coupled pair with C60(+) cations, detected at room temperature in micro-crystal devices. The strong dipolar coupling indicates long-lived next-neighbor pairing, which is new in organic EDMR. We discuss consequences for both, organic solar cell research and EDMR theory.

Hrubesch, Florian M.

Efficient electrical spin readout of NV- centers in diamond

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Using pulsed photoionization the coherent spin manipulation and echo formation of ensembles of NV- centers in diamond are detected electrically realizing contrasts of up to 17 %. The underlying spin-dependent ionization dynamics are investigated experimentally and compared to Monte-Carlo simulations. This allows the identification of the conditions optimizing contrast and sensitivity which compare favorably with respect to optical detection [1].

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Kraffert, Felix

Transient EDMR: Recent Progress and Challenges Ahead

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In this talk we report on the progress of our project on the development and application of transient electrically detected magnetic resonance (transient EDMR) spectroscopy. We present recent EDMR results from fully processed thin-film solar cells using polymer:fullerene blends as absorber layers and discuss the interplay between spin-dependent processes and charge transport in these devices.

The second part of the talk will be devoted to triplet excitons, which are encountered in various materials used in high-efficiency organic solar cells. Triplet excitons can, on the one hand, be involved in loss mechanisms and reduce the yield of separated charge carriers. On the other hand, they play an important role in processes such as singlet fission that provide the possibility of building solar cells with quantum efficiencies exceeding 100 %, i.e., devices delivering more than one electron and one hole per absorbed photon. Using transient EPR spectroscopy we study intermediate paramagnetic states generated upon fission of one singlet exciton into two separated triplet excitons. Particular emphasis will be given to strongly coupled triplet pairs in organic molecules that form quintet states.

Mathies, Guinevere

Efficient cross-effect DNP with trityl-nitroxide radicals.

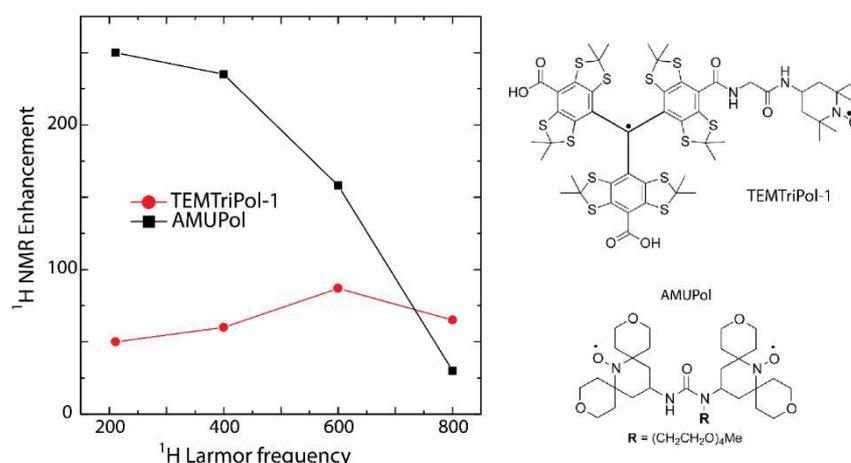
Guinevere Mathies,^a Marc A. Caporini,^b Frédéric Mentink-Vigier,^c Vladimir K. Michaelis,^a Yangping Liu,^d Melanie Rosay,^b Marc Baldus,^e Gaël de Paëpe,^c and Robert G. Griffin^a
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Dynamic nuclear polarization (DNP) is rapidly maturing as a method to enhance the sensitivity of nuclear magnetic resonance (NMR) experiments. In DNP, paramagnetic species are introduced into the NMR sample, often in the form of stable radicals or "polarizing agents". Via microwave irradiation at or near the electron Larmor frequency, the electron spin polarization is transferred to the nuclei, thereby enhancing the nuclear spin polarization and hence the NMR signal intensity. If DNP and NMR experiments are performed at the same magnetic field and temperature, a maximum signal enhancement of $\gamma_e/\gamma_{1H} = 658$ can be achieved for protons, where γ_e and γ_{1H} are the gyromagnetic ratios of electrons and protons, respectively.

The cross-effect (CE) is the form of DNP that is currently most successfully applied in magic-angle spinning (MAS) NMR structural studies. For CE DNP, biradicals, which are typically bis-nitroxides, are the most efficient polarizing agents. The chemical structure of these bis-nitroxides determines the NMR signal enhancement. The bis-nitroxide polarizing agent for CE DNP that currently gives the highest CE DNP enhancements is AMUPol, see Figure 1.

