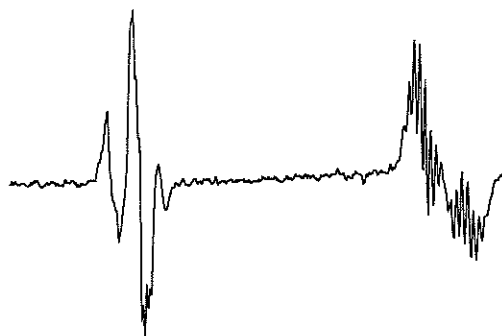




# **Eighth Meeting of the Benelux EPR Society**

**Programme  
Book of Abstracts  
List of Participants**



**May 29, 2000**

Ghent University (RUG)  
Department of Solid State Sciences  
Krijgslaan 281-S1/S2  
B-9000 Gent, Belgium

## The organising committee

F. Callens (local organiser),  
P. Matthys, S. Amira, K. Sabbe, G. Vanhaelewyn, H. Vrielinck,  
P. Gast (Secr. Benelux EPR Soc.),  
D. Schoemaker (Chairman Benelux EPR Soc.)

## Scientific Programme

- 09h00-10h00 : Registration, setup of posters, settlement of membership, coffee bar
- 10h00 : Welcome and Introduction by F. Callens
- 10h10 : Invited lecture : **A. Sienkiewicz**, Polish Academy of Science :  
*"Ultra-Wide Band Multi-Frequency High Field EMR Technique, a Methodology for Increasing Spectroscopic Information"*.
- 11h00 : **E. van der Horst**, University of Nijmegen :  
*"HF-EPR on Solid Molecular Oxygen"*.
- 11h25 : **S. Amira**, Ghent University :  
*"EPR Dosimetry with Teeth : Potential, Limitations and Prospects"*.
- 11h50 : **B. Gallez**, Université Catholique de Louvain :  
*"Monitoring of Tumor Oxygenation Using in Vivo EPR"*.
- 12h15 : Lunch
- 14h15 : **A. Kamlowski**, EPR Division Bruker, Karlsruhe :  
*"W-band EPR and ENDOR Experiments with the BRUKER E680 ELEXSYS Spectrometer"*.
- 14h40 : **Pham Thanh Huy**, University of Amsterdam :  
*"Magnetic Resonance Investigation of Gold and Gold-Hydrogen Complexes in Silicon"*.
- 15h05 : Coffee break
- 15h35 : **G. Janssen**, University of Antwerp :  
*"A 95 GHz ODMR Study of AgCl Nanocrystals Embedded in Crystalline KCl Matrix"*.
- 16h00 : **K. Sabbe**, Ghent University :  
*"X and Q-band Magnetic Resonance Study of Iridium Doped Silver Chloride Microcrystals"*.
- 16h25 : General Meeting of Benelux EPR Society
- 17h00 -18h30 : **Poster Session** : open for both the Benelux EPR Society and the Bilateral Workshop on Radiation-Induced Defects in Solids (May 30).

## Poster Session

- 1. Q-band EPR and ENDOR Study of Rh<sup>+</sup> in NaCl Single Crystals**  
H. Vrielinck, F. Callens and P. Matthys
- 2. Free Radicals Contained in Licorice-flavored Sweets can be Detected Non Invasively after Oral Administration to Mice using Low Frequency EPR**  
B. Gallez, C. Baudelet and R. Debuyst
- 3. EPR studies of Pharmaceuticals in Solid Phase**  
M. Gibella, A. Engalytcheff, A.-S. Crucq, B. Tilquin, P. Stocker, G. Lesgards and J. Raffi
- 4. Multifrequency EPR Study of Radicals Produced by Radiation in Shells and Corallite**  
G. Strzelczak, G. Vanhaelewyn, W. Stachowicz, E. Goovaerts, F. Callens and J. Michalik
- 5. EPR and ENDOR Study of Human Tooth Enamel Heated at 400°C**  
J. Sadlo, G. Vanhaelewyn, S. Amira, R. Morent, P. Matthys, F. Callens, J. Michalik and W. Stachowicz
- 6. Conduction Electron Spin Resonance (CESR) of Metallic Particles in Mesoporous Materials**  
M. Danilczuk, Jong-Sung Yu, D. Brown, L. Kevan and J. Michalik
- 7. Cationic Silver Clusters in Sodalites**  
J. Perlinska, H. Yamada and J. Michalik
- 8. EPR Study of Lewis-acid Sites in Zeolites Using NO as Probe Molecule**  
G. Catana, B.M. Weckhuysen and R.A. Schoonheydt
- 9. Dielectric Resonator-Based Resonant Structure for ESR Measurements at High Hydrostatic Pressures**  
A. Sienkiewicz, S. Garaj, M. Jaworski, C.P. Scholes and L. Forro

- 10. New Opportunities Offered by High-Field EPR/ENDOR in the Structural Characterisation of Mn(II) Sites in Aluminophosphate Zeolites**  
D. Arieli, D.E.W. Vaughan, K.G. Strohmaier and D. Goldfarb
- 11. Single Crystal High Frequency EPR of  $\text{Fe}_4(\text{OCH}_3)_6(\text{dpm})_6$**   
M. Stefan, A. Bouwen, E. Goovaerts, D. Gatteschi, R. Sessoli and L. Sorace
- 12. Nano-scale Structure of Rare Earth Doped Oxide Glasses as Studied by Electron Spin Echo Spectroscopy**  
S.B. Orlinskii and E.J. Reijerse
- 13. A CW/pulsed Heterodyne 190 GHz EPR Bridge**  
E.J. Reijerse, A.A.K. Klaassen and W.R. Hagen
- 14. Thermodynamics and Kinetics of Proton Exchange in pH-sensitive Imidazolyl Spinlabels as Studied by D-band EPR**  
E.J. Reijerse, V.V. Khramtsov and I.A. Grigor'ev
- 15. Lineshape effects of distributions in the zero field splitting parameters**  
A.H. Priem, A.A. Klaassen, E.J. Reijerse and W.R. Hagen

# ABSTRACTS

# Ultra-Wide Band Multi-Frequency High-Field EMR Technique: A Methodology for Increasing Spectroscopic Information

Andrzej Sienkiewicz<sup>&</sup>, Jerzy Krzystek<sup>\*</sup>, and Louis-Claude Brunel<sup>\*</sup>

<sup>&</sup>Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland;

<sup>\*</sup>Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Florida State University,  
1800 E. Paul Dirac Drive, Tallahassee, Florida 32310

We report methodology that combines an ultra-wide band multi-frequency microwave system with technology of high-magnetic fields for solving challenging problems in electron magnetic resonance (EMR) spectroscopy. This strategy has been made possible due to a novel EMR facility operating in an exceptionally wide range of microwave frequencies of 24 GHz to 3 THz, at the magnetic fields up to 17 T, and in the temperature range of 1.6 to 330 K. The basic configuration of the multi-frequency system works in a transmission mode and employs oversized cylindrical waveguides for routing the microwave power. Wide-band, low-noise, liquid helium cooled (4.2 K) InSb bolometer is used for the signal detection. This approach results in an extremely wide-band performance, thus making it possible to employ a variety of solid state millimeter and submillimeter microwave sources in combination with a far infrared laser (FIR) microwave source for performing multi-frequency EMR experiments. A complexity of resonant structures and related technical problems like microphonics at high magnetic fields are virtually eliminated. The system is simple, yet sensitive and revealed to be extremely advantageous while solving such problems as: observation of AFMR transitions in spin-ordered systems, *g*-factor resolution enhancement in complex organic radicals, and resonance signal detection in EMR-silent spin systems having integer-spin and large zero field splitting. Technical description of the multi-frequency high-field EMR facility is presented and results of its performance tests are given. The potential utility of using the multi-frequency high-field methodology in EMR studies is illustrated with selected examples of its recent applications.

