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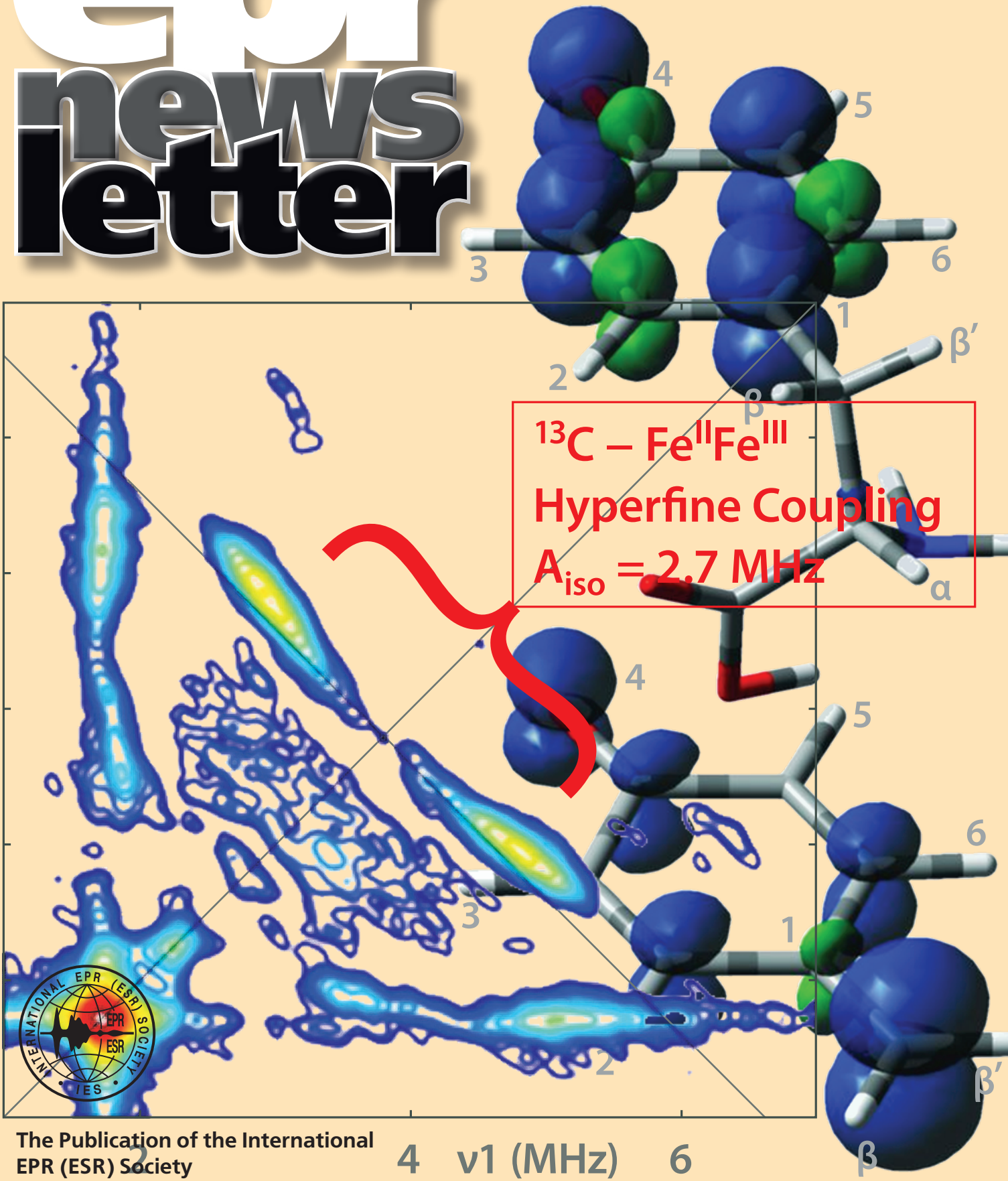

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Please feel free to contact us with items (news, notices, technical notes, and comments) or ideas for the *EPR newsletter*.

The *EPR newsletter* is published quarterly by the International EPR (ESR) Society and is available in electronic and printed form to all members of the Society. The deadlines for submission of news for upcoming issues: Spring March, 15; Summer June, 15; Fall September, 15; Winter December, 15.

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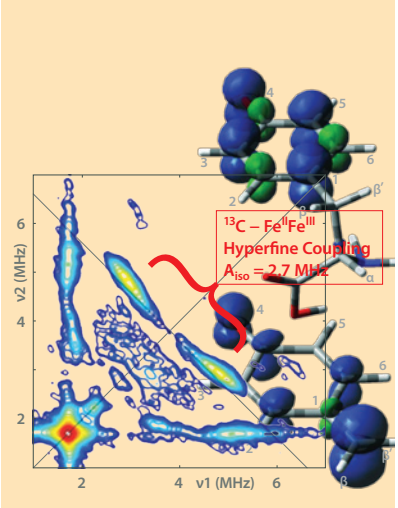

The cover picture illustrates aspects of research carried out by David Britt, recipient of the IES Gold Medal 2014. It shows (left) the radical SAM enzyme Biotin Synthase with HYSCORE indicating bonding of ^{13}C-labeled dethiobiotin substrate to the auxiliary 2Fe-2S indicating that the sulfur of biotin arises from sacrificial donation of a bridging sulfur; (right) The radical SAM enzyme HydG of the [FeFe] hydrogenase maturation pathway generates a 4-oxidobenzyl radical upon scission of the tyrosine substrate.

epr newsletter

The Publication of the International EPR (ESR) Society

volume 25 number 1-2 2015

ETH
Eidgenössische Technische Hochschule Zürich
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Editorial

Dear colleagues,

This issue welcomes two new IES sponsors, ELVA-1 and Oxford Instruments (see their ads on pages 18 and 10, respectively), who joined the great team of our sponsors: Active Spectrum, Adani Systems, Bruker BioSpin, Cryogenic Ltd., GMW, JEOL Japan & USA, Keycom, L&M EPR Supplies, Magnettech GmbH, Molecular Specialties, Norell, Research Specialties, Scientific Software Services, Virginia Diodes, Inc., and Wilmad-LabGlass. We look forward to long-term collaborations with them for our mutual benefit.

The support of our sponsors makes it possible for the society to expand and diversify its activities for your benefit, the IES members. In turn, our sponsors can now promote their products to the international magnetic resonance community. It is important that the efforts to get new sponsors continue. If you know of any other company that might be interested in collaboration with the IES, please feel free to inform their CEOs about us. Show them a copy of the EPR newsletter with the beautiful ads of our sponsors as an example. Do not be timid! If you make an attempt, there is a nonzero probability that you succeed. If you do not make an attempt, this probability is zero for sure. Another component of the IES budget is your dues. It is important that you pay them on time and also invite your colleagues and collaborators to join the IES. In the long run, this money returns to the members in many ways.

Please pay special attention to the photos and information in the Awards column (pp. 3, 4). This may help you to predict who will be featured in the forthcoming issues of the *EPR newsletter*. We heartily congratulate Gunnar Jeschke and Thomas Prisner, Robert Bittl, Joshua Biller, Andrin Doll, Dante Gatteschi, Robert Griffin, Edgar Groenen, Brian Hoffman, Sankaran Subramanian, Murali Krishna Cherukuri and Derek Marsh, Eric McInnes, Ilia Kaminker, and Vadim A. Atsarkin!

In accord with my promises in the editorial (24/3, p. 2) telling you about prospects for future issues of the *EPR newsletter* in 2015, in this issue please enjoy the success story of Nicholas Cox, John Weil Young Investigator Awardee 2014 (p. 5, see also 20/2-3, p. 7) and the reports about the research performed by Jackie Esquiaqui, Noah Horwitz, Alex Marchanka, and Zhelin Yu, recent IES Poster Awardees (pp. 6–10). Sabine Van Doorslaer continues her Present Meets Future column (pp. 16–18) featuring Heinz-Jürgen Steinhoff and his PhD student Daniel Klose (Daniel discussed his JEOL Prize research in 24/4, pp. 11, 12; see also 24/3, p. 3). The Guest of the Issue column, edited by Wolfgang Lubitz, hosts Howard Halpern with his exciting story about oxygen imaging with pulse spin lattice relaxation EPR (pp. 19–22). The concepts of effective spin and fictitious angular momentum are considered by Sushil K. Misra and Czeslaw Z. Rudowicz in the Tips and Techniques column (pp. 24–28) edited by Keith Earle.

The In Memoriam column is devoted to the late Graeme Hanson featuring contributions from his colleagues and friends and pays tribute to his multiple talents and activities (pp. 11–15). Many contributors to this column mentioned his editing of the EPR-Hot Topics column in the *EPR newsletter* (see 23/2, pp. 14, 15; 23/3, pp. 14, 15; 24/1-2, pp. 24, 25). It is good to know that the EPR-Hot Topics column, which was met with such enthusiasm by the magnetic resonance community, is to be continued. Starting from 25/3, this column is to be edited by Wolfgang Lubitz (wolfgang.lubitz@cec.mpg.de). Please address him with your proposals. You are welcome!

Laila Mosina

Awards

The Zavoisky Award 2014 to Gunnar Jeschke & Thomas Prisner

IES Fellows 2015

Dante Gatteschi
University of Florence,
Florence, Italy

Robert Griffin
Massachusetts Institute of Technology,
Cambridge, MA USA

Edgar Groenen
Leiden University,
Leiden, The Netherlands

Brian Hoffman
Northwestern University,
Evanston, IL USA

Sankaran Subramanian
Indian Institute of Technology Madras,
Chennai, India

IES Silver Medal 2015 in Biology/Medicine

Murali Krishna Cherukuri
Center for Cancer Research,
National Cancer Institute,
Bethesda, MD USA

Derek Marsh
Max Planck Institute for Biophysical Chemistry,
Göttingen, Germany

IES Silver Medal 2015 in Chemistry

Eric McInnes
University of Manchester,
Manchester, UK

IES Young Investigator Award 2015

Ilia Kaminker
Weizmann Institute of Science,
Rehovot, Israel

The 2014 Zavoisky Award is presented jointly to Professor Thomas Prisner, Goethe University Frankfurt (Main), and Professor Gunnar Jeschke, Swiss Federal Institute of Technology in Zurich (ETHZ), in recognition of their outstanding achievements in the development and application of pulse electron magnetic resonance (EPR) techniques at the borderline between EPR and NMR (nuclear magnetic resonance) for elucidating structure and dynamics of biological and organic supramolecular systems.

Thomas Prisner, in particular, is awarded for his achievements to optimize multi-frequency PELDOR spectroscopy for measuring intramolecular distances and orientations of spin-labeled proteins and single-stranded DNA molecules. In recent years, Thomas Prisner demonstrated that Dynamic Nuclear Polarization (DNP) is possible in the liquid state also at high magnetic fields (9.2 T). Using a high-power gyrotron microwave source, a 30-fold DNP enhancement of the NMR of water protons was obtained for an aqueous solution of a stable nitroxide radical salt. Thereby, he opened new avenues to achieve strong signal enhancement for NMR structure determination.

Gunnar Jeschke, in particular, is awarded for his achievements in experimental techniques and theoretical interpretations of dipolar EPR spectroscopy for structure determination with high precision on the nanoscopic level. In recent years, Gunnar Jeschke strongly contributed to the development of solid-state Photo-CIDNP MAS NMR to study transient radical pairs with tremendously enhanced NMR detection sensitivity. In parallel, he developed experimental strategies and theoretical evaluation tools for nitroxide-lanthanide spin labeling techniques which allowed for modeling protein structural transitions from sparse long-range spin-label distance constraints.

Photo above from left to right: Kev Salikhov, Chairman of the Zavoisky Award Committee, Thomas Prisner and Gunnar Jeschke.

Zavoisky Award 2015

Vadim A. Atsarkin
Kotel'nikov Institute for Radio Engineering and Electronics,
Russian Academy of Sciences,
Moscow, Russian Federation

Dante Gatteschi
University of Florence,
Florence, Italy

The Bruker Prize 2015 to Robert Bittl

From left to right: Prof Fraser Macmillan (UEA), Prof Graham Smith (St Andrews, Chair RSC ESR Group), Prof Robert Bittl (Freie Universität Berlin) and Dr Peter Höfer (Director for EPR, Bruker).

For details, see this newsletter, p. 32

The Bruker Thesis Prize 2015 to Joshua Biller

From left to right: Dr Peter Höfer (Bruker), Prof Graham Smith (St Andrews, Chair RSC ESR Group), Dr Joshua Biller (2015 Bruker Thesis Prize winner), and Profs Sandra and Gareth Eaton (Denver).

For details, see this newsletter, p. 32

The JEOL Student Lecture Prize 2015 to Andrin Doll

Dr Peter Meadows of JEOL (UK) Ltd and Prof Graham Smith (St Andrews, Chair RSC ESR Group) present Andrin Doll (ETH Zurich) with the JEOL Student Lecture Prize.

For details, see this newsletter, p. 32

John Weil IES Young Investigator Award 2014

Nicholas (Nick) Cox:

I am honored that the International EPR society selected me for the John Weil IES Young Investigator Award 2014 and for the opportunity to present my current research at the inaugural IES symposium held jointly with APES and SEST societies in Nara Japan. I thank the entire IES society for this recognition and support.

I encountered EPR spectroscopy during my PhD in Australia with Profs. Ron Pace and Elmars Krausz at ANU, but it was not until I started my postdoctoral studies that I first undertook pulsed EPR, when I joined the research group of Prof. Wolfgang Lubitz at the Max-Planck-Institute for Bioinorganic Chemistry (now Chemical Energy Conversion) located in Mülheim an der Ruhr, Germany. One of the first problems we tackled was the characterization of a metalloprotein called ribonucleotide reductase (RNR), which is responsible for production of nucleotide monomers used to make DNA. Our work concentrated on a particular type of RNR, which was long thought to only use a di-iron (Fe/Fe) cofactor. Using both crystallographic and EPR spectroscopy we could demonstrate that it instead contained a di-manganese (Mn/Mn) cofactor. This study, performed in collaboration with Drs. Hideaki Ogata, Ed Reijerse and Georg Auling (University of Hannover), employed multifrequency EPR (9–244 GHz) to ascertain the structure of the Mn-complex and its interaction with a nearby tyrosyl radical, a key component of the activated cofactor, which initiates the nucleotide reaction. We have recently extended this work to characterization of structurally similar bimetallic Mn/Fe-containing proteins. Working with Dr. Hannah Shafaat and in collaboration with researchers from the University of Stockholm, Drs. Julia Griese and Martin Högbom, we are studying the structural factors which tune the reactivity of these cofactors and allow the assembly of the heterodimeric as opposed to homodimeric cofactor, considering the similar ligand preferences of Mn^{II} and Fe^{II} and the structural similarity and proximity of the two metal binding sites.

My primary current research though in recent years has returned to Photosystem II, specifically the inorganic cofactor of this enzyme which catalyzes the water splitting in nature. Harnessing this reaction for industrial scale energy production and storage represents one of the great challenges of the 21st century. The cofactor is a tetramanganese calcium cofactor which displays both a high turnover number (TON $\approx 10^6$) and turnover frequency (TOF $\approx 500\ s^{-1}$). By way of comparison, Mn_2O_2Ca oxides, a chemically robust material, display an intrinsic water-splitting capacity eight orders of magnitude slower than the biological catalyst. The superior performance of the biological cofactor derives from its concerted mechanism for O-O bond formation using its unique geometry to bind and position the two substrate waters. Working with Leonid Rapatskiy we recently applied W-band ELDOR-detected NMR (ED-NMR) to this system to identify precisely what the substrate water sites of the cofactor are. As these two sites exchange rapidly with bulk water, the substrate oxygen atom can be labeled with ^{17}O ($I = 5/2$). We observed that one of the μ-oxo bridges of the complex can be efficiently labeled with ^{17}O suggesting this is one of the substrate water sites. The identity of the exchangeable bridge was later obtained in a recent study with Montserrat Perez Navarro and Thomas Lohmiller. This work was made possible by a strong in house collaboration with Dr. Anton Savitsky; whose instrumention improvements, in terms of both sensitivity and bandwidth, made these measurements possible. Similarly, strong external collaborative partners in France, Sweden and Germany, Drs. Alain Boussac, Johannes Messinger and Marc Nowaczyk were critical in the development of highly active biological preparations and sample protocols used to poise the cofactor in discrete catalytic states.

The research I presented in Nara is an extension of this earlier work, describing our most recent study using W-band pulse EPR to resolve the structure of the last metastable intermediate of the water splitting reaction. Our work shows that an additional water molecule needs to binds to the cofactor to form this intermediate and suggests that the O-O bond likely forms between two adjacent manganese-bound oxygens, the oxo-bridge described above and newly bound water molecule. This molecular level description of the catalytic cycle has come about from a close in-house collaboration with Dr. Dimitrios Pantazis from Prof. Frank Neese's department. His group including Drs. William Ames, Marius Retegan and Vera Krewald, are developing methods for the interpretation of magnetic resonance data from complicated, multi-metal systems which allows unified structural/functional models to be developed for the water oxidizing complex in PSII.

I'd like to close by thanking all those people I was not able to mention above including: Bill Rutherford, Chuck Dismukes, Paul Smith, Joseph Hughes, Warwick Hiller, Tom Wydrinsky, Alexey Silakov, Ethel Hüttel, Simon Drew and Derrick Kolling.

IES Poster Award 2014

Alexander Marchanka:

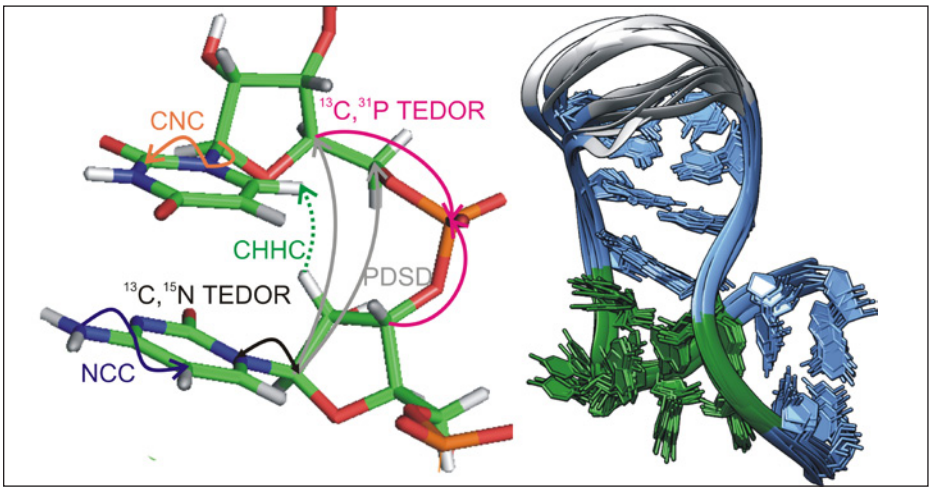
I would like to thank the organizers for inviting me to the International Symposium: Catalytic Systems for Chemical Energy Conversion, which was organized on the occasion of the 65th birthday of Prof. Wolfgang Lubitz. It was a great opportunity to share my research with this multidisciplinary audience. I would also like to express my sincerest gratitude to the International EPR (ESR) Society for awarding me the poster prize for my presentation.

In my presentation at the Symposium I had shown the usage of two magnetic resonance techniques: solid-state nuclear magnetic resonance spectroscopy (ssNMR) and EPR for structural characterization of RNA in large ribonucleoprotein complexes (RNP). ssNMR and EPR are applicable to biomolecular complexes of any size and are not limited by the availability of the complexes in crystalline form. The techniques are nicely complementary to each other. While ssNMR provides with local structural information on the atomic scale and short distance restraints up to 10 Å, EPR and in particularly PELDOR deliver valuable information on the global structural arrangement in distance range up to 80 Å.

Nucleic acids and RNPs play both a regulatory and a functional role in cellular processes; the elucidation of their activity mechanisms requires knowledge of their structure. Nucleic acids and RNP are difficult to crystallize; moreover, their size exceeds the molecular weight limit of solution state NMR technique. One of the research topics in our group at EMBL in Heidelberg (now on move to the University of Hannover) is the box C/D RNP, which performs posttranscriptional methylation of different substrate RNAs [1]. We are investigating this RNP with a plethora of different techniques, including ssNMR and EPR. With ssNMR we are aiming at understanding local structure of RNA in RNP complexes. ssNMR has been showing significant progress on structural characterization of membrane proteins and amyloid fibrils for the last years; however, ssNMR studies on RNA or RNP are limited by the lack of a general methodology. In the project I presented at the Symposium, I have been developing methodology for the structural characterization of RNA in RNP by solid-state NMR; I have been working on the 26mer box C/D RNA in complex with the L7Ae protein, a subcomponent of the box C/D RNP enzyme.

