

27th Meeting of the Benelux EPR Society

Delft, 24th May 2019

PROGRAM of the 27th Meeting of the Benelux EPR Society

9:45 Registration; Tea/Coffee

10:30 Opening: *Henk Vrielinck*

Session-I Chair: Etienne Goovaerts

10:40 Detecting low surface spin densities: from ultrasensitive magnetic force microscopy and easyMRFM towards single electron spin detection
Tjerk Oosterkamp (Leiden, NL)

11:10 Magnetic resonance study of energy upconversion in super-yellow PPV films doped with the triplet sensitizer palladium porphyrin
Ivan Sudakov (Antwerp, BE)

11:40 Spectroscopic and Quantum Chemical Investigation of Benzene-1,2-dithiolate-Coordinated Diiron Complexes with Relevance to Dinitrogen Activation
Maurice van Gastel (Mülheim, DE)

12:10 Lunch & Posters

Session-II Chair: Edgar Groenen

13:30 Forget capillaries and flat cells!
Ongoing EPR studies in Brussels on very large biological samples
Bernard Gallez (Brussels, BE)

14:00 Oxidative stress in healthy pregnancy and preeclampsia is linked to chronic inflammation, iron status and vascular function
Jacco Briedé (Maastricht, NL)

14:30 Nitrite binding to the ferric globin domain of GLB-33, a chimeric globin in *Caenorhabditis elegans* - a pH dependent spectroscopic investigation
Niels van Bremp (Antwerp, BE)

15:00 Tea/Coffee & Posters

Session-III Chair Freddy Callens

15:30 Magnetic Resonance Parameters from Multi-Frequency EPR: The 275 GHz Story of the DNP-Biradical AMUPol
Martina Huber (Leiden, NL)

16:00 Multi-Frequency EPR characterization of vanadium dopant sites in DUT-5(Al)
Kwinten Maes (Gent, BE)

16:30 Broadband tunable EPR spectroscopy of transition ions in metalloproteins and models
Fred Hagen (Delft, NL)

17:00 Closing remarks and Drinks

ABSTRACTS of ORAL PRESENTATIONS

Oosterkamp, T Detecting low surface spin densities: from ultrasensitive magnetic force microscopy and easyMRFM towards single electron spin detection	4
Sudakov, I Magnetic resonance study of energy upconversion in super-yello PPV films doped with the triplet sensitizer palladium porphyrin	5
Van Gastel, M Spectroscopic and quantum chemical investigation of benzene-1,2-dithiolate-coordinated diiron complexes with relevance to dinitrogen activation	6
Gallez, B Forget capillaries and flat cells! Ongoing EPR studies in Brussels on very large biological samples	7
Briedé, J Oxidative stress in healthy pregnancy and preeclampsia is linked to chronic inflammation, iron status and vascular function	8
Van Brempt, N Nitrite binding to the ferric globin domain of G:B-33, a chimeric globin in <i>Caenorhabditis elegans</i> – a pH dependent spectroscopic investigation	9
Huber, M Magnetic resonance parameters from multi-frequency EPR: The 275 GHz story of the DNP-biradical AMUPol	10
Maes, K Multi-frequency EPR characterization of vanadium dopant sites in DUT-5(Al)	11
Hagen, WR Broadband-tunable EPR spectroscopy of transition ions in metalloproteins and models	12

Detecting low surface spin densities: from ultrasensitive magnetic force microscopy and easyMRFM towards single electron spin detection

Tjerk Oosterkamp (Leiden, NL)

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Jelmer Wagenaar!

We use ultrasensitive magnetic force microscopy with very soft, high Q mechanical resonators at temperatures between 10 mK and 1 K. We position such an ultrasoft magnetically-tipped cantilever above our sample. Spins in the sample couple to the magnet on the cantilever. Varying temperature and magnet-sample distance enables us to extract spin densities from shifts in the cantilever's resonance frequency and quality factor.

We present a simplified version of this instrument, which we call the easyMRFM, which may pave the way to a broader application of this measurement technique.

Finally, we aim to use a single electron spin too bring a mechanical resonator in superposition. We present the progress for our experiments in this direction which should also be useful to image single spins with this scanning probe microscopy.

*put magn. nanoparticles in
Fe³⁺ in ferritine*

10K

Magnetic resonance study of energy upconversion in super-yellow PPV films doped with the triplet sensitizer palladium porphyrin.

Ivan Sudakov^a, Biniam Zerai Tedlla^a, Feng Zhu^b, Matthijs Cox^b, Bert Koopmans^b, Victoria L. Whittle^c, J.A. Gareth Williams^c, Etienne Goovaerts^a

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The energy conversion in single junction solar cells is limited by the Shockley-Queisser limit linked to the bandgap of the semiconducting material, which defines the energy loss after absorption of higher energy photons, and limits the absorption of photons at the low energy end. Novel device concepts to overcome this limit have been proposed, based on photon conversion processes involving triplet excitons in organic materials. Triplet-triplet fusion, or upconversion via triplet-triplet annihilation (TTA-UC), has already been demonstrated [1,2] to increase the performance of solar cell devices. Understanding of the processes limiting the efficiency of the TTA-UC is important for further optimization of such devices.

In this work, advanced electron paramagnetic resonance (EPR) techniques as well as optical absorption and fluorescence spectroscopy are applied to investigate the fate of charge excitations in so-called “super-yellow” poly-paraphenylene vinylene (SY-PPV) copolymer doped with the triplet sensitizer palladium (*meso*-tetraphenyl-tetrabenzoporphyrin) (PdTPBP). In this system TTA-UC has previously been studied [3], but was found to be quenched as soon as the sensitizer concentration in SY-PPV:PdTPBP films is increased above a few percent. As a function of sensitizer concentration in the films, triplet exciton (TE) and polaron (P) states are monitored by electrically- and optically detected magnetic resonance (EDMR and ODMR) and light-induced EPR, providing indications for TE-P annihilation as quenching mechanism. To shed light on the polaron-related processes, the well-known fullerene acceptor PCBM was introduced as electron trap in binary and ternary blends with the copolymer and the sensitizer. The nature and localization of the TE-P interactions will be discussed on the basis of these results.