We investigated the performance of trityl-nitroxide biradicals, called "TEMTriPols", as polarizing agents for CE DNP and found that they do not only give higher enhancements at the highest magnetic fields (see Figure 1),¹ but they also don't suffer from the detrimental depolarization effect.^{2,3} Compared to bis-nitroxides, trityl-nitroxide biradicals have a strong exchange interaction, J . We realized that this makes CE DNP more efficient as long as the total electron-electron interaction remains small compared to the ¹H Larmor frequency: $|-1/2d - J| < \omega_{01H}$. Our work has hereby provided a new guideline for the development of polarizing agents for CE DNP.

Figure 1: Field dependence of the CE DNP enhancement for the biradical polarizing agents AMUPol and TEMTriPol-1. All samples contained 10 mM biradical and 1 M ¹³C-urea in a frozen glassy matrix of d₆-glycerol:D₂O:H₂O 60:30:10 v:v:v (a.k.a. „DNP juice“). Enhancements are determined by comparing the signal strengths of ¹H-¹³C cross-polarization MAS NMR experiments with and without microwave irradiation.



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Möser, Jannik

Combined High- and Low-Frequency Electrically Detected Magnetic Resonance

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Electrically detected magnetic resonance (EDMR) is a versatile tool for probing spin-dependent charge transport and recombination processes: it provides sensitivities that are higher by several orders of magnitude in comparison to conventional EPR detection. In addition, EDMR is highly selective to those paramagnetic states affecting electronic transport and is thus the ideal spectroscopic method for studying performance-limiting defects in thin-film devices such as solar cells or transistors.

Recently, a 263 GHz/ 9.4 T EDMR set-up was presented [1], which improves the spectral resolution as compared to X-band frequencies. To differentiate between field-independent and field-dependent broadening mechanisms, and to analyze field dependencies of transport processes, multi-frequency experiments are required, ideally carried out using the same set-up to maintain the sample environment (e.g., illumination, electrical contacts). Therefore, we complemented the 263 GHz/ 9.4 T set-up with a detection scheme for EDMR in the range of 1 to 600 MHz, by integrating an RF coil into the 263 GHz sample probe. This approach enables EDMR at frequencies differing by three orders of magnitude within a single set-up. Here, we present first multi-frequency EDMR results and highlight their capability to unravel overlapping line-shape contributions in amorphous silicon solar cells.

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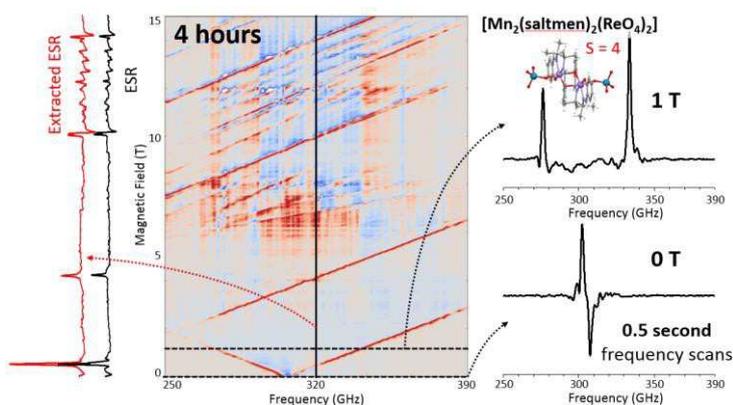
Neugebauer , Petr

High Frequency ESR Spectroscopy in Field and Frequency Domains

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Rodolphe Clérac² and Joris van Slageren¹

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Electron Spin Resonance (ESR) is a powerful technique to investigate electronic and magnetic properties of various materials. ESR at THz frequencies is of great interest in view of the large inherent spectral resolution and the possibility to investigate molecular systems with large magnetic anisotropies. We will present the recent progress in development of the combined High Frequency Field and Frequency Domain THz Electron Spin Resonance (HFESR/FDMR) spectrometer capable to investigate the electronic and magnetic properties of molecular systems, thin films and bulk materials in the very broad frequency range of 85-1100 GHz. The achieved FDMR measurement speed of less than 100 ms enables us to map the ESR signal in both field and frequency domain. A high resolution field vs. frequency map (10k x 10k points) can be obtained in very short time for full frequency band allowing to extract classical ESR spectra. Furthermore, the HFESR/FDMR setup was extended by possibility to study electron transport properties under microwave irradiation in solid state materials.



