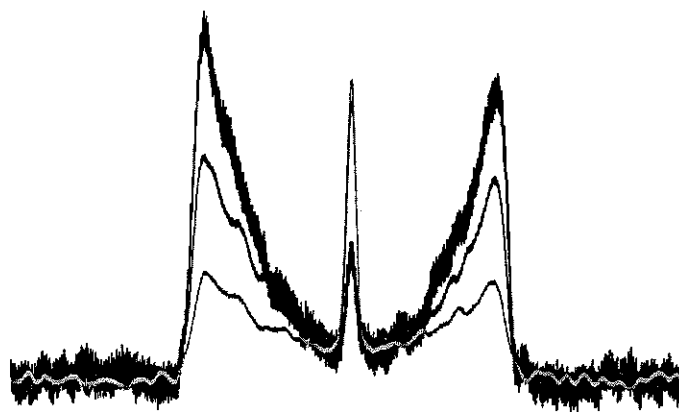


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Twelfth Meeting Of the Benelux EPR Society

Program and Abstracts



April 23, 2004
Department of Physics
University of Antwerp – Campus Drie Eiken
Antwerp, Belgium

Organization

August Bouwen

Sabine Van Doorslaer

Etienne Goovaerts ^a

Peter Gast ^b

^a Chairperson and ^b Secretary of the Benelux EPR Society

SCIENTIFIC PROGRAM

- 10:00-10:30 *Registration + poster display + coffee*
- 10:30 *Welcome*
- 10:35 **Stefano Ceola**, Universiteit Leiden O1
*Time resolved EPR of photo-excited paramagnetic systems
in liquid-crystal solvent*
- 11:00 **Mohammed A. Bahri**, Université de Liège O2
Quantification of lipid bilayer viscosity and fluidity effect induced by propofol
- 11:25 **Peter ter Heerdt**, Universiteit Antwerpen O3
*Determination of the zero field splitting interactions in a highly symmetric
tetra-iron (III) single-molecule magnet*
- 11:50 *Poster session*
- 12:30 *Lunch*
- 14:00 *Invited Talk*
Damien M. Murphy, Cardiff University
*Applications of EPR and ENDOR spectroscopy to studies in heterogeneous
and homogeneous catalysis*
- 14:45 **Serguei B. Orlinskii**, Universiteit Leiden O4
Probing the wave function of shallow Li and Na donors in ZnO nano particles
- 15:10 **Andre Stesmans**, Katholieke Universiteit Leuven O5
*Atomic origin of the B3 and B5 ESR spectra in neutron-irradiated
crystalline silicon*
- 15:35 **Patrick Carl**, Bruker Biospin GmbH, Rheinstetten O6
Innovations in intermediate frequency spectrometers
- 16:00 *Poster session + coffee break*
- 16:30 **Jacco J. Briedé**, Universiteit Maastricht O7
*In vivo spin trapping as a tool to detect LPS-induced oxidative stress in
different organs of the mouse*
- 16:55 **Evi Vinck**, Universiteit Antwerpen O8
*EPR and ENDOR study of neuroglobin, cytoglobin and
Fe(III)tetraphenylporphyrin (bis 4-methylimidazole)*
- 17:20 **Ernst van Faassen**, Universiteit Utrecht O9
Iron dithiocarbamates as spin traps of biological nitric oxide
- 17:45 *General Assembly of the Benelux EPR Society + Closing
Election of a new chairman*

LIST OF POSTER PRESENTATIONS

- Koen Beerten**, Katholieke Universiteit Leuven P1
ESR as a tool for dating geological quartz grains
- Sofie Cambré**, Universiteit Antwerpen P2
X-band ODMR-study of the preferential orientation of para-phenylene vinylene pentamers in polystyrene spin-coated films
- L. Hambach**, Université de Liège P3
ESR quantification of DMPC liposome viscosity change induced by the addition of cholesterol and/or cyclodextrin
- Martina Huber**, Universiteit Leiden P4
Spin-label EPR on proteins: distance, polarity and dynamics. Azurin as an example.
- Iulia Ioanitescu**, Universiteit Antwerpen P5
Comparing the heme pocket structure of human cytoglobin, tomato and drosophila hemoglobin
- Frank Loncke**, Universiteit Gent P6
Determination of spin Hamiltonian parameters for two Fe^{3+} impurity centres in Cs_2NaAlF_6 and Cs_2NaGaF_6
- Yevhen Polyhach**, Universiteit Antwerpen P7
W- and X-band EPR study of the impurity-defect centers in $Pb_{1-x}Sn_xGd_yTe$ crystals
- Franky Stevens**, Universiteit Gent P8
Ab initio investigation of X (O, S, Se) ions in alkali halides
- Florin Trandafir**, Universiteit Antwerpen P9
Nitrosyl binding modes in human neuroglobin
- Richard J. Tucker**, Cardiff University P10
 A^1H ENDOR and DFT study of weak solvent interactions with a Vanadyl Schiff-base complex
- Gauthier C.A.M. Vanhaelewyn**, Universiteit Gent P11
Q-band EPR and ENDOR of room and low temperature X-irradiated β -D-fructose single crystals
- Ravena Vasilini**, Université de Liège P12
Destruction of stearic acid nitrosyl radicals mediated by photoexcited pyropheophorbide-a methyl ester in liposomal systems
- Marieta Zdravkova**, Universiteit Gent P13
X- and Q-band EPR study of irradiated bone from human fingers

ORAL CONTRIBUTIONS

aan G. Selverius met laten zien

Invited Talk

Applications of EPR and ENDOR spectroscopy to studies in heterogeneous and homogeneous catalysis

Damien M. Murphy

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In the field of catalysis, the driving force for research is the improvement in catalyst performance, and specifically the increased reactivity and selectivity of the reaction. The key to this improvement, is a deeper understanding of the reaction mechanism, in order to adopt a molecular approach at how reactions occur at surfaces or at active sites in the homogeneous phase. This approach is only valid, if careful consideration is given to the experimental design. In other words, it is vitally important to study the reactions under realistic conditions and to take into consideration not only the strong (easily observable) interactions involved in the activation of the reagent, but also to the equally important weaker interactions operative over long range.