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Spectroscopic and Quantum Chemical Investigation of Benzene-1,2-dithiolate-Coordinated Diiron Complexes with Relevance to Dinitrogen Activation

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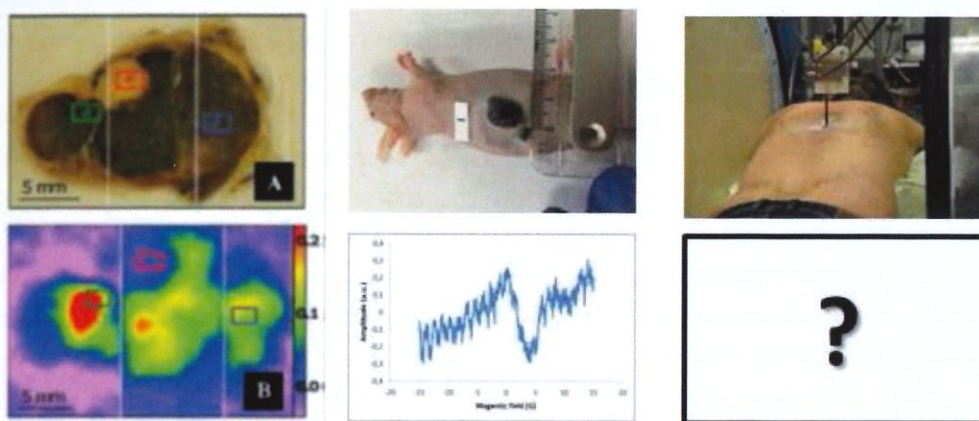
In this work, a benzene-1,2-dithiolate (bdt) pentamethylcyclopentadienyl di-iron complex [$\text{Cp}^*\text{Fe}(\mu\text{-}\eta^2\text{:}\eta^4\text{-bdt})\text{FeCp}^*$] and its [$\text{Cp}^*\text{Fe}(\text{bdt})(\text{X})\text{FeCp}^*$] analogues (where $\text{X} = \text{N}_2\text{H}_2, \text{N}_2\text{H}_3^-, \text{H}^-, \text{NH}_2^-, \text{NHCH}_3^-$ or NO^+) were investigated through spectroscopic and computational studies. These complexes are of relevance as model systems for dinitrogen activation in nitrogenase and share with its active site the presence of iron, sulfur ligands, and a very flexible electronic structure. Based on a combination of X-ray emission spectroscopy (XES), X-ray crystallography, Mössbauer, NMR and EPR spectroscopy, the geometric and electronic structure of the series has been experimentally elucidated. All iron atoms were found to be in a local low-spin configuration. When no additional X ligand is bound, the bdt ligand is tilted and features a stabilizing π -interaction with one of the iron atoms. The number of lone-pair orbitals provided by the nitrogen-containing species is crucial to the overall electronic structure. When only one lone-pair is present and the iron atoms are bridged by one atom, a three-center bond occurs and a direct Fe-Fe bond is absent. If the bridging atom provides two lone-pairs, an Fe-Fe bond is formed. A recurring theme for all ligands is σ -donation into the unoccupied e_g manifolds of both iron atoms and back-donation from the t_{2g} manifolds into the ligand π^* orbitals. The latter results in a weakening of the double bond of the bound ligand and in the case of NO^+ , it results in a weakening of all bonds that comprise triple bond. The electron-rich thiolates further amplify this effect, and can also serve as bases for proton binding. While the above observations have been made for the studied di-iron complexes, they may be of relevance for the active site in nitrogenase, where a similar N_2 binding mode may occur allowing for the simultaneous weakening of the N_2 σ bond and π bonds.

Forget capillaries and flat cells!
Ongoing EPR studies in Brussels on very large biological samples

C. Desmet, P. Danhier, L. Mignon, P. Leveque, E. Vanea, Q. Godechal, I. Tromme, J.F. Baurain, and B. Gallez

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The aim of this talk is to offer a journey in EPR characterization of melanin in melanoma, starting with freeze-dried thin slices obtained from human biopsies...to detection in living mice...to potential detection in melanoma patients (2 ongoing clinical studies in Brussels).



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melanin 2.003
10 G broad

biomagnetism of bees chitin, melanine

Oxidative stress in healthy pregnancy and preeclampsia is linked to chronic inflammation, iron status and vascular function

↳ making

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BACKGROUND: During normal pregnancy, placental oxidative stress (OS) is present during all three trimesters and is necessary to obtain normal cell function. However, if OS reaches a certain level, pregnancy complications might arise. In preeclampsia (PE), a dangerous pregnancy specific hypertensive disorder, OS induced in the ischemic placenta causes a systemic inflammatory response and activates maternal endothelial cells. In this study, we aimed to quantify superoxide concentrations (as a measure of systemic OS) using electron paramagnetic resonance (EPR) and correlate them to markers of systemic inflammation, iron status and vascular function.

METHODS: Fifty-nine women with a healthy pregnancy (HP), 10 non-pregnant controls (NP) and 28 PE patients (32±3.3weeks) were included. During HP, blood samples for superoxide, neutrophil to lymphocyte ratio (NLR), mean platelet volume (MPV) and iron status were taken at 10, 25 and 39 weeks. Vascular measurements for arterial stiffness (carotid-femoral pulse wave velocity (CF-PWV), augmentation index (AIx), augmentation Pressure (AP)) and microvascular endothelial function (reactive hyperemia index (RHI)) were performed at 35 weeks. In PE, all measurements were performed at diagnosis. CMH (1-hydroxy-3-methoxycarbonyl-2,2,5,5-tetramethylpyrrolidine) was used as spin probe for EPR, since the formed CM radical corresponds to the amount of superoxide.

RESULTS: Superoxide concentration remains stable during pregnancy ($p = 0.92$), but is significantly higher compared to the NP controls ($p < 0.0001$). At 25 weeks, there is a significant positive correlation between superoxide and ferritin concentration. ($p = 0.04$) In PE, superoxide, systemic inflammation and iron status are much higher compared to HP (all $p < 0.001$). During HP, superoxide concentrations correlate significantly with arterial stiffness (all $p < 0.04$), while in PE superoxide is significantly correlated to microvascular endothelial function ($p = 0.03$).

CONCLUSIONS: During HP there is an increased but stable oxidative environment, which is correlated to ferritin concentration. If superoxide levels increase, there is an augmentation in arterial stiffness. In PE pregnancies, systemic inflammation and superoxide concentrations are higher and result in a deterioration of endothelial function. Together, these findings support the hypothesis that vascular function is directly linked to the amount of OS and that measurement of OS in combination with vascular function tests might be used in the prediction of PE.