Pribitzer, Stephan

The Revival of TRIER

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The TRIER experiment has been tried ten years ago with monochromatic rectangular pulses at X-band frequencies and with the aim of measuring angles between electron spin-electron spin vectors. Although for model systems correlation peaks in 2D spectra could be seen and clearly assigned to the presence of more than two spins in the system, initial experiments were never followed up. This was mainly because sensitivity did not appear to be sufficient for measurements on biological systems and resolution of angles between spin vectors was poor in cases where the three distances differed significantly from each other.

There are two main reasons for assuming that the problems can be overcome now. First, sensitivity of DEER has increased by an order of magnitude by going from X-band to Q-band DEER. Second, sensitivity of TRIER depends on the product of the three excitation probabilities for three distinct fractions of spin packets. By changing from monochromatic rectangular pulses to passage pulses, improvement in excitation probability for each individual band of spin packets is now to be expected.

It may be possible to directly convert background-corrected two-dimensional time-domain data to a distance correlation map using multi-dimensional regularization.

Schnegg, Alexander

FD-FT THz-EPR for Magneto-Structural Correlations in Integer and Half-Integer High Spin Transition Metal Ions

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Zero field splittings (ZFS) provide important information about functional high spin states in e.g. proteins, synthetic catalytic complexes as well molecular nanomagnets (MNM) as single molecule magnets. Interest in ZFS is mainly triggered by two reasons. First, they determine the magnetic properties of MNM molecular nanomagnets and s. Secondly, ZFS can be employed as structural probes in transition metal ion complexes. In transition metal ions (TMI) ZFS may range from below $\sim 10^2$ cm⁻¹ (hundreds of MHz, e.g., in highly symmetric MnII complexes) to above $\sim 10^4$ cm⁻¹ (several THz, e.g., in octahedral CoII) have been observed. As a result, ZFS can induce spin- energy level splittings that are too large to be detected by conventional EPR techniques. Though we recently demonstrated that these cases are accessible limitation can be lifted by synchrotron-based Frequency Domain Fourier Transform THz-EPR (FD-FT THz-EPR). This method allows for mapping of the EPR transition energy/magnetic field landscape, in the range from 3 to 200 cm⁻¹ (100 GHz – 7 THz) and from -11 T to 11 T.

FD-FT THz-EPR set-up, which allows for mapping of the EPR transition-energy/magnetic-field landscape, from 3 to 200 cm⁻¹ (100 GHz – 7 THz) and from -11 T to 11 T.

Herein, we demonstrate how very large ZFS in integer-spin mono nuclear MnIII and CoI complexes can be extracted demonstrate for a MnII and and a CoI, both in S = 1 state, how very large ZFS can be determined bybased on advanced FD-FT THz-EPR measurements in combination with frequency- domain EPR simulations. In addition, we will discuss how complementary FD-FT THz-EPR and quantum-chemical calculations can be used to systematically study magneto-structural correlations in Co complexes with zero-field EPR ground state splittings up to THz frequencies and beyond.

Schöps, Philipp

Pushing SIFTER towards new application

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SIFTER (single-frequency technique for refocusing dipolar couplings)¹ is a not often used pulsed EPR (electron paramagnetic resonance) technique to measure distances between spin labels. However, it is possible to achieve a higher signal to noise ratio with SIFTER compared to PELDOR (pulsed electron electron double resonance, also called DEER)^{2,3} and DQC (double-quantum coherence)⁴. Drawbacks such as small modulation depths, artifacts resulting from inefficient pulse inversion and an ambiguity in the definition of the background function, have made previous SIFTER experiments ineffective. Here we show that it is possible to overcome the first two drawbacks by utilizing broadband pulses with nitroxide spin labels at X/Q - band frequencies⁵ or by using spin labels with narrow spectral width, for example triarylmethyl based radicals (TAM or trityl)⁶. The ambiguity in the definition of the background function is a general problem for single frequency techniques. By applying a three pulse sequence we were able to measure the non-mono exponential part of the SIFTER background and hence obtain a more quantitative description. Furthermore in SIFTER the background can be minimized by using small concentrations and broadband pulses leading to a large modulation depth. The high excitation efficiency achievable with broadband-SIFTER for nitroxides at X-band frequencies, made it also possible to excite multi-spin effects in systems consisting of more than two nitroxide radicals, which might be useful to quantify oligomeric states of proteins.