## HF - EPR ON SOLID MOLECULAR OXYGEN

E. van der Horst and P.J.M. van Bentum

High Field Magnet Laboratory, Toernooiveld 1, 6525 ED NIJMEGEN, The Netherlands

Molecular oxygen is a triplet spin system both in the gas phase and in the low temperature solid phase. Pure solid oxygen forms an anti-ferromagnetic lattice with a 25 K transition to an antiferromagnetic phase with two sublattices. It was recently shown that at this transition the effective molecular moment changes considerably [1].

Despite the relative abundance and importance of molecular oxygen surprisingly little is known about the spin dynamics in the solid state. For example, the value of the exchange interaction leading to a zero field splitting in the spectrum is not accurately known. Also, the disappearance of the EPR triplet spectrum at elevated temperatures is not well understood. Partly, this is due to the limitations of conventional low frequency EPR, which cannot resolve the full spectrum in integer spin systems.

In this contribution we will present the results of a multi-frequency EPR study on molecular oxygen in a solid nitrogen matrix, using frequencies up to 400 GHz and fields up to 16 T. The low temperature spectrum can be well described by a simple triplet with a zero-field splitting  $D$  of  $3.49 \text{ cm}^{-1}$ , even in concentrations as high as 20 %. The zero-field splitting turns out to be weakly temperature dependent up to a temperature of about 25 K. At higher temperatures the triplet spectrum vanishes and the spectrum transforms into a quasi-continuum centered around  $g=2$ .

This suggests that the triplet binding of the two unpaired electrons on the oxygen molecule is destroyed by thermal motion of the molecule in the host lattice. It is conceivable that the same mechanism is also the driving force behind the 25 K anti-ferromagnetic phase transition in pure solid oxygen.

Since molecular oxygen is a common impurity in chemical and biological systems, the present study provides a valuable reference for high field - high frequency EPR studies in general.

[1] Bermeo et. al., Journal of Low Temperature Physics, 1998, vol. 111, 287-302

## EPR dosimetry with teeth : potential, limitations and prospects

S. Amira, G. Vanhaelewyn and F. Callens  
Vakgroep Vaste-stofwetenschappen, Universiteit Gent,  
Krijgslaan 281-S1, B-9000 Gent.

EPR dosimetry with teeth is based on the assessment of radiation induced carbonate derived radicals in hydroxyapatite, which is the mineral component of teeth. The most stable radical,  $\text{CO}_2^-$ , is favourably used for dosimetric purposes. Especially at low doses, the evaluation of the dosimetric EPR signal is not a simple task, due to the presence of an overlapping native signal. A number of methods to isolate the dosimetric signal is combined with the additive dose method to determine the absorbed dose. All these methods imply a number of assumptions concerning the nature and behaviour of both the dosimetric and the native signal. How these assumptions may affect the dose reconstruction, using the  $\text{CO}_2^-$  radical will be discussed. The material presented here is for the greater part taken from the "2<sup>nd</sup> International Intercomparison on EPR Tooth Dosimetry". [1]

[1] "The 2nd International Intercomparison on EPR Tooth Dosimetry", A. Wieser, K. Mehta, S. Amira, D. Aragno, S. Bercea, A. Brik, A. Bugai, F. Callens, V. Chumak, B. Ciesielski, R. Debuyst, O.G. Dului, P. Fattibene, E.H. Haskell, R.B. Hayes, E.A. Ignatiev, V. Kirillov, E. Kleschenko, N. Nakamura, J. Nowak, S. Onori, B.P. Pass, S. Pivovarov, A. Romanyukha, A.I. Schames, O. Scherbina, S. Sholom, D.D. Tikounov, S. Toyoda, Rad. Meas., in press.



# Monitoring of tumor oxygenation using in vivo EPR

Bernard Gallez

Laboratory of Medicinal Chemistry and Radiopharmacy and Laboratory of Biomedical Magnetic Resonance, Université Catholique de Louvain, B-1200 Brussels, Belgium

Inadequate tumor oxygenation strongly contributes to the failure to cure some cancers by radiotherapy. Currently, there is a lack of adequate methodology able to measure accurately, sensitively, and non invasively the partial pressure of oxygen ( $pO_2$ ) in tissues. The development of such a methodology should improve the monitoring of the therapeutic approach (predictive assay for the radiosensitivity) and should lead to innovative interventions aiming at increasing the tumor oxygenation.

We have developed EPR oximetry methodology using a low-frequency EPR spectrometer (1.1 GHz) to quantify the  $pO_2$  in transplantable mouse tumor models. The principle of the method relies on the implantation of small paramagnetic particles of charcoals possessing a linewidth sensitive to oxygen. These compounds were calibrated in different media and were checked for the stability of the responsiveness to oxygen in vivo.

In this presentation, we will illustrate the power of this tool to assess the tumor oxygenation in different studies:

- . assessment of the effect of vasoactive agents in tumor models
- . assesment of the time course of action of these drugs as well as their efficacy
- . use of EPR to understand MRI contrast in imaging protocols sensitive to the oxygenation (Blood Oxygen Level Dependent imaging)
- . use of EPR to calibrate new tracers of hypoxia (nitroimidazole EF5)

## References

- B. Jordan, C. Baudelet, and B. Gallez. Carbon-centered radicals as oxygen sensors for in vivo Electron Paramagnetic Resonance: Screening for an optimal probe among commercially available charcoals. *MAGMA* 7, 121-129, 1998.
- B. Gallez, B. Jordan, C. Baudelet, P.-D. Misson. Pharmacological modifications of the partial pressure of oxygen in tumors. Evaluation using in vivo EPR oximetry. *Magn. Reson. Med.* 42, 627-630, 1999
- B. Jordan, P.-D. Misson, R. Demeure, C. Baudelet, N. Beghein, and B. Gallez. Changes in tumor oxygenation/perfusion induced by the NO donor, isosorbide dinitrate, in comparison with carbogen: monitoring by EPR and MRI. *Int. J. Radiat. Oncol. Biol. Phys.* in press
- K. Mäder and B. Gallez. Pharmaceutical applications of in vivo EPR. In: *Biological Magnetic Resonance*, Volume 20, L. Berliner, ed. in press
- B. Gallez and K. Mäder. Accurate and sensitive measurements of  $pO_2$  in vivo using low frequency EPR spectroscopy: how to confer biocompatibility to the oxygen sensors. *Free Rad. Biol. Med.* in press

## W-band EPR and ENDOR Experiments with the BRUKER E680 ELEXSYS Spectrometer

*Andreas Kamlowski, Peter Höfer, and Dieter Schmalbein  
Bruker Analytik GmbH, Rheinstetten, Germany*

High-frequency/high-field EPR is becoming more and more a routine technique in present-day EPR spectroscopy applications. With the advent of the BRUKER W-band 94 GHz ELEXSYS spectrometer series, this advanced field of EPR became accessible to a wider research community.

The increased spectral resolution is one of the main advantages of high-frequency/high-field EPR. For instance, the principal  $g$ -tensor components of organic or biological radicals become resolved at W-band while at X-band they may not. Concomitantly, the higher the Zeeman splitting, the higher the absolute sensitivity due to the enlarged population difference.

High-field EPR constitutes a major cornerstone in the so-called multifrequency EPR approach. Information is gathered at lower frequencies, *i.e.* S-, X- and Q-band and contrasted with the results at *e.g.* 94 GHz. This paves the way for studies on *e.g.* the molecular motion of nitroxide spin-labels providing valuable information on rotational correlation times and the environment of the label. A key advantage of multifrequency EPR is that field-dependent and field-independent contributions to the spectrum become disentangled. This implies that the parameters obtained via simulation are more reliable than obtained upon simulation of a single-frequency EPR spectrum.