In this talk, two examples will be given to illustrate how EPR and ENDOR have been used to explore these two facets of heterogeneous and homogeneous catalysis. In the first example (mainly incorporating EPR), the reactive oxygen species (ROS) involved in the heterogeneous photocatalytic oxidation of organics will be discussed, illustrating how these intermediates can only be detected under selective experimental conditions. In the second example (mainly incorporating ENDOR), the very weak interactions between an enantioselective homogeneous catalyst and a series of chiral substrates will be discussed, illustrating how the chiral information is transferred from the metal - ligand complex (or catalyst) to the substrate. Because these interactions are so weak, they can quite often remain un-detected by other experimental/spectroscopic techniques but their contribution is nevertheless crucial to the enantioselective performance of the catalyst.

TiO₂ (Rutile) O₃⁻ formative

TiO₂ · E_g = 3eV

TiO₂ (Anatase) O₂⁻ formative!

↓
hv → Ti³⁺
O⁻ O₂⁻ ...) surface

Time resolved EPR of photo-excited paramagnetic systems in liquid-crystal solvent

S. Ceola^{*,&}, L. Franco[&], C. Corvaja[&]

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In this work Time-Resolved EPR was used to study the anisotropy of the electron-dipolar interaction of the triplet state of photo-excited organic molecules dissolved in a liquid-crystal solvent.

The systems studied, C₆₀ mono-adducts and an Azo dye, are organic molecules widely used as partners in Donor-Acceptor (D-A) systems [1]. These D-A systems could be initiators of the charge-transfer process in photovoltaic devices for converting solar light into electrical energy.

The anisotropy of the liquid-crystal solvent is the key for the study of the principal directions of the dipolar tensor. The quantitative evaluation of the ordering of the solute molecule in the liquid crystal was achieved both theoretically [2] and experimentally [3].

In this way the relative orientation of the dipolar-interaction tensor with respect to the molecular structure for both the C₆₀ mono-adducts and the Azo dye was found [4]. These findings were used to clarify an energy-transfer (ET) step in the photo-physical path of a covalently linked D-A system comprised of the C₆₀ mono-adduct and the Azo dye. The photo-excitation of the Azo dye moiety is followed by singlet-singlet ET to the C₆₀ unit. Then an ISC process in the fullerene moiety creates the corresponding triplet-excited state, which decays rapidly to the Azo dye triplet state. The existence of such a triplet-triplet ET step could only be identified once the analysis of the TR-EPR spectra of the dyad was completed.

[1] Cattarin S.; Ceroni P.; Guldi D. M.; Maggini M.; Menna E.; Paolucci F.; Roffia S.; Scorrano G.; *J. Mater. Chem.* 1999 9, 2743-2750.

[2] Ferrarini A.; Moro G. J.; Nordio P. L.; in *Physical Properties of Liquid Crystal : Nematics*, (D. A. Dunmur, A. Fukuda, G. R. Luckhurst eds, INSPEC, London 2001) Chp. 2.3, p.p. 103-112

[3] Mazzoni M.; Franco L.; Ferrarini A.; Corvaja C.; Zordan G.; Scorrano G.; Maggini M.; *Liq. Cryst.*, 2002, 29 203-208.

[4] Ceola S.; Corvaja C.; Franco L.; *Mol. Cryst, Liq. Cryst.* 2003, 394, 31-43.

Quantification of lipid bilayer viscosity and fluidity effect induced by propofol

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A. SERET, and M. HOEBEKE

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Quantification of viscosity change in membrane is crucial for understanding of many signalling processes and diseases. In this work, we have established standard curves allowing us to quantify the value of microviscosity at different depth inside liposome membrane by measuring Electron Spin Resonance order parameter and correlation time of stearic spin probes spectrum. At room temperature, local microviscosities were 277.26, 64.42 and 63.62 cP, respectively in dimyristoyl-L- α phosphatidylcholine (DMPC) liposome membrane at the different depths 8, 10 and 21 Å. In the gel state (10°C), the corresponding viscosities increased to 752.26, 359.75 and 342.4 cP. Propofol (2,6-diiso propyl phenol) is extensively used for induction and maintenance of general anaesthesia. Propofol (PPF) has a unique phenolic structure that is not present in any other conventional anaesthetic. Lipophilic propofol is presumed to penetrate into and interact with membrane lipids inducing changes in membrane fluidity. Therefore, it is important to quantify the change in microviscosity induced by propofol in order to better understand the molecular mechanism of its anaesthetic action. The addition of propofol in DMPC liposomes above the phase-transition temperature (23.9°C) did not change viscosity. At 10°C, an increase of PPF concentration from 0 M to 1.0×10^{-2} M for a constant lipid concentration induced mainly a decrease in the value of viscosity. Above 10^{-2} M PPF, no further decrease was observed and the viscosity at the studied depths (8, 10 and 21 Å) took the following values 350, 130 and 170 cP respectively. The concentration 10^{-2} M was identified as the incorporation limit of propofol in DMPC liposomes.

Determination of the zero-field-splitting interactions in a highly symmetric tetrairon(III) single-molecule magnet.