The pipeline for the structure determination by NMR includes several steps. First, one has to prepare uniformly and/or selectively labeled samples. Next, unambiguous assignment of resonances of different nucleus is needed to map NMR signals to specific spin systems. Finally, distance and angular restraints are measured and used in structure calculations. Our protocol for structure determination of RNA by ssNMR implies two approaches: nucleotide-type specific labeling of RNA and usage of multidimensional heteronuclear correlation experiments. At the first step, we developed methods for the intranucleotide assignment of resonances [2]. To accomplish this goal we used CNC and $^{13}C,^{15}N$-TEDOR experiments (see figure, left) to measure ribose-base connectivities and obtain the assignment of ribose/base spin systems. The NCC experiment was used for the complete resonance assignment in the bases. For the unambiguous assignment and measurement of the distance restraints we used $^{13}C,^{15}N$-TEDOR-PDSD, $^{13}C,^{31}P$-TEDOR, CHHC and NHHC experiments at long mixing times. Recently, we published the protocol and the first structure of an RNA determined solely by solid-state NMR technique [3] (see figure, right). Solid-state NMR has a great potential and our approach will hopefully pave the way for structural characterization of RNA in large RNPs.

While ssNMR is able to determine local structure, it cannot provide information about global molecular fold. With EPR we aim at elucidating the structural arrangement of the box C/D RNP at different stages of the enzyme catalytic cycle. The structure of the box C/D RNP was determined recently both in the apo-state (no substrates bound) and in the holo state (all substrates bound): the two structures were found to be substantially different [1]. To determine the structural arrangement of the RNA in the box C/D RNP, we label the substrate RNAs at different positions and measure distances between two spin labels in different conformational states of the enzyme by PELDOR. This work is performed in collaboration with the group of Prof. C. Kreutz (University of Innsbruck) and the group of Prof. T. Prisner (University of Frankfurt). At the current stage of the project, PELDOR has provided unique long range structural information on the RNA conformation. Finally, PELDOR in combination with solution state NMR, SAXS and SANS techniques will allow the structural characterization of the box C/D RNP at different stages of the catalytic



Left-hand side is magnetization transfer schemes in different solid-state NMR experiments; right-hand side is bunch of 10 ssNMR structures.

cycle. Please, look for the report of this study in the near future.

The work presented here would have not been possible without the support of many people. I would like to acknowledge my current advisor, Dr. Teresa Carlomagno at EMBL, Heidelberg, where I moved in the beginning of 2012. I also would like to acknowledge close collaboration between our group, the group of Prof. C. Kreutz and the group of Prof. T. Prisner for the work on the box C/D enzyme. I also would like to express my gratitude to my former supervisors Prof. Wolfgang Lubitz and Dr. Maurice van Gastel for their help and support during my doctoral and postdoctoral studies at the Max Planck institute for Bioinorganic Chemistry in Mülheim a.d. Ruhr and at the University of Bonn.

1. Lapinaite, A., Simon, B., Skjaerven, L., Rakwalska-Bange, M., Gabel, F., Carlomagno, T. The structure of the Box C/D enzyme reveals regulation of rRNA methylation. Nature **2013**, 502, 519–523.
2. Marchanka, A., Simon, B., Carlomagno, T. A suite of solid-state NMR experiments for intranucleotide RNA resonance assignment in a 21 kDa protein-RNA complex. Ang. Chem. Int. Ed. **2013**, 52, 9996–10001.
3. Marchanka, A., Simon, B., Althoff-Ospelt, G., Carlomagno, T. RNA structure determination by solid-state NMR spectroscopy. Nat. Commun. **2015**, 6:7024. doi: 10.1038/ncomms8024.

IES Poster Award 2014

Jackie Esquiaqui:

The annual Rocky Mountain Conference provides an exciting forum for leading scientists in the field of electron paramagnetic resonance (EPR) spectroscopy to participate in insightful discussions, engaging presentations, and informative sessions highlighting pioneering efforts of advancements in the field of EPR. As a graduate student pursuing a Ph.D. in Chemistry, I am most grateful to have attended the 56th annual Rocky Mountain Conference in Copper Mountain, Colorado and I am humbly honored to have been awarded the "Best Student Poster" award for the 37th International EPR Symposium. I give my sincerest thank you to the organizers and judges of the 2014 EPR symposium for providing me an occasion to present my research and for your highly regarded recognition through this award. I especially thank my supervisor Dr. Gail Fanucci for her incredible mentorship, guidance, support, and her dedication to encouraging and providing her students with the opportunity to attend and present their work at local and national meetings.

My doctoral research is centralized on utilizing site-directed spin labeling (SDSL) and EPR spectroscopy to answer biologically relevant questions regarding dynamics and conformational sampling of the large RNA glycine riboswitch. RNA riboswitches are segments of mRNA located in the 5' untranslated region of many prokaryotic transcripts that can independently and selectively recognize and bind a cognate ligand without the obligate aid of any protein counterpart (Serganov & Patel, 2012b). Riboswitch ligand binding induces conformational changes in RNA secondary and tertiary structure that alters expression of downstream genes associated with the bound ligand (Serganov & Patel, 2012a). Questions regarding changes in dynamics and RNA structural rearrangement in the ligand unbound to ligand bound form are well-suited for study by both CW and pulsed EPR spectroscopy techniques and are of interest for further understanding of the effectuated genetic regulation of genes in these organisms. The latter has been implicated in the potential targeting for development of novel antibiotics and in furthering the design of engineered aptamers for genetic regulation (Blount & Breaker, 2006; Wieland, Auslander, & Fussenegger, 2012).

Biological SDSL-EPR is diverse and can include the study of biomolecules such as proteins, lipids, and nucleic acids through use of varying EPR methods. SDSL-EPR does not restrict the molecular size of the biomolecule studied and requires a small sample quantity which is advantageous for many biological systems of interest. For naturally diamagnetic protein systems, the well-established and successful methodology of SDSL has allowed for facile incorporation of site specific nitroxide spin labels that can be interrogated by EPR spectroscopy. In recent years, advancements in the field of RNA SDSL have provided numerous methods for incorporation of spin labels through site specific chemical modification of synthetically produced RNA (Zhang, Cekan, Sigurdsson, & Qin, 2009). However, synthetic RNA production imposes a limitation upon the length (~40 nucleotides) of chemically modified RNA that can be cost-efficiently generated, thus, restricting the size of RNA that can be studied by EPR spectroscopy. To achieve SDSL of larger RNAs (such as many riboswitches which exceed 100 nucleotides) alternative methodologies must be implemented.

The focus of my poster presentation encompassed methodological design and successful employment of SDSL of the 232 nucleotide *Vibrio cholerae* glycine riboswitch to study backbone dynamics within an important, previously identified, interaction known as the leader-linker interaction. To overcome the challenge of spin labeling this large RNA, the methodology of splinted ligation, alongside synthetic RNA strategies, was employed (Esquiaqui, Sherman, Ionescu, Ye, & Fanucci, 2014). This scheme involves use of a short, chemically modified, synthetically produced RNA that is first spin labeled and subsequently ligated enzymatically to a large RNA fragment containing the remaining riboswitch sequence which has been generated using standard *in vitro* transcription procedures. Successful RNA SDSL, ligation, and purification of the full length glycine riboswitch were achieved allowing for investigation of site specific changes in backbone dynamics. The glycine riboswitch is comprised of two binding domains (aptamers) that can each bind one molecule of glycine to induce genetic expression of genes important for the catabolism of glycine within the cell (Mandal et al., 2004). Previous biological studies have

identified formation of a leader-linker interaction that influences glycine binding affinity and interaptamer interactions (Sherman, Esquiaqui, Elsayed, & Ye, 2012). To provide spectroscopic evidence for the formation of this interaction, SDSL, in conjunction with X-band CW EPR, was used to probe three sites with predicted variability in local dynamics based upon RNA folding in the absence and presence of salts and glycine ligand. Our results showed differential backbone dynamics at each of the three sites probed in agreement with the predicted changes upon formation of the leader-linker interaction (Esquiaqui et al., 2014).

Successful utilization and optimization of both enzymatic and synthetic RNA techniques has provided us an approach to spin labeling large RNAs such as the glycine riboswitch for studies using EPR spectroscopy and we are hopeful that our optimized methods may be an additionally useful tool in the RNA-SDSL EPR community (Esquiaqui, Sherman, Ye, Fanucci, 2014). We are excited to be continuing this work through multifrequency CW EPR and Double Electron-Electron Resonance (DEER or PELDOR) studies to investigate local dynamics and conformational sampling of the glycine riboswitch.

Blount, K.F. & Breaker, R.R. (2006). Riboswitches as antibacterial drug targets. Nat. Biotechnol. **24**(12), 1558–1564.

Esquiaqui, J.M., Sherman, E.M., Ionescu, S.A., Ye, J., & Fanucci, G.E. (2014). Characterizing the Dynamics of the Leader-Linker Interaction in the Glycine Riboswitch with Site-Directed Spin Labeling. Biochemistry **53**(22) 3526–3528.

Mandal, M., Lee, M., Barrick, J.E., Weinberg, Z., Emilsson, G.M., Ruzzo, W.L., & Breaker, R.R. (2004). A glycine-dependent riboswitch that uses cooperative binding to control gene expression. Science **306**(5694), 275–279.

Serganov, A. & Patel, D.J. (2012a). Metabolite recognition principles and molecular mechanisms underlying riboswitch function. Annu. Rev. Biophys. **41**, 343–370.

Serganov, A. & Patel, D.J. (2012b). Molecular recognition and function of riboswitches. Curr. Opin. Struct. Biol. **22**(3), 279–286.

Sherman, E.M., Esquiaqui, J., Elsayed, G., & Ye, J.D. (2012). An energetically beneficial leader-linker interaction abolishes ligand-binding cooperativity in glycine riboswitches. RNA **18**(3), 496–507.

Wieland, M., Auslander, D., & Fussenegger, M. (2012). Engineering of ribozyme-based riboswitches for mammalian cells. Methods **56**(3), 351–357.

Zhang, X., Cekan, P., Sigurdsson, S.T., & Qin, P.Z. (2009). Studying RNA using site-directed spin-labeling and continuous-wave electron paramagnetic resonance spectroscopy. Meth. Enzymol. **469**, 303–328.

Esquiaqui, J.M., Sherman, E.M., Ye, J., & Fanucci, G.E. (2014). Site-directed spin-labeling strategies and electron paramagnetic resonance spectroscopy for large riboswitches. Meth. Enzymol. **549**, 287–311.

IES Poster Award 2014

Noah Horwitz:

First and foremost, I would like to thank my co-authors, without whom my presentation would not have been possible. Eric Margulies and Dr. Leah Shoer performed important optical experiments, Dr. Matt Krzyaniak and Prof. Raanan Carmieli were invaluable in helping me understand my EPR data, and my advisor Prof. Michael Wasielewski has provided support and advice throughout my graduate career. I would also like to thank the organizers of the International EPR Symposium and Rocky Mountain Conference on Magnetic Resonance for the opportunity to present my work and the US Department of Energy Office of Science Graduate Fellowship for funding my attendance.

In my poster presentation at the symposium, I discussed how EPR spectroscopy can be used to follow spin polarization in systems that undergo photoinduced electron transfer. My research focuses on organic compounds containing an electron donor (D) and an electron acceptor (A) that undergo electron transfer (ET) following photoexcitation, producing a pair of free radicals. Similar structures, in which the donor and acceptor are held in close proximity by either covalent or noncovalent interactions, form the basis of photosynthetic reaction centers and organic photovoltaics. Because ET typically proceeds from a photoexcited singlet state, the two spins in the radical pair remain anticorrelated as a consequence of angular momentum conservation. The initial state of this spin correlated radical pair (SCRP) is a maximally-entangled Bell state [1, 2], which gives rise to a uniquely polarized EPR signal.

As noted above, SCRPs occur naturally in photosynthetic reaction center proteins, and similar D-A molecules are being developed for use in organic photovoltaics (OPVs) and solar fuels synthesis [3]. Previous research indicates that stable radicals coupled to D-A systems can increase the rate of intersystem crossing from the excited state [4], a possible energy loss process, but can also reduce the rate of charge recombination [5], a major loss process in OPVs. A better understanding of spin dynamics in SCRPs could lead to new ways to improve OPV efficiency by reducing these loss processes [6]. As one example, recent work has shown reduced charge recombination rates from triplet radical pairs in OPVs [7], and this effect has been exploited through incorporation of stable radicals into the active layer of an OPV [8]. Additionally, the unique non-equilibrium spin state formed in SCRPs upon photoexcitation could serve as the basis for new information processing technologies based on electron spins: so-called molecular spintronics [9].

I am studying synthetic organic molecules containing D-A systems covalently-linked to one or more stable radicals with the aim of understanding how interactions with additional spins influence the D-A system. Covalently-linked systems have the advantage of fixed distances between components, allowing the coupling strength between them to be controlled via synthetic modifications. At the symposium, I presented on the synthesis and characterization of a series of molecules containing a phenylenediamine electron donor and a naphthalenediimide (NDI) electron acceptor coupled to either a nitroxide (TEMPO) or allyl (BDPA) stable radical. In a control molecule containing no stable radicals, we use transient optical absorption spectroscopy to observe the expected picosecond charge separation to form an SCRP that undergoes charge recombination in hundreds of nanoseconds - slow enough to observe the SCRP by transient continuous wave EPR techniques. Mixing between the initially populated ▶

singlet SCRP state and triplet SCRP states is driven by the different magnetic environments of the two radicals, and these triplet SCRPs recombine to an EPR-active triplet excited state localized on the NDI acceptor.

In the molecule containing a TEMPO radical, we observed polarization of the TEMPO following ET and charge recombination in the D-A system. This polarization transfer from an SCRP to a stable radical has been observed before in similar molecules (10), and may be useful in spintronics applications as a way to build up an initial polarized state for other operations. Preliminary transient optical absorption data on this molecule shows that the presence of TEMPO speeds up charge recombination. While this is partly due to the electronic effect of the polar TEMPO group, rates of charge recombination and triplet formation will be monitored to see if the coupling between TEMPO and the reduced acceptor radical influences the relative recombination rates of singlet and triplet radical pairs.

With BDPA, the expected polarization transfer was not observed. Instead, SCRP and NDI triplet signals are observed to be nearly identical to those from the control molecule. However, an additional set of lines are observed in the EPR spectrum, which persist after the SCRP has recombined. Since the new signal is too broad to be due to polarized BDPA, it may arise from an interaction between the BDPA radical and the NDI triplet. Transient nutation experiments are planned to determine if these new signals arise from a quartet state involving BDPA and NDI triplet. Such quartet states have been observed before, but only in molecules where the 3 spins involved are in close proximity [4, 11]. Additionally, we will try to measure or estimate the coupling between BDPA and the donor radical to see if it is in a different coupling regime than the TEMPO-containing molecule.

While preliminary, these results show some interaction between BDPA and the SCRP. Future work to narrow down what is happening in the BDPA-containing molecule and determine why it differs from the TEMPO-containing molecule should help complete our understanding of the range of interactions that can occur in these multi-spin organic systems.

1. Salikhov, K.M., et al. Appl. Magn. Reson. **1**, 195–211 (1990)
2. Salikhov, K.M., et al. Appl. Magn. Reson. **31**, 237–252 (2007)
3. Wasielewski, M.R. Chem. Rev. **92**, 435–461 (1992)
4. Colvin, M.T., et al. J. Phys. Chem. A **115**, 7538–7549 (2011)
5. Chernick, E.T., et al. J. Am. Chem. Soc. **128**, 4356–4364 (2006)
6. Poluektov, O.G., et al. Phys. Chem. Chem. Phys. **11**, 6750–6756 (2009)
7. Rao, A., et al. Nature **500**, 435–439 (2013)
8. Zhang, Y., et al. Nat. Commun. **3**, 1043 (2012)
9. Epstein, A. J. MRS Bulletin **28**, 492–499 (2003)
10. Colvin, M.T. et al. J. Phys. Chem. A **117**, 5314–5325 (2013)
11. Teki, Y. & Matsumoto, T. Phys. Chem. Chem. Phys. **13**, 5728–5746 (2011)

IES Poster Award 2014

Zhelin Yu:

It is an honor to be invited to write this article about my research for the EPR Newsletter. First, I would like to thank the organizers of the 2014 International EPR Symposium and Rocky Mountain Conference on Magnetic Resonance for providing me an opportunity to share my research work with pioneers and leaders in this research community. I would also like to acknowledge my supervisors, Prof. Gareth R. Eaton and Prof. Sandra S. Eaton, at University of Denver for their support and guidance in my graduate career.

My presentation at the symposium was about rapid-scan electron paramagnetic resonance (EPR) of immobilized nitroxides. In rapid-scan EPR the magnetic field is scanned through resonance in a time that is short relative to the electron spin relaxation times. The directly-detected quadrature signal is obtained using a double-balanced mixer with the reference at the resonator frequency. By contrast conventional continuous wave (CW) EPR uses phase sensitive detection at the modulation frequency [1]. Among organic radicals, a very important case is immobilized nitroxide spin labels. We demonstrate that the technology developed in our laboratory for rapid scans can be extended to perform 155 G wide sinusoidal scans, which are wide enough to encompass the full spectrum of an immobilized nitroxide. Rapid scans were obtained for ^{14}N-perdeuterated tempone (^{14}N-PDT) and ^{15}N-PDT in sucrose octaacetate and for T4 lysozyme doubly spin labeled with iodoacetamide spiro cyclohexyl nitroxide in a trehalose glass at room temperature.

CW and rapid-scan spectra were recorded on a Bruker E500T spectrometer using a Bruker Flexline ER4118X-MD5 dielectric resonator. The sinusoidal scans were generated with the recently described scan driver [2]. The scan coils were constructed from 200 turns of Litz wire (255 strands of AWG44 wire). The coil constant was 37.7 G/A, which is sufficient to generate scans up to 155 G wide with scan frequencies up to 13.4 kHz. Mounting the coils on the magnet, rather than on the resonator, reduces the oscillatory background signal induced by the rapid scans.

The region of the power saturation curves in which signal amplitude increases linearly with B_1 extends to higher B_1 for the rapid-scan experiments than for CW, which permits use of higher microwave power without saturating the signal. In a rapid scan experiment the spin system is on resonance for a time that is shorter than in conventional CW, so higher B_1 can be used without saturation. The use of higher power and resulting increase in signal amplitude is a significant contributor to the improved signal-to-noise (S/N) for rapid-scan spectroscopy. The microwave power for data acquisition was selected using the following criterion. A linear least-squares fit through the signal amplitudes at the lowest 5 or 6 microwave powers was extrapolated to higher B_1. The B_1 selected for data acquisition was the point at which the experimental signal amplitude was about 5% lower than the amplitude predicted by linear extrapolation of the non-saturated signal amplitude. The B_1 used for data acquisition for ^{14}N-PDT, ^{15}N-PDT and T4 lysozyme were 24, 22, and 25 mG, respectively, for CW and 49, 39, and 77 mG, respectively, for rapid scan. The modulation frequency for the CW spectra was 100

kHz. The modulation amplitudes: ^{14}N-PDT in sucrose octaacetate (0.63 G), ^{15}N-PDT in sucrose octaacetate (0.9 G), ^{14}N-spin label on T4 lysozyme (1.8 G), were about 20% of ΔB_{pp}. These combinations of parameters result in less than 2% line broadening relative to spectra obtained at lower modulation amplitude and smaller B_1. The scan frequencies for the rapid scan signals were limited by the constraints of the coil driver. At these scan frequencies the signal bandwidths were less than the resonator bandwidth, so resonator bandwidth did not contribute to spectral broadening.

The rapid-scan signals were deconvolved and background corrected. The resulting spectra are the sum of up-field and down-field scans. The experimental dispersion spectra were converted into absorption spectra for summation with the experimental absorption spectra. A post-processing Gaussian filter was applied to both CW and rapid-scan spectra. The cut-off frequency for the low-pass filter was selected to cause no more than 2% broadening of the full width at half maximum of the absorption spectra or the ΔB_{pp} linewidth for first-derivative spectra. S/N is the peak-to-peak signal amplitude (for CW) or signal amplitude (for rapid scan) divided by the rms noise in baseline regions of the spectrum.

The S/N for the rapid-scan absorption spectra is 6–30 times that for the CW first derivative spectra, which is a substantial advantage for weak signals. The improved S/N for rapid-scan relative to CW spectra comes from three factors: (i) differences in signal amplitudes due to excitation of a small portion of the spectrum in the CW experiment vs excitation of the entire spectrum in rapid scan, (ii) the ability to use higher B_1 without power saturating the signal, and (iii) the differences in the noise spectral densities in CW and rapid-scan spectra. The S/N improvement for slowly tumbling spin-labeled protein samples that is provided by rapid scan EPR will be highly advantageous for biophysical studies.

The results and a full discussion of their implications subsequently were published in *Journal of Magnetic Resonance*, **247**, 67–71, (2014).