This presentation will highlight the main features as well as configuration possibilities of the W-band ELEXSYS spectrometer. Moreover, selected EPR and ENDOR applications will be presented. In addition, CW-EPR spectra will be compared to simulations obtained with BRUKER's EPR Simulation Suite: *XSophe-XeprView-Sophe*

We are grateful to our customers for the interesting applications and for giving permission to present the data. Demo licenses for *XSophe-XeprView-Sophe* are available on request: [www.bruker.de/wwwesr](http://www.bruker.de/wwwesr)

## Magnetic resonance investigation of gold and gold – hydrogen complexes in silicon

P. T. Huy, C. A. J. Ammerlaan and T. Gregorkiewicz  
Van der Waals – Zeeman Institute, University of Amsterdam  
Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands

Transition metals are important impurities in the semiconductor materials, especially in silicon. If present in the materials, the transition metals create several deep levels within the band gap of the semiconductor, as a result of which the electronic properties of the materials or devices are changed dramatically. Transition metals are also easily involved in impurity-pair or complex formation and precipitation processes.

Gold in silicon, due to its technological importance and to its vital role in the understanding of the electronic properties of transition metal impurities, is one of the most studied defects. Substitutional gold in silicon is known to introduce two levels in the band gap. The deep acceptor and donor levels are at  $E_C-0.54$  eV and  $E_V+0.35$  eV, respectively. In spite of this, however, some controversy has remained concerning the relevant details of its electronic structure.

In the present study, by introducing hydrogen at high temperature in an atmosphere of water vapor ( $H_2O$  or  $D_2O$ ), an effort has been made to elucidate the atomic and electronic structure of defects related to gold and gold – hydrogen complexes. We report on three new EPR centers labeled Si-NL62, Si-NL63 and Si-NL64 which based on the analysis of the experimental observations will be assigned to a gold-impurity pair, and gold-gold – hydrogen pair and a complex of  $Au-H_2$ , respectively.

Corresponding author: Mrs. G. Janssen, (address for correspondence only) University of Antwerp (UIA), Physics Department, Universiteitsplein 1, 2610 Antwerpen(Wilrijk), Belgium, [grietj@uia.ua.ac.be](mailto:grietj@uia.ua.ac.be), fax: +32 3 820 2470

A 95GHz ODMR STUDY OF AgCl NANOCRYSTALS EMBEDDED  
IN CRYSTALLINE KCl MATRIX

G. Janssen<sup>+</sup>, E. Goovaerts<sup>+</sup>, S. V. Nistor\*, A. Bouwen<sup>+</sup>, D. Schoemaker<sup>+</sup>,  
H. Vogelsang\*\* and W. von der Osten\*\*

<sup>+</sup> Physics Department, University of Antwerp (UIA), B-2610 Antwerpen, Belgium

\* National Institute for Materials Physics, POB MG-7 Magurele, 76900 Bucharest, Romania

\*\* Fachbereich Physik, Universität-GH D-33095 Paderborn, Germany

The defect properties of silver chloride (AgCl), an indirect bandgap material with NaCl crystal structure, have been extensively studied due to its importance as photosensitive material. Various optical and magnetic resonance studies have shown the holes to be localized on a Ag<sup>+</sup> lattice ion as a self-trapped hole (STH), the hole trapping being accompanied by a tetragonal J-T distortion of the surrounding Cl<sup>-</sup> ions [1]. Furthermore, the STH weakly binds an electron forming a self-trapped exciton (STE). The electron is in a very diffuse hydrogen-like 1s orbital, extending at least up to the 90<sup>th</sup> silver shell, while the hole is strongly localized essentially in one lattice cell [2,3]. Nanocrystals (NCs) of AgCl in a crystalline (alkali halide) matrix with radii close to the spatial extension of the STE have been successfully prepared [4]. Due to the spatial confinement effect only the recombination of the STE has been observed, the distant electron-hole pair ("donor-acceptor") and impurity STE (Br<sup>-</sup>) recombination are absent.

We present here optically detected magnetic resonance (ODMR) spectra of AgCl NCs embedded in the KCl single crystal lattice. Detection was performed via the change of the photoluminescence (PL) intensity under modulated W-band (95 GHz) microwave excitation. As in a previous ODMR study [4] in the Q- band (35GHz) only the STE-spectra are observed, due to spatial confinement and impurity exclusion. Moreover, through increased resolution we have been able to determine more accurately the g-values and zero-field splitting of the triplet state. The angular variation of the spectra can be described using parameter values very close to those of the STE in bulk AgCl. Spectral changes have been observed between different samples, which seem to result from variation in the NCs properties .

[1] K. S. Song and R. T. Williams, in *Self-Trapped Excitons*, vol. 105 of *Solid State Sciences*, ed. by M. Cardona, Springer, Berlin 1993.

[2] O. G. Poluektov, M. C. J. M. Donckers, P. G. Baranov and J. Schmidt, *Phys. Rev.* **B47**, 10226 (1993).

[3] M. T. Bennebroek, A. Arnold, O. G. Poluektov, P. G. Baranov and J. Schmidt, *Phys. Rev.* **B53**, 15607 (1996).

[4]. H. Vogelsang, O. Husberg, U. Köhler, W. van der Osten and A. P. Marchetti, *Phys. Rev.* **B** (to be published)

# X and Q-band magnetic resonance study of iridium doped silver chloride microcrystals.

K. Sabbe, H. Vrielinck, F. Callens

Vakgroep Vaste-stofwetenschappen, Universiteit Gent,  
Krijgslaan 281-S1, B-9000 Gent.

D. Vandenbroucke

Agfa-Gevaert Research Laboratories  
Septestraat 27, B-2640 Antwerp, Belgium

Irradiation at low temperature ( $T < 120\text{K}$ ) of iridium doped AgCl microcrystals with X-rays leads to the formation of a single  $\text{Ir}^{2+}$  complex. The comparison between X and Q-band EPR (Electron Paramagnetic Resonance) spectra shows that the defect has a small orthorhombic distortion. Pulse-anneal to temperatures higher than 170K converts the complex into a second  $\text{Ir}^{2+}$  complex with axial symmetry. This conversion is monitored with X-band ENDOR (Electron Nuclear Double Resonance), which allows a consistent spectrum decomposition and interpretation. For both defects a model is proposed and the general EPR and ENDOR parameters are in agreement with the parameters for  $\text{Ir}^{2+}$  complexes in NaCl and AgCl single crystals [1-4].

[1] Eachus R.S. and Graves R.E., *J. Chem. Phys.*, **65**(4), 1976, p. 1530

[2] A.P. Manchetti, R.S. Eachus, *Adv. in Photochem.*, **17**, 1992, p. 145

[3] Vugman, N. V. and Pinhal, N. M., *Mol. Physics*, **38** (6), 1979, p. 1999

[4] M. Zdravkova, K. Sabbe, F. Callens, E. Dobbeleir, P. Matthys, *Imag. Science J.*, **47**, 1999, p. 63

## Q-band EPR and ENDOR study of a cubic $\text{Rh}^+$ centre in NaCl single crystals

H. Vrielinck, F. Callens and P. Matthys

Department of Solid State Sciences

Krijgslaan 281 - S1, B9000 Gent, Belgium

In a recent X-band ENDOR study of X-ray irradiated  $\text{NaCl}:\text{Rh}^{3+}$  single crystals, a paramagnetic centre has been identified as a  $\text{Rh}^+$  ion (with  $4d^8$  configuration) on a substitutional  $\text{Na}^+$  position [1]. The ENDOR analysis demonstrated that the centre has an effective spin  $S = 1$  and octahedral site symmetry. However, apart from a weak  $\Delta M_S = 2$  transition, the EPR spectrum of this centre remained undetected in X-band.