Nitrite binding to the ferric globin domain of GLB-33, a chimeric globin in *Caenorhabditis elegans* - a pH dependent spectroscopic investigation

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Globins are heme-containing proteins known for their involvement in oxygen storage and transport and their capacity to reduce nitrite to NO. The globin superfamily is well-studied across different species, but the discovery of 34 globin genes in the model organism *Caenorhabditis elegans*, all diverse in gene and proteins structure, is surprising considering the simple anatomy of this nematode [1]. One of them is GLB-33 that is mainly expressed in the neuronal tissues of the nematode and from homology modeling it is suggested to consist of a 7 α -helical transmembrane domain and a heme-containing globin domain (GLB-33GD). The first is similar to a Phe-Met-Arg-Phe-amide neuropeptide receptor whereas the latter is a myoglobin-type molecule. From X-band continuous wave EPR experiments and simulation of the principal g-values on recombinantly expressed GLB-33GD, we found that it consists of two LS-forms which translates to Fe-OH⁻ ligation. The hydroxo ligated heme pocket itself is furthermore characterized in detail with electron spin echo envelope modulation (ESEEM), hyperfine sublevel correlation (HYSCORE) and electron-nuclear double resonance (ENDOR) spectroscopy. Uncommonly, the hydroxo ligated state remains present at mildly acidic conditions. Next to this unusual behavior, GLB-33GD shows faster nitrite reductase activity than any other reported globin [2]. Here, we use the combination of optical, vibrational and EPR spectroscopy to reveal that nitrite does not easily bind the ferric heme iron since it remains strongly hydroxo ligated as previously confirmed. Mildly acidic conditions were needed to obtain maximal nitrite coordination and the effect of acidity on recombinantly overexpressed GLB-33GD and on the GLB-33GD[NO₂⁻]-complex was studied. Furthermore, we conclude from resonance Raman spectroscopy with ^{14/15}NO₂⁻ and mass spectrometry that nitrovinyl heme is formed at low pH-values via the substitution of a vinyl proton with NO₂.

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Magnetic Resonance Parameters from Multi-Frequency EPR: The 275 GHz Story of the DNP-Biradical AMUPol

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To understand the dynamic nuclear polarization (DNP) enhancements of biradical polarizing agents, the magnetic resonance parameters need to be known. We describe a tailored EPR approach to accurately determine electron spin–spin coupling parameters using a combination of standard (9 GHz), high (95 GHz) and ultra-high (275 GHz) frequency EPR. Comparing liquid- and frozen-solution continuous-wave EPR spectra provides accurate anisotropic dipolar interaction D and isotropic exchange interaction J parameters of the DNP biradical AMUPol. We found that D was larger by as much as 30% compared to earlier estimates, and that J is 43 MHz, whereas before it was considered to be negligible.

A combination of frozen and liquid solution measurements and a systematic approach to determine the tensor parameters of the zero-field splitting parameter D , the exchange interaction J , and the hyperfine A and G tensors are described.*

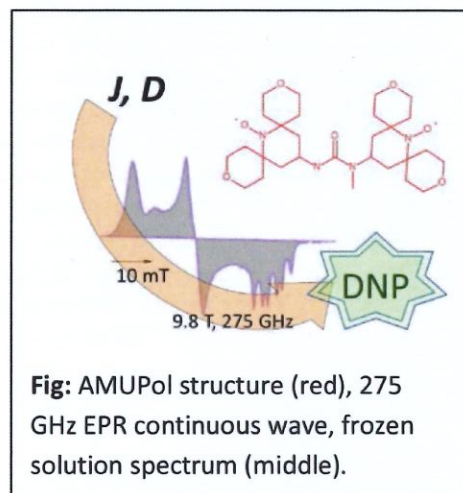


Fig: AMUPol structure (red), 275 GHz EPR continuous wave, frozen solution spectrum (middle).

* P. Gast, D. Manc E. Zurlo, K. L. Ivanov, M. Baldus and M. Huber *Phys.Chem.Chem.Phys.*,2017, 19, 3777

Multi-Frequency EPR characterization of vanadium dopant sites in DUT-5(Al)

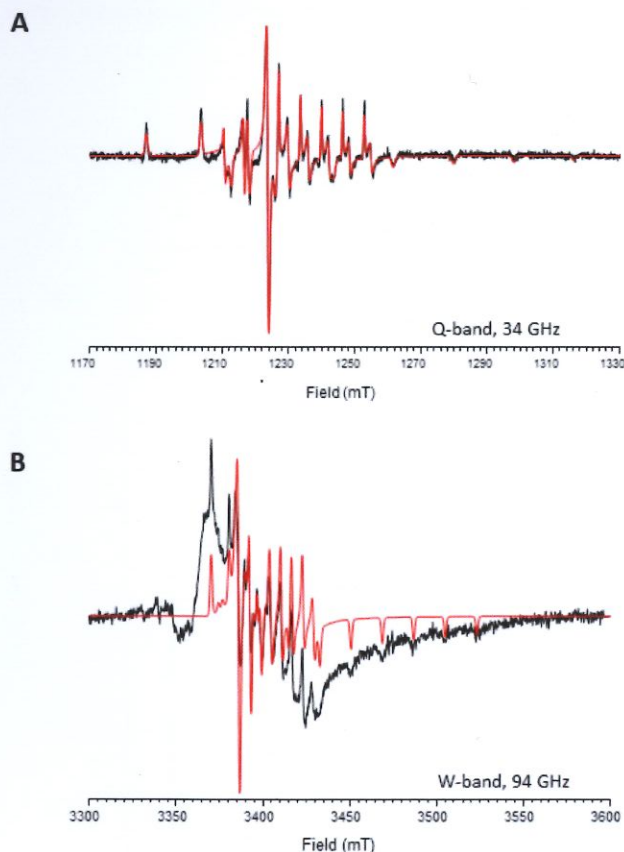
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Metal-Organic Frameworks (MOFs) are ordered porous crystalline materials constructed of metal ions connected by organic linkers. Because of their many interesting properties, a diverse scale of applications are being explored (e.g., catalysis, gas adsorption, separation and storage). For the research presented here we use DUT-5(Al), which consists of Al(OH) chains linked together by biphenyl-4,4'-dicarboxylate (BPDC), creating a rigid lattice with large one-dimensional pores. In $(V^{IV}=O)BPDC$, i.e. COMOC-2(V), part of the framework exhibits the breathing phenomenon: the framework can reversibly change from an open (large pore) to a closed (narrow pore) structure [1]. Recently EPR spectroscopy using $V(IV)$ as a paramagnetic probe was able to distinguish between the large pore and the narrow pore state of V-doped MIL-53(Al) ($(Al^{III}OH)BDC$, BDC: 1,4-benzenedicarboxylate) [2-4]. In mixed $(Al^{III}OH)_x(V^{IV}=O)_{1-x}BPDC$ MOFs, an EPR spectral component was observed that showed similar characteristics as $V^{IV}=O$ in large pore MIL-53(Al), but also other components were found [5].