1. S.S. Eaton, R.W. Quine, M. Tseitlin, D.G. Mitchell, G.A. Rinard, G.R. Eaton, Rapid scan electron paramagnetic resonance, in: S.K. Misra (ed.), Multifrequency Electron Paramagnetic Resonance, Wiley, 2014, pp. 3–67.
2. R.W. Quine, D.G. Mitchell, S.S. Eaton, G.R. Eaton, A resonated coil driver for rapid scan EPR, Conc. Magn. Reson., Magn. Reson. Eng. **41**B, 95–110, (2012)

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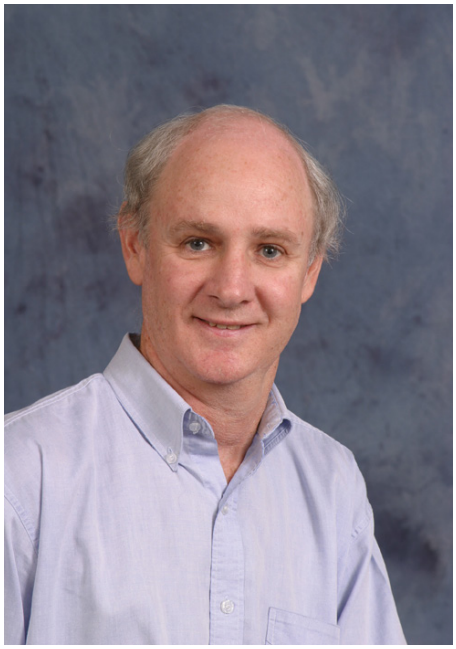

Graeme Hanson (1955–2015)

The Centre for Advanced Imaging acknowledges the passing of Professor Graeme Hanson on 25th February 2015. His family, colleagues and the science community have lost a passionate researcher who is internationally recognised for excellence in his chosen field.

Graeme was born on 16 July 1955 in Melbourne and grew up in Box Hill with his parents Mavis Jean and Richard Wallace Hanson and younger brother John. Graeme's primary and secondary schooling was at local state schools after which he attended La Trobe University Bundoora, Victoria, completing a BSc with Honours. He continued his PhD under the supervision of Professor Wedd (Bioinorganic Chemistry), with additional supervisors Prof. John R. Pilbrow (EPR Spectroscopy) and Dr. Robert Scopes (Enzymology).

It was during these formative years that Graeme was introduced to the technique which was to dominate his professional area of expertise and to establish his scientific reputation. That technique was EPR, Electron Paramagnetic Resonance. After La Trobe, Graeme moved to Harvard University with Bert Vallee for several years, to Monash University and then commenced lecturing in the School of Chemistry at the University of Queensland in 1987.

After 2 years in the Chemistry Department at UQ Graeme joined the Centre for Magnetic Resonance to establish the EPR facility. Over the next 25 years, that EPR facility was expanded, equipped and reequipped to become ultimately the best EPR facility in Australia and recognized internationally. He was promoted to Professorial Research Fellow in 2003 and continued to lead the EPR Group at the Centre for Advanced Imaging from 2010. Graeme's extensive collaborations were acknowledged by others, being appointed Honorary Professor at the School of Life and Environmental Sciences, Deakin University, a Fellow of the Royal Australian Chemical Institute (RACI) and treasurer of the Society of Biological Inorganic Chemistry.

His distinguished career focused on utilising synergistic approaches of both theoretical and experimental continuous wave and pulsed EPR spectroscopy to address important scientific challenges in the biological and chemical arenas. A successful collaboration with the EPR Division of Bruker Biospin, Germany resulted in the development and commercialisation of the computer simulation software suites (XSophe-Sophe- XeprView, Molecular Sophe and iResonanz) which were pivotal in his scientific endeavours and ensured that Graeme's research was at the forefront in the application of EPR. Application of the software suites to the characterisation of organic free radicals, active sites in metalloenzymes, model transition metal ion complexes, dinuclear copper cyclic peptide complexes capable of fixing carbon dioxide and metallo-drugs has provided many ground-breaking and novel insights.

Graeme contributed to the wider scientific endeavour as a Fellow of the Royal Australian Chemical Institute; German Chemical Society Lecturer (University of Kaiserslautern); RACI Schools Lecturer, Vice President of the International EPR Society (2015–2017), Treasurer of the Society of Biological Inorganic Chemistry, 2007–2015; Board member and Treasurer of ANZMAG,1995–2004; Vice President of the Asia Pacific EPR Society, 2006–2010; Fellow of the RACI; Member of the International Society of Magnetic Resonance, Australian Society of Biophysics, Society of Biological Inorganic Chemistry, ANZMAG, the American Chemical Society (ACS), Royal Society of Chemistry and the RACI.

Since Graeme's passing there have been many condolence messages sent from the scientific community and the sincere respect and affection for Graeme from this community is palpable. In their messages several people commented on Graeme's work-life balance and devotion to his family, exemplified by this comment from Trevor Hambley: "On a personal level, I'd say what I remember most was Graeme's unwavering, unequivocal, and enthusiastic commitment to his family and to his work – it was on a level that is hard to match."

Graeme's personal passions were many and varied. He loved travel, fireworks, camping in the Australian bush and sports. Growing up he loved bike riding and playing cricket, badminton, table tennis and tennis, which he played at club level into his early 20s. His love of sports grew with his son's successful involvement in soccer, with Graeme volunteering many hours to coaching, managing and running local teams and clubs. He had a long involvement in the Scouting Movement, beginning as a Cub and progressing through Scouts to Rovers, becoming Queen Scout.

Graeme was a proud father and devoted husband, he passed away after a brief illness and is survived by his wife Lyn and children Jeff, Harry, Johanna and Adrian.

* * *

I first met Graeme in 1978 when his honours supervisor, Dr Tony Wedd, at Latrobe University (now Emeritus Professor of Inorganic Chemistry, Melbourne University), sent him to me to learn about EPR Simulations. Graeme was working on some Mo(V) compounds. I equipped him with the main program I had developed almost a decade earlier, which he quickly modifed to incorporate the naturally occrring Mo isotopes.

As I was on sabbatical in the USA during the whole of 1979, I did not meet up with Graeme again until my return in 1980 by which time he was immersed in his PhD, also under Tony Wedd, on a range of Mo-O and W-O compounds and isotopically enriched Mo in the molybdenum enzyme, Xanthine Oxidase. His early grounding in enzymology was overseen by another LaTrobe University scientist, Dr. Robert Scopes (author of *Protein Purification: Principles and Practice*, Springer).

Upon my return in 1980, we undertook to construct an S-Band bridge to operate with our Varian E12 Spectrometer; this was completed and became operational in late 1981. With a suitably designed rectangular cavity it was possible to operate at 2, 2.9 and 4 GHz, and at liquid helium temperature. One could switch frequencies during experiments. As LaTrobe University only possessed a Varian E-9 instrument operating down to 77 K, the work could not be carried out there but

only in my lab. Graeme quickly familiarised himself with operating the S-Band bridge and did, in fact, observe the hoped for resolved hyperfine structure from the weaker isotopes. On looking back to that time, it is clear he was starting to think about how the simulation program could be made more general.

During my visit to Prof Bert Vallee's Group at the Harvard Medical School early in 1983, Bert asked if I could think of someone who could assist with their work on cobalt substituted enzymes such as carboxypeptidase. The person needed a good background in inorganic chemistry, preferably also a background in enzyme biochemistry as well as a first-rate background in EPR spectroscopy. I immediately thought of Graeme who, in due course, spent two years in Vallee's Group.

During 1985-7, on returning to Australia, Graeme spent two years as a Post-Doc in my Group and, in fact, ran my Group for most of 1986 while I was away in a neighbouring Government Lab working on my book. More importantly, in collaboration with my PhD student, Geoff Sinclair, Graeme returned again to the question of how to generalise EPR simulations. In those days we had an LSI11 computer in the lab and he and Geoff developed a convenient data entry procedure, but as the programs were still reliant on perturbation theory they could never be totally general. This period was a point of departure from reliance on the University's mainframe computer as the LSI11 performance was competitive and it was under their control in the lab and not hindered by scheduling on the mainframe.

Graeme purchased one of the very first IBM PC's back in 1985. While today's PCs and Laptops are many times more powerful than those first PCs, he sensed that some day such small computers would be adequate for the kind of software development he had in mind.

After leaving my group in the Physics Department at Monash University, Graeme spent two years as a Lecturer in Chemistry at the University of Queensland. Following this he moved to the Centre for Magnetic Resonance (CMR), responsible for EPR Spectroscopy. During Graeme's many years at CMR (now called Centre for Advanced Imaging) he built up an impressive suite of spectrometers; CW at S-, X- and Q-band frequencies, Endor, Eldor and more recently pulsed EPR.

About 20 years ago, Graeme and his Group embarked on a successful collaboration with the EPR Division of Bruker Biospin, Germany. This led to the development and commercialisation of the computer simulation packages – XSophe-Sophe-XeprView, Molecular Sophe and, more recently, iResonanz. Dr Chris Noble (a Physics PhD from Monash University) worked on later developments with Graeme. This software was pivotal in his own work and is also used by many researchers around the world. Graeme wanted more than a spin Hamiltonian as the outcome of experimental work and, in recent years, made good use of Density Functional Theory software to asssist with relating the spectroscopy to the chemistry.

It is worth pointing out that the development of XSophe, the first of the commercial simulation suites, was carried out with Dr Deming Wang (a former PhD student of mine) who came up with the SOPHE grid, a way of covering orientations over a sphere based on the roof tiling on the Sydney OPera HousE. Scaling up or down to finer or coarser grids was easily achieved, and avoided the limitations of working with spherical polar coordinates (θ, ϕ). And by using computer diagonalisation of the spin Hamiltonian matrices for spins $S = 1/2$ to $7/2$, the packages have become more general. These simulation packages all included tables of nuclear spins and isotopic abundances from the whole Periodic Table with default settings for the naturally abundant isotopes. EPR Spectra involving enriched isotopes could be simulated by in-putting the actual isotopic percentages.

These various simulation packages have assisted with characterisation of organic free radicals, active sites in metalloenzymes, model transition metal ion complexes, dinuclear copper cyclic peptide complexes capable of fixing carbon dioxide, and metallo-drugs leading to many ground-breaking and novel insights.

It was fitting that the University of Queensland promoted Graeme many years ago to the position of Professorial Research Fellow, with the title of Professor.

Graeme's *EPR ⇒ Hot Science* feature in recent *EPR Newsletters* (23/2, 23/2 & 24/1-2) fulfilled his desire to make forefront research accessible to the general EPR reader. It is good that one example involved his Group.

Whilst my first impression of Graeme, back in 1978, was of a fairly quiet young man, I realised just a few years later that under that apparently quiet demeanour was a very talented young man. I think he was probably a bit apprehensive having to visit a Physics Department on that first visit!

Over the years, Graeme discovered a talent for organisation. In 1995 we organised EPR95 at Sydney University just prior to the ISMAR Symposium, with an attendance of around 50. When Graeme asked if I would consider joining him and Mike Davies as a Co-Organiser of APES08 in Cairns, North Queensland, I was at first a little apprehensive, particularly as the world was in the middle of the GFC. True to form Graeme convinced us to go ahead. Though smaller than previous APES's, it paid its way and turned out to be a very good conference indeed.

I have lost track of all the conferences that Graeme has had a hand in organising. However, I refer to the last such conference AsBIC7 (7th Asian Biological Inorganic Chemistry Conference) held from 30 November to 5th December 2014 where he was one of the two Conference Organisers. This was a remarkable commitment given that he had been diagnosed with a serious illness.

In recent years Graeme somehow found time to join Larry Berliner as Co-Editor of several issues of Biological Magnetic Resonance.

There is much evidence of involvement in the wider scientific world: Fellow of the Royal Australian Chemical Institute(RACI); RACI Schools' Lecturer; German Chemical Society Lecturer (University of Kaiserslautern); Treasurer, Society of Biological Inorganic Chemistry, 2007–2015; Board member and Treasurer of ANZMAG (Australian and NZ Magnetic Resonance Society),1995–2004; Vice President, Asia Pacific EPR Society, 2006–2010; Member, International Society of Magnetic Resonance, Australian Society of Biophysics, American Chemical Society (ACS) and The Royal Society of Chemistry.

The esteem within which Graeme was held in the EPR Community was well recognised in his recent appointment as Vice President (Asia-Pacific) of the International EPR Society. The pity is that he will not be able to complete his term.

There was much more to Graeme than his scientific work. He loved travel, camping in the Australian bush and sports. While growing up he participated in many sports, particularly tennis, which he played at club level into his early 20s. He had a long involvement in the Scouting Movement, beginning as a Cub and progressing through Scouts to Rovers, ultimately becoming a Queen's Scout.

Graeme was very much a family man, justly proud of his children whether for academic success or on the sporting field. His love of sports grew with his sons' successful involvement in soccer, with Graeme volunteering many hours to coaching, managing and running local teams and clubs. I often wondered how he managed to fit in his research and his involvement with the wider scientific com-

munity, and yet also make time to ensure his son's got to soccer practice and then being there to support them in competition.

A proud father and devoted husband, Graeme passed away after a brief illness. He is survived by his wife, Lyn, and children Jeff, Harry, Johanna and Adrian. The EPR Community has lost one of its hardest workers and many of us have lost a good and personal friend and respected colleague.

To Lyn and the family we all add our condolences at this time.

John Pilbrow (Melbourne, Australia)
May 5th, 2015

A Tribute To Graeme Hanson from a Close Friend

I have known Graeme Hanson for several decades. Graeme and I would meet at various EPR meetings around the world and quickly became scientific colleagues and close friends. I had the pleasure of visiting him at the University of Queensland (UQ) during the early 1990s while on sabbatical in Melbourne. I also returned to that region of the world in 2008 when Graeme was the main organizer of the Sixth Asia-Pacific EPR/ESR Symposium in Cairns. Despite his being constantly busy and frequently unable to attend many sessions, he always had time for his friends. Graeme and I would schedule regular Skype calls to discuss science, the IES and issues of life and family. Graeme had the unique talent (as do many excellent scientists) of taking on more responsibilities and projects than a normal scientist might not be able to juggle. He would 'burn the midnight candle' to complete manuscripts, grant proposals and the like, including joint proposals on which he and I were collaborating.

Since Graeme had extensive experience as an officer in large international scientific professional organizations, such as ICBIC, I would frequently request his advice on IES issues that I encountered as both Vice President-Americas and Interim President. As a result, Graeme accepted the position as IES Vice President – Asia starting 2015, a position that he was only able to serve for less than two months.

The times I most cherish were his visits to Denver to attend the Rocky Mountain International EPR Symposia. Graeme, my wife Barbara and I would frequently attend an opera in Central City and have wonderful gourmet dinners together. The most memorable was one late afternoon when Graeme returned to Denver airport to discover that they had cancelled his trip and rebooked him for the next morning. I suggested that Graeme find the airport bus that dropped him just near our home and we spent a delightful evening dinner and discussion before bringing him back to the airport the next day.

We collaborated on several books in the Biological Magnetic Resonance series: *High Resolution EPR: Applications to Metalloenzymes and Metals in Medicine*, Vol 28 and *Metals in Biology: Applications of High-Resolution EPR to Metalloenzymes*, Vol 29 (2009). In collaboration with Takeji Takui, we are in production of another volume entitled: *Electron Spin Quantum Computing: Electron Spin-Qubit Based Quantum Computing and Quantum Information Processing* that is currently in production for a 2015 copyright date. Amazingly, we were in the process of signing a contract for yet another volume on metalloenzymes that was sitting on Graeme's desk. I intend to proceed ahead on this volume, which will also carry his name as coeditor.

I was also one of the few people outside of his close family circle to know about his cancer diagnosis. We discussed the treatment, the prognosis and his professional travel and scientific plans for the future which I kept totally confidential until he informed the organizers that he was unable to attend the November, 2014 APES/SEST/IES meeting. Despite at least two terrible setbacks and long hospital stays during the interim, I was shocked to hear that his weakened condition overcame him so soon. I think of Graeme every day; I remember our frequent telephone calls, past travels and always dreaming up new plans for future scientific collaborations and publications. The profession has lost a real pioneer and contributor and I (and my family) have lost a dear friend.

Lawrence Berliner

* * *

The EPR community has lost a valued colleague. Since others have provided much important information about Graeme Hanson's scientific career, we will add only a few brief comments about our interactions with him. Graeme was a frequent attendee of the International EPR Symposium at the Rocky Mountain Conference, and happily came to our lab to help with implementation of his program Sophe. He was very expert with computers and provided invaluable assistance. When we visited Brisbane he was a gracious and attentive host in spite of the many tasks he had to work on to make the conference successful. With joint interests in a wide range of EPR spectroscopy, in similar paramagnetic species, and in stimulating wider appreciation of the importance and applications of EPR, we enjoyed our mutually beneficial interactions with Graeme.

Sandra Eaton
Gareth Eaton

* * *

When asked to write a tribute to Professor Graeme Hanson, at first I hesitated to reply. Though it is a truly an honor to write about such a remarkable person and fine scholar, I was afraid that my thoughts might not do justice to his accomplishments.

I am not sure whether it was at an EPR conference at Denver or ICBIC where I first met Graeme. I do remember I was a postdoc at that time. I found him looking at my poster presentation of the enzyme Nitrogenase and asked him many questions regarding the spectroscopical interpretation of the data. He stayed for quite a time and enthusiastically answered my questions, which inspired me a lot.

After I became a regular participant of APES (Asia-Pacific EPR/ESR Symposiums), I made more frequent personal contact with him, and discovered how generous and passionate he was. Among many meetings with him, the most memorable was in 2010. It had been a busy time preparing for APES2010, held in Jeju, Korea. I asked him many favours concerning many aspects of the symposium. He willingly helped me a lot.

In the summer of that year, we met again at EUROMA, Florence. Graeme, Hitoshi and I gathered at Palazzo Pitti one evening to discuss the selection of the APES Young Scientist Awards. We spent more time chatting about the Renaissance than the awards! On the starry night, Graeme introduced me the best place in the Earth to observe the Milky Way, Uluru (also known as Ayer's Rock) in Central Australia. I have not been there yet. If I ever visit Uluru, it will remind me of Graeme who told about this place. Not many weeks before the symposium, I urgently asked him to bring the "ready-to-present" frames and certificates for the APES Young Scientist Awards. I was surprised when he showed up with "huge" frames made in Australia – all the way to Korea. Without his central role, organizing APES2010 and publishing the special issue of *Applied Magnetic Resonance* for APES2010 would not have beeen possible.


TAKEN BY WOLFGANG LUBITZ

When I heard about his illness back in November, while at APES2014, I was shocked because I had read his column. "EPR ⇒ Hot Science", in the *EPR newsletter* last summer! I hoped he would be back. It is sad to realize that there will be no more meeting with such a fine scholar. But his name, Professor Graeme Hanson, will shine for a long time.

Hong-In Lee
Daegu, Republic of Korea

* * *

With great sadness we have received the message that our dear colleague Graeme Hanson (59) passed away on February 25, 2015 – only a few months after he had been diagnosed with kidney cancer. Graeme was a Professorial Research Fellow and head of the EPR group at the Centre for Advanced Imaging (CAI) at the University of Queensland, Brisbane, Australia. He was Honorary Professor at Deakin University, a Fellow of the Royal Australian Chemical Institute and was engaged and served in several professional organizations, e.g. the Society of Bioinorganic Chemistry, the Australian and New Zealand Magnetic Resonance Society, the Asia-Pacific EPR Society, and was recently elected by the International EPR Society (IES) as Vice President.

Graeme Hanson is well-known in the field of EPR for his development of computer simulation software suites that allow correlating the parameters from different types of EPR experiments with the molecular (electronic and geometric) structure of the investigated system. This is realized through a simultaneous application of EPR simulations, modeling and quantum chemical calculations. His five patents relate to this unique software development and have led to the commercialization of several programs together with Bruker Biospin (XSophe-Sophe-XeprView, Molecular Sophe and iResonanz). These programs are now used by many scientists around the world working in EPR and related fields, including researchers in our Max Planck Institute that has been visited by Graeme many times during the last decade.

Furthermore, Graeme has published a large number of excellent innovative papers in his main research field, the structure and function of metalloproteins. Many of them are highly cited, in particular his work on the role of copper ions in Alzheimer's disease, his extensive spectroscopic work on molybdoenzymes and on acid phosphatases, for which he described the first case of a dinuclear mixed-metal (Fe-Mn) center and characterized its electronic structure. Another class of interesting systems to which Hanson and coworkers have contributed is vanadium pharmaceuticals, which are used in the therapy of diabetics. Furthermore, his recent study on dinuclear copper cyclic peptides, which convert carbon dioxide to carbonate, might become of importance in the field of CO_2 fixation.

In recent years Graeme Hanson has been one of the most active EPR spectroscopists in Australia. It is due to his strong engagement, excellent planning and sedulous work that Australia has now a National Centre for Advanced Imaging, including EPR, in Brisbane, where difficult problems in chemical, biological and medical research can be solved in which paramagnetic species play a critical role. Hosted by Graeme Hanson, I had the pleasure to visit the CAI last year. It is located in a beautiful new building and is unique in the Australia/New Zealand/Oceania region with respect to instrumentation, computer facilities, software and dedicated personnel. Graeme's engagement and impact has contributed much to establish this Centre. It is good to hear that his laboratory and work will be continued in the future by Jeffrey Harmer.

Graeme's influence on the whole field is best noticed by the fact that he has been invited to many international EPR conferences to present his work. He had particularly strong ties to Germany both professionally and personally. Last summer he came to our institute as a guest of an EPR Symposium – a long way from Brisbane. In Australia he has also organized or co-organized a large number of national and international symposia and conferences. I have visited many of these meetings related to Magnetic Resonance, EPR, and Bioinorganic and Biological Chemistry. I vividly remember the last Conference in the Gold Coast in December 2014 (AsBIC-7) that he had organized together with his colleague Sue Berners-Price, which was a great success. The photo is from Graeme and his wife Lyn, taken at the conference dinner of the AsBIC-7.