In this work the results of a Q-band EPR and ENDOR study of this  $\text{Rh}^+$  centre are presented. It is shown that X and Q-band provide mutually consistent and complementary information. The observation of the  $\Delta M_S = 1$  EPR spectrum in Q-band, consisting of a broad single quantum and a much narrower double quantum transition, allows an accurate determination of the  $g$  value of the centre and confirms that its cubic symmetry. The Q-band ENDOR transitions are assigned to the  $M_S = 0$  multiplet of the first shell Cl nuclei, which was not observed in X-band.

- [1] H. Vrielinck, M. Zdravkova, F. Callens and P. Matthys, *J. Chem. Soc. Faraday Trans.* **94**, 2999-3002 (1998)

# Free radicals contained in liquorice-flavored sweets can be detected non invasively after oral administration to mice using low frequency EPR\*

Bernard Gallez, Christine Baudelet, René Debuyst

Laboratory of Medicinal Chemistry and Radiopharmacy and Laboratory of Biomedical Magnetic Resonance, Université Catholique de Louvain, B-1200 Brussels, Belgium

## 1. Introduction

Liquorice, the underground part of the *Glycyrrhiza* species, is one of the most frequently used constituent in natural medicine, but also a flavour used in many sweets (cachou). Recently, the phenolic constituents of liquorice have been found to exhibit a variety of effects such as antioxidant activity. A recent study elucidated the phenolic constituents of liquorice with scavenging radicals activities. They showed that these liquorice phenolics were able to be oxidized into stable radicals (1). The aim of this study was to demonstrate the presence of free radicals in liquorice preparations (particularly in sweets), and eventually to observe the fate of these free radicals after oral administration to animals.

## 2. Material and methods

A total of ten preparations containing liquorice were tested: pieces and powder of liquorice, and several commercial liquorice-flavoured sweets. The samples were analyzed using X-Band EPR spectrometer for the characterization of the radicals (g-value and linewidth). One of the sample (Cachou Lajaunie) presented a strong EPR signal and was used for in vivo studies. 1 ml of a suspension (containing 1 g of finely divided cachou) was administered to four anesthetized mice and EPR spectra were recorded non invasively using a low-frequency EPR spectrometer (1.1 GHz). A great sensitivity was obtained by laying the animal stomach down on top of the coil as the organ under study was close to the area of reception.

## 3. Results

All samples contained a free radical with a g-value of 2.003-2.004 and a linewidth of 6.8 to 9 Gauss. One of the sample (Cachou Lajaunie) presented a strong EPR signal with a g-value of 2.0029 and a linewidth of 0.52 Gauss. When administered to mice, the signal recorded from the stomach region was rather stable as the signal decreased of approximately 20 % over the time of observation (80 minutes). That indicates a very low reactivity of these radicals in the biological media. It is likely that the decrease of this signal is due to the gastric emptying.

## 4. Conclusion

This study is the first report demonstrating non invasively the presence of free radicals in vivo coming from the food. We are further investigating the possibility to monitor using EPR the fate of free radicals coming from irradiated food. This study emphasized that the non invasive detection of free radicals in the gut using low frequency EPR is not limited to the use of spin labels (2).

## 5. References

- (1) Hatano T, Takagi M, Ito H, Yoshida T [1997] *Chem. Pharm. Bull.* 45: 1485-1492.
- (2) Gallez B, Mäder K, Swartz HM [1996] *Magn. Reson. Med.* 36: 694-697

\* : to be published in a forthcoming issue of *Journal of Nutrition*

## EPR studies of pharmaceuticals in solid phase

M. Gibella<sup>1</sup>, A. Engalytcheff<sup>1</sup>, A-S Crucq<sup>1</sup>, B. Tilquin<sup>1</sup>, P. Stocker<sup>2</sup>, G. Lesgards<sup>2</sup>, J. Raffi<sup>3</sup>

<sup>1</sup> Unité d' Analyse Chimique et Physico-chimique des Médicaments, Université Catholique de Louvain, U.C.L.  
72.30, Avenue E. Mounier, 72, B-1200 Bruxelles

<sup>2</sup> Laboratoire de Chimie des Produits Naturels, Université d' Aix-Marseille, Faculté de Saint-Jérôme, 13397  
Marseille cedex 20, France

<sup>3</sup> Laboratoire de Recherche sur la Qualité des Aliments, Commissariat à l' Energie Atomique (DSV/DEVM) et  
Université d' Aix-Marseille, Faculté de Saint-Jérôme, 13397 Marseille cedex 20, France

Sterilization by high-energy ionizing radiations (  $\gamma$  rays, electron beams ) arouses more and more interests thanks to its numerous advantages.  $\gamma$  rays induce almost no rise in temperature which make them usable to sterilize thermosensitive drugs for example. Moreover, the high penetration of those rays lead to the possibility of terminal sterilization. Nevertheless, there is still a lack of knowledge concerning the radio-initiated chemical mechanisms and this method can't be used yet with all the guarantees required. At last, radiosterilization is not permitted in all the countries and a method to differentiate irradiated from non-irradiated products would be very useful.

Electron Paramagnetic Resonance (E.P.R.) can be used both for studying radiolytic mechanisms and for detection of irradiated drugs. Five antibiotics have been studied by ESR : three belonging to the penicillins group (anhydrous ampicillin, amoxicillin, cloxacillin sodium salt) and two to the cephalosporins group (ceftazidime and cefuroxime sodium salt). The influence of several parameters such as the irradiation dose, the temperature of irradiation and the time of storage have been investigated. Comparison between spectra have been investigated and some mechanisms are suggested.



## Multifrequency EPR Study of Radicals Produced by Radiation in Shells and Corallite.

*G.Strzelczak\*<sup>1</sup>, G.Vanhaelewyn<sup>2</sup>, W.Stachowicz<sup>1</sup>, E.Goovaerts<sup>3</sup>, F.Callens<sup>2</sup> and J. Michalik<sup>1</sup>.*

*1. Institute of Nuclear Chemistry and Technology, Warsaw, Poland.*

*2. Ghent University, Ghent, Belgium*

*3. University of Antwerpen, Antwerpen, Belgium*

Shells of two sea molluscs *Venus* and *pearl oyster* and corallite (*white coral*) were exposed to the action of ionising radiation ( $\gamma$  and X-rays) and examined by EPR spectroscopy at room temperature in X, Q and W band. The EPR spectra of natural shells recorded in X band are complex and not easy to interpret, because of spectrum overlap.

The spectra recorded in Q or W bands are much better resolved and assignment of individual paramagnetic species in complex spectra is definitely easier.

The spectroscopic parameters of most paramagnetic centres detected in irradiated shells are very close to those of specific paramagnetic species produced in synthetic crystalline carbonates.

The most stable, long living paramagnetic centres identified in all investigated shells are anion radicals  $\text{CO}_2^-$  (isotropic and orthorhombic).

Additional signals recorded in pearl oyster, which are well visible in Q and W bands, were attributed to isotropic  $\text{SO}_2^-$  and axial  $\text{SO}_3^-$  species.

The assignment was confirmed by computer simulation.

## EPR and ENDOR Study of Human Tooth Enamel Heated at 400°C

J. Sadlo<sup>1</sup>, G. Vanhaelewyn<sup>2</sup>, S. Amira<sup>2</sup>, R. Morent<sup>2</sup>, P. Matthys<sup>2</sup>, F. Callens<sup>2</sup>,  
J. Michalik<sup>1</sup>, W. Stachowicz<sup>1</sup>

<sup>1</sup>Institute of Nuclear Chemistry and Technology  
*ul. Dorodna 16, 03-195 Warsaw, Poland*

<sup>2</sup>Laboratory for Crystallography and Study of the Solid State  
*Krijgslaan 281-S1, 9000 Gent, Belgium*

Powdered tooth enamel heated at 400°C has been examined with electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR) and ENDOR-induced EPR (EIEPR) and compared with hydroxyapatite synthesized at high temperature. Experiments at both X (9.5 GHz) and Q-band (34 GHz) have been performed. The EPR spectra of the tooth enamel X-irradiated at room temperature consist mainly of signals assigned to O<sup>•</sup> and CO<sub>2</sub><sup>•</sup> radicals. The X and Q-band ENDOR results show that the O<sup>•</sup> radical is located at an A site and interacts with unequivalent sets of <sup>31</sup>P nuclei and two unequivalent protons. This supports the model proposed for synthetic hydroxyapatite. The EIEPR results show that the <sup>31</sup>P and <sup>1</sup>H resonances originate from both O<sup>•</sup> and CO<sub>2</sub><sup>•</sup> radicals and that <sup>23</sup>Na and <sup>19</sup>F resonances originate only from a CO<sub>2</sub><sup>•</sup> radical located probably at the surface.