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Shiddiq, Muhandis

Microresonators for High-Frequency Optically-Detected Magnetic Resonance

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Planar microresonators have better conversion efficiency than conventional resonators and higher sensitivity for small samples^{1,2}. We present new designs for high-frequency optically-detected magnetic resonance (ODMR) experiments. The existing planar microresonator designs are based on the microstrip model that requires metallization on the rear side of the substrate. This back-metallization makes incorporating laser in ODMR experiments difficult. A possible solution to this problem is to build coplanar waveguide (CPW) microresonators that require metallization only on one side. We will discuss CPW microresonators' geometry and coupling technique to produce high microwave magnetic fields at the sample position for high frequency setup.

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Sperlich, Andreas

Observation of Spin States involved in Organic Electroluminescence Based on Thermally Activated Delayed Fluorescence

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Organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) have high potential for economical and sustainable lighting applications. The efficiency of the TADF pathway is only partially governed by the spin statistics of injected electrons and holes, in which the intermediate exciplex state at the interface of two molecules is formed in the emissive singlet spin configuration with a probability of only 25%, while 75% of excitations are in a non-radiative triplet state. The most commonly used approach to access the triplet states are phosphorescent materials containing a heavy metal atom like iridium or platinum. The strongly increased intersystem crossing (ISC) rate yields internal efficiencies of emission as high as 100%. In a recently introduced class of materials, the energetic separation between the singlet- and triplet exciplex spin configurations is in the range of thermal energy, enabling an efficient reverse intersystem crossing (RISC) from triplet- to singlet states without the use of heavy metals. In this study, we report the first application of electroluminescence detected magnetic resonance (ELDMR) techniques on TADF materials and indubitably proof the involvement of spins in the emergence of TADF electroluminescence. Temperature dependent studies of bilayer devices revealed that such spin-dependent processes of light emission are truly thermally activated.

Weichselbaumer, Stefan

pEPR Experiments at Millikelvin Temperatures using Adiabatic Pulses.

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Pulsed electron paramagnetic resonance at temperatures comparable to or below the level splitting naturally offers larger sensitivity due to a close to unity polarization of the spin ensemble. At these temperatures superconducting microwave circuits offer minimal microwave power dissipation, low noise, and small mode volumes which further improve the detection sensitivity. Additionally, this regime is generally unexplored with respect to spin relaxation and coherence times.

We present pulsed electron paramagnetic resonance (EPR) spectroscopy on a spin ensemble of phosphorous donors in isotopically purified ²⁸Si using superconducting niobium lumped element microwave resonators. These combine high quality factors and small mode volumes. In particular, we perform EPR in the so-called strong coupling regime, where excitations are coherently exchanged between the phosphorus spin ensemble and the microwave resonator. In our presentation, we focus on coherence time measurements and discuss the impact of the resonator on the obtained results. Additionally, we highlight experimental aspects originating from the geometry and in particular the B1 field inhomogeneity of the microwave resonator. We further present initial results in the direction of the implementation of adiabatic pulses, which are known to be able to compensate these B1 field inhomogeneities.

Zeier, Robert

From modeling to optimization in multi-spin systems.

We discuss the analysis and optimization of control pulses in multi-spin systems. In particular, we present analytically derived, time-optimal pulses for electron-nuclear polarization transfers [1] which improve on previously known approaches. We highlight prerequisites and techniques for modeling and simulation of spin systems in general. And additional methods then enable numerical optimizations, and finally analytic approaches. We also outline how fundamental symmetries of spin systems might limit the potential of control pulses.

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Auth, Michael

Ambipolar Charge Transfer In Single-Wall Carbon Nanotube Based Bulk-Heterojunctions