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Within the family of tetrairon(III) Single-Molecule Magnets (SMMs) with an $S = 5$ spin ground state [1,2], the compound $[\text{Fe}_4(\text{thme})_2(\text{dpm})_6]$ (**1**) is unique in that it has crystallographically-imposed D_3 molecular symmetry (Hdpm = dipivaloylmethane, H_3thme = 1,1,1-tris(hydroxymethyl)ethane) [3]. The Fe_4 units are iso-oriented in the crystal lattice (space-group $R\bar{3}c$), with their unique axes parallel to the three-fold crystal axis. As a consequence, **1** is an ideal system for the determination of second- (D) and fourth-order zero-field splitting (zfs) parameters by single-crystal EPR spectroscopy.

This work presents a detailed CW W-band EPR study on single crystals of **1**. A four-circle X-ray diffractometer was used to orient the crystals perpendicular on or parallel to specific crystallographic directions. Then very precise angular variations in crystalline and principal planes were performed to establish the zfs interaction. As already indicated by magnetic measurements [3], the second-order axial zfs parameter ($D = -0.442 \text{ cm}^{-1}$) is about twice as large as that of $[\text{Fe}_4(\text{OCH}_3)_6(\text{dpm})_6]$ (**2**) [1]. Due to the larger D value and the strictly axial symmetry, **1** is expected to display SMM behavior at higher temperature than **2**. Finally, an angular variation in the perpendicular plane shows a 60 degrees modulation of the field positions of several resonance lines, which can be attributed to the appearance of higher order zfs terms in the spin hamiltonian.

[1] A. Bouwen, A. Caneschi, D. Gatteschi, E. Goovaerts, D. Schoemaker, L. Sorace and M. Stefan, *J. Phys. Chem. B* 105, 2658-2663 (2001).

[2] R. W. Saalfrank, I. Bernt, M. M. Chowdhry, F. Hampel and G. B. M. Vaughan, *Chem. Eur. J.* 7, 2765-2769 (2001).

[3] A. Cornia, A. C. Fabretti, P. Garrisi, C. Mortalò, D. Bonacchi, R. Sessoli, L. Sorace, A. L. Barra and W. Wernsdorfer, unpublished results.

→ do intensity calculations agree with

||| Where left $S=4$? → look @
BS³

**Probing the wave function of shallow Li and Na donors
in ZnO nano particles.**

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Celso de Mello Donegá and Andries Meijerink

Debye Institute, Utrecht University, The Netherlands

EPR and ENDOR experiments on ZnO nano particles reveal the presence of shallow donors related to interstitial Li and Na atoms. The shallow character of the wave function is evidenced by the multitude of ^{67}Zn ENDOR lines. Further, by the hyperfine interactions with the ^7Li and ^{23}Na nuclei that are much smaller than for atomic lithium and sodium. In the case of the Li-doped nano particles an increase of the hf interaction with the ^7Li nucleus and with the ^1H nuclei in the $\text{Zn}(\text{OH})_2$ capping layer is observed when reducing the size of the nano particles. This effect is caused by the confinement of the shallow-donor 1s-type wave function that has a Bohr radius of about 1.5 nm, i.e., comparable to the dimension of the nano particles.

Atomic origin of the B3 and B5 ESR spectra in neutron-irradiated crystalline silicon

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The electron spin resonance (ESR) technique was used to study neutron-irradiated defects in c-Si as a function of anneal temperature T_{an} . For T_{an} in the sub 200 °C range, the ESR response is dominated by the Si-P3 and Si-P6 spectra, as observed before; At $T_{an}=200$ °C, a low symmetry center, labeled as Si-H8 and only once reported before, appears; Here, a hyperfine doublet, corresponding to interaction with one ^{29}Si nucleus, is resolved. These defects are mentioned here for reasons of completeness.

In the T_{an} range ≥ 250 °C, the anneal region of main focus, two other paramagnetic defects become dominant. The first concerns the long known Si-B3 center of tetragonal symmetry, yet of still undecided atomic nature. Mapping of the full angular magnetic field direction dependence of known and newly resolved ^{29}Si hyperfine structure enables an apparently conclusive identification: K-band (~ 20.5 GHz) ESR spectra simulations show that the defect electron wave function has its strongest hyperfine interaction with two equivalent Si sites in a first shell, a next interaction with four equivalent Si sites in a second atomic shell, and a next interaction with eight equivalent sites in a third shell. On the basis of these K-band spectra, it is found that the data comply with recent theoretical calculations on the tetra-interstitial (I_4), hence it is identified with B3.

Second, a still unidentified defect, termed Si-B5, is observed. The defect shows some similarities to the previously reported Si-B4 defect, yet it appears quite distinct from it. The B5 defect exhibits two doublets originating from hyperfine interaction with four and six equivalent Si sites. Here, the tri-interstitial I_3 is proposed as provisional defect model. On the basis of the annealing behavior and their symmetry, the possible linking of these paramagnetic B_3 and B_5 centers with the optically active X and W centers, respectively, is discussed.

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2 mag \rightarrow dispersief deel!
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Innovations in Intermediate Frequency Spectrometers

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By the application of the intermediate frequency concept, the spectrometers components, such as pulse forming units and detection system, available at X-band can be utilized for the development of spectrometers operating at other frequencies (ex. S-, Q-, and W-band). This concept has been successfully applied at W-band and more recently at Q-band frequencies. EPR spectroscopy at Q-band frequencies provides several advantages over conventional X-band frequencies. These advantages have been successfully exploited in CW-EPR for the analysis of complex systems. Pulse-EPR, pulse-ELDOR and pulse-ENDOR methods also gain from performance at Q-band and offer a wide array of tools for analysis of structure and dynamics. To exploit these advantages at Q-band, a versatile CW/ Pulse Q-band spectrometer and resonators have been developed.