# CONDUCTION ELECTRON SPIN RESONANCE (CESR) OF METALLIC PARTICLES IN MESOPOROUS MATERIALS.

M. Danilczuk<sup>1</sup>, Jong-Sung Yu<sup>3</sup>, D. Brown<sup>2</sup>, L. Kevan<sup>4</sup> and J. Michalik<sup>1</sup>

<sup>1</sup> Institute of Nuclear Chemistry and Technology, 03-195 Warsaw, Poland,

<sup>2</sup> University of Huddersfield, Huddersfield HD1 3DH, UK

<sup>3</sup> Hannam University, Taejon 306-791, Korea

<sup>4</sup> University of Houston, Houston, TX 77204 - 5641, USA

Some years ago Kawabata predicted that conduction electron spin resonance (CESR) signal of small metal particles would be modified from that of the bulk [1]. The modification should occur only when the size of the metal particles become very small. Below a certain size the energy differences  $\delta$  between the electronic levels is sufficient to block the relaxation induced by the spin-orbit coupling. This relaxation mechanism is the dominant one for the bulk metal. According to Kawabata, the size effect takes place if  $\delta \gg h\omega_z$  and  $h/\tau \ll \delta$ , where  $\delta = 1/D_{Ef}$ ,  $D_{Ef}$  is the density of states at the Fermi level,  $h\omega_z$  is the Zeeman energy, and  $\tau$  is a relaxation time which is derived from the theory of Elliott [2] and is given by  $\tau = d/V_F \Delta g^2$  ( $d$  - diameter of particles,  $V_F$  - Fermi velocity, and  $\Delta g^2 = g_{bulk} - g_e$ ). The theory predicts that the linewidth  $H_{pp}$  is proportional to the size of particles:  $H_{pp} = 4.86d^2$ , where  $d$  in nm (1)

Small metal particles have been produced by hydrogen reduction of AIMCM-41 synthetic mesoporous materials exchanged with  $Pd^{2+}$ ,  $Pt^{2+}$  and  $Ag^+$  cations. Two types of AIMCM-41 with Si/Al = 10 and 30 and thus different cation capacity have been used. The lattice structure of AIMCM-41 materials remains the bunches of aluminosilicate nanotubings.

The effective reduction temperature to produce CESR signals depends on the type of exchangeable cation. The lowest temperature is required for Pd-AIMCM-41. For samples with Si/Al = 10 a strong CESR singlet with  $\Delta H_{pp} = 4.5G$  at  $g = 2.003$  is observed after hydrogen reduction at 70 °C. The sample with Si/Al = 30 reduced under the same conditions gives the signal with similar EPR parameters but lower intensity.

To generate CESR signal in Ag-AIMCM-41 the reduction temperature above 500 °C is needed. The CESR signals of silver clusters are narrower ( $H_{pp} = 3 G$ ) and appear at  $g = 2.007$ . Again, signal intensity for samples with Si/Al = 30 is much lower than for AIMCM-41 with higher Si/Al ratio.

In Pt-AIMCM-41 CESR signal with  $H_{pp} = 5.8 G$  and  $g = 2.002$  of Pt particles reaches its maximum at 350 °C for both Si/Al ratios, however signal intensity for samples with Si/Al = 30 is smaller by about fivefold.

The diameters of metal particles calculated from eq.1 are 0.78 nm for Ag, 0.96 nm for Pd and 1.09 nm for Pt. Although those diameters are smaller than the average diameter (3.5 nm) of AIMCM-41 channels the ESR results indicate that the particle size is constrained and therefore determined by AIMCM-41 channel diameter.

This conclusion is based on the fact that the size of metal particles is independent on cation loadings in AIMCM-41. It proves that metal particles are located inside AIMCM-41 channels. If metal agglomeration proceeded on the external surfaces of AIMCM-41 crystallites one would expect that bigger clusters would form in materials with higher metal loadings.

## References

1. A.Kawabata, *J. Phys. Soc. Jpn.* **29**, 902 (1970).
2. R.J. Elliott, *Phys. Rev.*, **96**, 266 (1954)

## Cationic Silver Clusters in Sodalites

*Joanna Perlińska<sup>1</sup>, Hiro Yamada<sup>2</sup> and Jacek Michalik<sup>1</sup>*

<sup>1</sup>Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

<sup>2</sup>National Institute for Research in Inorganic Materials, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

As we showed earlier silver agglomeration process in  $\gamma$ -irradiated sodalites is strongly dependent on the temperature of sodalite hydrothermal synthesis. In dehydrated silver sodalites synthesised above 150°C we observed isotropic septet with ESR parameters  $A_{\text{iso}} = 80$  G and  $g_{\text{iso}} = 1,997$ . We assigned this signal to  $\text{Ag}_6^{5+}$  cluster which is formed by electron capture by six  $\text{Ag}^+$  cations located in the same cage. In contrast, in dehydrated silver sodalites synthesised at 95°C only  $\text{Ag}_5^{n+}$  clusters, represented by ESR sextet with  $A_{\text{iso}} = 92$  G and  $g_{\text{iso}} = 1,987$ , are stabilised.

The aim of the present work is to check the effect of different anions as hydroxyl, oxalate, halogens and their loadings on the nuclearity of stabilised silver clusters. It was found that  $\text{Ag}_6^{5+}$  clusters are formed more efficiently in  $\text{F}^-$ -sodalites than in  $\Gamma^-$ -sodalites. We postulate that this effect is caused by different degree of dehydration. At the same dehydration temperature big anions efficiently block water migration path. As the result, in the cages with residual  $\text{H}_2\text{O}$  molecules  $\text{Ag}_6^{5+}$  clusters cannot be formed. In  $\text{F}^-$ -sodalites  $\text{Ag}_6^{5+}$  clusters are produced independently on  $\text{F}^-$  loadings whereas in sodalites with  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\Gamma^-$  hexameric clusters are generated only for low anion loadings.

## EPR study of Lewis-acid sites in zeolites using NO as probe molecule

Gabriela Catana, Bert M. Weckhuysen and Robert A. Schoonheydt

*Centrum voor Oppervlaktechemie en Katalyse, Katholieke Universiteit Leuven,  
Kardinaal Mercierlaan 92, B-3001 Heverlee, Belgium*

The acid properties of zeolites are responsible for their catalytic activity with respect to a variety of industrially important reactions. One can distinguish two types of acid centers: (i) Bronsted acid sites, assigned to bridging OH groups in the zeolite structure; (ii) Lewis acid sites, which can be cations or aluminium defect centers. The structure of the latter, the so-called 'true Lewis sites', is still controversially discussed.

In this paper we report recent results about EPR measurements for the characterization of true Lewis acid sites in zeolites, using NO as probe molecule. From previous catalytic studies it is known that the activity of the catalyst depends both on its structure type and on its chemical composition. Therefore we investigated samples with two structure types (faujasite and MFI) and with different aluminium content, namely the commercial USY (Si/Al = 5.4-36.9) and ZSM-5 (Si/Al = 16.5-39) series. The EPR spectra of adsorbed NO (1.4 Torr) were recorded with a Bruker ESP300E spectrometer in X-band (9.5 GHz) at 115 K.