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The exceptional electrical conductivity of Single-Wall Carbon Nanotubes (SWNT) makes them potentially interesting to improve charge transport in organic photovoltaics (OPV). Additionally, their near infrared absorption bands can improve the spectral response of conventional polymer-fullerene bulk-heterojunctions. Until now, only few OPV devices containing purified semiconducting SWNTs were reported and characterized regarding the charge transfer properties of solar cell absorbers. Also the use of doped SWNTs for optoelectronic devices is a promising field for future application. For this study we used purified and n-doped semiconducting (6,5)-SWNT samples, which we firstly investigated regarding their doping properties. Therefore, we performed quantitative Electron Paramagnetic Resonance (EPR) measurements using a CuSO₄ spin standard. Our results confirmed exceptional purity of (6,5)-SWNTs with respect to unintentional doping, dangling bonds or catalyst residue. The doping level of intentionally n-doped SWNTs is under investigation right now. Furthermore, we tested purified (6,5)-SWNTs in combination with known OPV donors and acceptors, namely the fullerene acceptor PC60BM and the conjugated polymer P3HT. With EPR, we found specific signatures for charge carriers localized on either (6,5)-SWNTs, P3HT or PC60BM and revealed the potential ambipolarity of (6,5)-SWNTs, leading to either hole transfer from PC60BM or electron transfer from P3HT. The properties of surfaces and interfaces of solids play an important role for a variety of technologically important fields ranging from semiconductor devices to heterogeneous catalysis. The role of defects on these surfaces and interfaces is particularly crucial to understand the properties of these systems. A major step is the microscopic understanding of these properties, which is still challenging due to the large complexity of most technologically used surfaces or interfaces and the lack of appropriate methodology. To this end the investigation of model surfaces under well-defined ultrahigh vacuum conditions provides a possibility to address some of these issues. EPR spectroscopy has proven to be a very versatile method to investigate paramagnetic point defects on semiconductor surfaces and interfaces, however, the conventional detection scheme suffers from insufficient sensitivity to cope with the low defect density of high quality devices. However, electrically detected magnetic resonance (EDMR) has shown to be able to overcome this sensitivity gap and was used successfully in the past to characterize defects in semiconductor devices and in particular at interfaces of such systems.

In this contribution we will present our current efforts to set up an EDMR experiment working under ultra-high vacuum (UHV) conditions to investigate defects on semiconductor surfaces. Recent advancements and challenges of a working set up as well as first successful steps towards an investigation of single crystal silicon surfaces will be discussed.

Berndhäuser, Andreas

In-cell measurement of the Trityl-Iron distance in CYP101 via RIDME.

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Structure determination of biomacromolecules under in-cell conditions is a relevant yet challenging task. EPR distance measurements have proven to be a valuable tool in this endeavor. Trityl radicals are highly persistent and exhibit a long relaxation time, thus allowing to overcome many limitations to which nitroxide spin labels are subjected to. Here, we present the in-cell measurement of the Trityl-Iron distance in CYP101 via RIDME.

Bloos, Dominik

Application of High Frequency Microwave Spectroscopy on Electron Transport of Solid State Materials

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Among the multiple experimental methods for the investigation of the electronic structure of materials and molecules, High Frequency Electron Paramagnetic Resonance (HF-EPR) is an outstanding method, because of its high g-value resolution and the access to large energy splittings. Additionally, the HF-EPR setup can be used to study electron transport properties in solid state materials.

We will present the recent progress in development of the HF-EPR Spectrometer in Stuttgart. The achieved measurement speed of up to less than 100 ms in frequency domain enables us to map the EPR signal in both field and frequency domain. A map with high resolution (10k x 10k points) can be obtained in less than 4 h and can be used to extract classical field domain EPR spectra in the given frequency range. Besides EPR, we used the spectrometer to measure electron transport of solid state materials. Measurements of graphite showed unexpected oscillations at high fields, which is a hint for a flat band near the Fermi level of graphite, caused by ABC stacking or topological defects. Finally we were able to measure the evolution of weak localization in SiC buffers, which are used as substrates for epitaxial graphene.

Bondarenko, Elena

Modular bio-orthogonal site-directed spin labeling for EPR spectroscopy in vivo and in vitro

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Site-directed spin labeling (SDSL) EPR spectroscopy has emerged as a powerful technique to study the structure and conformational dynamics of biomolecules in vitro. The application of this technique in vivo poses two major problems: (i) Specificity of the labeling reaction and (ii) stability of the paramagnetic species¹. Our current approach to address these issues includes “click chemistry”², a highly specific and biocompatible reaction between azide and alkyne moieties, in combination with the site-directed incorporation of unnatural amino acids into proteins. With GFP as a model protein site-directed spin labeling was performed in *E. coli* cells. Complexes of Gd³⁺, introduced in 2007 as potential spin labels³, are stable in the reducing intracellular environment. We show that these spin labels provide valuable information about side chain mobility and interspin distances extracted from cw EPR spectroscopy.