The limited availability of high-power microwave sources and amplifiers at W-band frequencies has imposed limitations on pulse-EPR experiments, through restrictions in pulse excitation bandwidth. To overcome this limitation, the W-band Power Upgrade Module was developed. The spectrometer capabilities have been increased by providing up to 100 mW of pulse output power and an increase in detection sensitivity. The increase in experimental flexibility is demonstrated for pulse-ENDOR and pulse-ELDOR.

Q Reson

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***In vivo* spin trapping as a tool to detect LPS-induced oxidative stress in
different organs of the mouse**

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Oxidative stress induced by the increased formation of (oxygen) radicals including the increased formation of lipid peroxidation free radicals are involved in the induction and progression of multiple diseases as cardiovascular diseases, pulmonary health problems and cancer. ESR/EPR in combination with spin trapping techniques offers a valuable tool to detect and identify this increased radical formation, not only in *in vitro* experiments, but also *in vivo* in different laboratory animals (i.e. rat, mouse). In order to detect and identify free radical formation in the mouse, we performed experiments with this so-called *vivo spin* trappings techniques in this animal.

For induction of *in vivo* radical formation, two laboratory mice were injected intraperitoneal (i.p.) with a single dose of LPS (lipopolysaccharide), a bacterial membrane component that induces severe inflammation. Twenty-three hours later, these and two other control mice were injected with the spin trap α -(4-pyridyl-1-oxide)-N-tert-butylnitron (POBN) and killed one hour later. Target organs (lung, liver, heart, spleen, kidney and thymus) and blood plasma were removed and stored. Subsequently, radical spin trap adducts in different organs were extracted with a Folch lipid extraction and extracts were measured at the ESR. Significantly increased POBN-trapped free radical formation was detected in the liver of LPS treated mice. Apart from the lung, all other organs showed a non-significant increase in radical formation. Values of the hyperfine splitting constants revealed that POBN-trapped carbon centered lipid radical adduct were detected. Furthermore, LPS-treated mice showed a significantly increased vitamin C radical signal in blood plasma.

All in all, these experiments show that the *in vivo* formation of lipid peroxidation free radical products in different organs of the mouse can be measured and identified by ESR. Detection and modulation of this formation in different laboratory mouse models offers the opportunity to develop and improve beneficial strategies for prevention and health care in different diseases.

EPR and ENDOR study of neuroglobin, cytoglobin and Fe(III)tetraphenylporphyrin (bis 4-methylimidazole)

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Neuroglobin and cytoglobin are two recently discovered members of the globin family. Neuroglobin is mainly expressed in the brain, while cytoglobin is expressed in all tissues studied so far. The function of these globins is still unknown. In this work we will present X-band CW EPR, pulsed EPR and ENDOR spectra of the ferric form of these globins. The CW EPR spectra are typical for low-spin Fe(III) complexes. In the pulsed EPR spectra the contributions of the histidine and porphyrin nitrogens and the nearest protons can be identified. As a comparison the HYSCORE spectra of Fe(III)tetraphenylporphyrin (bis 4methyl-imidazole) are shown. This system can serve as a model for the prosthetic group of neuroglobin and cytoglobin, as these globins are characterized by a bisimidazole coordination in the absence of an external ligand. The EPR parameters, derived by simulation of the CW EPR and HYSCORE spectra will be presented. Comparison between the EPR data for the model compound and the globins reveal interesting structural information on the heme pocket of the newly discovered globins.

Frog spectrum
Kermit ← experiment model
Lobster - spectrum. wt

Iron dithiocarbamates as spin traps of biological nitric oxide.

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Iron dithiocarbamate complexes [1] are widely used for spin trapping of nitric oxide radicals in liquids and heterogenous biological materials like plants, mammalian tissue homogenates or biopts. The iron atom of the dithiocarbamate complexes strongly binds the NO ligand to form a stable mononitrosyl iron complex (MNIC). In reduced charge state, the NO-Fe^{2+} -dithiocarbamate adduct is paramagnetic ($S=1/2$) and may be quantified with EPR at 77 K or at room temperature. It has recently become clear that the yield of paramagnetic nitrosyl adducts depends not just on the NO levels, but is strongly affected by the presence of superoxide radicals and the redox properties of the sample.

We demonstrate that the adduct yield of a conventional NO trapping experiment often seriously underestimates the total NO production, and that the degree of this error depends on the type of tissue. More reliable estimates of the true NO production result from a more sophisticated ABC trapping protocol. With ABC the yields of paramagnetic MNIC are enhanced by scavenging of superoxide in the living test animal or cell culture. The scavenging is achieved by suppletion of a known quantity of exogeneous MNIC-DETC complexes. A well defined dosage of exogenous MNIC-DETC may be administered by adding an oversupply of DETC to a known quantity of dinitrosyl-iron-thiosulfate (DNIC) complexes. The DNIC-thiosulfate reacts with free DETC into an equimolar quantity of MNIC-DETC.

The table below gives a representative example of MNIC yields in mice. The mice were treated for four hours with the inflammatory agent lipopolysaccharide (2 mg LPS/kg). Incubation with iron and DETC was 30 minutes. The yields are in nmole MNIC per gram of wet tissue and have an accuracy of ca. 20 % or 30 % for conventional and ABC method, respectively.

Tissue type	Conventional NO trapping (N=5)	ABC method (N=10)
liver	54	160
lung	18	15
kidney	36	300
spleen	2.0	60
brain	14	100

The first column gives the MNIC yields as obtained via conventional NO trapping with Fe-DETC. These amounts underestimate the total NO production because an unknown fraction of NO is lost to superoxide. This NO loss is avoided in the ABC method, where the final yields are higher, accordingly. The data show that the majority of NO is lost to superoxide in brain, kidney and spleen. Liver and lung, on the other hand, have lower superoxide levels.

[1] A. Vanin, A. Huisman and E. van Faassen, *Iron dithiocarbamate as spin trap for nitric oxide detection: Pitfalls and successes*. Meth.Enzym. 359 (2002) 27-42.