Graeme has been a proud father of four children. For me it was amazing to see how well he managed the balance between his personal and professional life, receiving strong support from his wife Lyn.

For all of us his early death is a great tragedy. We have lost a very good scientist, a great person and a dear friend! He will be sorely missed.

Wolfgang Lubitz
(MPI for Chemical Energy Conversion;
Mülheim/Ruhr, Germany)

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On Feb. 25, 2015, sudden notices from Dr. Jeffrey Harmer and Prof. John Pilbrow telling that Graeme Hanson passed away on Feb. 24 gave me a great shock because we communicated about the IES budget few days before. He just started as the Vice President for Asia-Pacific of IES in January, 2015, and we were expecting his deep contributions to IES. He was also starting a new column "EPR-Hot Science" in the *EPR newsletter*, and I regret so much that we are not able to read his new column anymore.

I knew Graeme for some time through the activities of APES (Asia-Pacific EPR/ESR Society) and we were close friends. He served actively as the country representative of Australia/New Zealand, Vice President and Advisory Council Member of APES. He also organized the wonderful Asia-Pacific EPR/ESR Symposium (APES2008) in Cairns, Australia with Prof. J. Pilbrow and Prof. M. Davies. I specially remember APES2008 because he was very kind to organize the award lecture for me on the occasion of my Silver Medal for Instrumentation of IES. Graeme also visited Kobe to give an invited talk at the Molecular Photoscience Research Center International Workshop "Low Energy Excitations in Condensed Phases" just after giving an invited talk at a Joint Conference of the International Symposium on Electron Spin Science and the 46th Annual Meeting of the Society of Electron Spin Science and Technology (ISESS-SEST2007, Nov. 6–9, 2007, Shizuoka, Japan). At the time he was giving nice talks related to the EPR software, which he was developing. I remember going up to the Roko Mountain just behind our university with Graeme and Elena after the workshop and we enjoyed the beautiful view of Kobe from the top of the mountain. Moreover, I specially remember the day when Graeme, Hong-In Lee and myself discussed about the coming APES2010 in Jeju, Korea, at the reception of Joint EUROMAR2010 and ISMAR in Florence, Italy. The weather was fine and very nice atmosphere in the garden but we were discussing about the APES Young Investigator Award or how to support students to APES2010 etc. and drinking wine. I can recall the day clearly. I also met Graeme very often at various conferences. Last time I met him was International Symposium "Catalytic Systems for Chemical Energy Conversion", July 23–25, 2014, Mueheim an der Ruhr, Germany to celebrate the 65th Birthday of Prof. Wolfgang Lubitz. Graeme looked fine at the time and he was very kind to present a big painting carried from Australia to Wolfgang. He was really a kind and nice person.

Graeme called me several times on the phone to discuss various things because we were in the similar time zone. At the end of October, 2014, Graeme called me on the phone. "Hi, Hitoshi." It started as usual but what he was going to tell me was not so easy. He was appointed as the invite speaker at the Joint Conference of APES2014, the 1st International EPR (ESR) Society Symposium, SEST2014 (APES-IES-SEST2014, Nara, Japan, Nov. 12–16, 2014) but he told me that he cannot come to Nara because he has to go through the therapy due to his cancer. It was completely unexpected for me because nothing seemed wrong with him when I met him in July. I could not find the proper words to tell him at the beginning. Then he told me that he wants to make the presentation through the internet, which did not happen at the end because the therapy affected him much more than he expected. However, as he started to communicate with us through e-mail normally after the conference and served as the Vice President of IES, I thought his therapy was going well. Then the sudden notice on Feb. 25 came to me.

Graeme, we will miss you sadly. I would like to express my heartfelt condolences to his family and his colleagues.

Hitoshi Ohta,
President of IES (International EPR (ESR) Society), Vice President of APES (Asia-Pacific EPR/ESR Society),
Molecular Photoscience Research Center,
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PRESENT MEETS FUTURE

Edited by
Sabine Van Doorslaer

Science progresses through the interaction of senior and junior scientists. This 'Present meets future' feature, relates the views and experiences of Dr. Daniel Klose (who recently started a postdoc at ETH Zurich) and his 'PhD father' Prof. Dr. Heinz-Juergen Steinhoff (University of Osnabrueck).

How did your career in science and EPR start? Where does your fascination for science originate from?

Daniel: Somehow nature with all its intricate and beautiful features has always fascinated me, and still does so today. Seeking to unravel and understand how it works was one factor that led to a great appeal of physics for me in high school and also later during my studies of physics in Osnabrueck. Hence, my first dream was rather to become a physicist. When it came to choosing specializations, it was more difficult, yet life sciences were a strong interest already. So with much curiosity but in need for some advice, luckily talking to Prof. Steinhoff about my interests and situation, he helped me to join the EPR group of Prof. Chris Kay at UCL, London, for getting a taste of both nanotechnology as well as life sciences projects and for learning EPR spectroscopy. So it was a splendid and diverse experience in London for almost a year that ended with a brilliant event: Chris was local organizer of the RSC EPR meeting in London in 2008. Hence, I returned highly motivated and inspired to Osnabrueck having decided to continue in life sciences & EPR spectroscopy.

Heinz-Juergen: My childhood's dream was to become an architect. During my last years in school, however, I became much more interested in electronics, physics and biology. And it was my biology teacher, who gave me the opportunity to make my own experiments in the school's biology laboratory after lectures and thereby he strengthened my interests in natural sciences. The interest in the combination of physics and biology accompanied my entire studies so that I decided to make my Diploma in biophysics. When I asked Albrecht Redhardt, who was the head of the institute of biophysics at the Ruhr-University Bochum at that time, for a Diploma project, he showed me a laboratory shelf full of waveguides, attenuators, phase shifters and klystrons, and said: "Set up an EPR spectrometer". At that time I was not aware of any relation between EPR spectroscopy and biophysics, but I was fascinated by the quantum nature of magnetic resonance and by the given chance to train my skills in high frequency physics. As soon as the spectrometer was finished, the first spectra recorded included those of spin labelled haemoglobin. The interesting temperature dependence of the spectra, which revealed a glass transition around 180 K, stimulated my interest to use EPR spectroscopy later to study protein architecture and dynamics and their relation to function.

What accomplishment in your scientific career are you very proud of?

Heinz-Juergen: As our work on molecular biophysics and EPR spectroscopy requires team work I have students and co-workers from different disciplines in my laboratory. I have tried to find a good balance between theoretical and experimental physicist, biologists and chemists. With pleasure I follow the development of successful interaction among the members of the team generating new ideas, and I very much enjoy our joint learning of something new. With each discovery and successfully finished PhD thesis, I feel proud of these accomplishments together with my group members.

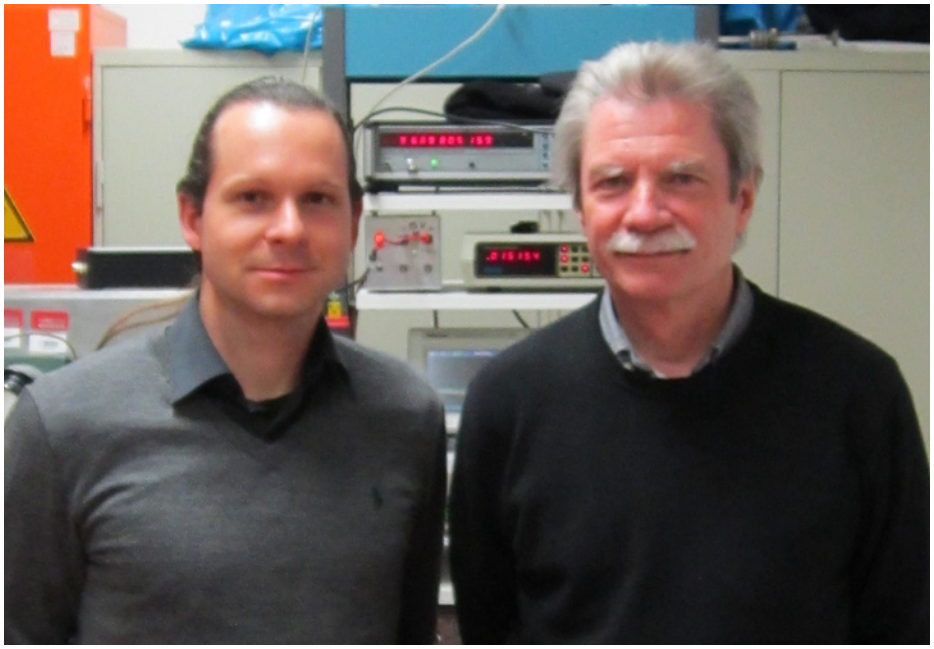
Daniel: This for me is a rather difficult question since I see most of my projects so far as densely interconnected team work where everybody contributes to the often longer process rather than to singular achievements. But maybe the time-resolved EPR spectra on the spin-labeled HAMP domain mutants are a good example, or the awesome event when the click chemistry worked with spin labels for the first time, and also the first molecular dynamics simulations with newly-parameterized molecules give always a very pleasant and rewarding feeling.

Can you describe one of the most enjoyable moments in your (short or long) scientific career?

Heinz-Juergen: I remember it vividly: It happened when I visited the laboratory of Wayne Hubbell, UCLA, in the early 90s. We were looking for possible light-induced conformational changes of bacteriorhodopsin and had prepared a couple of samples with spin labels bound to different sites in the cytoplasmic part of the protein. I had set up a self triggered flash light with focus on the sample in the EPR cavity, the output of the EPR spectrometer plugged into a second lock-in amplifier with the flash trigger signal as reference. At that day, Wayne and his wife Cherie had invited me for an outdoor barbecue dinner. In order to be in time for the appointment I had to leave the laboratory before I had seen any signal, but just started recording with a couple of B-field scans. After a wonderful dinner in the Santa Monica Mountains we returned to the laboratory around midnight, where a clearly recorded light-minus-dark difference EPR spectrum waited for us to be discovered. What an enjoyable day! This experiment paved the way for my later EPR-based findings on light-induced conformational changes in light-sensitive proteins and protein complexes.

Daniel: For me this is clearly meeting people from the scientific community, discussing and exchanging views and ideas and exploring what might be possible in the future. For me some facets of envisioning the future are for instance to know how things have developed in the past, or to see what is happening beyond the rim of one's own tea cup... So for this, conferences both in the EPR community as well as with mixed communities are very valuable, and on such events meeting people like Klaus Möbius is simply inspiring. I'm very grateful for those shared insights and inspiration. The younger generations need to know what they are carrying on after all...

Choosing a scientific career is not always an easy road to go. What were the problems that you met (or are still having) in pursuing your scientific career and your EPR dream?



Daniel Klose (°1982) studied Physics at the University of Osnabrueck (DE) from 2003 till 2009. From September 2007 to May 2009, he was an Honorary Research Assistant at UCL (UK). In this period, he got fascinated by EPR. Daniel continued to do his PhD in Biophysics at the University of Osnabrueck. From March 2015, he is postdoctoral research assistant at the ETH Zurich (CH). After being already the runner up for the JEOL Prize in 2013, he obtained the JEOL Prize 2014. He has received many other prizes and awards, including the "Greta Pifat Mrzljak Award" (Croatia, 2012), an "International Travel Award" of the American Biophysical Society for the "Biophysical Society Meeting" in Baltimore (USA, 2015) and several poster prizes.

Heinz-Juergen Steinhoff (°1954) studied Physics at the Ruhr-University Bochum (DE) where he continued to obtain a PhD in 1985 and habilitated in 1991. From 1992–1999 he was associated professor at the same university. During this time, he spent 1 year as a visiting professor at UCLA with Wayne Hubbell. From 1999–2001 he worked as a senior scientist at the Max Planck Institute for Molecular Physiology, Dortmund. Since 2002, he holds the chair for Macromolecular Physics at the Department of Physics at the University of Osnabrueck (Germany). From 2005–2007 and from 2010–2011 he was dean of the Department of Physics at this university. In the period 2008-2010 he was member of the Senate of the University of Osnabrueck.

Daniel: Sure it's not always easy, but is any advanced career really easy and safe? So as long as it works, as long as there is curiosity and passion, why not go on? People should try to live a happy life and that can mean different ways for different people and it's good that this world is so diverse... It's certainly true that science is clearly not the easiest way to go, especially imagining to combine both work and family life one day, but many inspiring examples of people I know show that it's possible with good teamwork, and to me it totally appears worth pursuing for the chance to explore one's interests and curiosities and for the freedom to make choices and plans. Especially in the early stage of the career, for the first and second post-doc phase, these choices though seem to determine the chances and risks. So, having a wise and active mentor helps significantly! Following the current political discussion about possible developments of the general conditions for young researchers therefore gives some hope for the future and I think from the early researchers' point of view, tenure track is certainly a way to go for the academic institutions in the competition for the best future researchers.

Heinz-Juergen: Before I got the call of the chair of Macromolecular Physics at the University of Osnabrueck, I had to keep delicate balance between working as a scientist in successive fixed-term jobs at a university and taking responsibility and care of my family with two daughters. In the early 90s I felt like moving out of academia because there seemed to be no perspective for a safe position. However, I had great luck that my wife had a fixed job during this period. And the uncertain perspective was more than enough balanced by my enthusiasm for scientific work and my great pleasure to teach students, thus giving me confidence to pursue my scientific career.

Daniel, what are your expectations and plans for your further career? Do you want to stay in academia?

Daniel: For sure I would love to continue in academic research in the future, if possible! For the future I guess the combination of techniques will continue to be essential to address complex biophysical problems, and also the current development of techniques for in vivo spin labeling EPR is very interesting for me. It would be great to be able to study large membrane protein complexes in vivo in the future. The amounts of sample currently needed require careful planning, but I think several methods are already waiting to be applied to larger systems and I think it would be great for the whole EPR community to see such efforts turn out fruitfully.

Heinz-Juergen, are there specific expectations that you cherished as a young researcher that have come true? Or did your career take turns that you never anticipated at the start, but that have been fulfilling nevertheless? Is there an old scientific dream that you still want realize?

Heinz-Juergen: My dreams have come more than true: Every day I have the privilege to think about fascinating problems, work on the development of new experiments and eventually witness new discoveries. My goal now is to push the spin-labelling EPR method to make it applicable for the study of protein conformation, interaction and dynamics in the native environment, i.e., in the live cell.

How do you see the future of EPR and your role in this?

Daniel: The future of EPR? Hopefully bright, especially with all the fascinating and important developments currently going on that are culminated in the DFG priority program. I hope they can be continued as intensely. The same applies from my point of view for the COST actions in Europe, which are an important support for the young people. And about a role for me in the future of EPR, I can only say it would be a great pleasure ... ;)

Heinz-Juergen: I am fascinated by recent developments in EPR methodology, which include increased sensitivity, the application of very high frequencies and fields, new pulse schemes, and miniaturisation which renders an EPR spectrometer on a single chip possible. I am convinced that EPR has a great future in material and life sciences to study the structure and dynamics of matter. I see my role in enhancing the visibility of EPR

especially in the field of structural biology, where this technique is very well suited and often without competition for the analyses of structural heterogeneity of proteins and protein complexes on a length scale in the nm range and for characterization of their conformational dynamics. For that purpose I am always looking for interesting applications and I have been establishing a couple of very fruitful collaborations in this field.

Are there matters that you think the EPR community should pay more attention too?

Daniel: I'd like to say that the support for the young people in the field of EPR is great and important! We are grateful for that and I hope it will always be kept up to such an extent. I hope all people who wish can actually benefit from this support and exchange of experiences. Another idea would be to pay more attention to going to other conferences that focus on topics where EPR is a suitable technique to address the questions at hand, such as specialized meetings on certain classes of proteins or certain applications in nanotechnology. This could enhance the visibility of EPR spectroscopy outside the EPR community and allow for more applications of the techniques in the future.

Heinz-Juergen: I have always enjoyed the cordial atmosphere when I have met with my colleagues on EPR conferences. This is what the EPR community makes so special. I sincerely wish that this will continue in future so that the next generations of EPR scientists also profit from this friendly environment. Or to say it with the words of Klaus Möbius: "Science is best done with friends".

Oxygen Imaging with Pulse Spin Lattice Relaxation EPR: Animal Studies and the Path to Human Images

Howard Halpern

Quantitative Images of Living Animal Tissues.
Human images of structures beneath the skin of humans are a product of the last 119 years of science and technology development, beginning with Wilhelm Roentgen's discovery of the X-ray [1] and the film based images of dense bony tissue in late 1895 and early 1896. Since then a number of imaging modalities have been developed with sensitivity to normal and abnormal states of the soft tissues of animals and humans. The same time period has witnessed the development of a number of spectroscopies which reveal the structure of solid and liquid states of matter, the basis for processes evolving in these states [2]. But living samples are, most often, heterogeneous. Spectroscopic imaging has been a development of the past three decades where the spectroscopic process information could be localized within a subvolume in a living sample [3, 4]. In particular, spectroscopic images of the animal or human tissues are now possible.

Why Molecular Oxygen Imaging with Dissolved Spin Probes?
EPR of small molecular spin probes, molecules with molecular weight of from one to ten times that of a simple sugar molecule provide quantitative spectroscopic measures of crucial physiologic properties of the various pharmacologic compartments of the enormously complex living system. These include the concentration or partial pressure of molecular oxygen, the thiol-disulfide balance or redox state, the related local bioreduction capability, the acidity (pH), the temperature, the presence of specific oxygen centered free radicals, and many others [5]. We believe that the ability of an EPR image to specifically quantify molecular oxygen dissolved in the life supporting solvents of a living animal and eventually a human to be the most important of these. The absence of oxygen in the heart, brain, peripheral tissues and the cancers of human patients is responsible for the death of greater than half of our species, and the evaluation of treatments and pharmaceutical agents to ameliorate the hypoxic state promises to prolong the useful and involved lives of all of us [6].

Low Frequency for Human Application.
For eventual human application EPR imaging needs to be done under unusual conditions. For deep penetration into the body of a human with minimal nonresonant loss of signal amplitude, magnetization excitation frequencies of the order of hundreds of MHz, the excitation frequency of a modern MRI, appear necessary [7, 8]. However, unlike the MRI multi Tesla superconducting magnets, at 250 MHz, EPR images are obtained with a magnetic field of only 9 mT, obtained with simple copper air core magnets. For small animal experiments, used to rapidly and efficiently evaluate treatment and pharmaceutical effectiveness, higher L- band frequencies may be of advantage as they promise higher signals. For in vivo EPR images, relaxation rates of even the most slowly relaxing aqueous spin probes are five to six orders of magnitude faster than those of a water hydrogen nucleus, requiring fixed stepped gradients and modest power requirements.

Spin Probe Sensitivity to Molecular Oxygen (O_2 or pO_2).
Several techniques for oxygen measurement and imaging have been used since Backer and Budker's [9] seminal paper in the late 70s, which described the broadening of spectral lines by spin exchange with oxygen. The underlying mechanism has been thought to be Heisenberg Spin Exchange (HSE) [10].

Progress in Dissolved Spin Probe Oxymetry.
A spin probe is dissolved in the relevant solvent to report, through increase in its spin packet line width or, equivalently, its relaxation rates, the rate of interaction with dissolved oxygen. Line broadening has, until recently, been the principle means of dissolved spin probe oxymetry. Recent pulsed oxygen images using tri-aryl methyl radicals, specifically partially deuterated OX063 have taken advantage of that spin probe's $1/(6\,\mu s^{-1})$ hypoxic spin lattice relaxation rates, which enables pulse measurement and imaging at the frequencies referred to above [11]. Inversion recovery imaging not only increases signal to noise by nearly a factor of two relative to electron spin echo imaging, but has reduced the confounding sensitivity of spin probe to self relaxation or broadening by nearly an order of magnitude, making the spin probe measurement, to within one to two torr, an absolute measurement or image for animal application [12].

Application of EPR imaging to Cancer Biology.
A number of laboratories have developed spin probe based EPR oxygen measurement ▶

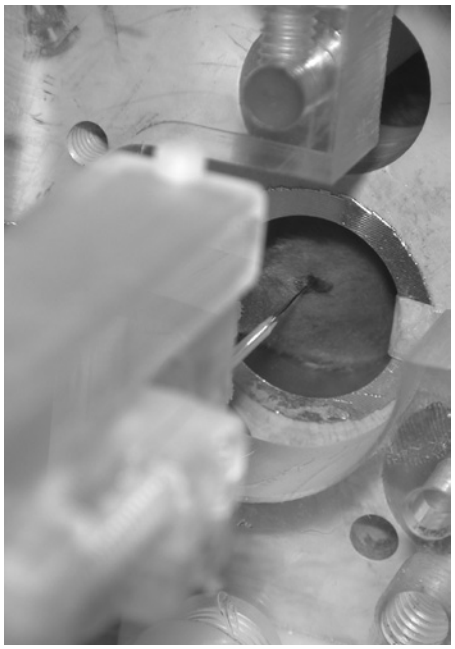


Fig. 1. Oxylite™ probe, mounted in the stereotactic frame, penetrating the FSa tumor in the hind leg of a C3H mouse immobilized in the EPR resonator. The Oxylite™ probe was advanced to the length of the tumor. Spatial coordinates of probe tip can be controlled within 1 millimeter accuracy. For scale, the diameter of the tumor bearing inductive element of the resonator (the hole through which the tumor bearing leg extends) is 16 mm. In an example of an x-ray of the Oxylite™ location in the tumor, it is seen curving away from the direction of the needle used to penetrate the animal skin [19].

techniques based on various spin probes and spectroscopies including spectral spatial continuous wave localized spectroscopies and images; and pulse based images [13–18]. We describe here work in our laboratory focusing on images of tumors in small animals – mice, although we have demonstrated both pulse and continuous wave EPR images from rats and rabbits. We will also describe, briefly our ideas for the progression of the technique of spin lattice relaxation (SLR) based imaging of oxygen tension in tumors to human subjects.