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Bunzmann, Nikolai

Investigation of spin states in organic light emitting diodes based on thermally activated delayed fluorescence via multi-frequency ELDMR and EDMR techniques

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The major drawback of conventional fluorescent organic light emitting diodes (OLEDs) is the fact, that only 25% of injected electrons and holes form emissive singlet excitons, whereas 75% form longliving triplets, which decay non-radiatively. However, if the used materials are designed to exhibit an energy splitting ΔE_{ST} between the singlet and triplet state in the order of thermal energy $k_B T$, reverse intersystem crossing (RISC) from triplets to singlets is strongly enhanced. Therefore, so-called thermally activated delayed fluorescence (TADF) is induced, allowing for a dramatic increase of efficiency, which is why TADF OLEDs provide high potential for economical and sustainable light sources. In order to investigate the role of spins in the TADF process, electrically and electroluminescence detected magnetic resonance (EDMR, ELDMR) techniques are applied. Transitions between triplet substates, which are split in an external magnetic field, are driven by a tunable microwave source, realized by a non-resonant stripline. By evaluating the dependence of multi-frequency ELDMR and EDMR spectra on changes in experimental conditions, detailed information of the investigated spin system can be obtained.

Gerstmann, Uwe

NV centers in SiC polytypes: identification, modeling and basic properties

U. Gerstmann (Uni Paderborn)

The NV center in diamond has been studied for decades due to its potential applications in quantum computing and nano-sensing. In particular silicon carbide (SiC) provides an interesting alternative, providing direct equivalents in form of nitrogen-donor silicon-vacancy (NCVSi) pairs. Since SiC exists in many different polytypes it gives a wide playground for various NV centers with different optical and symmetry properties.

Here, we present recent results on NV- spin-triplet centers in the three polytypes 3C (the direct diamond equivalent), 4H and 6H. Based on photo-EPR spectroscopy at cryogenic to room temperatures, comparative DFT calculation are performed whereby the full set of EPR parameters, g-tensors, hyperfine splittings as well as zero-field splittings (ZFS) is calculated for the relaxed defect structures. Whereas ^{14}N hyperfine splittings provide a clear fingerprint of the NCVSi centers [1], the ZFS parameters are crucial to attribute the different spectra to the inequivalent lattice sites involved in the hexagonal polytypes [2]. Since optical initialization of the groundstate proceeds in particular for the axial symmetric pairs, selective excitation in 4H/6H SiC suggests an easy preparation of unidirectional spin ensembles.

[1] H.J. von Bardeleben et al., Phys.Rev.B **92**, 064104 (2015).

[2] S.A. Zargaleh et al., Phys.Rev.B **94**, 060102(R) (2016).

Godt, Adelheid

Gd(III) and Mn(II) complexes and molecular rulers for testing and development of EPR techniques

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The complex Gd(III)-PyMTA1 was found to be a valuable label for Gd-based DEER techniques² and RIDME³ and the corresponding Mn(II)-PyMTA turned out to be suitable for Mn-based RIDME.⁴ Therefore, we are presently working on making complexes with PyMTA as the ligand ready for bioconjugation to peptides.

To meet the demand of a concrete EPR technique in respect to ZFS and relaxation times, we work on a comparative study of a few, structurally quite different ligands (DOTA, TAHA, NO₃Pic, PCTA, PicDTTA). Additionally the combination of the two spin labels, Gd(III) and nitroxyl radical, is investigated.

In our contribution we will present the syntheses of ligands and rulers together with some results of the spectroscopical investigations.

1. Qi et al. *Synthesis*, **2016**, DOI 10.1055/s-0035-1561660.
2. Dalaloyan et al. *Phys. Chem. Chem. Phys.* **2015**, *17*, 18464–18476; Doll et al. *Phys. Chem. Chem. Phys.* **2015**, *17*, 7334; Doll et al. *J. Magn. Reson.* **2015**, *259*, 153; Qi et al. *J. Am. Chem. Soc.* **2014**, *136*, 15366.
3. Razzaghi et al. *J. Phys. Chem. Lett.* **2014**, *5*, 3970.
4. Keller et al. *Phys. Chem. Chem. Phys.* **2016**, DOI 10.1039/C6CP04884F.

Jeschke, Gunnar

Optimization of shaped pulses for EPR- Dos and Don'ts

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Control of electron-nuclear spin systems in microcrystalline or glassy samples is more complicated than in the NMR scenarios where optimal control techniques are usually applied. In EPR, spectral width typically exceeds resonator bandwidth, there is significant microwave field inhomogeneity, and spin Hamiltonian parameters exhibit broad distributions due to their anisotropy. The levels are connected by both allowed and incompletely forbidden transitions, which leads to longitudinal and transverse interference when several transitions are passed sequentially. A large number of nuclear spins can contribute significantly to such interference effects. Furthermore, the parameter to be optimized is not necessarily the efficiency of a transfer between two product operators, as it is the case in formalized optimal quantum control.