↳ kun je hier experimenteel op NMR gebruiken
↳ echt in vivo en H.F. ipvg?

POSTER CONTRIBUTIONS

ESR as a tool for dating geological quartz grains

Koen Beerten^a and Andre Stesmans^b

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One of the main concerns in geological research is the age determination of sediments. Sedimentary deposits consist of eroded material that is transported mostly by wind (aeolian deposits) or water (fluvial deposits) before it is deposited and subsequently buried. Quartz grains derived from sedimentary deposits contain paramagnetic defects (detectable by ESR), which may act as a geological clock. The crucial assumption is that sunlight bleaching before burying serves as a zeroing mechanism, i.e., the ESR signal intensity should be properly set to zero prior to burial of the grains. However, natural bleaching in some natural environments may be limited resulting in incomplete bleaching of the ESR signal.

To compensate for the lower bleaching sensitivity, especially in fluvial environments, in this poster the single grain approach is explored and presented, as has previously been done in optically stimulated luminescence (OSL) dating¹. In this method, an age determination is produced for a number of individual grains, and this provides the possibility to discriminate insufficiently bleached grains which otherwise would be responsible for an age overestimate. Consequently, these grains are excluded from the final age calculation.

Palaeodose distributions from a variety of sedimentary deposits are shown and discussed, including desert sand, fluvial sands and fluvio-aeolian deposits. The results suggest that a population of well bleached grains is present in each deposit.

1. A. S. Murray and R. G. Roberts, *Earth and Planetary Sci. Lett.* 152, 163 (1997)

X-band ODMR-study of the preferential orientation of *para*-phenylene vinylene pentamers in polystyrene spin-coated films

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After the discovery of electroluminescence in *para*-phenylenevinylene (PPV), efforts have been done to improve the performance and to understand the properties of these conjugated molecules. The π -conjugated polymers, like derivatives of PPV, combine semi-conducting properties with the properties of other conventional polymers, such as low mass, good mechanical properties and good processing ability.

In this work we use X-band Optical Detected Magnetic Resonance (ODMR) to study spin-coated films from a PPV-derived pentamer. A 1:1 blend of polystyrene (PS) and the pentamer is dissolved in a 1%wt solution in CHCl_3 and then spin coated at different spin coating speeds. Varying the angle of the magnetic field with the plane of the film, changes in the spectral shape of the ODMR-spectrum are observed. These changes indicate that the pentamers do not randomly occupy all possible orientations as would be in a powder. Simulations of these ODMR-spectra show that almost all pentamers have their backbones close to parallel to the film plane, while only a small percentage pentamers do have their backbones perpendicular to this plane, depending on the preparation method of the different films studied (other pentamer, solvent, spin coating speed).

ODMR is demonstrated to be a powerful technique for the characterization of the orientation of oligomers in a spin coated film.

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ESR quantification of DMPC liposome viscosity change induced by the addition of cholesterol and/or cyclodextrin

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At room temperature, the effect of cholesterol at various percentages on dimyristoyl-L- α phosphatidylcholine (DMPC) membrane liposome has been studied quantitatively. Order parameter (S) and/or correlation time (τ_c) of stearic spin probe (n -DSA) have been calculated from their ESR spectrum. Previously established standard curves (*) allow us to quantify the value of viscosity (η) from S and τ_c . The 5, 12, 16 -DSA have their nitroxylradical group attached at various position along the alkyl membrane chain and then explore the liposome at 8, 10 and 21 Å respectively. At the depth of 8 Å (5-DSA), the progressive addition of cholesterol induces an increase of η from 277.26 cP to a maximum value of 678.98 cP for a 20% mole fraction of cholesterol. We notice that a supplementary addition of cholesterol continues to induce a progressive change on the deeper layers. Thus for a depth of 10 Å (12-DSA), η increases from 64.42 cP to a maximum value of 159.21 cP for a 25% mole fraction of cholesterol. At a depth of 21 Å (16-DSA), η increases from 63.62 cP to 108.77 cP. In this case, a 40% mole fraction of cholesterol is necessary to reach the maximum value of viscosity.

Cyclodextrins are cyclic oligosaccharides with a hydrophilic outer surface and a lipophilic central cavity. They can interact with appropriately sized molecules and form water-soluble inclusion complexes with many lipophilic water-insoluble drugs. Some of cyclodextrins are supposed to penetrate into membrane and to provoke some modifications of the membrane liposome. Extraction of cholesterol can be monitored by a change of the membrane viscosity. In our study, we demonstrate quantitatively that the addition of cyclodextrin (RAMEB) in saturated DMPC liposomes solution, at room temperature, does not change the viscosity. However, the ESR spectrum shows that the solubilisation of RAMEB in DMPC liposomes leads to a leaving of the spin label outside the membrane.

(*) Quantification of Lipid bilayer viscosity and fluidity effect induced by propofol (submitted). M.A.Bahri, B.Heyne, P.Hans, A.Seret, A. Mouithys-Mickalad and M.Hoebeke

**Spin-label EPR on proteins: distance, polarity and dynamics.
Azurin as an example.**

Michela Finiguerra, Irene M.C. van Amsterdam[&], Miguel Prudencio[&],
Sharmini Alagaratnam[&], Marcellus Ubbink[&], Martina Huber

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The utility of spin label EPR has advanced significantly in recent years. Owing to the techniques of molecular biology (site-directed mutagenesis) the spin label can be placed at virtually any position of interest in a protein, and modern EPR techniques reveal interactions and dynamic ranges not previously accessible.