Validation of the Oxymetry in Animals. We have validated the oxygen images in animals in three sets of experiments. In the first, we compared the pO_2 from image voxels (volume elements) with point phosphorescence quenching measurements using an Oxylite fiberoptic probe [19]. The location of the end of the 200 μ diameter optical fiber was stereotactically located in the FSa mouse fibrosarcoma tumor and registered with the EPR oxygen image of the tumor, just after tumor pO_2 imaging, inside the imaging resonator/sample holder without disturbing the tumor location. The leg born tumor in our resonator with the stereotactically registered fiberoptic probe is shown in Fig. 1. Figure 2 shows examples of the pO_2 measured in the Oxylite tracks as the probe was withdrawn from the tumor as well as orthogonal slices of the pO_2 image surrounding the assigned position of the track in the tumor.

In the second validation, we compared pO_2 images of the tumor with quantitative enzyme-linked immunosorbent assay (ELISA) determinations of the concentration of the hypoxia induced protein Vascular Endothelial Growth Factor from stereotactically localized biopsies from FSa fibrosarcomas. The scatter plot in Fig. 3 shows typical biological scatter and high statistical significance from 12 biopsies showing about 3/4 of the variation in the protein concentration is associated with the mean pO_2 from the approximately 100 image voxels localized to the biopsy volume [20].

A key question concerning the pO_2 images that have been obtained with SLR pulsed technology is the relevance of its resolution, approximately 1 mm. This third validation asks whether or not these images can show, based on the fractions of tumor voxels with pO_2 less than a particular threshold, that they can predict outcomes of treatment of tumors of a given size to a given radiation dose, the 50% tumor control dose. Figure 4 shows the results of treating two different kinds of tumor, a syngeneic mouse mammary tumor, MCa4, and a syngeneic fibrosarcoma,

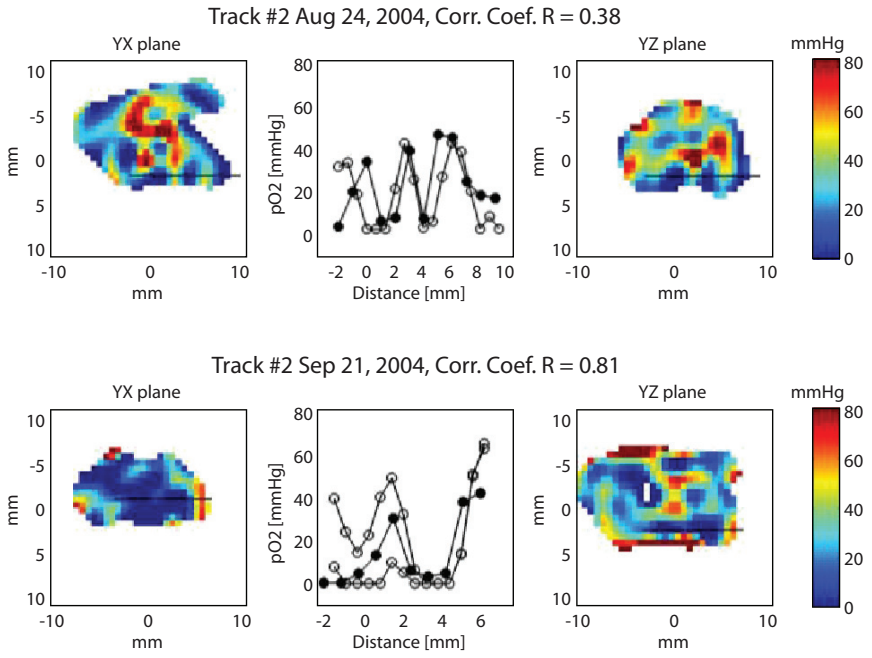


Fig. 2. Upper and lower panels show, on each side of the pO_2 plot, orthogonal planes from pO_2 images of a tumor bearing mouse leg both of which include the track of the Oxylite™ probe. Left: Tumor oxygenation sagittal slice with quantitative color maps. The color map provides a quantitative measure of the oxygen in each of the (0.66 mm)^3 voxels. Middle: plot of the oxygen values from the Oxylite™ track (filled circles) and the track (black line in the images) and pO_2 image (open circles). On the lower plot, image pO_2 values from adjacent image "tracks" bracket the Oxylite™ values. Right: Coronal slice shown in Fig. 3 with a quantitative color map. This is the perpendicular slice. The assumed location of the glass fiber probe within the pO_2 images as strictly along the axis of the imaging resonator was shown to be inexact from high resolution x-rays obtained from similarly prepared tumors. In the face of large pO_2 gradients in the tumor tissue as large as 50 torr/mm, seen in Fig.2, this makes the agreement between the Oxylite™ measurements and the pO_2 image all the more remarkable.

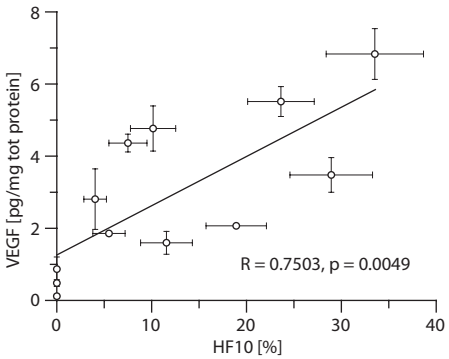


Fig. 3. Correlation between hypoxia and VEGF content. Fraction of voxels in the biopsy with pO_2 less than 10 torr, HF10 from the EPR oxygen image vs VEGF concentration in picograms per microgram of total protein.

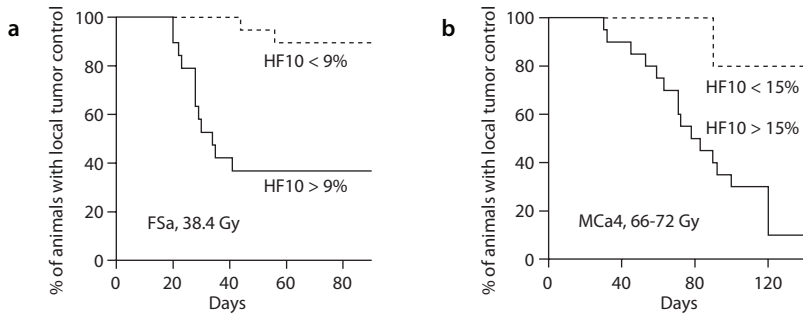


Fig. 4. Kaplan-Meier plot showing the percent of animals with local tumor control as a function of time after treatment with a single dose of X-rays. **a** FSA tumors were treated with 33.8 Gy. 90% of tumors (17 out of 19) with HF10 less than 10% were controlled at 90 days after treatment. In contrast, only 37% of tumors (7 out of 19) were controlled at 90 days when their HF10 was higher than 10%. Wilcoxon test shows that HF10 > 10% threshold was a significant predictor of tumor failure ($p = 0.0138$) for FSa tumors. **b** MCa4 tumors treated with a single dose in the range of 66-72 Gy. 80% of tumors (4 out of 5) with HF10 ≤ 15% were controlled at 120 days after treatment, whereas 15% (3 out of 20) with HF10 > 15% were controlled at 120 days. Wilcoxon test shows that HF10 > 15% threshold was a significant predictor of tumor failure ($p = 0.0193$).

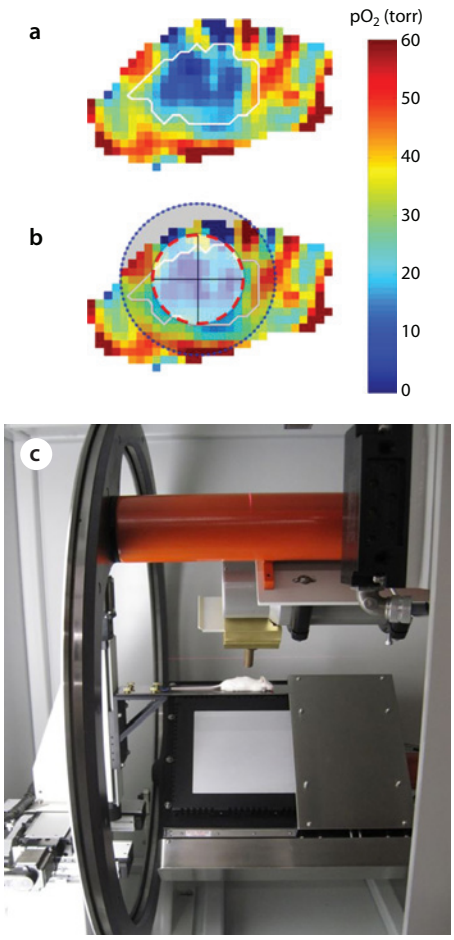


Fig. 5. EPR oxygen image of the leg tumor. **a** Oxygen map with tumor contour transferred from the registered MRI image. **b** Boost (red line) and anti-boost (shaded area) as determined by the boost planning software. **c** Precision X-ray XRAD225Cx image-guided biologic irradiator/CT imager.

FSa grown in C3H mice. Using a threshold of 9% of voxels with pO_2 less than 10 torr for FSa, tumors and 15% for MCa4 tumors, the probability for tumor control was significantly better for the hypoxic fraction less than the threshold than for the hypoxic fraction larger than the threshold. This validates the biomedical relevance of images with the 1 mm spatial resolution [21].

Tests of localizing radiation to regions of the tumor with high hypoxic fraction.
Given the success in identification of regions within a tumor whose voxels are hypoxic, does treating only these regions of tumors with extra 'boost' dose increase the tumor cure? Prior to human applications, this needs to be demonstrated in animal models. Figure 5a shows hypoxic region defined in a mouse MCa4 breast tumor, and a spherical volume for radiation boost treatment in addition to the TCD_{50} dose applied to the entire tumor. Figure 5b shows an XRAD225Cx system to precisely deliver the boost dose to the indicated region. A trial comparing the tumor control using such a boost with treatment to a well oxygenated shell of similar volume (an "anti-boost") is underway [22].

Proposed strategy for identifying resistant, hypoxic regions in tumors of human patients.
The initiating idea behind our EPR imaging effort that begun over 30 years ago, was the eventual imaging of oxygen in the tumors of human patients. The low field and frequency were chosen to make EPR O_2 images possible deep in the tumors of patients [23]. However the success of our O_2 images in small animals has required use to consider that initial human images must be done with two further constraints: 1) reduced spin probe injection amounts into human subjects to minimize the whole body concentration of the spin probe and 2) reduced tissue volume subjected to the radiofrequency magnetization excitation to allow for local increase in specific absorption rate (SAR) without threat to the well-being of a patient. To this end, we have 1) investigated the pO_2 distributions from mouse model tumors derived from locally (intratumoral and interarterial) injected spin probe and 2) designed a local bimodal excitation/detection system. Intratumoral injection into a relatively large 10 ml (~2.7 cm diameter) local human tumor reduces the whole body spin probe dose by four orders of magnitude in a 70 kg (~70,000 ml) human subject. The biomodal excitation/detection system shown in Fig. 6 physically decouples the excitation magnetic field from the detection coil, different from the more common phase decoupling used in, for example, birdcage resonator designs [24].

Summary.
We have brought the technology for the EPR imaging of oxygen to a point where quantitative images of oxygen in the tissues and tumors of living animals with 1–2 torr pO_2 resolution and 1 mm spatial resolution can be obtained from 10 minute oxygen images. We have validated the oxygen images and demonstrated that they predict cure from radiation therapy. We are in the process of validation the potential use of EPR oxygen images in guiding radiation to resistant portions of animal tumors. Finally, a path to initial human application is suggested, using low dose means of spin probe delivery and local power deposition and detection.

Acknowledgements: I would like to acknowledge useful suggestions by Dr. Boris Epel and Prof. Michael Bowman. This work took place at the University of Chicago as part of the Center for EPR Imaging In Vivo Physiology supported by the National Institute for Biomedical Imaging and Bioengineering grant EB002034 and also National Cancer Institute grant CA098575.

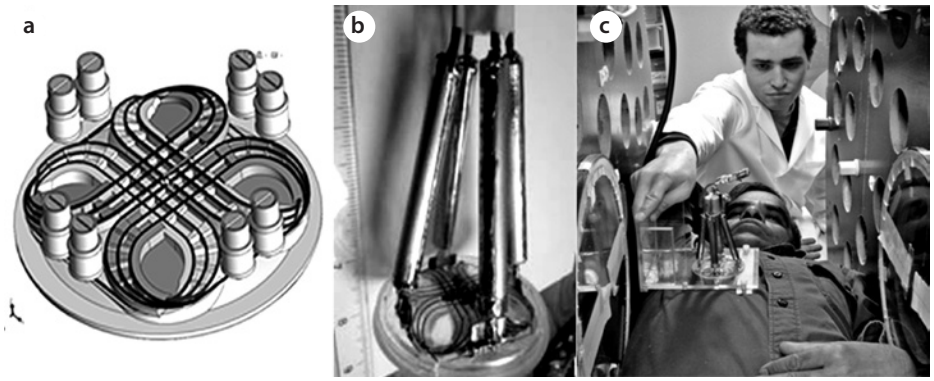


Fig. 6. a Design drawing of bimodal surface coil with geometric decoupling. **b** Bimodal surface coil as built. **c** Placement of surface coil.

1. Rontgen WC. On a new kind of rays. Science 1896;3:227–31.
2. Condon EU, Shortley GH. The Theory of Atomic Spectra. Cambridge: University Press 1935.
3. Lauterbur PC, Levin DN, Marr RB. Theory and simulation of NMR spectroscopic imaging and field plotting by projection reconstruction involving an intrinsic frequency dimension. J Magn Reson 1984;59:536–41.
4. Maltempo MM. Differentiation of spectral and spatial components in EPR imaging using 2-D image reconstruction algorithms. J Magn Reson 1986;69:156–61.
5. Swartz HM, Khan N, Buckey J, et al. Clinical applications of EPR: overview and perspectives. NMR Biomed 2004;17:335–51.
6. Longo DL, Fauci AS, Kasper DL, Hauser SL, Jameson JL, Loscalzo J, eds. Harrison's Principles of Internal Medicine. 18th edn. New York: McGraw Hill 2011.

7. Halpern HJ, Spencer DP, Vanpolen J, et al. Imaging radio-frequency electron-spin-resonance spectrometer with high-resolution and sensitivity for in vivo measurements. Rev Sci Instrum 1989;60:1040–50.
8. Bottomley PA, Andrew ER. RF magnetic field penetration, phase shift and power dissipation in biological tissue: implications for NMR imaging. Phys Med Biol 1978;23:630–43.
9. Backer JM, Budker VG, Eremenko SI, Molin YN. Detection of the kinetics of biochemical reactions with oxygen using exchange broadening in the ESR spectra of nitroxide radicals. Biochim Biophys Acta 1977;460:152–6.
10. Dirac PAM. Principles of Quantum Mechanics. 4th (paperback) edn. Oxford: Oxford University Press 1982.
11. Mailer C, Sundramoorthy SV, Pelizzari CA, Halpern HJ. Spin echo spectroscopic electron paramagnetic resonance imaging. Magn Reson Med 2006;55:904–12.
12. Epel B, Bowman MK, Mailer C, Halpern HJ. Absolute oxygen R imaging in vivo with pulse electron paramagnetic resonance. Magn Reson Med 2013; in press?
13. Khan N, Hou H, Hein P, et al. Black Magic and EPR Oxymetry: From Lab to Initial Clinical Trials. New York: Plenum Publishers 2005.
14. Salikhov I, Walczak T, Lesniewski P, et al. EPR spectrometer for clinical applications. Magn Reson Med 2005;54:1317–20.
15. Khan N, Williams BB, Hou H, Li H, Swartz HM. Repetitive tissue pO_2 measurements by electron paramagnetic resonance oximetry: current status and future potential for experimental and clinical studies. Antioxid Redox Signal 2007;9:1169–82.
16. Williams BB, Khan N, Zaki B, Hartford A, Ernstoff MS, Swartz HM. Clinical electron paramagnetic resonance (EPR) oximetry using India ink. Adv Exp Med Biol 2010;662:149–56.
17. Ellis SJ, Velayutham M, Velan SS, et al. EPR oxygen mapping (EPROM) of engineered cartilage grown in a hollow-fiber bioreactor. Magn Reson Med 2001;46:819–26.
18. Zweier JL, Chzhan M, Wang PH, Kuppusamy P. Spatial and spectral-spatial EPR imaging of free radicals and oxygen in the heart. Research on Chemical Intermediates 1996;22:615–24.
19. Elas M. Electron paramagnetic resonance oxygen images correlate spatially and quantitatively with oxylite oxygen measurements. Clinical Cancer Research 2006;12:4209–17.
20. Elas M, Hleihel D, Barth ED, et al. Where it's at really matters: in situ in vivo vascular endothelial growth factor spatially correlates with electron paramagnetic resonance pO_2 images in tumors of living mice. Mol Imaging Biol 2011;13:1107–13.
21. Elas M, Magwood JM, Butler B, et al. EPR oxygen images predict tumor control by a 50% tumor control radiation dose. Cancer Res 2013;73:5328–35.
22. Epel B, Redler G, Pelizzari C, Tormyshev VM, Halpern HJ. Approaching oxygen-guided intensity-modulated radiation therapy. Adv Exp Med Biol 2015; in press.
23. Halpern HJ, Yu C, Peric M, Barth E, Grdina DJ, Teicher BA. Oxymetry deep in tissues with low-frequency electron paramagnetic resonance. Proc Natl Acad Sci USA 1994;91:13047–51.
24. Epel B, Redler G, Tormyshev V, Halpern HJ. Towards human oxygen images with electron paramagnetic resonance imaging. Adv Exp Med Biol 2015; in press.

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Concepts of zero-field splitting Hamiltonian ($\tilde{H}_{ZFS}$), crystal-field Hamitonian (H_{CF}), effective and fictitious spins

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There is quite a bit of confusion in the literature in referring to the crystal-field (CF) Hamitonian, H_{CF}, as the zero-field splitting (ZFS) Hamiltonian, $\tilde{H}_{ZFS}$, and *vice-versa* as evidenced in a large number of published papers dealing with transition metal (TM) or rare-earth (RE) ions. To resolve this, it is important to clearly understand the concepts of effective spin and fictitious angular momentum. It is the purpose of this article to explain these in simple terms, so that EPR practitioners without a sophisticated theoretical background can use them correctly. Relevant references have been included. In this context, this article describes the pros of referring correctly to these terms and the cons of their incorrect usage. In order to facilitate the discussion, some basic concepts are reviewed first.

I. Phenomenon of continuous-wave EPR: Effective spin, fictitious spin, and fictitious angular momentum

EPR (Electron Paramagnetic Resonance) is also referred to as ESR (Electron Spin Resonance) and EMR (Electron Magnetic Resonance); the term EPR will be used hereafter. In continuous-wave (CW) EPR spectroscopy [1], a microwave radiation field is applied to the sample continuously, and the EPR signal is recorded while sweeping an external magnetic field over a chosen range, normally over 0.0–0.9 T (Tesla; 1 T = 10,000 Gauss) at X-band (~10 GHz). There are certain advantages of using X-band spectrometers. However, over the years, spectrometers at higher frequencies, over 1000 GHz, and lower, to several hundred MHz have also been developed. When the difference between a pair of energy levels matches the energy of the microwave quantum and the transition probability of interaction with the excitation field, normally applied perpendicular to the swept magnetic field, is non-zero, the microwave radiation is resonantly absorbed by the sample.

(i) Effective spin Hamiltonian and effective spin. In EPR the energy levels between which resonant absorption of microwave radiation takes place at room and lower temperatures become relevant. These energy levels of a paramagnetic ion, embedded in an environment consisting of charged ligands and paramagnetic ions, are referred to as the ground manifold. It includes the ground state and the energy levels that lie within a few cm^{-1} in energy of the ground state, which are accessible to EPR at microwave frequencies by a reasonable value of the external magnetic field. The ground manifold does not, in general, have the isotropic behavior possessed by a free spin. The Hamiltonian that describes the ground manifold is referred to as the effective spin Hamiltonian (SH) [2–6]. It contains quantum mechanical operators expressed in terms of the effective spin ($\tilde{S}$) as well as operators that depend on the nuclear spin (I), if there is a non-zero nuclear spin present. Furthermore, the form of SH must be consistent with the point- group symmetry of the environment.