In the present study we further explore the EPR spectrum of mixed $(Al^{III}OH)_x(V^{IV}=O)_{1-x}BPDC$ MOFs. Spin-Hamiltonian parameters were derived from X- (9.5 GHz) and Q-band (34 GHz) spectra and resulting simulations were compared to W-band (94 GHz) spectra. Doping DUT-5(Al) with low (1% - 7%) concentrations of V^{IV} reveals two components in the EPR spectrum measured in vacuum: a narrow-line and a broad-line component. Going to higher (9%+) concentrations of V^{IV} reveals two additional spectral components: a narrow-line component of isolated vanadyl centers, and a broad structureless line of the V-concentrated phase ($V^{IV}=O$) BPDC.

Figure 1: Room temperature powder EPR spectra of DUT-5(Al), doped with 3% V^{IV} . A: Q-band (34 GHz) large pore spectrum, obtained by elimination of the broad-line component from the spectrum measured in vacuum ($p \approx 0.3$ mbar). B: W-band (94 GHz) spectrum measured in vacuum ($p \approx 2$ mbar). Black - experiment, red - simulation large pore component.

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Cluster system

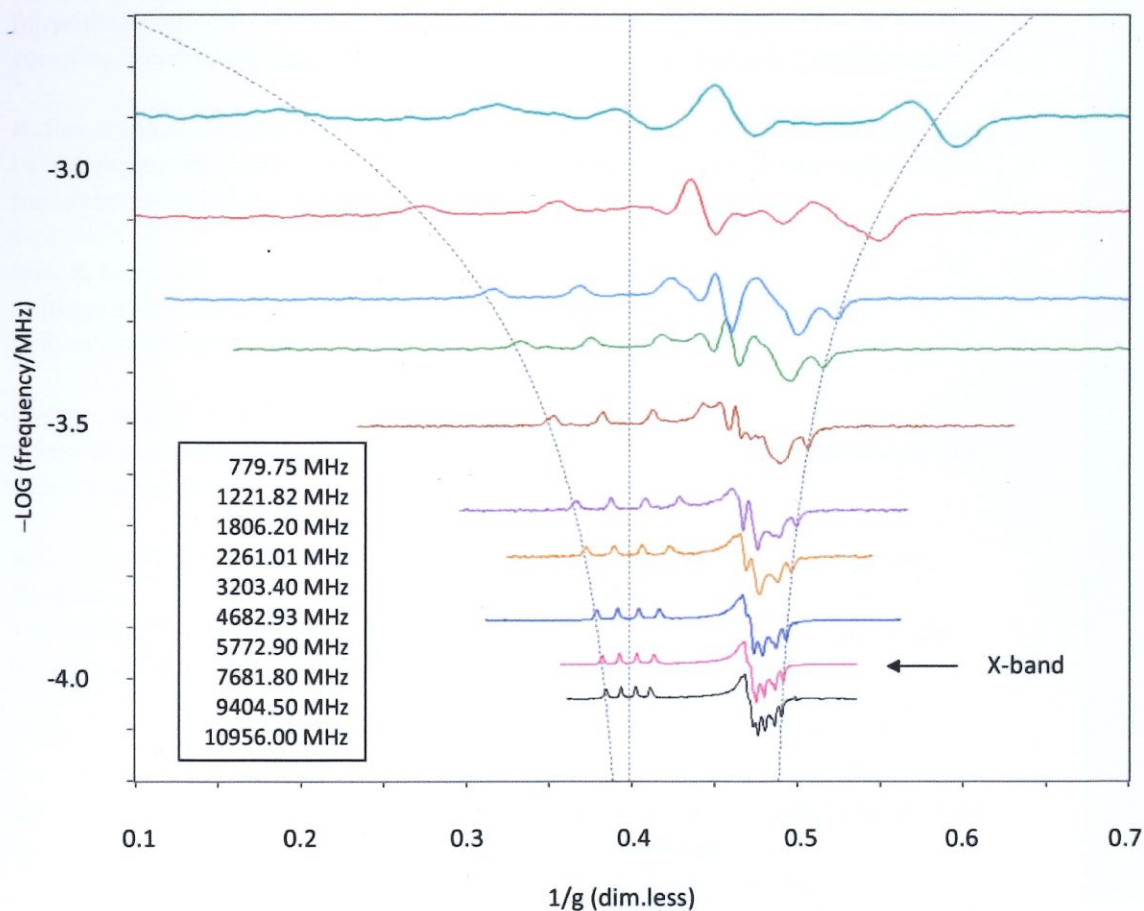
Broadband tunable EPR spectroscopy of transition ions in metalloproteins and models

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Analysis of the EPR of transition ion complexes requires data taken at different microwave frequencies because the spin hamiltonian contains operators linear in the frequency as well as operators independent of the frequency. In practice data collection is hampered by the fact that conventional EPR spectrometers have always been designed to operate at a single frequency only. Here, a broadband instrument is described and tested that – presently – operates from 0.5 to 12 GHz and whose sensitivity approaches that of single-frequency spectrometers. Multi-frequency EPR from a low-symmetry Cu(II) spectroscopic model (see figure) is globally analyzed to illustrate a novel approach to reliable determination of the molecular electronic structure of transition ion complexes from field-frequency 2D data sets. The methodology is applicable to various classes of metalloproteins.