Protein dielectric properties in the vicinity of the spin label are obtained by high-field EPR on spin-labelled proteins [1]. In particular, the higher spectral resolution of high-field EPR, here 95 GHz EPR, allows to measure and correlate g-tensor parameters and hyperfine information from which polarity/proticity properties are derived. Dynamical parameters are obtained from the relaxation properties of the spin labels [2], and by high-field EPR also the anisotropy of the motion of the spin label can be determined [3].

We have prepared spin-labeled variants of the blue-copper protein azurin. Different positions are spin labeled by site-directed mutagenesis, and we explore the possibilities for studying dynamics, distances and polarities at these positions. The spin labels in azurin (Zn) K27C and azurin (Zn) S118C show different mobilities using standard and high-field EPR, and in a double mutant, a long distance between two labels is measured by a pulsed, two-frequency EPR method.

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Comparing the Heme Pocket Structure of Human Cytoglobin, Tomato and Drosophila Hemoglobin

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Human cytoglobin (Cygb), tomato hemoglobin (Hb) and Drosophila Hb are recently discovered globins. Their function is still debated. Combined CW-EPR and optical measurements reveal that the heme iron is hexacoordinated in both the ferrous and ferric form of the proteins. The g values of the Fe(III) forms are typical for a His-Fe³⁺-His ligation. This differs from the high-spin aquomet form observed for ferric vertebrate Hbs and myoglobins. The differences in the EPR parameters of the three types of globins and the influences of pH and temperature on the CW-EPR spectra will be discussed. A preliminary pulsed EPR analysis of the ferric human cytoglobin will be given. Using HYSCORE, the hyperfine and nuclear quadrupole couplings of the heme and histidine nitrogens can be identified and compared with known EPR/ENDOR data of vertebrate Hbs and cytochromes.

Determination of spin Hamiltonian parameters for two Fe^{3+} -impurity centres in $\text{Cs}_2\text{NaAlF}_6$ and $\text{Cs}_2\text{NaGaF}_6$

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Lately, hexagonal Cs_2NaMF_6 crystals ($M = \text{Al}, \text{Ga}$; $R\bar{3}m$ space group [1,2]) doped with Cr^{3+} have gained interest because of their possible application as active medium in optically pumped tunable solid state lasers emitting in the red to near IR. When studying these (hydrothermally grown) crystals with EPR and ENDOR, in order to determine the spin Hamiltonian parameters of the Cr^{3+} centres [3], we found a considerable concentration of Fe^{3+} -impurity centres ($3d^5$, $S=5/2$). This Fe^{3+} -impurity was also present in the melt-grown $\text{Cs}_2\text{NaAlF}_6:\text{Cr}^{3+}$ crystals studied earlier by Fargin et al. [4].

In this work we present the determination of g-tensors and zero field splitting parameters for these Fe^{3+} centres in $\text{Cs}_2\text{NaAlF}_6$ and $\text{Cs}_2\text{NaGaF}_6$, at room temperature and at 20K. As for Cr^{3+} , two inequivalent centres were observed. In view of the resolved superhyperfine interaction with six equivalent ^{19}F nuclei, visible in X (9.5 GHz)- and Q (34.0 GHz)-band EPR-spectra, we could conclude that Fe^{3+} substitutes for the two inequivalent M^{3+} ions in the unit cell, as did Cr^{3+} . By observing the interaction with the nearest ^{23}Na nuclei using ENDOR, we could distinguish the two sites. In order to separate the overlapping EPR spectra of the two centres in the ab-plane, Q-band ENDOR-Induced EPR measurements were performed.

Finally, the g-tensors and zero field splitting parameters for these two centres were determined using the EasySpin program package [5] and compared with the results for the Cr^{3+} -dopant.

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W- and X-BAND EPR STUDY OF THE IMPURITY-DEFECT CENTERS IN $\text{Pb}_{1-x-y}\text{Sn}_x\text{Gd}_y\text{Te}$ CRYSTALS

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PbTe-SnTe solid solutions belong to the group of IV-VI semiconductors that are important materials for the purpose of near and far-infrared electronics. Electrophysical parameters of these materials are crucially determined by their defect system. Doping with rare-earth elements was found to be a very effective approach to control the defect system of the lead and tin tellurides.

Conventional X-band EPR method has previously been successfully applied to study the spectroscopic properties of the Gd ions doped into the PbTe matrix. EPR study also revealed useful information about the behaviour of the defect system of this matrix [1]. That is not the case for the PbTe-SnTe solid solutions in which lead atoms are substituted by Sn atoms in metal sublattice. It is known, that Sn atoms cause local disordering in the crystalline matrix. As a result, defect system and correspondently electro-physical properties of the crystal are changed. Impurity Gd ions in that case could serve as an excellent EPR active probe reflecting Sn induced changes of the crystalline matrix on the local scale.

Sn-induced disordering are responsible for the difficulties in the observation of well-defined EPR signals from $\text{Pb}_{1-x-y}\text{Sn}_x\text{Gd}_y\text{Te}$ single crystals. Instead, a badly resolved spectrum is usually observed. The present work we took is attempt to "catch" the very beginning of the disordering process by studying $\text{Pb}_{1-x-y}\text{Sn}_x\text{Gd}_y\text{Te}$ solid solutions with low concentration of the Sn atoms. For that purpose high quality single crystals of nominal composition $x = 0.05$ and $y = 0.01$ were grown by the Bridgman method.

Several kinds of the EPR active centres were revealed. Combined X-and and W-band experiments have shown that the experimentally observed EPR spectrum for the chosen Sn content is dominated by that originated from the Gd^{3+} ions in cubic sites. Fine structure is resolved only partially for that centre because of the significant spread of the spin Hamiltonian (SH) parameters as compared to the EPR spectrum of the Gd ions in the PbTe matrix. However the value of the SH parameters appeared to be nearly the same for both cases. Another EPR signal with $g \approx 2$ was observed in X-band experiment, which position does not depend on the orientation of the magnetic field with respect to the crystallographic axes. The intensity of the signal increases with increasing of the concentration of the free electrons in the sample. Additional anisotropic signals with 90° periodicity while rotating magnetic field in the (100) plane are also observed.