(ii) Fictitious spin and fictitious angular momentum. The fictitious spin, denoted by S', is used to describe the particular subset of N distinct lowest-lying energy levels of a paramagnetic ion out of the total manifold of N_t energy levels ($N < N_t$). This subset of energy levels can be considered to be equivalent to a spin multiplet, to which a fictitious spin operator $\boldsymbol{S}'$ is ascribed, characterized by the spin quantum number S', and associated with its magnetic quantum number $M_{S'}$ ($-S' \le M_{S'} \le +S'$), so that $N = 2S' + 1$ [2–6]. It is thus apparently an angular momentum, but it does not have the transformation properties of a true angular momentum under rotation of coordinate axes, so it is really a fictitious angular momentum. On the other hand, the fictitious-spin operator, $\boldsymbol{S}'$, has been sometimes denoted incorrectly by the effective spin operator ($\tilde{\boldsymbol{S}}$) [4]. It is noted that the above definition implies that the fictitious spin, S', has, in fact, no direct relationship with the true electronic spin, S, or the effective spin, $\tilde{S}$, of the spin system of a paramagnetic ion being considered. This is because the natures of the spin operators $\boldsymbol{S}$, $\tilde{\boldsymbol{S}}$, and $\boldsymbol{S}'$ are quite different from each other. The simplest and most often encountered case of the fictitious spin S' is $S' = 1/2$, which may be employed for systems of any origin exhibiting two distinct lowest lying energy levels, which are well separated from the higher levels, e.g. Kramers doublets for odd-electron systems [1–3].

(iii) Effective spin versus true electronic spin. In order to avoid confusion, one should always use the terms effective spin ($\tilde{S}$) and the effective SH for transition ions with an orbitally non-degenerate ground state. On the other hand, for transition ions in crystals exhibiting an orbital singlet ground state represented by the true electronic spin S, the quantum number S is equal to the quantum number $\tilde{S}$ associated with the effective spin operator $\tilde{\boldsymbol{S}}$. Importantly, the main difference between the operators $\boldsymbol{S}$ and $\tilde{\boldsymbol{S}}$ is in their nature, which is determined by the respective distinct basis of states in which they act, i.e. $\{|S, M_S\rangle\}$ and $\{|\tilde{S}, \tilde{M}_S\rangle\}$, respectively. This difference applies also to the respective Hamiltonians (see below) used to describe the system in the two spaces. In spite of this fact, the two types of spins and the associated quantities are often inappropriately mixed up in the EPR literature.

II. Concept of crystal field

The interaction of the electrons of a paramagnetic ion embedded in a crystal with its surroundings can be described, in the first approximation, in terms of an electrostatic crystal field potential V_{CF}, i.e. the crystal field (CF) Hamiltonian, $H_{CF} = qV_{CF}$, where q is the charge on the ion. In order to estimate its effect, one has to first compare its magnitude, i.e. the energy level spacings of the ion when embedded in a crystal, relative to the energy spacings of the free ion. In the case of transition elements, these can be classified into three main categories according to their order of magnitude, as follows [4, 7–10].

(i) Weak CF. In this case, the distance between a spin-orbit multiplet (J, L, S) and the next one (J', L, S), where J and J' are the total angular momenta, is larger than the crystal-field energy. (Here J, J' are determined by the vector sum of $\boldsymbol{L}$, the orbital angular momentum, and $\boldsymbol{S}$, the spin angular momentum: $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$). The degeneracy $2J + 1$ of ▶

each multiplet is partially or wholly lifted. In a first approximation, one can neglect the admixture from neighboring multiplets, so that J remains approximately a good quantum number. It applies reasonably well to the rare-earth group, for which the spin-orbit coupling (SOC) is larger, and the crystal field is smaller than that in the iron group as a rule. The CFs are small for the rare-earth group [4] due to the ligand ions being pushed further away by the extended 5s, 5p orbitals, rather than the 4f electrons being shielded by the 5s and 5p electrons of the external closed shells, as commonly believed.

(ii) Intermediate CF. In this case, J is not at all a good quantum number, and the multiplet structure disappears. Application of perturbation theory requires that the effect of H_{CF} on an (L, S) term should be considered first, and then one should calculate the effect of the SOC on wave functions and the energy levels as modified by the CF. The effect of admixtures from neighboring terms (L', S') may be neglected in the first approximation when calculating the splitting of a given (L, S) term. (N.B.: S' here is not the fictitious spin but rather the 'S-value' for the neighboring term.) Thus, L, and to a better approximation S, remain good quantum numbers. However, in more accurate calculations these admixtures should be taken into account. This situation applies to many compounds of the iron-group ions. Often, the CF potential can be split into terms of decreasing symmetry V_{CF1}, V_{CF2}, etc., out of which only the first term is much larger than the SOC constant, λ, which makes the calculation difficult. In that case, one first considers the effect of V_{CF1}, followed by taking into account simultaneously the terms in λ and V_{CF2} as perturbations, and so on.

(iii) Strong CF. In this case, the CF energy is larger than the electrostatic repulsion energy responsible for the LS-coupling. Then the term structure disappears, and L is not even approximately a good quantum number. One then considers how each one-electron orbit is modified by the CF and how the degeneracy of individual electron levels is lifted. A new configuration of minimum energy is then built up by placing the various electrons in the new orbitals, referred to as "crystal-field configuration". The electron-electron interaction is now treated as a perturbation, thereby partially lifting the degeneracy of the crystal-field configuration. New levels are thus introduced, called analogously "CF terms" with new good quantum numbers, which replace the total orbital angular momentum quantum number L. This situation is applicable mainly to the 4d (palladium)- and 5d (platinum)-group ions, and also to certain complexes of the 3d (iron)-group ions. It is noted that the strong CF case is generally associated with covalent bonding, for which it is inadequate to use the wave functions strictly localized on the ion to describe the magnetic behavior of the ion, although the main features of the magnetic properties of the ion can still be described within the framework of the CF theory. This is because many of these properties are determined from the symmetry of the surrounding ligands without considering their specific interactions with the paramagnetic ion.

III. Total Hamiltonians

For the iron-group and rare-earth ions, which are the ones of interest here, the total Hamiltonians are described as follows.

(i) Iron-group ions ($3d^n$ electrons) in the lowest-lying orbital singlet states. These ions sense the CF directly without being shielded by any extra shell of electrons, the total physical Hamiltonian consists of the following terms [2–9]:

$$H = H_0 + V, \text{ where}$$
$$H_0 = H_{FI} + H_{CF},$$
$$V = H_{SO} + H_{SS} + H_{Ze}. \qquad (1)$$

In Eq. (1), the subscripts define the various terms: FI (free ion) – the electrostatic interactions between the electrons in the free paramagnetic ion being considered, CF – the crystal (or ligand) field, SO – the spin-orbit, SS – the electronic spin-spin, and Ze – the Zeeman electronic interaction. The separation of H, in Eq. (1), into the zero-order Hamiltonian, H_0, and perturbation, V, enables one to carry out the required perturbation calculations as desired. The explicit form of the crystal-field Hamiltonian, H_{CF}, which parameterizes the effect of the electric field due to surrounding ligands acting on the paramagnetic ion being considered, depends on the local site symmetry characterized by the point-symmetry group G [4, 7–9]. Most EPR studies on iron-group ions involve only the manifold corresponding to the lowest orbital singlet, i.e. the set of $2S + 1$ spin states $\{|\Gamma_\alpha\rangle|S, M_S\rangle\}$ belonging to the ground state $^{2S+1}L(3d^n)$ multiplet split by H_{CF}. Here the orbital part, $|\Gamma_\alpha\rangle$, transforms according to the irreducible representation Γ_α of the group G of H and $|S, M_S\rangle$ denotes the $2S + 1$ spin states of the (true) total electronic spin operator of the ion, S, characterized by its electronic magnetic quantum number, M_S. The eigenvalues of H in Eq. (1) within the ground orbital singlet state, $\{|\Gamma_\alpha\rangle|S, M_S\rangle\}$, excluding H_{Ze}, define the physical zero-field splitting (ZFS), which is also referred to as the fine-structure splitting. As described below, the microscopic spin Hamiltonian (MSH) theory [2–4] enables derivation of the relations between the physical ZFS energies and the parameters of the effective SH defined in Section I.

(ii) Rare-earth ions ($4f^n$ electrons). For these electrons the basis of states and the explicit form of the contributions included in Eq. (1) differ from those for the iron-group ($3d^n$) ions discussed above. Nevertheless, for the S-state $4f^7$ (Gd^{3+}, Eu^{2+}) ions, the final result of derivation of the ZFS, i.e. fine structure, is essentially the same as described in (i) above, since they exhibit an orbital singlet ground state. For non-S-state ions, the ground states involve wavefunctions of total J and their description requires different procedures [4, 9].

IV. Crystal-field Hamiltonian (H_{CF}) in the ground-multiplet approximation

(i) General form of H_{CF}. For the $L(d^N)$-multiplet of the TM ions or the $J(f^N)$-multiplet of the RE ions the crystal-field (CF) Hamiltonian, H_{CF}, can be expressed as

$$H_{CF} \propto \chi_{lm}(\boldsymbol{T}), \qquad (2)$$

where $\boldsymbol{T}$ is the orbital angular momentum $\boldsymbol{L}$ $(=\sum_i \boldsymbol{l}_i$, where $\boldsymbol{l}_i$ is the orbital angular momentum of the single ith electron) for the $L(d^N)$-multiplet of the TM ions, or the total angular momentum $\boldsymbol{J}$ $(=\sum_i \boldsymbol{j}_i, \boldsymbol{j}_i = \boldsymbol{l}_i + \boldsymbol{s}_i$, where $\boldsymbol{s}_i$ is the spin angular momentum of the ith electron) for the $J(f^N)$-multiplet of the RE ions, see e.g. [9, 11]. Here, the operators $\chi_{lm}(\boldsymbol{T})$ may transform either as the spherical harmonics Y_{lm}, i.e. the spherical-tensor operators (STO), or their combinations, known as the tesseral-harmonics, i.e. the tesseral-tensor operators (TTO) [2, 3]; see Appendix I.

(ii) Explicit forms of H_{CF}. H_{CF} is expressed in terms of the extended spin operators (ESO), O_k^q ($\boldsymbol{J}$ or $\boldsymbol{L}$) [12, 13], within a given $L(d^N)$-multiplet or $J(f^N)$-multiplet or of a transition ion, see, e.g. [14] and references therein, as:

$$H_{CF}(\text{ESO}) = \sum_{k,q} B_k^q O_k^q \ (J \text{ or } L), \qquad (3)$$

where $B_k^q = A_k^q \langle r^k \rangle \theta_k = C_k^q \theta_k$, the crystal-field parameters (CFPs) B_k^q (A_k^q, C_k^q) are all real, and the so-called multiplicative Stevens factors $\theta_k = \alpha$, β, and γ for the rank $k = 2$, 4, and 6, respectively, have been tabulated, e.g. in [1, 4]. The summation in Eq. (3) includes all q components governed by the local site symmetry and group theory [1, 4]. The limit to the ranks k ($k \le 2l$) for the operators acting ▶

within the ground multiplet and the associated CFPs arises from the orbital quantum number (l) of a given configuration, namely, $L(d^N)$: $l = 2$ yields $k = 2$ and 4 and $J(f^N)$: $l = 3$ yields $k = 2$, 4, and 6. Usually, only the even k terms are considered. The implicit dependence of the ESOs, O_k^q, in H_{CF} on $\boldsymbol{J}$ or $\boldsymbol{L}$ should always be kept in mind [14].

V. Mapping the total physical Hamiltonian into the effective spin Hamiltonian

Introduction of the effective spin $\tilde{\boldsymbol{S}}$. The transition from the total physical Hamiltonian, $H_0 + V$, as given in Eq. (1), to the effective SH, $\tilde{H}_{eff}$, involves a mapping, which can be represented in general form as [2, 3]:

$$H_0 + V \rightarrow \tilde{H}_{eff} \equiv \tilde{H}_{SH} \equiv \tilde{H}_{ZFS} + \tilde{H}_{Ze} = \sum A_{lm}\,\chi_{lm}(\tilde{\boldsymbol{S}}) + \mu_B\,\boldsymbol{B}\cdot\boldsymbol{g}\cdot\tilde{\boldsymbol{S}}, \quad (4)$$

where A_{lm} denotes the ZFS parameters associated with a given generic type of the tensor operators, and χ_{lm}, which are operators built up from the components of the effective spin operator $\tilde{\boldsymbol{S}}$, of even rank l ($l = 2$, 4, and 6 for $\tilde{S} \le 7/2$, the commonly occurring cases, such that for the effective spin $\tilde{S}$, $l \le 2\tilde{S}$, where the projections for a given l are labeled $-l \le m \le l$ according to their transformations under rotations, and the relevant values of m depend on the site symmetry). In Eq. (4), and hereafter, a tilde over H represents the fact that H is a function of the effective spin, $\tilde{S}$.

Effective spin-Hamiltonian approaches. Two alternative approaches exist to obtain an effective SH: the 'derivational' microscopic SH (MSH) approach and the 'constructional' generalized SH (GSH) approach [2, 3].

(i) MSH approach. Here $\tilde{H}_{eff}$ is derived from $H_{phys} \equiv H_{FI} + H_{CF}$ for a given 'spin' system for a selected subspace of the totality of states for a paramagnetic species. The first MSH derivation, based on perturbation theory, is due to Pryce [15], who derived a Hamiltonian, which later became known as the spin Hamiltonian [2, 3]. This approach enables derivation of analytical expressions. Another major approach used in the MSH theory is based on full diagonalization of H_{phys} using a projection method, which ordinarily requires significant computer programming. Here the energy levels, E_a, of the physical Hamiltonian, obtainable by full diagonalization of H_{phys}, are projected onto the energy levels, ε_b, of a suitably parameterized spin Hamiltonian $\tilde{H}_{ZFS}$, calculated in a parametric way within its own basis of effective spin states $\{|\tilde{S}, \tilde{M}_S\rangle\}$. The MSH approach expresses the experimental parameters, measured by EPR and related techniques, in terms of more fundamental microscopic parameters, obtainable from other independent spectroscopic techniques.

(ii) GSH approach. The GSH is based on the method of invariants [2, 3]. Each term is a rotationally invariant (scalar) combination of the polynomials formed from the relevant spin operators, which are the effective spin $\tilde{S}$ and the nuclear spin, I, as well as the external quantities B (magnetic field) and/or E (electric field). The operator polynomials describing GSH [2, 3] can be expressed in terms of any of the tensor-operators $\{\chi_{lm}\}$, described in Appendix I below, in the general form:

$$H_{spin} = H_{ZFS} + (H_{Ze} + H_{Hoze}) + (H_{HF} + H_{HOHF}) + (H_{Zn} + H_{HOZn}), \quad (5)$$

where

$$H_{ZFS} = \sum A_{lm}\,\chi_{lm}(\tilde{S}),$$

$$(H_{Ze} + H_{Hoze}) = \sum_{l,m}\sum_{l',m'} P_{Ze}(l,m;l'm')\chi_{lm}(\tilde{S})\chi_{l'm'}(B),$$

$$(H_{HF} + H_{HOHF}) = \sum_{l,m}\sum_{l',m'} A(l,m;l'm')\chi_{lm}(I)\chi_{l'm'}(\tilde{S}),$$

$$(H_{Zn} + H_{HOze}) = \sum_{l,m}\sum_{l',m'} R_{Zn}(l,m;l'm')\chi_{lm}(I)\chi_{l'm'}(B).$$

In Eq. (5), the first single-tensor term represents the ZFS part of GSH, while the double-tensor combinations are described as follows: (i) $P_{Ze}(lm, l'm')\chi_{lm}(\tilde{S})\chi_{l'm'}(B)$ with $l = l' = 1$ represent the linear Zeeman electronic (Ze) terms, whereas those with $l > 1$ and/or $l' > 1$ represent the higher-order Zeeman electronic (HOZe) terms, which are not included in the 'conventional' SH given by Eq. (4); (ii) $A_{HF}(lm, l'm')\chi_{lm}(I)\chi_{l'm'}(\tilde{S})$ with $l = l' = 1$ represent the linear hyperfine (HF) terms $\tilde{S}$.A.I, whereas those with $l > 1$ and/or $l' > 1$ represent the higher-order hyperfine (HOHF) terms; and (iii) $R_{Zn}(lm, l'm')\chi_{lm}(I)\chi_{l'm'}(B)$ with $l = l' = 1$ represent the linear Zeeman nuclear (Zn) terms, whereas those with $l > 1$ and/or $l' > 1$ represent the higher-order Zn (HOZn) terms [2, 3]. Recently, higher-order field-dependent terms (HOFD) in SHs for transition ions and their implications for high-magnetic field and high-frequency EPR measurements have been discussed in [16].

VI. Explicit forms of spin Hamiltonians

A spin Hamiltonian (SH) includes two major terms: $\tilde{H}_{ZFS}$ and $\tilde{H}_{Ze}$, and is described either by the simple 'conventional' form, excluding 4th and higher order operators, as follows:

$$\tilde{H}_{spin} = \tilde{H}_{ZFS} + \tilde{H}_{Ze} = \tilde{S}.D.\tilde{S} + \mu_B B.g.\tilde{S} \quad (6)$$

or, the SH form expressed using the extended Stevens (ES) operators (ESO), O_k^q, [1, 12, 13], including up to 6th order operators, as follows:

$$\tilde{H}_{ZFS} = \sum_{k=2,4,6}\sum_{q=-k}^{k} B_k^q O_k^q(\tilde{S}_x, \tilde{S}_y, \tilde{S}_z) = \sum_{k=2,4,6}\sum_{q=-k}^{k} f_k b_k^q O_k^q. \quad (7)$$

Here, $\tilde{H}_{ZFS} \propto \chi_{lm}(\boldsymbol{X})$, where $\boldsymbol{X}$ may be either the effective spin, $\tilde{\boldsymbol{S}}$, or the fictitious 'spin', $\boldsymbol{S}'$ – see Appendix I. The scaling factors in Eq. (7) are defined as:

$$f_k = 1/3,\ 1/60,\ \text{and}\ 1/1260 \ \text{for}\ k = 2,\ 4,\ \text{and}\ 6, \quad (8)$$

respectively. These factors are missing in some publications as pointed out in [2, 3, 17].

It is first noted that $\tilde{H}_{ZFS} \propto \chi_{lm}(\boldsymbol{X})$ in Eq. (7), where $\boldsymbol{X} = \tilde{\boldsymbol{S}}$ (effective spin) or $\boldsymbol{S}'$ (fictitious spin), whereas $H_{CF} \propto \chi_{lm}(\boldsymbol{T})$, where $\boldsymbol{T} = \boldsymbol{L}$ or $\boldsymbol{J}$ in Eq. (3). The Hamiltonian $\tilde{H}_{ZFS}$ is a function of the effective spin, $\tilde{S}$ or fictitious 'spin', S', whereas H_{CF} is defined within a given ground $L(d^N)$-multiplet of the TM ions or $J(f^N)$-multiplet of the RE ions. It is noted that $\boldsymbol{X}$ and $\boldsymbol{T}$ are physically different operators. However, the mathematical forms of $\tilde{H}_{ZFS}$ and H_{CF}, expressed in terms of the operators $\boldsymbol{X}$ and $\boldsymbol{T}$, respectively, are the same for a given point-symmetry group, G, under which they are invariant, except for the additional presence of odd-order ($l = 1$, 3, 5) terms in H_{CF} only when G is characterized by a non-centrosymmetric point-group symmetry, wherein spatial inversion is not allowed. The non-zero matrix elements of odd-order CF terms exist only between states belonging to different configurations [8, 9]. In practice, the odd-order CF terms have rarely been used. The two Hamiltonians are expressed in terms of tensor operators, which are similar only in terms of their transformation properties, but have different physical origin, as manifested in their dependence on the relevant angular momentum operators, $\boldsymbol{X} = \tilde{\boldsymbol{S}}$ or $\boldsymbol{S}'$, in $\tilde{H}_{ZFS} \propto \chi_{lm}(\boldsymbol{X})$, or $\boldsymbol{T} = \boldsymbol{L}$ or $\boldsymbol{J}$ in $H_{CF} \propto \chi_{lm}(\boldsymbol{T})$. However, if this dependence on the specific angular momentum operators is not ▶

explicitly indicated in terms of the operators $\boldsymbol{X}$ or $\boldsymbol{T}$, the two Hamiltonians, expressed symbolically only in terms of the ESO as $O_l^m = \chi_{lm}$, would appear identical in form.

VII. Confusion between H_{CF} and $\tilde{H}_{ZFS}$

Confusion between $\tilde{H}_{ZFS}$ and H_{CF} is common in the literature, and can occur by referring incorrectly to (i) the true ZFS quantities as CF quantities, see [14] and references therein, or (ii) the converse, see [18] and references therein. Confusion (i) includes the following aspects (a) referring to parameters or Hamiltonians, which are by their physical context, in fact, 'ZFS parameters' or 'ZFS spin-Hamiltonians', as 'CF parameters' or 'CF Hamiltonians'; (b) using incorrectly the nomenclature 'strong, intermediate and weak CF schemes', described in Section II for H_{ZFS}, which is well defined only for H_{CF} (see, e.g. [8–10, 19]) and not for $\tilde{H}_{ZFS}$, in context with perturbation calculations involving $\tilde{H}_{ZFS}$ and $\tilde{H}_{Ze}$; (c) using the notation valid for the ZFS parameters for the parameters which are, in fact, CF parameters; (d) applying incorrectly the point-charge model or related models to $\tilde{H}_{ZFS}$ to calculate, e.g. B_k^q or b_k^q in Eq. (7), which are applicable only to CF parameters, to derive relations between the structural parameters, e.g. the ligand-paramagnetic ion distances.