Here we show on the example of pump pulses in 5-pulse DEER how optimization of shaped pulses can be performed in the EPR context by relying on computationally efficient simulations with the SPIDYAN toolbox. We discuss the gains that can be achieved with respect to hyperbolic secant pulses and the current limitations of our approach.

Kallies, Wolfgang

Optimum Control Pulses – Convergence and Applications

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Optimal control theory provides tools to improve pulse performance and robustness by tuning thousands of pulse parameters at feasible computational costs [1]. Individually optimized pulses have been applied to NMR as well as EPR systems [2]. Previously it was shown that the concurrent optimization of pairs of 90° pulses offers substantial gains in pulse performance compared to individually optimized pulses [3]. We extended the idea of cooperative pulses to combinations of excitation and refocusing pulses of the Hahn Echo sequence. In this context, a new approach was developed to avoid local minima and to significantly improve the convergence of the optimization for the cooperative pulses.

In addition we examined robust and selective inversion pulses for EDMR experiments [4], where a combination of heuristic search algorithms and optimal control methods was used.

[1] N. Khaneja et al., 172, 296 (2005)

[2] P. Schöps et al., 250, 55 (2015)

[3] M. Braun et al., New J. Phys. 16, 115002 (2014)

[4] H. Huebl et al., Phys. Rev. Lett 100, 177602 (2008)

Kern, Michal

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 at the orders of tens microseconds (Figure 1a) [1]. Although these are exhibited mainly at temperatures lower than 10 K, the molecular nature of these systems offers the possibility for extended chemical tailoring for higher coherence times.

However, local addressing of molecular qubits is very challenging and for successful device development, these qubits will need to be interfaced with conventional semiconductor technology.

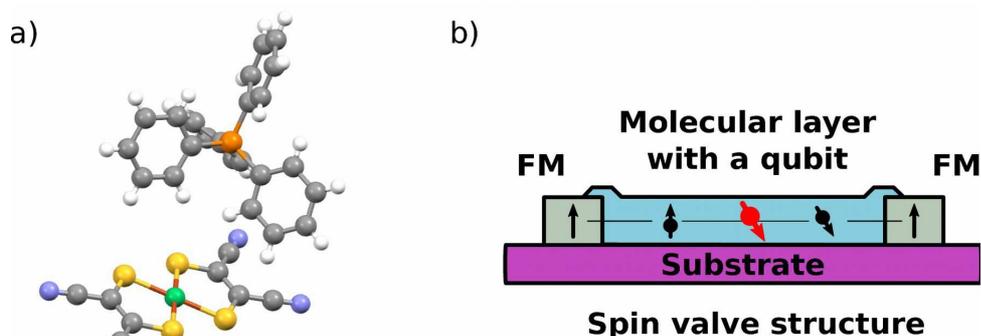


Figure 1: a) Molecular qubit (PPh4)2[Cu(mnt)2] with coherence time of 68 microseconds. b) Possible device architecture based on the spin valve effect, where FM stands for ferromagnetic electrodes.

To overcome this challenge, we plan to use spin polarized charge carriers in a spin valve geometry with various spin transport possibilities to program/readout of the quantum state of the qubits. We have already started to study spin injection into Ge channels from Mn5Ge3 ferromagnetic (FM) electrodes via the Hanle effect. By using the 3 terminal geometry, we have observed proof of successful spin injection and transport, with spin diffusion length of 367 nm [2].

For the investigation of spin transport in organic layers and crystals we have designed possible device architecture (Figure 1b with the possibility of adding a tunneling oxide layer on top of the electrodes) and we are currently intensively exploring this direction.

[1] K. Bader et al. Nat. Commun. 5 (2014) 5304

[2] I. A. Fischer et al. Appl. Phys. Lett 105 (2014) 222408

Kultaeva, Anastasiia

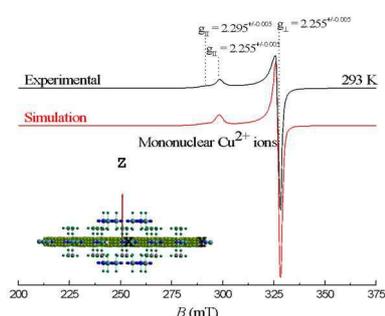
EPR Study of the Isostructural Elastic Layer-Structured Metal-Organic Framework (ELM-11)

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In the present work report we present an EPR study of a novel elastic layer-structured metal-organic framework compound (ELM) with the chemical formula $[\text{Cu}(\text{bpy})_2(\text{BF}_4)_2]_n$, where bpy denotes 4,4'-bipyridine. In this two-dimensional (2D) layered structure the bpy molecules bridge the Cu^{2+} ions in x-y plane to form parallel layers that are connected by the BF_4 ions.¹

The later bind axially to the Cu^{2+} ions. Cw X-band EPR spectra have been recorded for powder samples and small single crystals at room temperature. Single crystal studies were done using dielectric resonators. The g tensor parameters including the orientation of its principal axes frame have been obtained. A comparison of our results with the XRD single crystal structure indicate the presence of an interlayer exchange coupling between the Cu^{2+} ions which is likewise supported by the angular dependence of the linewidth of the Cu^{2+} EPR signals.