In all cases NO molecule trapped by the electric field of an electron deficient site has an EPR signal characterized by a slightly anisotropic g-tensor. The spectra show a partially resolved hyperfine splitting, caused by the interaction of electrons with nitrogen ( $I = 1$ ) and aluminium ( $I = 5/2$ ) nuclei. The experimental spectra were simulated to estimate the g-factors and the hyperfine splitting constants and then double integrated to determine the spin concentrations. The strength of the probed acid sites was discussed based on the  $g_{zz}$  values of the different EPR spectra. The spin concentrations were correlated for each structure type with the amount of the extra-framework aluminium species determined from  $^{27}\text{Al}$  MAS NMR measurements and chemical analysis. For the investigated set of samples a good correlation was obtained with the test catalytic reactions and with other spectroscopic techniques, e.g. infrared spectroscopy of CO adsorbed on Lewis-acid sites at low temperature.

## Dielectric Resonator-Based Resonant Structure for ESR Measurements at High Hydrostatic Pressures

Andrzej Sienkiewicz\*†, Slaven Garaj†, Marek Jaworski\*, Charles P. Scholes‡, and László Forró†

\*Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland;

† Institut de Génie Atomique, Département de Physique, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland;

‡ Chemistry Department, SUNY at Albany, Albany, NY 12222, USA

We report a newly developed microwave probehead for performing sensitive ESR measurements at high hydrostatic pressures. The system consists of two sub-assemblies: 1) the double-stacked dielectric resonator (DR) resonant structure, and 2) the miniature sapphire- or diamond-anvil pressure cell (i.e. SAC or DAC). The BeCu-made body forms the outer shell of the probehead and accommodates the resonant structure, as well as provides a precise guidance for movable metallic parts of the pressure cell. The microwave resonant structure is designed around commercially available high dielectric ( $\epsilon_r = 30$ ) ceramic DRs from MuRata-Erie North America. The resonant frequency of the lowest cylindrical  $TE_{018}$  mode of the double-stacked DRs separated by a distance of 4.9 mm is of ca. 9.3 GHz. The spacing between the DRs easily accommodates two metallic cylindrical elements that are terminated with sapphire or diamond anvils. The metallic gasket, a prerequisite element of the SAC or DAC, is also accommodated in the spacing between the DRs. Both SAC and DAC are ruby-calibrated. The green light (He-Ne laser,  $\lambda = 514.3$  nm) is used for excitation of the pressure-sensitive red light fluorescence from  $Cr^{3+}$  in ruby. The highest reachable pressures (up to 2 GPa for the SAC and 4 GPa for the DAC) are mainly limited by imperfections of the mechanical guidance of the movable elements. The newly developed apparatus was used for high-pressure Conduction Electron Spin Resonance (CESR) studies of an orthorhombic phase conducting polymer,  $K_1C_{60}$ . We could follow the CESR linewidth ( $\Delta H_{pp}$ ) broadening up to the pressures in the range of  $\sim 1.5$  GPa. The observed broadening of  $\Delta H_{pp}$  with increasing hydrostatic pressure for the metallic-phase of  $K_1C_{60}$  supports the one-dimensional scenario for the orthorhombic phase of this compound.

## New Opportunities Offered by High-Field EPR/ENDOR in the Structural Characterization of Mn(II) Sites in Zeolites

D. Arieli<sup>1</sup>, D.E.W. Vaughan<sup>2</sup>, K.G. Strohmaier<sup>3</sup> and D. Goldfarb<sup>1</sup>

<sup>1</sup> Department of Chemical Physics, Weizmann Institute of Science, Rehovot, 76100

<sup>2</sup> Penn. State University, Pennsylvania <sup>3</sup> Exxon Research and Engineering Company, New Jersey

High-Field EPR/ENDOR is an active field of techniques which provide unique and direct structural information on paramagnetic ions in catalytically active sites of zeolites. Moreover, it can be implemented for developing mechanisms of formation of aluminosilicate, aluminophosphate (AIPO) or silicoaluminophosphate (SAPO) molecular sieves. The precise atomic architecture of catalytic sites in zeolites plays a major role in the design and optimization of new inorganic solid catalysts.

We study the incorporation of low levels of high-spin Mn(II) (Mn/Al~0.001) into five selected members out of the extended family of AIPO/SAPO type zeolites. The structures cover a range of channel morphologies (from the smallest aperture of sodalite, 2.2 Å, up to an opening of ~7.5 Å, found in the new family of large-cage structures, UCSB-n), and a variety of framework densities (ranging from 12 to 19 T sites/ 1000 Å<sup>3</sup>). W-band EPR and <sup>31</sup>P/ <sup>1</sup>H ENDOR experiments were carried at 4 K, from which we determine the location of Mn(II) in the final products, as well as its intermediate environments during SAPO formation.

Mims and Davies ENDOR spectra, recorded at a field set to one of the  $| -1/2, m_I > \Rightarrow | +1/2, m_I >$  <sup>55</sup>Mn hyperfine components consist of a symmetric <sup>31</sup>P doublet separated by a hyperfine coupling of 5-8 MHz. The larger opened structures show a relatively smaller couplings compared to the denser morphologies. Matrix lines of <sup>27</sup>Al and <sup>31</sup>P appear as well at their respective Larmor frequencies. These findings provide a direct evidence for framework substitution of Mn(II) for Al in all types of structures. The position and line shape of the <sup>31</sup>P doublets indicate that they originate primarily from an isotropic coupling between <sup>31</sup>P and the  $\pm 1/2$  manifolds of Mn(II). We have further used this <sup>31</sup>P ENDOR signature complemented by <sup>1</sup>H ENDOR as a probe for the investigation of zeolite formation. We followed the synthesis course of SAPO-5 by measuring the ENDOR spectra of samples, quenched at different stages of formation. While the XRD patterns indicate the initiation of structural organization only after 20 Hr, a relatively weak <sup>31</sup>P doublet, splitted by 4 MHz, appear in the corresponding ENDOR spectrum already after 4 Hr of synthesis. The splitting of this doublets increases to 7 MHz during the zeolite crystallization, but its intensity reaches a maximum concomitant with the appearance of a crystalline structure in the XRD pattern. The time evolution of the <sup>1</sup>H ENDOR spectra shows a continuous decrease in the amount of matrix protons as well as in the number of ligating water molecules. Based on the above observations we assign the initial <sup>31</sup>P doublet to the incorporation of Mn(II) into tetrahedral sites of disordered 1D and/or 2D zeolite precursors. These precursors are later transformed to the final 3D crystalline structures.

# SINGLE CRYSTAL HIGH FREQUENCY EPR OF $\text{Fe}_4(\text{OCH}_3)_6(\text{dpm})_6$

M. Stefan<sup>1,2</sup>, A. Bouwen<sup>1</sup>, E. Goovaerts<sup>1</sup>

<sup>1</sup>*Department of Physics, University of Antwerp (UIA), Universiteitsplein 1, 2610 Antwerp, Belgium*

<sup>2</sup>*Institute of Atomic Physics (NIMP), POB MG-7 Magurele, 76900 Bucharest, Romania*

and

D. Gatteschi<sup>3</sup>, R. Sessoli<sup>3</sup>, L. Sorace<sup>3</sup>

<sup>3</sup>*Department of Chemistry, University of Florence, Via Maragliano 77, 50144 Florence, Italy*

Molecular clusters with a large number of magnetic ions have attracted increasing interest due to the fact that some of them show slow relaxation of the magnetisation at low temperature. The large relaxation time is determined by the presence of a large  $S$  spin ground state and an Ising type anisotropy, which corresponds to a negative zero field splitting. High field EPR spectroscopy is a very appropriate method for investigating the energy levels of these clusters, as it allows the study of systems with large zero field splitting and broad lines.