Aspects (a) and (b) above lead to a misunderstanding of the different physical natures of $\tilde{H}_{ZFS}$ in Eqs. (4)–(7) and H_{CF} in Eqs. (1)–(3), causing confusion between the two. Fortunately, this involves only a mistake in the description, as exemplified by the phrase 'the crystal field Hamiltonian in the spin Hamiltonian notation' used in the context of H_{CF} [20], or 'the crystal-field spin Hamiltonian' used to describe $\tilde{H}_{ZFS}$ [21–23]. Aspects (c) and (d) are quite serious since they may lead to erroneous numerical results [2, 14, 18]. As an example of the confusion in question, i.e. the factual usage of the relations for invalid direct conversions between the CF parameters and the ZFS ones, one can quote from [24]: '... the following relations between the conventional ZFS parameters D and E and CF parameters B_k^q: $D = 3B_2^0$, $E = B_2^2$ ...' As discussed in [25], such relations are valid only for intra-conversion of ZFS parameters, as a consequence their usage in [24] leads to errors of substance. Note that the readers may also benefit from the relevant discussion of CF Hamiltonian, as distinct from SH, which can be found, in, e.g. the books [1, 4–6, 9–11, 26, 27].

The interrelated terms used at the transition between the physical (crystal field, or equivalently ligand field (LF)) Hamiltonians and the effective (spin) Hamiltonians, denoted as CF (LF) ↔ SH (ZFS) transition, have recently been thoroughly discussed [28]. A visualization of this transition between the physical and effective energy levels, as well as the pertinent terms used, is depicted in Fig. 1 [29].

The explanations of symbols used in Fig. 1, adapted from [29], are as follows.

***H* – physical full electronic Hamiltonian:** HF – Hartree-Fock, CSCF – central self-consistent field, f.i. – free ion, es – the electrostatic interactions between the electrons in a free-ion, CF – the crystal (or ligand) field, SO – the spin-orbit, SS – the electronic spin-spin; H'_{es} – residual electronic repulsion, H_{CF} – CF Hamiltonian with CFPs B_{kq} in Wybourne notation [2, 11].

Ψ – respective wave functions: (A) single-electron wave functions consisting of the radial

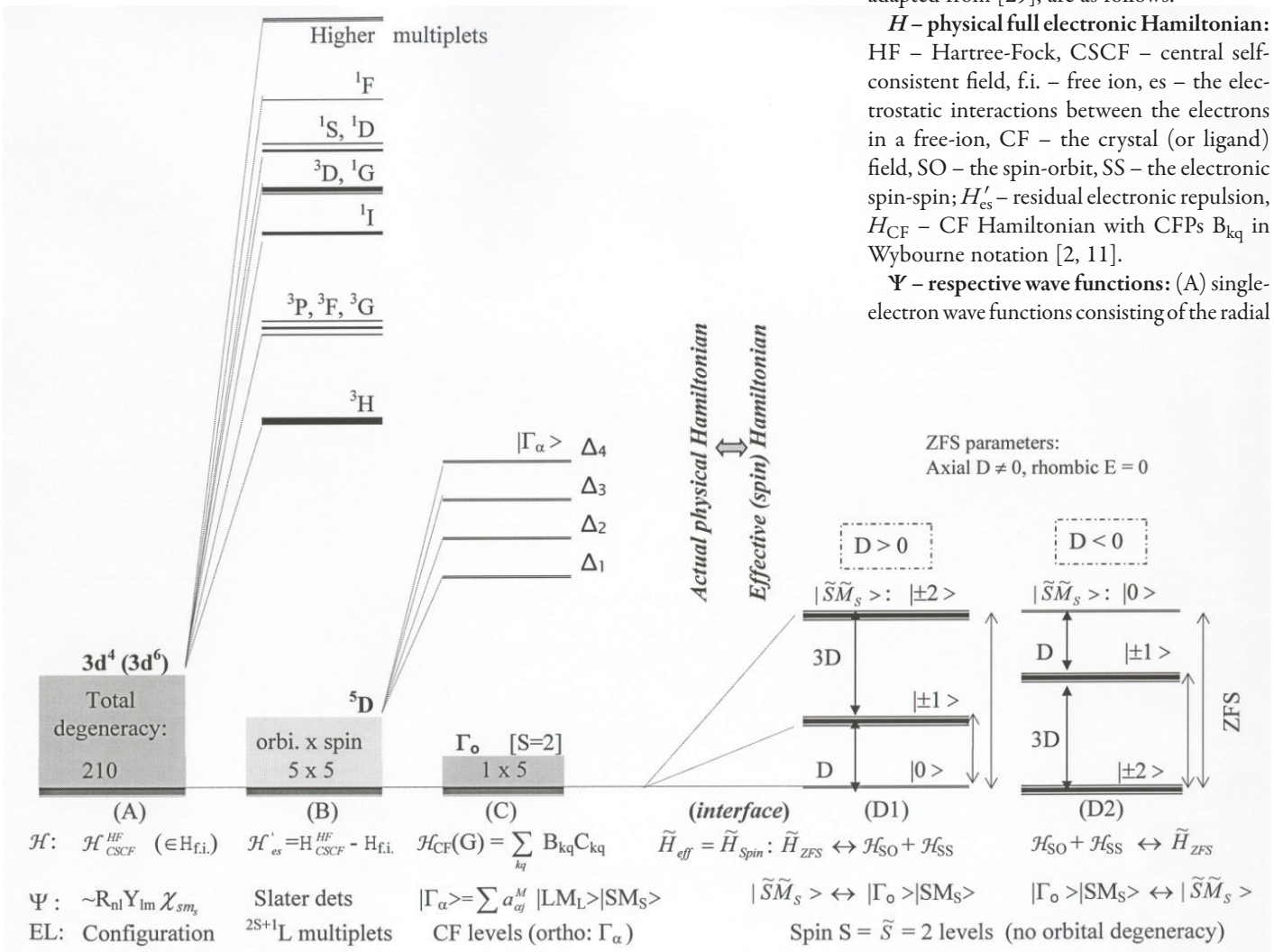


Fig. 1. Schematic representation of the physical energy levels (first three schemes) and the effective ones (last two schemes), which illustrates the CF (LF) ↔ SH (ZFS) transition for the selected 3d^4 (3d^6) ions in crystals.

part (R_{nl}), the spherical harmonics (Y_{lm}), and the spin part (χ_{sm_s}); (B) Slater determinants (dets) built-up from the single-electron wave functions; (C) the wave functions of the total orbital angular momentum $\boldsymbol{L}$ and the total spin momentum $\boldsymbol{S}$ transforming according to a given irreducible representation Γ_α of a given point-symmetry group G.

Appendix I. Tensor-operators

Tensor operators are collectively denoted by the generic symbols $\{\chi_{lm}\}$ for operators and A_{lm} for the associated parameters in Eqs. (4) and (5). These forms apply to almost all major tensor-operator notations [2, 3]. These tensor-operator notations offer the following advantages: (i) separate conventional spin-operator combination are replaced by one-operator symbol, χ_{lm}, with specified l and m values, and (ii) their transformation properties are well defined and tabulated [12, 13]. The most representative symbols originally introduced for the operators and their coefficients, which define the ZFS (or CF) parameters, are described below [2].

(i) Tesseral-tensor operators (TTO). Historically conventional SH notations were initially expressed in the Cartesian coordinates as in the case of initial (very early) forms of $H_{CF} \propto (x, y, z)$. Later, the tesseral harmonics (Z^c_{kq}, Z^s_{kq}) and the spherical ($Y_{kq}(\theta, \Phi)$) ones [2] were introduced in the CF theory [8–10]. These early notations for H_{CF} led to the operator-equivalent technique [4, 19, 26], due to Stevens [27, 30]. This involved replacing (x, y, z) in H_{CF} by the corresponding orbital angular momentum operators (L_x, L_y, L_z), then symmetrizing them, e.g. replacing x^2y^2 (= y^2x^2) by $(L_x^2 L_y^2 + L_y^2 L_x^2)/2$. Applying this technique to $H_{CF} \propto (x, y, z)$ and employing the real tesseral harmonics $Z^c_{kq} \propto (x, y, z)$, Stevens [30] introduced an incomplete set of the tesseral-tensor operators (TTO), which were the "operator equivalents" of only the real tesseral harmonics. Specifically, in this way the operators, $O^q_k(L)$ with the components q limited to $k \geq q \geq 0$ were proposed. They were later referred to as Stevens operators [4].

Classification of tesseral-tensor operators. The various commonly used tesseral-harmonics operator equivalents, i.e. tesseral-tensor operators (TTO), may be classified into, see [2] and references therein:

(a) The usual Stevens operators, where the q values are limited only to the positive integers and zero ($k \geq q \geq 0$); with the coefficients B^q_k (or the 'rescaled' b^q_k).

b) The extended Stevens (ES) operators, O^q_k, where the q values include also the negative integers, i.e. here $-k \leq q \leq +k$; with the coefficients B^q_k (or the 'rescaled' b^q_k).

c) The normalized Stevens (NS) operators, O^m_n, which are, in fact ES operators, each multiplied by certain normalizing factor with the coefficients B^m_n.

d) The normalized combinations of spherical tensor (NCST) operators, T_{lm}, which are simply related to the NS operators O^m_n, and at the same time are linear combinations of the STO; with the coefficients B_{lm}, described below.

(ii) Spherical-tensor operators (STO). Any operators $\chi_{lm}(\boldsymbol{X}$ or $\boldsymbol{T})$ that transform as the spherical harmonics Y_{lm} belong to the category of the spherical-tensor operators (STO). The operators of this category play only a rather secondary role in EPR studies compared to the dominant extended Stevens (ES) operators (ESO), O^q_k [1–3, 12, 13, 17], described above.

References

1. Misra S.K. (ed), 2011, Multifrequency Electron Paramagnetic Resonance: Theory and Applications (Wiley-VCH: Weinheim); Erratum, Misra S.K., Rudowicz C., http://www.wiley-vch.de/publish/dt/books/ISBN3-527-40779-0/
2. Rudowicz C., 1987, Magn. Reson. Rev. 13, 1; Erratum, ibidem, 1988, 13, 335.
3. Rudowicz C., Misra S.K., 2001, Appl. Spectrosc. Rev. 36, 11.
4. Abragam A., Bleaney B., 1970 & 1986 Electron Paramagnetic Resonance of Transition Ions (Oxford: Clarendon Press; New York: Dover).
5. Spaeth J.-M., Niklas J.R., Bartram R.H., 1992, Structural Analysis of Point Defects in Solids. Springer Series in Solid-State Sciences Vol. 43, (Berlin: Springer).
6. Atherton N.M., 1993, Principles of Electron Spin Resonance (Oxford: Ellis Horwood).
7. Figgis B.N., Hitchman M.A., 2000, Ligand Field Theory and its Applications (Wiley-VCH: New York).
8. Griffith J.S., 1961, The Theory of Transition-Metal Ions (Cambridge: Cambridge University Press).
9. Altshuler S., Kozyrev B.M., 1974, Electron Paramagnetic Resonance in Compounds of Transition Elements (New York: Wiley).
10. Sugano S., Tanabe Y., Kamimura H., 1970, Multiplets of Transition-Metal Ions in Crystals, p.10 (New York: Academic Press).
11. Liu G., Jacquier B. (eds.), 2005, Spectroscopic Properties of Rare Earths in Optical Materials (Tsinghua University Press and Springer: Berlin).
12. Rudowicz C., 1985, J. Phys. C18, 1415; Erratum, ibidem, C18, 3837.
13. Rudowicz C., Chung C.Y., 2004, J. Phys.: Cond. Matter. 16, 5825.
14. Rudowicz C., Karbowiak M., 2014, Physica B 451, 134.
15. Pryce M.H.L., 1950, Proc. Phys. Soc. A63, 25.
16. Rudowicz C., 2013, Nukleonika, 58, 341.
17. Rudowicz C., 2000, J. Phys.: Cond. Matter. 12, L417.
18. Rudowicz C., Karbowiak M., 2015, Physica B 456, 330.
19. Pilbrow J.R., 1990, Transition-Ion Electron Paramagnetic Resonance (Oxford: Clarendon Press).
20. Hüfner S., 1978, Optical Spectra of Transparent Rare Earth Compounds (New York: Academic Press).
21. Beijerinck H.C.W., Willemsen B., 1970, Physica 47, 515.
22. Bhargava S.C., Kundsen J.E., Mörup S., 1979, J. Phys. C12, 2879.
23. Roelfsema K.E., den Hartog H.W., 1976, Phys. Rev. B13, 2723.
24. Pandey S., Kripal R., 2013, Acta Phys. Polonica A123, 101.
25. Rudowicz C., Karbowiak M., 2014, Acta Phys. Polonica 125, 1215.
26. Mabbs F.E., Collison D., 1992, Electron Paramagnetic Resonance of d Transition-Metal Compounds. (Amsterdam: Elsevier).
27. Stevens K.W.H., 1997, Magnetic Ions in Crystals (Princeton: Princeton Univ. Press).
28. Rudowicz C., Karbowiak M., "Disentangling intricate web of interrelated notions at the interface between the physical crystal field Hamiltonians and the effective spin Hamiltonians", Coordination Chemistry Reviews, accepted (2014).
29. Rudowicz C., Sung H.W.F., 2001, Physica B 300, 1.
30. Stevens K.W.H., 1952, Proc. Phys. Soc. 65, 209.

56th Annual Rocky Mountain Conference on Analytical Chemistry: 37th EPR Symposium

Copper Mountain, Colorado, USA, July 13–17, 2014

Left to right: Meghan Kohne, Claire Motion, David Waters, Hitoshi Ohta, and IES Poster Awardees Noah Horwitz, Zhelin Yu and Jackie Esquiaqui.

The 2014 EPR Symposium kicked off at Copper Mountain, Colorado, on the day of the 2014 FIFA World Cup Final. Participants in both the EPR and Solid State NMR Symposia watched together at the Incline Bar and Grill, at the foot of the Copper Mountain ski resort, as Germany and Argentina battled on the soccer pitch in Brazil. Given the high level of German participation at the Conference, the conference mood was certainly buoyed by the German victory.

The scientific program began on Monday morning, July 14, and was packed with 54 talks and 42 posters over three days, with talks on topics ranging from nanomagnets and organic solar cells to protein dynamics and in-vivo EPR oxymetry. EPR Symposium sessions were chaired by Steve Lyon (spin devices in inorganic and organic materials), John McCracken (Biological macromolecules), Fraser MacMillan (Functional dynamics of macromolecular complexes), Christoph Boehme (Methods, including high-field/high frequency EPR) and Dane McCamey (Materials – quantum information to nanomagnetism). Taking advantage of the co-location with the SSNMR Symposium, a packed joint session addressed mechanisms and methods of DNP.

Several prizes were awarded. The EPR Symposium continued the tradition, established in 2013, of awarding prizes for best student posters. The invited speakers served as judges, organized by co-chair Kurt Warncke. Each winner received a check, with funds contributed by both the IES and the Symposium, and a book on EPR generously donated by the author, Lawrence Berliner. This year's Piette Award winner, introduced by Sandra Eaton, was Periannan Kuppusamy (Dartmouth), who delivered a fascinating lecture entitled "EPR Oxymetry: of Mice and Men".

The formal scientific program of the Symposium closed with a business meeting on the afternoon of Wednesday, July 16. It was announced that next year's EPR Symposium will be held in Snowbird, Utah – the first time the meeting has moved out of Colorado. The chair and co-chair of this meeting will be Kurt Warncke and John Morton. However, this was not the end of the EPR related activities.

Just a few days before the EPR Symposium began, Gary Gerfen received the official word that the NSF had awarded a Research Coordination Network (RCN) grant entitled "SHARED EPR Research – Supporting, Highlighting and Advancing REcent Developments in EPR Research". This is a 5-year award that gives the US EPR community an opportunity to plan strategically, share technology, develop collaborations, educate its members and increase its profile. One of the important activities funded by this award will be an annual workshop on Grand Challenges in EPR. Thursday morning, July 17, was devoted to a stimulating discussion aimed at identifying some of these grand challenges.

The 37th EPR Symposium was a great success, and we are looking forward to the 38th next year in Snowbird.

Mark Sherwin

Joint Conferences of APES, IES and SEST (APES-IES-SEST2014)

Nara, Japan, November 12–16, 2014

Joint Conference of 9th Asia-Pacific EPR/ESR Symposium, 1st IES Symposium and the 53rd Annual Meeting of The Society of Electron Spin Science and Technology (APES-IES-SEST2014) has been held at Todaiji Cultural Center (main sessions) and Nara Prefectural New Public Hall (poster session), Nara, Japan, during Nov. 12–16, 2014. The venue was situated in the heart of tourist attraction, Nara Park, next to Todaiji Temple with Great Buda statue. The conference followed the tradition of APES and covered all aspects of EPR/ESR. It attracted 279 participants (including 68 students and ? high school students) from 22 countries, which was a record for APES. We think that the joint conference with IES, which was the first IES Symposium even in the joint form, and the attractive venue gave very good influences to attract scientists from all over the world. We had 8 plenary lectures, 26 invited talks, 5 IES award talks, 30 oral talks and 130 posters, which include 2 APES Young Scientist talks and 4 SEST Award talks. Plenary lecturers and invited speakers were recommended by the program committee and selected by the committee with the initiative of each session chairperson. Moreover, as we also had the excursion and AGM's of APES, IES and SEST, the schedule was relatively tight even we had parallel sessions for invited, IES award and oral talks. However, the sessions were well organized without much delay due to the efforts of chairpersons and the cooperation of speakers.

The first day (Nov. 12) started at 13:00 with the opening address of H. Ohta and Messages from APES and IES Presidents, Prof. T. Takui and Prof. K. Moebius, followed by three Plenary Lectures, "Magic Matrix Effects on Protein Dynamics Decoded by High-Field EPR" by Prof. K. Moebius, "Recent Progress in Theory of ESR in Strongly Correlated Spin Systems" by Prof. M. Oshikawa, and "Very High Sensitivity Orientational PELDOR" by Prof. G. Smith. Then after 5 oral presentations of SEST Excellent Presentation Award Competition among students and PD's, the participants enjoyed the welcome reception at Nara Women's University nearby. Several kinds of Japanese sakes were prepared for the tasting but it was just the beginning.

The second day (Nov. 13) started with the Plenary Lecture "The New Spin Probes for Biochemical Applications" by Prof. E. Bagryanskaya followed by two parallel sessions "Spin Chemistry" and "Dosimetry & Dating". After lunch Prof. L. J. Berliner gave the Plenary Lecture "Harden M. McConnell – the

Life of a Giant in Magnetic Resonance". It was followed by two parallel sessions "Quantum Spin System" and "*In vivo* Imaging". After the break APES Young Scientist Award presentations "Nanoscale magnetic resonance with single electron spin sensor under ambient conditions" by Dr. Fazhan Shi and "Towards the structural design of piperidine nitroxides for in vivo measurement probe" by Dr. Toshihide Yamasaki were given. Then we had APES General Meeting organized by the APES President, T. Takui, and following Office Bearers for the APES Council for 2014–2016 were elected.

President: Prof. Subray Bhat (India)
Vice-President: Prof. Elena Bagryanskaya (Russia)
Vice-President: Prof. Hitoshi Ohta (Japan)
Immediate Past President: Prof. Takeji Takui (Japan)
Secretary: Prof. Ramakrishna Damle (India)

Country/Regional Representatives:

Australia/New Zealand (Australasia): Prof. Simon Drew
China: Prof. Yong Li
India: Prof. K. N. Anuradha
Japan: Prof. Tadaaki Ikoma
Republic of Korea: Prof. Hong-In Lee
Russia (Siberia): Prof. Albert Ziatdinov
Philippine: Prof. Christopher Ambe
Thailand: Prof. Noppawan Morales
Turkey: Prof. Muhammed Acikgoz

Advisory Council Members:

Prof. Sa-Ouk Kang (Former Vice-President, Republic of Korea
Prof. Czeslaw Rudowicz (Founder President, Poland, formerly Hong Kong

During the meeting the next APES2016 was decided to be held at Vladivostok (Russia/Far East) with the initiatives of Prof. E. Bagryanskaya and Prof. A. Ziatdinov. After the General Meeting the participants moved to Nara Prefectural New Public Hall and the Bruker seminar was held where the participants enjoyed the reception after the seminar.

The third day (Nov. 14) started with two Plenary Lectures, "Overhauser Dynamic Nuclear Polarization at a Magnetic Field of 9.2 T" by Prof. Thomas F. Prisner and "Protein Dynamic Structure Revealed by High Sensitivity Pulse Dipolar ESR Distance Measurements" by Prof. Jack H. Freed, followed by two parallel sessions "DNP (Dynamic Nuclear Polarization)" and "Photo Synthesis & Protein Distance Measurement". This time the organizers were putting some emphases on DNP with the help from NMR side, Prof. T. Fujiwara (Chairperson). In the afternoon the SEST General Meeting was held, where the SEST report was given by the SEST President K. Takeshita and the SEST Executives, followed by SEST Award presentations "Electron Spin Resonance Studies of Organic Electronic Materials and Devices" by Prof. Shin-ichi Kuroda and "*In Vivo* EPR Imaging Studies of a Brain Disease Mouse Model" by Prof. Hirotada Fujii. Then SEST Young Investigator Award presentations "High-frequency ESR Studies of Molecule-based Conductors and Magnets" by Dr. Yugo Oshima and "Time-Resolved Spectroscopic Study on Paramagnetic Intermediates Generated by Photochemical Reactions" by Dr. Tomoaki Yago were given. In the evening the Poster Session was held at Nara Prefectural New Public Hall where drinks including beers and wines were served to encourage the discussions. As a new attempt three poster presentations by high school students were performed. Their qualities were high and students were willing to discuss with senior scientists. We think they had good experiences and the attempt was rather successful. After the poster session SEST+APES Young Scientists Meeting was held at Nara Women's University where young scientists had good communications with the presenters, Dr. Alexey Alfonsov, Dr. R. Mutoh and Dr. Z. Fu.