ABSTRACTS of POSTER PRESENTATIONS

- Abednatanzi, S, Gohari Derakhshandeh, P, Leus, K, Vrielinck, H, Callens, F, Schmidt, J, Savateev, A, van der Voort, P** 14
Mechanistic study of metal-free oxygen activation by porous triazine frameworks for selective aerobic oxidation
- Cnockaert, V, Vrielinck, H, Crivits, T, Blanpain, B, Verbeken, K** 15
Determination of the concentration of ferric iron in lead silicate glasses using quantitative EPR
- d'Hose, D, Danhier, P, Jordan, B, Gallez, B** 16
Validation of an EPR analytical toolbox enabling the simultaneous measurement of oxygen consumption rate and mitochondrial superoxide production by tumor cells
- Gohari Derakhshandeh, P, Abednatanzi, S, Tack, P, Muniz-Miranda, F, Liu, Y-Y, Everaert, J, vanden Bussche, F, Vincze, L, Stevens, CV, van Speybroeck, V, Callens, F, Leus, K, Vrielinck, H, van der Voort, P** 17
Bipyridine covalent triazine framework beyond a catalyst support for an iridium complex: elucidating the promotional role of support in aerobic oxidation catalysis
- Hafideddine, Z, Loreto, S, Aerts, S, Cool, P, Meynen, V, Dewilde, S, van Doorslaer, S** 18
Development of globin-based iosensors: the immobilization of neuroglobin in mesoporous matrices
- Nys, K, May, NV, Ching, HYV, Gál, GT, van Doorslaer, S** 19
Distinguishing the cis/trans geometric isomers of bis-ligand copper(II)-hydroxypyridinecarboxylic acid complexes using EPR and DFT
- Nyssen, P, Mouithys-Mickalad, A, Hoebeke, M** 20
Effect of morphine and propofol on the activation of equine neutrophils: an EPR spin trapping study
- Sidabras, JW, Sommer, C, Duan, J, Winkler, M, Happe, T, Suter, D, Lubitz, W, Reijerse** 21
Technical advances for studying nano-liter volume [FeFe]-hydrogenase single crystals using electron paramagnetic resonance
- Welker, G, de Wit, M, Benschop, T, Hoekstra, F, van de Stolpe, G, Prokscha, T, Bossoni, L, Oosterkamp, T** 22
Detecting low surface spin densities: iron-doped palladium measured with muon spin rotation and ultrasensitive magnetic force microscopy

Mechanistic study of Metal-free Oxygen Activation by Porous Triazine Frameworks for Selective Aerobic Oxidation

Sara Abednatanzi^a, Parviz Gohari Derakhshandeh^a, Karen Leus^a, Henk Vrielinck^b, Freddy Callens^b, Johannes Schmidt^c, Aleksandr Savateev^d, Pascal Van Der Voort^a

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Oxygen activation is a critical step in ubiquitous heterogeneous oxidative processes, most prominently in catalysis, electrolysis, medical and pharmaceutical applications. We present here our findings on metal-free O₂ activation on porous triazine frameworks (PTFs) as an important class of N-rich materials. The tunable structure of PTFs provides a great opportunity to modulate the distribution of N heteroatoms. A series of highly porous PTFs are constructed with predictable and controllable nitrogen doping, which serve as a model system for an in-depth study of O₂ activation. Interestingly, PTF materials present a remarkably high oxygen activity. The O₂ activation process was further studied in the formation of aldehydes and ketones via selective aerobic oxidation of alcohols as well as direct imine formation through aerobic oxidative coupling of amines. For the first time, a detailed mechanistic study of O₂ activation over PTFs was made and the role of nitrogen heteroatoms was comprehensively investigated. The electron paramagnetic resonance (EPR) and control experiments provide strong evidence for the reaction mechanism proving the applicability of PTF materials to effectively activate oxygen into superoxide species due to the presence of N-rich functionalities within the framework. Moreover, this report highlights the importance of a self-templated procedure to introduce a large number of N functionalities for the development of well-defined metal-free catalytic materials. This work offers the hope for developing inexpensive and high-performance alternatives to metal-based materials not only for catalysis but also for bio-related applications dealing with O₂ sensing and activation.

Determination of the concentration of ferric iron in lead silicate glasses using quantitative EPR

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The possibility of using X-band electron paramagnetic resonance (EPR) for the selective measurement of the concentration of ferric iron in lead silicate glasses is explored. The goal is to develop a fast and accurate experimental procedure for the determination of the fraction of Fe^{3+} centers in $\text{PbO-SiO}_2\text{-Fe}_x\text{O}_y$ glasses containing both Fe^{3+} and Fe^{2+} . In this way the oxidation or redox state of the glass can be determined by performing a complementary analysis for the determination of the total amount of iron present. Such measurements are relevant for pyrometallurgical recycling processes of some non-ferrous metals as they rely on the oxidation or reduction of metals present in molten lead silicate slags. The relative fractions of Fe^{3+} and Fe^{2+} present in these slags is a direct measure of the oxidation balance during processing. The high X-ray absorption of Pb present makes conventional Mössbauer analysis difficult. Quantitative X-band EPR could provide a viable alternative for other cumbersome methods such as wet-chemical analysis and synchrotron XANES, which are known to have specific practical issues. This is especially true since desktop X-band EPR spectrometers are already available today. For this study, a range of synthetic lead silicate glasses containing 0 to 8 wt% of Fe_2O_3 were prepared for EPR analysis. Two different approaches were compared for processing the acquired EPR spectrum for Fe^{3+} quantification. The first one is based on the total EPR intensity by double integration of a broad EPR spectrum. The second one is based on the relative intensity of two distinct features in the EPR spectrum of Fe^{3+} species in glassy materials. These features are the characteristic peaks around $g = 4.3$ and $g = 2$ for ferric iron in amorphous oxides. Reproducibility of the measurement procedure was checked on two spectrometers: a Bruker ESP300E and a Varian E-line spectrometer, both operated at room temperature. It was found that double integration of the EPR spectrum is a feasible approach but that variation in the sensitivity of the spectrometer and the broad character of the spectrum introduce large uncertainties. The second approach, based on the ratio of the peak-to-peak height of two different features of the Fe^{3+} spectrum, provides much higher accuracy, even between the two spectrometers with slightly different settings. This approach also enables faster measurements since a spectrum over a smaller range in magnetic field is sufficient for quantification compared to double integration. On the downside, the influence of the matrix for this approach is still unknown. The matrix refers here to the other compounds in the glass besides Fe^{3+} . The exact influence of the amounts of SiO_2 , PbO , Fe^{2+} and any other EPR-silent compounds in the glass is expected to be limited or easily compensated for, based on measurements found in literature. Nevertheless, this issue needs to be studied in more detail and will be subject of future work.