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Ab initio investigation of X^- ($X = O, S$ and Se) ions in alkali halidesF. Stevens^{a,b}, H. Vrielinck^a, F. Callens^a and M. Waroquier^b^a*Department of Solid State Sciences, Ghent University, Krijgslaan 281-S1, 9000 Ghent, Belgium*^b*Laboratory of Theoretical Physics, Ghent University, Proeftuinstraat 86, 9000 Ghent, Belgium*

In spite of the apparent simplicity of mono-atomic X^- ($X = O, S$ and Se) defects in alkali halides, relatively little is known about the precise incorporation of these chalcogen ions this class of lattices. Using Electron Paramagnetic Resonance (EPR), X^- ions with tetragonal, orthorhombic-I and monoclinic-I g tensor symmetry were observed. Because interpretation of experimental EPR results in terms of the geometry and the defect structure is not a trivial task, the location and nearest environment of the mono-atomic defects in the alkali halide lattice could not be convincingly established yet for any of these three classes. Therefore, taking the available experimental parameters as computational targets, these data have been further interpreted by suitable quantum chemical calculations using Density Functional Theory (DFT) methods.

The final assignment of a defect structure to a particular class of X^- ions is based on the quantitative and qualitative reproduction of experimental g and hyperfine values.

Conformations involving a next nearest neighbor and nearest neighbor halide vacancy are proposed as plausible defect structures for the X^- ions with tetragonal and orthorhombic-I g tensor symmetry respectively. For the mono-atomic ions with monoclinic-I symmetry, a perturbed interstitial defect model is suggested.

Using a similar cluster in vacuo approximation based on DFT, EPR parameters of both di- [1-3] and tri-atomic [4-5] chalcogen ions in alkali halide lattices were studied. Therefore, this work is an extension of our previous research on chalcogen doped alkali halides.

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Nitrosyl Binding Modes in human Neuroglobin

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The function of neuroglobin (Ngb), a recently identified member of the globin superfamily, is yet unknown. Several possibilities have been suggested, amongst which an involvement in the NO metabolism.

EPR studies and optical measurements show that the heme iron in Ngb is hexacoordinated in both the ferrous and ferric form of protein. The axial ligands were identified as histidines at positions E7 and F8. Preliminary pulsed EPR results on ferric human Ngb will be shown.

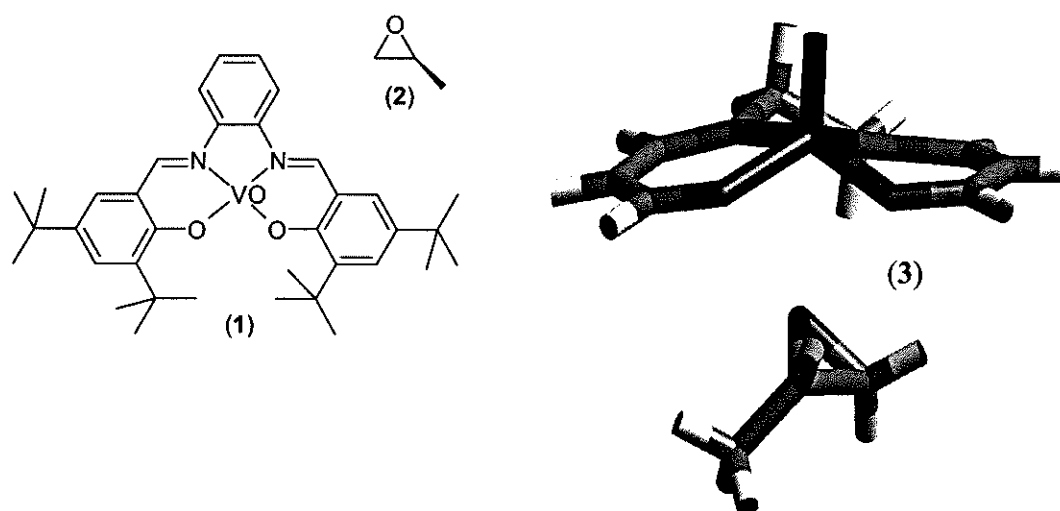
Escherichia coli cell cultures with low O₂ concentration overexpressing proteins generate nitric oxide (NO). When wild type human Ngb is overexpressed in *E. coli* cell cultures grown under anaerobic conditions, the protein is predominantly in the F8His-Fe²⁺-E7His form, whereby a small percentage of the protein is in the nitrosyl ferrous form (F8His-Fe²⁺-NO). In contrast, under the same conditions, the E7-Leu and E7-Gln mutants of the protein are mostly in the nitrosyl ferrous form. This indicates an important role of the E7 residue in stabilizing the exogeneous NO ligand. The differences in the temperature dependence of the CW-EPR spectra of wild-type, E7-Leu and E7-Gln hNgbNO will be related to the heme pocket structure. Comparisons will be made with vertebrate hemoglobins and myoglobins.