We report here the results of W-band EPR studies on well orientated single crystals of  $\text{Fe}_4(\text{OCH}_3)_6(\text{dpm})_6$  (where Hdpm = dipivaloylmethane) with monoclinic symmetry (space group  $C2/c$ ). The basic unit of this system is a planar tetranuclear Fe(III) cluster with ground spin state  $S = 5$ , which shows the characteristic behaviour of a single-molecule magnet [1].

The measurements were performed with a continuous wave W-band EPR spectrometer (Bruker E600) with cylindrical cavity operating at 95 GHz, equipped with a superconducting magnet mounted on a rotating base. Angular variations of the spectra were obtained in different planes and at different temperatures. The resulting spectra showed the characteristic pattern of a quasi-axial system, with the symmetry axis perpendicular to the plane formed by the four iron ions. At 5K only the low field part of the spectrum could be observed, confirming the negative sign for the  $D$  parameter. The spectra taken at 25 K showed the normal 10 lines pattern and with increasing temperature the lines became broader, until above 200 K only a single broad line could be observed. The linewidths increase towards the outermost peaks of the spectra, from small  $|M|$  to large  $|M|$ , suggests a local strain induced effect.

## References

- [1] A. L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli and L. Sorace, *J. Am. Chem. Soc.* **121**, 5302 (1999)



## **Nano-scale structure of rare earth doped oxide glasses as studied by electron spin echo spectroscopy**

*S.B. Orlinskii\* and E.J. Reijerse*

\*Kazan state University

University of Nijmegen

The study of nano-scale ordering in rare earth doped oxide glasses is very important with respect to their applications in optical communications, vitrification of radio-active waste and the production of colloration in glasses. In this contribution it will be demonstrated that in phosphate glassed doped with Tb(III) ions, the number of phosphorus atoms and their distance to the metal center can be estimated using Electron Spin Echo Envelope Modulation (ESEEM) in combination with model calculations. The Tb-Tb distance is probed through the effect of the dipolar interaction on the phase-relaxation time as a function of the magnetic field. It turns out that using these techniques two types of Tb centers can be distinguished, each with a characteristic distribution in local structure parameters.

## A CW/pulsed heterodyne 190 GHz EPR bridge

E.J. Reijerse, A.A.K. Klaassen, W.R. Hagen.

*Department of Molecular Spectroscopy, University of Nijmegen. Toernooiveld, 6525 ED Nijmegen.*

A 190 GHz EPR bridge is described based on a doubled 95 GHz system. The starting point of this development is a pulsed heterodyne 95 GHz bridge (Krymov) produced by the Donetsk physical technical institute. The 250 mW output of this bridge is doubled using a high power doubler (20 mW @ 190 GHz) developed in the Rutherford Appleton Laboratory (UK). The exciting power is led through a quasi-optical system and fed into a non-resonant sample holder. The signal power is downconverted in a 95 GHz balanced mixer with integral doubler (ELVA-1) to 1.82 GHz. The LO for this mixer is generated from the 7 GHz master oscillator and the 70 MHz reference oscillator in the main unit using an external single sideband mixer (Anaren) and a separate IMPATT multiplier and amplifier train (ELVA-1). The magnetic resonance signal is analysed and converted to DC in the quadrature mixer of the 95 GHz main unit. The properties of the key elements in this setup (doubler, mixer, LO-unit) are described in detail.

## Thermodynamics and kinetics of proton exchange in pH-sensitive imidazolyl spinlabels as studied by D-band EPR.

*E.J. Reijerse, V.V. Khramtsov\*, I.A. Grigor'ev\**

Department of Molecular Spectroscopy, University of Nijmegen.

(\*) Russian Academy of Science, Siberian branch, Novosibirsk

Imidazolyl spin-labels have been developed over the last decades to monitor proton reactions in various areas in chemistry and bio-chemistry. At conventional EPR frequencies the HFI is the main parameter causing the spectral difference between the protonated and unprotonated spin label. At 130 GHz the difference in g-factor is dominating the spectral changes during the proton exchange reaction. The perdeuterated and  $^{15}\text{N}$  labeled amidine spin label: 4-Amino-2,2,5,5-tetramethyl-3-imidazoline-1-yloxy has been studied at D-band (130 GHz) at its pK value (pH = 6.1) in a temperature range 10-50 C and a buffer concentration series both in protonated and deuterated solvents. Due to the much large spectral difference at D-band the exchange reaction can be followed to much higher exchange rates. In this contribution we present the improved kinetic and thermodynamic parameters as well as the isotope effect in this proton exchange reaction.

# Lineshape Effects of Distributions in Zero Field Splitting Parameters

A.H. Priem, A.A. Klaassen, E.J. Reijerse and W.R. Hagen  
Department of Molecular Spectroscopy, NSR Center, Nijmegen, The Netherlands

The EPR spectra of high spin systems are of considerable interest in inorganic and bioinorganic chemistry.

The quantitative analysis of such EPR spectra is accompanied by a number of experimental and theoretical difficulties. The most obvious problem encountered is the often relatively large zero field splitting between the Kramer's doublets ( $M_s = \pm 1/2, \pm 3/2, \pm 5/2 \dots$ ) For instance, this has limited nearly all studies on biological high spin Fe(III) to only one (or two) intra-doublet transition.

A less obvious problem are the lineshape effects generated by distributions in zero field splitting (ZFS) parameters  $D$  and  $E$ . A typical example is the X-band spectrum of Fe(III) EDTA, which consists of a sharp  $g=4.3$  absorption, and relatively broad shoulders. Without taking the effects of a distribution in the ZFS parameters into account, this spectrum is impossible to simulate. Determining ZFS distributions from X-band spectra alone is not possible, since the X-band spectra only yield the ratio  $E/D$ .

Using high frequency EPR the ZFS parameters and distributions in ZFS parameters can be determined directly. As will be shown, spectra simulated this way show a good fit for X, Q and D-band.

# **LIST OF PARTICIPANTS**

**Bernard Gallez**  
Catholic University of Louvain  
Lab. Chem. Med.  
Avenue Mounier 73.40  
B-1200 Bruxelles  
e-mail : [gallez@cmfa.ucl.ac.be](mailto:gallez@cmfa.ucl.ac.be)

**Paul Matthys**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281-S I  
B-9000 Gent  
e-mail : [Paul.Matthys@rug.ac.be](mailto:Paul.Matthys@rug.ac.be)

**Gauthier Vanhaelewyn**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281-S1  
B-9000 Gent  
e-mail : [Gauthier.Vanhaelewyn@rug.ac.be](mailto:Gauthier.Vanhaelewyn@rug.ac.be)

**Henk Vrielinck**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281-S1  
B-9000 Gent  
e-mail : [Henk.Vrielinck@rug.ac.be](mailto:Henk.Vrielinck@rug.ac.be)

**Kris Sabbe**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281-S1  
B-9000 Gent  
e-mail : [Kris.Sabbe@rug.ac.be](mailto:Kris.Sabbe@rug.ac.be)

**Dirk Schoemaker**  
Physics Department  
University of Antwerp  
B-2610 Wilrijk  
e-mail : [schmaker@uia.ua.ac.be](mailto:schmaker@uia.ua.ac.be)

**Etienne Boesman**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281-S1  
B-9000 Gent

**Freddy Callens**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281-S1  
B-9000 Gent  
e-mail : [freddy.callens@rug.ac.be](mailto:freddy.callens@rug.ac.be)

**Rene Debuyst**  
Catholic University of Louvain  
Avenue Mounier 72.20  
B-1200 Bruxelles  
e-mail : [debuyst@fysi.ucl.ac.be](mailto:debuyst@fysi.ucl.ac.be)

**Etienne Goovaerts**  
Physics Department  
University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk  
e-mail : [goovaert@uia.ua.ac.be](mailto:goovaert@uia.ua.ac.be)