Validation of an EPR analytical toolbox enabling the simultaneous measurement of oxygen consumption rate and mitochondrial superoxide production by tumor cells

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A growing body of evidence indicates that mitochondria play a key role in cancer progression and response to treatment. Inhibition of the oxygen consumption rate (OCR) of tumor cells by several drugs has been shown to enhance the efficacy of radiationtherapy by increasing tumor pO₂ and subsequently stabilizing radiation-induced DNA-damage (1).

Mitochondria are also the major producer of superoxide and other downstream ROS in the cell, the main source of superoxide being complex I and III. Superoxide may trigger cell death when produced in large excess but, at moderate levels, it was suggested to be a key driver promoting cancer cell migration and metastasis (2). Therefore, these dual dose-dependent effects are important to study when considering the effect of a drug as a potential radiosensitizer in radiationtherapy. So far, no technology is able to assess simultaneously the consumption of oxygen and the leakage of superoxide from the electron transport chain.

This "EPR mitochondrial Toolbox" relies on the use of two EPR spin probes (¹⁵N-PDT and ¹⁴N-CMH) labelled with different nitrogen isotopes allowing the simultaneous measurement of two nitroxides EPR spectra, thereby enabling dynamic and simultaneous measurement of mitochondrial OCR and superoxide respectively in isolated mitochondria. Perdeuterated nitroxides as ¹⁵N-PDT are very sensitive probes to measure oxygen levels in a medium using EPR-oximetry. On the other hand, CMH is the best EPR tool to detect sensitively and specifically superoxide in complex biological media, like demonstrated recently by Scheinok S. (3) in our lab. As a first step, this toolbox was tested on a validated model mimicking mitochondrial function (respiration and superoxide production) using hypoxanthine (HX) and xanthine-oxidase (XO) where XO catalyses the oxidation of HX into xanthine generating superoxide. Secondly, it was also tested on a "whole cell" model of superoxide production using RAW 364.7 macrophages treated with PMA, stimulating the NADH oxidase (NOX) to consume oxygen and produce superoxide.

This innovative approach will allow studying the effects of compounds on the electron transport chain in order to prove their efficiency in alleviating tumor hypoxia, but also to measure their potential impact on metastasis induction.

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Bipyridine Covalent Triazine Framework beyond a Catalyst Support for an Iridium Complex: Elucidating the Promotional Role of Support in Aerobic Oxidation Catalysis

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Synergistic catalysis holds great promise to enhance the catalytic performance of heterogeneous catalysts suffering from sluggish reaction kinetics. Accordingly, much effort has been dedicated to the development of bimetallic catalyst systems in which the two promoter elements display synergistic benefits compared to their monometallic counterparts. However, the use of bimetallic catalysts inescapably raises the cost of preparation and the environmental issues. This study discovers a spectacular synergistic effect when using a bipyridine covalent triazine framework (bipy-CTF) as a nanoporous support for an Ir^{III} complex in the aerobic oxidation of alcohols. A detailed mechanistic study is reported to provide insights into the function of the bipy-CTF in this synergistic catalysis. The electron paramagnetic resonance (EPR) and *in-situ* XANES analyses provide strong evidence for the reaction mechanism proving the applicability of bipy-CTF to activate oxygen and alcohols, resulting in an enhancement of the performance of the Ir complex to exceed largely the activity of the homogeneous counterpart. To the best of our knowledge, this is an unprecedented report on promoting the activity of a heterogeneous catalyst through its solid support. More generally, the presented findings reveal an important step toward using CTFs in industrial sustainable applications dealing with oxygen activation such as oxidation of organic compounds and oxygen reduction reactions.

Development of globin-based biosensors: the immobilization of neuroglobin in mesoporous matrices

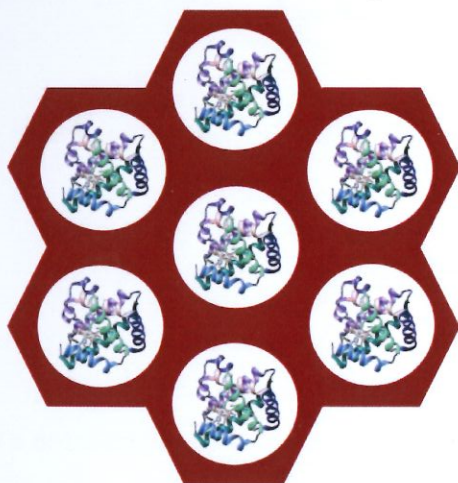
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Globin-based biosensors are a promising tool to accurately sense and detect certain molecules of interest. In recent years, there is a high demand for the detection and monitoring of particular toxic byproducts in for example waste water management. Many proteins, such as globins, are highly selective and sensitive for the detection of small molecules like H₂O₂, H₂S and NO. The electrochemical activity is governed by the heme group of the globin, where the change of the oxidation state of the heme iron can be detected in biosensing applications. However, the stability of globins outside their biological environment is limited, but can be prolonged by incorporation or immobilization of the globins in a suitable matrix. Moreover, the immobilization can also improve the activity in the appropriate environment. In particular, the properties of the immobilization matrices should avoid loss of the protein activity and leaching or degeneration of the proteins. For the encapsulation of the globins, SBA-15-type silica (SiO₂) and titanium dioxide (TiO₂) are used. These mesoporous materials show high biocompatibility and potentially good



retention of the protein activity. Here we study the incorporation of the vertebrate globin neuroglobin (NGB). NGB is predominantly expressed in the nervous system and the protein structure displays the typical globin fold. NGB is extremely stable under pH and temperature conditions known to denature other globins and, under *in vitro* conditions, it is redox active. Via electron paramagnetic resonance (EPR) the ferric heme centre can be studied and consequently the stability and state of the globin and its heme group can be checked before and after immobilization.