A ^1H ENDOR and DFT study of weak solvent interactions with a Vanadyl Schiff-base complex

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An angular selective ENDOR study, in combination with DFT calculations, was used to investigate the subtle diastereomeric effects of a vanadyl complex in frozen solution. The present work illustrates for the *first time* the use of ENDOR spectroscopy to measure diastereomeric interactions between a chiral paramagnetic complex-Vanadyl salen (1) and a chiral substrate-Propylene oxide (2). Our work has indicated that whilst EPR spectroscopy is not sensitive enough to discriminate between the weakly bonded diastereomeric complexes formed between chiral [VO(salen)] and chiral epoxides in solution, ENDOR spectroscopy can discriminate between such diastereomers. Whilst ENDOR spectroscopy has been widely and elegantly used for structural determination of complex biosites¹, it has not been broadly applied in the area enantioselective catalysis. The assignment of features in the ENDOR spectra as coordinated epoxide fragments has been confirmed using a range of solvents, the use of structurally less elaborate ligands, selective deuteration of ligand protons and the use of a per-deuterated chiral substrate (Propylene oxide- d_6). A complimentary DFT study has also been used to confirm the assignments and has yielded accurate structural information that is in excellent agreement with the data obtained from the simulation of the experimental ENDOR data. Such coordinated epoxide complexes have been proposed as reaction intermediates in the enantioselective ring opening kinetic resolutions of racemic epoxides^{2,3}, but to date have not been observed in solution. We therefore report the direct observation of a coordinated epoxide in frozen solution-(3, simplified model) and for the first time demonstrated the use of a paramagnetic complex as a chiral ENDOR shift reagent.



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Q-band EPR and ENDOR of room and low temperature X-irradiated β -D-fructose single crystals

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Irradiated sugars have been examined by Electron Magnetic Resonance (EMR) techniques from many points of view. Most of these investigations were stimulated by other research topics and applications. For example, sugar radicals are believed to play a major role in the radiation damage to deoxyribose nucleic acid (DNA).

One serious drawback in the study of irradiated solid state sugars is the occurrence of many, sometimes very similar, radicals which can complicate the analysis of the EMR spectra. Furthermore, the nature of the observed radicals is temperature dependent, leaving the primary radiation defects mostly unobserved after irradiation at room temperature (RT). Examination of spectra from low temperature (LT) irradiated sugars, offers the opportunity to study the pristine radiation defects. The spectral evolution from LT to RT can in principle provide information about radical reactions that could eventually explain the observed radical products at RT.

In order to acquire resonance data of LT (liquid N₂ in this case) X-irradiated single crystals, a prototype continuous wave Q-band EPR/ENDOR cryostat/cavity was used, developed by the EPR group at the University of Oslo. This special equipment allows to in-situ X-irradiate an oriented (e.g. by means of XRD) single crystal at LT. The latter procedure circumvents important practical obstacles.

The special Q-band cavity was used to study the LT X-ray induced radicals in β -D-fructose single crystals. The ENDOR measurements show the presence of at least six carbon-centered radicals. By means of EI-EPR it was observed that three of the radicals exhibit one large and two small hydrogen hyperfine couplings and the other three radicals mainly show a single large hyperfine coupling. In total, six hydrogen hyperfine tensors were completely determined. The results for the LT radicals are compared with the results of ongoing Q-band measurements on RT X-irradiated fructose single crystals. Plausible radical models are put forward and discussed.

Destruction of Stearic Acid Nitroxyl Radicals Mediated by Photoexcited Pyropheophorbide-a Methyl Ester in Liposomal Systems

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Photodynamic therapy (PDT) is a new treatment modality that selectively destroys malignant, premalignant, and benign lesions in patients and is initiated by the selective accumulation of a photosensitizing agent in malignant tissue.

The sensitizer is harmless unless and until activated by light of the appropriate wavelength. Several groups have recently reported the antitumor efficacy of pheophorbide- and pyropheophorbide-based photodynamic therapy. Among these compounds, pyropheophorbide-a methyl ester (PPME) is a photosensitizer of the second generation. He has received increasing attention because its strong absorption above 600nm (which is optimal for effective penetration through tissue) and its high production of $^1\text{O}_2$. PPME has also no dark cytotoxicity.

In this work, four spin-labeled stearic acids (n-DSA) have been included into dymiristoyl-L- α -phosphatidylcholine (DMPC) large unilamellar liposomes, in order to study the photochemical behaviour of PPME towards nitroxyl radicals situated at various depths in lipids bilayers.

Visible illumination of the dye, either free in ethanol or bound to liposomes, leads to the reduction of the electron spin resonance signal of the label. In homogeneous solvent like N_2 -saturated ethanol, the series of n-DSA studied are reduced at similar rates in the presence of photoexcited PPME. In the N_2 -saturated liposomes, PPME is localised in the bilayer and the efficiency of the interaction between PPME and spin labels depends on the depth at which the nitroxyl moiety is localized.

Our results demonstrate that photoexcited PPME is able to destroy the paramagnetism of spin-labeled doxyl stearic acid incorporated in liposome by a electron transfer (Type 1 photoreaction).

X- and Q-band EPR study of irradiated bone from human fingers

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Tooth enamel and bone are integrated dosimeters which record the radiation history of the skeleton. During irradiation, electrons and holes become trapped in the crystalline component of the material (hydroxyapatite). Most radicals are very stable at room temperature and can be measured using EPR spectroscopy. The radiation-induced CO_2^- signal is proportional to the administered radiation dose and can be used for estimating it. Parallel to the radiation-induced signal a broad "native" signal is also present which is supposed to be due to the organic component of the material. Tooth enamel is much more studied by EPR due to its higher sensitivity to irradiation and due to the lower contribution of the native signal which masks the dosimetrically important signal (CO_2^-) especially at doses lower than 10 Gy. In bone the nature of the formed centers except the signal of CO_2^- is not well established. We are studying bone irradiated at high dose (> 1 kGy) using X- and Q-band EPR. The spectra at high frequency look more complex than at lower frequency because of a larger number of superimposed components becomes resolved. As the hydroxyapatite is the main component in teeth and bones, the identification of some species is made using the existing data for irradiated tooth enamel. The radicals CO_2^- and CO_3^{3-} are formed but the most important contribution, however, is coming from the CO_2^- radical. The native signal in bone is more complex after irradiation and shows additional features.

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