¹Volodymyr Bon, Negar Kavooosi, Irena Senkovska, and Stefan Kaskel, ACS Appl. Mater. Interfaces, 2015, 7 (40), pp. 22292–22300,

Masaaki Saito

Linear-scaling electronic structure methods which can be applicable to large, real-life molecules in the domain-based local pair-natural orbital (DLPNO) framework

We have developed a series of linear-scaling electronic structure methods which can be accurately and reliably applicable to large, real-life molecules in the domain-based local pair-natural orbital (DLPNO) framework. The Coupled-Cluster with Singles and Doubles (CCSD) approach serves as a fundamental tool for the accurate model chemistry and gives accurate energy and the electronic wave function for most of the chemically interesting species. However, the prohibitively high computational cost has limited its applicability only up to approximately 30 atoms. By using the DLPNO technique (DLPNO-CCSD), we have shown that it is possible to calculate the accurate electronic wave function for those closed-shell molecules which are composed of more than 1,000 atoms at CCSD level in the common computational environment, overcoming the inherent high computational cost. In this session, we report the development of the open-shell version of the DLPNO-CCSD method and the several applications to several semi-realistic systems such as [NeFe] Hydrogenase and the oxygen evolving complex (OEC) in the photosystem II (PSII).

Calculation of the magnetic property with the present approach is currently being developed in our group to deliver a powerful tool for theoretical spectroscopy.

Ronneburg, Hendrik

Current efforts to set up an EDMR experiment working under ultra-high vacuum (UHV) conditions to investigate defects on semiconductor surfaces

The properties of surfaces and interfaces of solids play an important role for a variety of technologically important fields ranging from semiconductor devices to heterogeneous catalysis. The role of defects on these surfaces and interfaces is particularly crucial to understand the properties of these systems. A major step is the microscopic understanding of these properties, which is still challenging due to the large complexity of most technologically used surfaces or interfaces and the lack of appropriate methodology. To this end the investigation of model surfaces under well-defined ultrahigh vacuum conditions provides a possibility to address some of these issues. EPR spectroscopy has proven to be a very versatile method to investigate paramagnetic point defects on semiconductor surfaces and interfaces, however, the conventional detection scheme suffers from insufficient sensitivity to cope with the low defect density of high quality devices. However, electrically detected magnetic resonance (EDMR) has shown to be able to overcome this sensitivity gap and was used successfully in the past to characterize defects in semiconductor devices and in particular at interfaces of such systems.

In this contribution we will present our current efforts to set up an EDMR experiment working under ultra-high vacuum (UHV) conditions to investigate defects on semiconductor surfaces. Recent advancements and challenges of a working set up as well as first successful steps towards an investigation of single crystal silicon surfaces will be discussed.

Schnegg, Alexander

FD-FT THz-EPR with Improved Versatility and Spectral Range

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Frequency Domain Fourier Transform (FD-FT) THz-EPR based on coherent synchrotron radiation (CSR), provides a powerful tool for the detection of high spin states exhibiting very large Zero field splittings. Herein, we describe the performance of our recently up-graded FD-FT THz-EPR set-up, employing the special low \square short-bunch CSR mode in a quasi continuous wave detection scheme. This scheme allows for EPR measurements in Voigt and Faraday configurations, as well as in transmission and induction mode. In addition variable alignments of the linearly polarized radiation with respect to the static external magnetic field are possible.

However, in addition to its stable broad-band high power spectrum, CSR offers another very promising characteristic, time dependence. The time structure of the THz radiation results from the fact, that CSR is generated by ps or even sub-ps long electron bunches in the storage ring. Thereby, ultra-short THz pulses with high repetition rate can be generated. As we have shown recently this radiation has excellent properties for laser-pump THz-probe experiments, due to the tunability of the excitation spectrum. Based on these achievements, we discuss the prospects of time resolved FTIR and FD-FT THz-EPR experiments.

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