Distinguishing the *cis/trans* geometric isomers of bis-ligand copper(II)-hydroxypyridinecarboxylic acid complexes using EPR and DFT

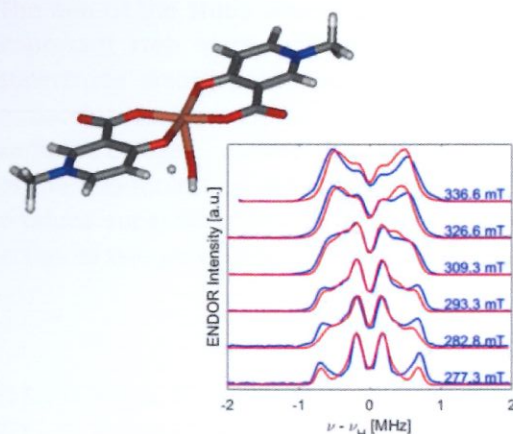
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Metal ions are crucial for life but excessive uptake or a genetic disorder might perturb metal homeostasis and cause significant health problems. A disproportionate amount of copper in the body damages biomolecules in cells and has proven a role in the development of cancer, cirrhosis, atherogenesis and neurodegenerative diseases. Chelation therapy provides a way of removal or attenuation of these toxic ions. However, there are significant side effects for the patient besides the risk of complex formation involving displacement to more dangerous sites in the body [1,2].

The quest for new chelating compounds recently resulted in synthesis of hydroxypyridinecarboxylic acids (HPCs), based on deferiprone (3-hydroxy-1,2-dimethylpyridin-4(1H)-on), which is widely used in chelation therapy. The development of new chelators requires a high stability of the metal complexes, fast formation kinetics, high selectivity and low toxicity. Moreover, it is important to have a good structural knowledge of the complex under physiological conditions, given the coexistence of *cis/trans* geometric isomers.



Here, we present a study on four HPCs which were investigated earlier by single-crystal X-ray diffraction (SXRD) and showed full *cis* or *trans* coordination [3]. X-band CW EPR at room temperature and at 77 K exploited the paramagnetic character of the bis-ligand Cu(II) complexes to differentiate them. However, only small differences were observed, not allowing elucidation of the geometric isomerisation of the complexes in solution. Therefore we turned to a combined approach of density functional theory (DFT) and X-band Mims ENDOR enabling

a detailed analysis of the hyperfine interactions of the unpaired electron with the ligand protons. This way, insight was obtained in the *cis/trans* geometric isomers of the Cu(II)-HPC complexes demonstrating a more complicated image than the SXRD results.

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Effect of morphine and propofol on the activation of equine neutrophils: an EPR spin trapping study

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Inflammation is a complex physiological phenomenon involving chemical and enzymatic mechanisms. During this event, Polymorphonuclear Neutrophil Leukocytes (PMNs) play an important role by producing reactive oxygen species (ROS) and releasing myeloperoxidase (MPO), an oxidant enzyme. The latter one has two main activities: chlorination and peroxidase, which participate in the host defense against micro-organisms like bacteria and virus.

Inflammatory pathologies induce an excessive stimulation of the PMNs and therefore an uncontrolled production and release of ROS and MPO in the extracellular medium. This causes severe damages on the surrounding tissues, leading to pathologies like rheumatoid arthritis, atherosclerosis, [1,2] A possible pathway to control this excessive inflammation and treat chronic pathologies is to regulate the neutrophil functions. The research of potential anti-inflammatory molecules, able to inhibit the oxidant enzymes like MPO and/or to scavenge ROS, is an important part of biomedical research. The design of new anti-inflammatory molecules has been the subject of many publications. [3] An alternative is to give a second life to clinical-used molecules, presenting antioxidant and anti-inflammatory properties. Propofol (PPF) and morphine meet these two requirements. Indeed, besides their analgesic and anesthetic actions, morphine and propofol present antioxidant properties and have been shown to be ROS and radical scavengers. [4,5,6] Morphine even presents an inhibitory action on PMN's degranulation. [7]

The aim of the study was to investigate and compare the action of propofol and morphine on an important step of the inflammation pathway, the respiratory burst and more precisely on the superoxide anions production, using EPR spectroscopy. Therefore, the reductive action of these molecules has been first investigated on an enzymatic system, used to produce superoxide anions: xanthine oxidase - xanthine, via spin trapping. This study has been completed with the investigation of the two molecules action on a cellular system. Indeed, isolated equine PMNs have been used to produce superoxide anions. The action of morphine and propofol has also been compared to the action of two polyphenols, gallic acid and quercetin.

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The non-innocent role of spin traps

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DMPO (5,5-Dimethyl-1-pyrroline N-oxide) plays an important role as a spin trap in the EPR study of systems containing free radicals and paramagnetic centers in chemistry and biology[1]. However, since DMPO is often used at high concentrations, it can potentially undergo a significant amount of non-innocent side reactions, not just spin-trapping the radicals. In this work we investigated the chemical behavior of DMPO in the presence of Cu(II) compounds, which are often used in homogenous catalysis[2]. We have used CW EPR and HYSCORE to study the interaction of Cu(II) with DMPO in DMSO in the absence or presence of a competing pyridine ligand. We found that DMPO can coordinate to the Cu(II) ion and we identify the new species by combining the EPR simulations with the DFT computations.