**Peter Gast**  
University of Leiden, Huygens Lab.  
Postbus 9504  
NL-2300 RA Leiden  
Nederland  
e-mail : [gast@biophys.LeidenUniv.nl](mailto:gast@biophys.LeidenUniv.nl)

**Mariana Stefan**  
Physics Department  
University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk  
e-mail : [mstefan@uia.ua.ac.be](mailto:mstefan@uia.ua.ac.be)

**Eric Van der Horst**  
Catholic University of Nijmegen  
Toernooiveld 1  
NL-6525 ED Nijmegen  
Nederland  
e-mail : [ericvdh@sci.kun.nl](mailto:ericvdh@sci.kun.nl)

**René Dekeyser**  
Agfa-Gevaert  
Septestraat 27  
B-2640 Mortsel  
e-mail : [Rene.Dekeyser@belgium.agfa.com](mailto:Rene.Dekeyser@belgium.agfa.com)

**Marc Penders**  
Bruker Belgium  
Kareelovenlaan 4  
B-1140 Brussel  
e-mail : [mp@bruker.be](mailto:mp@bruker.be)

**Juergen R. Niklas**  
Technical University,  
Bergakademie Freiberg  
Institut für Experimentelle Physik,  
Silbermannstraße 1  
D-09599 Freiberg (Germany)  
e-mail : [niklas@physik.tu-freiberg.de](mailto:niklas@physik.tu-freiberg.de)

**Jacek Michalik**  
Institute of Nuclear Chemistry and  
Technology  
Dorodna 16  
PL-03-195 Warsaw  
Poland  
e-mail : [esrlab@orange.ichtj.waw.pl](mailto:esrlab@orange.ichtj.waw.pl)

**Andrzej Plonka**  
Lodz Polytechnic Institute of Applied  
Radiation Chemistry  
Wroblewskiego 15  
PL-93-590 Lodz  
Poland  
e-mail : [anplonka@ck-sg.plodz.pl](mailto:anplonka@ck-sg.plodz.pl)

**Andrzej Sienkiewicz**  
Institute of Physics  
Polish Academy of Sciences  
Al. Lotnikow 32/46  
PL-02-668 Warsaw  
Poland  
e-mail : [sienk@delta.ifpan.edu.pl](mailto:sienk@delta.ifpan.edu.pl)

**Jan van Bentum**  
Departm. High Field Magnet Lab.  
University of Nijmegen  
Toernooiveld 1  
NL-6525 ED NIJMEGEN  
Nederland  
e-mail : [jvanb@sci.kun.nl](mailto:jvanb@sci.kun.nl)

**Alix Engalytcheff**  
Catholic University of Louvain  
Avenue Mounier 72.30  
B-1200 Bruxelles  
e-mail : [alix.engalytcheff@cham.ucl.ac.be](mailto:alix.engalytcheff@cham.ucl.ac.be)

**Andreas Kamlowski**  
BRUKER Analytik GmbH  
EPR Division  
Silberstreifen  
D-76287 Rheinstetten  
Germany  
e-mail : [andreas.kamlowski@bruker.de](mailto:andreas.kamlowski@bruker.de)

**Pham Thanh Huy**  
Semiconductor Materials Group  
Van der Waals- Zeeman Inst.  
University of Amsterdam  
Valkenierstraat 65-67  
NL-1018 XE Amsterdam  
e-mail : [pthuy@wins.uva.nl](mailto:pthuy@wins.uva.nl)

**Griet Janssen**  
Physics Department  
University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk  
e-mail : [grietj@uia.ua.ac.be](mailto:grietj@uia.ua.ac.be)

**Gabriela Catana**  
Centrum voor Oppervlakte-chemie en Katalyse  
Catholic University of Leuven  
Kardinaal Mercierlaan 92  
B-3001 Heverlee  
e-mail : [gabriela.catana@agr.kuleuven.ac.be](mailto:gabriela.catana@agr.kuleuven.ac.be)

**Jan Van Nuyen**  
Physics Department  
University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk  
e-mail : [janvn@uia.ua.ac.be](mailto:janvn@uia.ua.ac.be)

**Dafna Arieli**  
Department of Chemical Physics  
Weizmann Institute of Sciences  
Rehovot, 76100  
Israel  
e-mail : [dafna.arieli@agr.kuleuven.ac.be](mailto:dafna.arieli@agr.kuleuven.ac.be)

**Sergei Pashenko**  
University of Leiden  
Huygens Lab.  
Postbus 9504  
NL-2300 RA Leiden  
Nederland  
e-mail : [pashenko@biophys.LeidenUniv.nl](mailto:pashenko@biophys.LeidenUniv.nl)

**Igor Borovihk**  
University of Leiden  
Huygens Lab.  
Postbus 9504  
NL-2300 RA Leiden  
Nederland  
e-mail : [borovihk@biophys.LeidenUniv.nl](mailto:borovihk@biophys.LeidenUniv.nl)

**Marc Danilczuk**  
Institute of Nuclear Chemistry and  
Technology  
Dorodna 16  
PL-03-195 Warsaw  
Poland  
e-mail : [mdan@orange.ichtj.waw.pl](mailto:mdan@orange.ichtj.waw.pl)

**Joanna Perlinska**  
Institute of Nuclear Chemistry and  
Technology  
Dorodna 16  
PL-03-195 Warsaw  
Poland  
e-mail : [asia@orange.ichtj.waw.pl](mailto:asia@orange.ichtj.waw.pl)

**Waclaw Stachowicz**  
Institute of Nuclear Chemistry and  
Technology  
Dorodna 16  
PL-03-195 Warsaw  
Poland  
e-mail : [stach@orange.ichtj.waw.pl](mailto:stach@orange.ichtj.waw.pl)

**Grazyna Strzelczak**  
Institute of Nuclear Chemistry and Technology  
Dorodna 16  
PL-03-195 Warsaw  
Poland  
e-mail : [grazyna@orange.ichtj.waw.pl](mailto:grazyna@orange.ichtj.waw.pl)

**Jarek Sadlo**  
Institute of Nuclear Chemistry and Technology  
Dorodna 16  
PL-03-195 Warsaw  
Poland  
e-mail : [sadlo@orange.ichtj.waw.pl](mailto:sadlo@orange.ichtj.waw.pl)

**Sami Amira**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281-S1  
B-9000 Gent  
e-mail : [sami.amira@rug.ac.be](mailto:sami.amira@rug.ac.be)

**Rino Morent**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281-S1  
B-9000 Gent  
e-mail : [rino.morent@rug.ac.be](mailto:rino.morent@rug.ac.be)

**Ed Reijerse**  
Departm. High Field Magnet Lab.  
Catholic University of Nijmegen  
Toernooiveld 1  
NL-6525 ED Nijmegen  
Nederland  
e-mail : [rey@sci.kun.nl](mailto:rey@sci.kun.nl)

**Wiesiek J. Szweryn**  
Catholic University of Nijmegen  
Toernooiveld 1  
NL-6525 ED Nijmegen  
Nederland  
e-mail : [wiesiek@sci.kun.nl](mailto:wiesiek@sci.kun.nl)



**Adri Klaassen**

Catholic University of Nijmegen

Toernooiveld 1

NL-6525 ED Nijmegen

Nederland

e-mail : [Adri.Klaassen@sci.kun.nl](mailto:Adri.Klaassen@sci.kun.nl)

**Alex Priem**

Catholic University of Nijmegen

Toernooiveld 1

NL-6525 ED Nijmegen

Nederland

e-mail : [alexp@sci.kun.nl](mailto:alexp@sci.kun.nl)

**Ewald Pauwels**

Ghent University

Vakgroep Subatomaire en Stralingsfysica

Proeftuinstraat 86

B-9000 Gent

e-mail : [ewald@moldyna9.rug.ac.be](mailto:ewald@moldyna9.rug.ac.be)