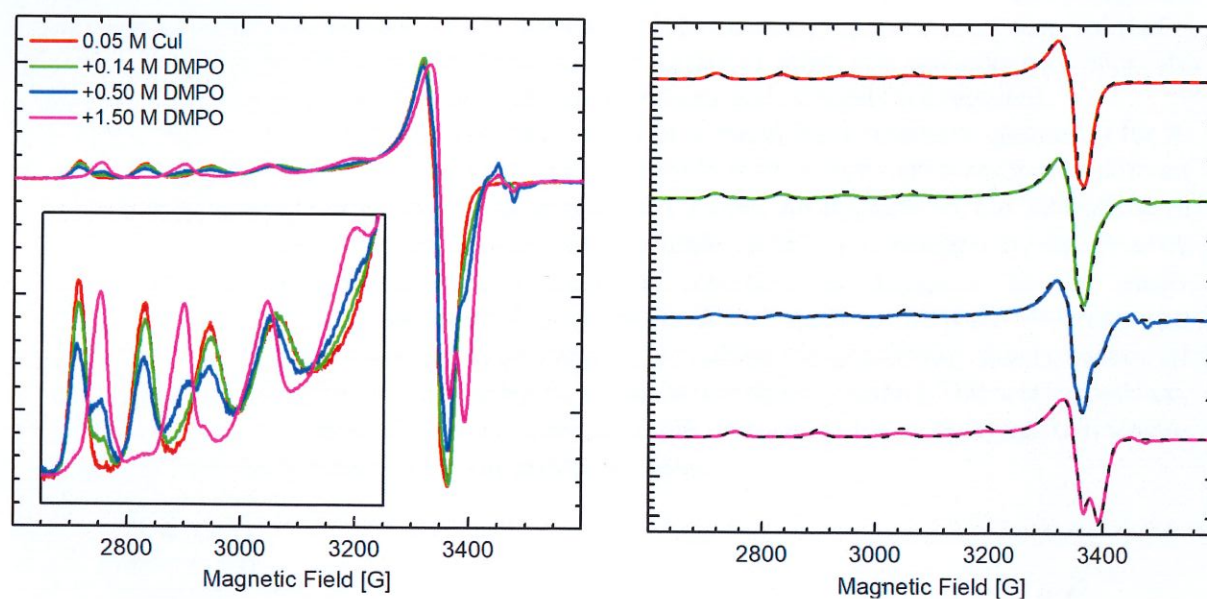


Figure 1. *left* X-band cw-EPR spectra of 0.05 M CuI in DMSO with increasing concentration of DMPO recorded at 100 K. Each spectra has been normalised to the double integral i.e. total number of spins. *right* The spectra stacked with corresponding simulated spectra (black dash).

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Technical Advances for Studying nano-Liter Volume [FeFe]-Hydrogenase Single Crystals using Electron Paramagnetic Resonance

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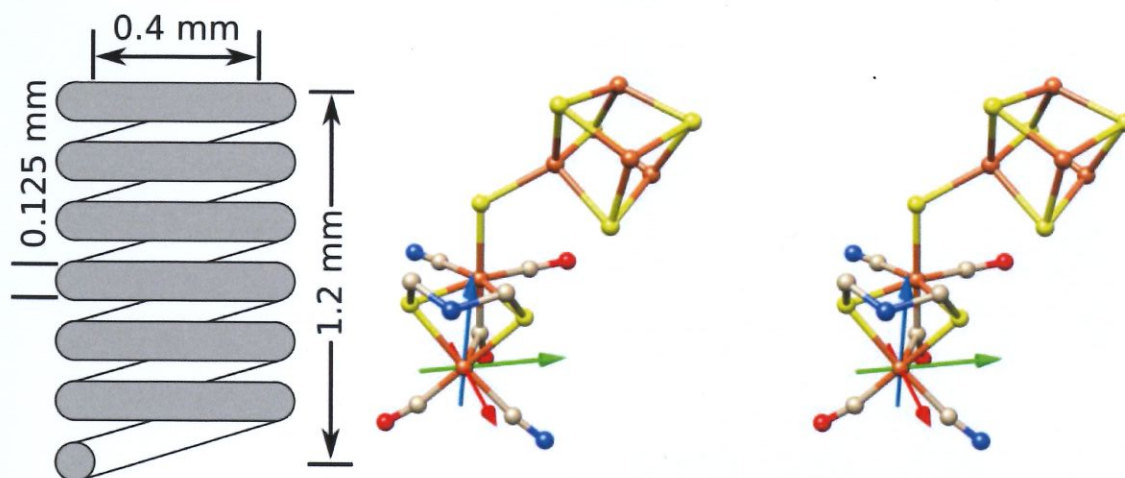
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The study of catalytic states with effective paramagnetic centers in protein single crystals using Electron Paramagnetic Resonance (EPR) spectroscopy can be highly informative. Such studies are used to resolve g - and hyperfine tensors of the active site and relate the electronic structure to enzyme geometry. Previous work on the active-site of [NiFe]-hydrogenase used a $2 \times 0.5 \times 0.5 \text{ mm}^3$ (500 nL) single crystal.[1] However, typical crystal sizes of [FeFe]-hydrogenase are 50 times smaller in volume. In order to meet the challenges of nano-liter volume single crystal studies, further technical advances and methods are required.

Here we present the design and fabrication of a micro-helix resonant geometry for X-band CW and pulse EPR experiments.[2] The micro-helix is a 6.5-turn helical resonator with an inner diameter of 0.4 mm and a total length of 1.2 mm. An increase in the EPR absolute sensitivity by a factor of up to 28 (for non-saturable samples) is realized by significantly reducing the active volume. The micro-helix assembly is designed to be easily exchangeable in standard commercial equipment. A first study on an [FeFe] Hydrogenase single crystal from *Clostridium pasteurianum* (Cpl) enabled the preliminary determination of the full g -tensor within the molecular frame of the active site (H-cluster). This work opens up, for the first time, the possibility to use advanced EPR techniques for studying protein single-crystals of dimensions typical for X-ray crystallography.



Left: geometry of the μ -helix; Right: Stereo view of the g -tensor in the H-cluster

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Detecting low surface spin densities: iron-doped palladium measured with muon spin rotation and ultrasensitive magnetic force microscopy

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We investigate 100nm thin films of palladium with 2ppm and 170ppm iron doping at temperatures between 20mK and 150K. These samples serve as a test bed for comparing two methods to determine electron spin densities: muon spin rotation and ultrasensitive magnetic force microscopy.

In our muon spin rotation measurements, spin-polarized muons are implanted into a sample at different depths, thereby probing the local magnetic environment. This allows us to selectively measure at the film surface or interface only and to investigate the effect of interface and surface spins. Furthermore, we position an ultrasoft magnetically-tipped cantilever above our sample. Spins in the sample couple to the magnet on the cantilever. Varying temperature and magnet-sample distance enables us to extract spin densities from shifts in the cantilever's resonance frequency and quality factor.

TRAVEL INFORMATION for the Benelux EPR Society meeting in Delft on May 24, 2019

TRAVEL by PUBLIC TRANSPORTATION

Travel by train to Delft Central Station

Take bus 69 (every 7.5 min)

After 15 min get off at the 5th stop 'TU Kluiverpark' (just before the stop you passed our building on your left side and the nuclear reactor on your right side)

Walk south 100 meter to the TNW South Building 58

TRAVEL by CAR

Get to the A13 between Rotterdam and The Hague

Get off at exit Delft Zuid (rightmost lane: TU)

At exit end (traffic lights) turn left onto Huismansingel

Continue for 700 meter until end of road

Turn right onto Heertjeslaan

After 350 meter take right exit "TNW" onto van der Maasweg facing Building 58

On your left is the free 4-story parking structure

LOCATION of Meeting:

TNW (=Technische Natuurwetenschappen) Building 58, van der Maasweg 9 , 2629HZ Delft

Enter Atrium, go up to second floor to

Auditorium: Kronigzaal



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