The fourth day (Nov. 15) started with the IES General Meeting where the IES President K. Moebius gave the IES report followed by the IES Award Ceremony and the IES Gold Medal presentation "EPR Investigations of Photosynthetic and Bioenergy-Related Enzymes" by Prof. R. David Britt. After the break the "IES Award Session" continued with the presentations "Recent Development of the PELDOR Theory" by Prof. Kev M. Salikhov (IES Fellow), "Ferromagnetic Resonance Studies of Spin-Orbit Effects in Heavy Atom Organic Radical Ferromagnets" by Prof. Stephen Hill (IES Silver Medal for Instrumentation), "Quasi-Optical Pulsed EPR and ENDOR at very high Frequencies" by Prof. Johan van Tol (IES Silver Medal for Instrumentation), "The structure of nature's water splitting catalyst prior to O-O bond formation: an EPR and DFT study" by Dr. Nicholas Cox (John Weil Young Investigator Award), and "Dynamic and Electronic Characteristics of Photo- generated Radical Pairs Revealed by Real-time Observation of the Spin Dynamics" by Dr. Tomoaki Miura (IES Young Investigator Award). The Chairperson Prof. L. Berliner did a great job to finish the tight session within the scheduled time. Unfortunately the "Instrumentation" Session had to go parallel to the "IES Award Session" due to the tight schedule. In the af-

ternoon the Excursion was organized. Because of the busiest season in Nara we regret that we can only take mainly foreign participants to the bus tour to visit Horyuji Temple and sake brewery "Okura-honke". We hope that the foreign guests enjoyed the excursion and the other guests enjoyed exploring around the Nara Park. In the evening the Banquet was held at the restaurant "Half Time" in Nara National Museum. The Banquet started by the welcome address of SEST Chairperson Prof. A. Kajiwara, followed by the SEST President Prof. K. Takeshita and the toast by the Honorary Chair of Symposium Prof. Hideo Utsumi. At the Banquet the huge variety of Japanese sake from Nara area was provided for the tasting, which was explained by our expert Dr. Yuki Matsuoka. Then speeches by IES Executives (Prof. L. Berliner and Prof. H. Schwartz), Prof. G. Smith, Prof. S. Dzuba and Prof. Yong Li. APES Founder President Prof. C. Rudowicz also joined the speech. Then the participants enjoyed the Gagaku, the traditional Japanese music with Sho (mouthorgan) by Tetsuji Hayashi, Jushichigen (17-string koto) by Keita Orimoto and Japanese traverse flute by Naomi Koizumi. Not only the traditional court music but also it included "Amazing Grace". The participants also enjoyed taking photos with them. The Banquet came to an end with the introduction of next APES2016 by Prof. E. Bagryanskaya and the closing remark by H. Ohta.

The final day (Nov. 16) started with the Plenary lecture "Clinical Applications of EPR" by Prof. Harold M. Swartz followed by the parallel sessions "Biology" and "Quantum Computing". In the afternoon the parallel sessions "Material Science, Electric Devices, Spintronics" and "Free Radicals and Theory" continued. Then the conference came to the closing. During the closing session Yuta Matsuoka and Hiroki Nagashima received the SEST Excellent Presentation Awards. Dr. Alexey Alfonsov, Fumitoshi Ema, Wataru Koinuma, and Takeshi Yamane received the IES Poster Awards, which include the certificate, the $200 cash and the one year IES membership. Dr. Yung Szen Yap and Tsubasa Okamoto received the APES Poster Awards, which include the certificate and the 20,000 JPY cash. Finally H. Ohta thanked all participants, the members of organizer, students, and particular emphasis on our secretary Ms. Y. Ogawa who really communicated with all participants in all aspects.

Following the tradition since APES2010, APES-IES-SEST2014 supported two APES Young Scientist Awardees and 4 APES2014 Travel Bursaries for students and post-docs to attend the symposium. 14 SEST students were also supported by the SEST Student Research Awards. Two IES Young Investigator Awards, Two SEST Young Investigator Awards, 4 IES Poster Awards, and 2 APES Poster Awards were awarded. Therefore, we really put some emphases to encourage young people during this symposium.

APES-IES-SEST2014 was the first attempt to have a joint symposium with IES. In order to attract the participants to join IES, the registration fee (40,000 JPY) was reduced 7,000 JPY for regular participants and 3,500 JPY for students if you join IES while it costs $36/year for regular IES member and only $6/year for student IES member. It encouraged Japanese to join IES and it increased about 75, which is three times the number to the former year. Moreover, we gained about 60 participants from outside Asia-Pacific area within total 279 participants and it attracted 33 sponsors. We think that the impact of Joint IES Symposium was huge and such attempt will expand to other EPR/ESR related conferences.

Finally we would like to thank APES, IES, SEST, Kobe University, Morino Foundation, Inoue Foundation, all sponsors and the participants for their supports to make the symposium rather successful.

Hitoshi Ohta, APES and IES Chairperson
Atsushi Kajiwara, SEST Chairperson

48th Annual International Meeting of the ESR Spectroscopy group of the Royal Society of Chemistry

Southampton, UK, March 29 – April 2, 2015

The 48th Annual International Meeting of the ESR Spectroscopy group of the RSC was held at the Marwell Hotel, Southampton 29th March – 2nd April 2015. The RSC meeting is the longest continuously running international EPR conference and is well known both for its very high quality and friendly, informative and engaging atmosphere. The conference was attended by 94 delegates from 12 countries, and was hosted by Dr Ilya Kuprov of the University of Southampton. The hotel was in splendid wooded grounds, directly adjacent to the famous Marwell Zoo which was also the destination for the free afternoon.

The scientific highlight was the 2015 Bruker Prize Lecture given by Prof Robert Bittl of Freie Universität Berlin. His lecture on "*EPR on more than one unpaired electron: too many spins?*" gave a brilliant overview of his wide-ranging interests, specifically focussing on multi-electron systems ranging from quantum biology to inorganic and organic materials. Prof Bittl is the 30th Winner of the Bruker Prize and joins an esteemed list of previous winners from all over the globe.

The conference opened with a plenary lecture from Prof David Parker (Durham) on "*Understanding shift and relaxation processes for lanthanide PARASHIFT agents*", and further plenaries were given by Prof Frank Neese (MPI für Chemische Energiekonversion) on "*Theoretical approaches to mononuclear single molecule magnets*", Prof Thomas Prisner (Frankfurt) on "*Applications of broadband pulses for*

dipolar spectroscopy", and Prof Michael Wasielewski (Northwestern University) on "*Spin coherence and polarization transfer within photogenerated three-spin systems*".

Invited lectures were given by Prof Peter Hore (Oxford, "*Animal navigation using magnetically sensitive spins*"), Prof Elena Bagryanskaya (Novosibirsk, "*New approaches for distance measurements in nucleic acis using advanced SDSL with nitroxyl and trityl radicals*"), Prof Damien Murphy (Cardiff, "*Catalytic chemistry of low-valent transition metal complexes*"), Prof Song-I Han (California Santa Barbara, "*Probing interfaces and interactions by Overhauser DNP and EPR*", and Dr Will Myers (Oxford, "*Applications of pulsed dipolar spectroscopy in circadian mechanics*"). The meeting was closed with an excellent tutorial lecture from Prof Gunnar Jeschke (ETH Zurich) on "*The dos and don'ts of DEER and DEERAnalysis*" which is available from the conference website via esr-group.org.

The 2015 JEOL Student Prize Lecture competition was won by Andrin Doll (ETH Zurich) with an excellent presentation on "*High-sensitivity Gd(III) DEER with composite chirp pulses.*" The runners up were Christopher Engelhard (Freie Universität Berlin, "*Cellular metabolites enhance light sensitivity through alternate electron transfer pathways in Arabidopsis cryptochrome*") and Claire Motion (St Andrews, "*Enhancing sensitivity and modulation depth in high field PELDOR experiments*"). Further excellent lectures were given in this session by Angeliki Giannoulis (St Andrews, "*Metal ions in PELDOR spectroscopy*"), Gary Wolfowicz (UCL, "*Improving spin coherence and control in donors in silicon*") and Bouchra Hajjaj (St Andrews, "*Development of new radical labelling strategies for cysteine rich proteins*").

Graham Smith with Dinar Abdullin (Bonn) and Christoph Meier (Berlin), winners of the Poster Prizes.
Taken by Arthur Heiss

The meeting also saw the inaugural Bruker thesis prize. Theses defended in the preceeding two-year period were eligible and the standard of the applications was exceptional. The winner of the 2015 prize was Dr Joshua Biller (currently at the National Institute for Standards and Technology, USA) for his 2014 thesis on "*Nitroxide radicals for low frequency electron paramagnetic resonance imaging (EPRI)*" supervised by Profs Gareth and Sandra Eaton (Denver). The winner is invited to lecture on their thesis work, and Josh gave an outstanding presentation on "*Frequency dependence of nitroxide relaxation from 250 MHz to 34 GHz*".

The prizes for the best poster was won by Dinar Abdullin (Bonn) for his poster "*Comparison of different EPR techniques for Fe(III)-nitroxide distance measurements*", and Christoph Meier (Freie Universität Berlin) for his poster "*Electrically detected HYSCORE on conduction band tail states in ^{29}Si-enriched microcrystalline silicon*". As has been the case in recent years the overall quality of the posters was excellent.

The conference was a great success and many thanks go to Prof Ilya Kuprov for the organisation. The RSC ESR Group Committee would also like to thank Bruker and JEOL for their continued sponsorship and support of this meeting, including two receptions with free bars which helped bring people together in the evenings. The committee would also like to acknowledge the RSC for sponsoring a number of PhD travel bursaries, and the support of Active Spectrum, Adani, Cryogenic and Hall Scientific, who all exhibited at the meeting. At the RSC ESR Group AGM, Drs Chris Wedge (Warwick) and Emma Carter (Cardiff) were elected as Ordinary Members. Prof Jeschke was re-elected as international representative, while Dr Dima Svistunenko joins the committee as the 2016 conference organiser. Drs Janet Lovett (St Andrews) and Stephen Brookes (JEOL UK Ltd) retired from the committee in 2015, and were thanked for all their hard work on behalf of the RSC ESR group. The 49th International Meeting of the RSC ESR Group will be held at the University of Essex 3-7th April 2016. Information about the meetings can be found at the website esr-group.org.

The delegates of the 48th Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry.

Prof. E. J. L. McInnes
Secretary to the RSC ESR group
Prof. G. Smith
Chair of the RSC ESR group

Market place

POSITIONS

Research Scientist (Postdoctoral associate)
The Institute of Macromolecular Chemistry AS CR, v.v.i. seeks a postdoctoral associate / research scientist to join the Laboratory of electron paramagnetic resonance of polymer systems (EPR)
Requirements: University degree and PhD in the field of chemistry, physical chemistry or physics / Practical experience with the method of electron paramagnetic resonance (EPR) / Knowledge of and working experience with polymers and EPR imaging will be an advantage / Stays abroad will be an advantage / Good knowledge of English language / Good publication activity / Independence, reliability.
Details about research work can be obtained from RNDr. Petr Štěpánek, DrSc., stepanek@imc.cas.cz
Candidates should submit a structured CV emphasizing experience relevant to the advertised position, a motivation letter and a list of publications and other results to e-mail: fencl@umch.cz HR department tel. (420) 296 809 385.

Available: Used EPR Spectroscopist
Old, but well maintained EPR Spectroscopist, with wide application experience, seeks opportunity to support active research group. EPR- based publications over 5 decades, most recently 2011, mass spectrometry publications to 2014. Experience in the study of transient organic and organometallic free-radicals; transition metal complexes; spin-trapping; spin probe; radical ions; matrix isolation

and γ-radiolysis techniques; photocatalysis; polymer degradation and stabilisation etc. Has Bruker, Varian and JEOL operating experience, plus track record in NMR and mass spectrometry techniques. Would prefer to work in biochem/biological area, but would consider anything interesting. Opportunity arises due to restructure of Research Department in Australian steel company after 26 years faithful service. Excellent grant writing skills, 100% success rate. Speaks English, German and some French.

Please Contact: Phil Barker pba02985@bigond.net.au or pbarker@uow.edu.au to receive user logbook and publications list.

Postdoctoral Associateships in Magnetics at NIST

We offer postdoctoral opportunities in magnetics at the National Institute of Standards and Technology in Boulder, Colorado, USA. Annual salary is $65,600 plus benefits. Appointments are for two years. Application deadlines are 1 February and 1 August annually (but inquire earlier).

The application process is competitive. Typical successful applicants have a strong research background and academic record. Letters of reference and an original research proposal are required.

U.S. citizenship and a background investigation are required (no exceptions).
www.nist.gov/pml/electromagnetics/magnetics

EPR Specialist Position at Johns Hopkins

Postdoctoral or specialist (staff) position is available immediately to study membrane proteins at the Johns Hopkins University School of Medicine in Baltimore, Maryland, USA. We study conserved membrane enzymes with implications for human health (see Nature Chem Biol 8:759, eLife 1:e00173, and Nature Rev Micro 7:411), and are generously funded by the National Institutes of Health (NIH) and the Howard Hughes Medical Institute (HHMI). The project uses site-directed spin labeling (SDSL) with nitroxide probes to study the dynamics, distance measurements, and saturation kinetics with CW-EPR methods. The applicant must have at least 3 years of prior experience in SDSL, EPR, spectrum simulations, and distance measurements as evidenced by publications. Experience with membrane proteins is preferred but not essential. Position will come with generous salary and benefits, depending on experience and record of achievement. Interested applicants please send detailed CV and contact information for 3 references to rosanna@jhmi.edu.

Research Positions – Advanced EPR of Biochemical and Chemical Systems

Several research positions (doctoral and postdoc level) are presently available in the Biophysical Chemistry Department of the Max Planck Institute for Chemical Energy Conversion in Mülheim/Ruhr, Germany. We are looking for highly motivated young scientists in the field of Electron Paramagnetic Resonance who are interested in studying biochemical and chemical systems related to the topic of the institute.

In-house projects: Photosynthetic systems (reaction centers, water oxidation) / Hydrogenase enzymes and related model systems / Radical enzymes and protein maquettes.

Collaborative projects: EPR instrumental developments dedicated to EPR studies of (single) protein micro crystals / Advanced EPR investigation of highly reactive chemical intermediates and their weakly bound intermolecular complexes.

Our lab is equipped with 10 modern EPR spectrometers covering the frequency range from 2 to 244 GHz capable of the complete repertoire of CW EPR and pulse techniques (ENDOR/TRIPLE, ELDOR, ESEEM) in combination with laser excitation and freeze quench techniques. More details can be found on our website: www.cec.mpg.de.

Candidates should have project relevant knowledge and be trained in Magnetic Resonance Spectroscopy, preferably in EPR. Candidates with an interest in EPR instrumental development and microwave engineering are specifically encouraged to apply.

Please send your application including CV and the scope of scientific interests to:
Prof. Wolfgang Lubitz
Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany
e-mail: wolfgang.lubitz@cec.mpg.de

Bruker BioSpin Corp

Bruker BioSpin Corp is looking for a highly motivated individual to join our EPR Service team to install and support high technology EPR Spectrometer Systems in customer research labs. This individual will install and service our EPR Spectrometer Systems and train customers for basic operation of the equipment. A BS in electrical engineering, electronics or related fields or equivalent experience is required. Experience diagnosing and repairing electronic, electromechanical and/or mechanical equipment is required. General understanding of analog electronics, digital electronics, high voltage circuitry/circuits, microwave technology, vacuum technology, cryogenics; strong technical skills on analytical instrumentation required.

Please send resume, cover letter and salary requirements to bruker.jobseprfse0620@bruker-biospin.com

EQUIPMENT

Wanted: Badly needed certain parts of, or even a complete Bruker X-Band microwave unit from the mid-seventies, the one which came with the Bruker B-ER 420 system. Particularly, the klystron heating and protection board, B-E-Z 10. Please contact Prof. Dr. Wolfgang E. Trommer, Department of Chemistry, TU Kaiserslautern, P.O.Box 3049, D-67653 Kaiserslautern, Germany. E-mail: trommer@chemie.uni-kl.de.

EPR parts, electronics and hardware

Pulse generators, amplifiers, frequency counters, etc. We also offer X-band cavities, waveguide, klystrons, cells, etc. for Varian instruments.

Please contact techepr03@gmail.com for availability and pricing.

Design and construction of EPR electronics

The University of Denver can supply electronic design and construction services for EPR applications. Low-noise pulse amplifiers, low-noise 100 kHz preamplifiers, boxcar integrators, and pulse timing systems are available. We also supply a conversion kit to convert Varian field-control units to voltage-controlled scan operation. A 6-digit 1-ppm frequency counter is available in X-, C-, S-, L-band, or MHz versions. Complete microwave/RF bridges from 150 MHz to L-, S-, or C-band are available from designs previously built and tested at the University of Denver.
Please contact: Richard W. Quine, e-mail: rquine@du.edu, phone: 1-303-871-2419

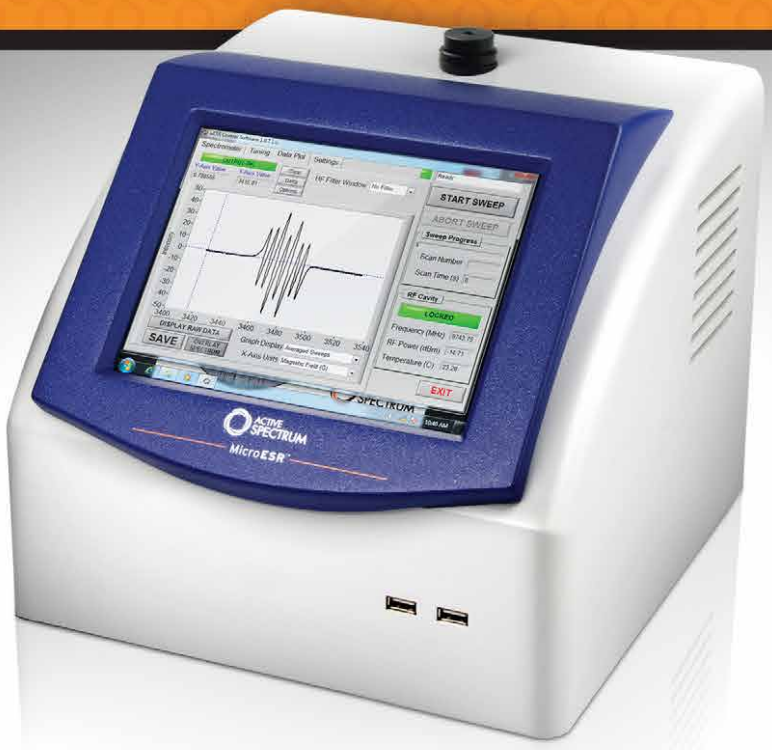
Available: Used Varian EPR equipment

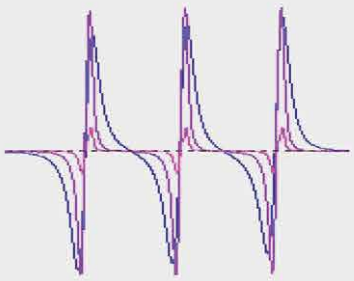
(1) Varian E-104 EPR spectrometer with vertical style bridge and e-line fieldial. (2) Varian E-9 EPR spectrometer. Both available with warranty and continued service support. (3) Varian TM cavity with flat cell holders and flat cells. (4) Varian E-257 variable temperature controller with heater sensor and insert holder. (5) Varian E-272B field/frequency lock accessory.

Please contact: James Anderson, Research Specialties, 1030 S. Main St., Cedar Grove, WI 53013, USA. phone/fax: 1-920-668-9905, e-mail: janderson36@wi.rr.com

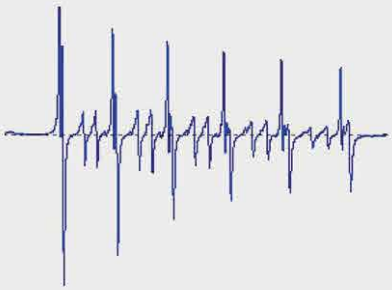
Micro-ESR

A cost effective teaching tool for undergraduate **chemistry and physics**





Spin-Spin Exchange



Forbidden Transitions

Spin Trapping to Elucidate Free Radical Reaction Mechanisms

SOME LABORATORY CONCEPTS:

- Free radicals
- Hyperfine Splitting
- g-factor
- Kinetics
- Electron Density
- Transition Metals
- Spin Trapping
- Sample Concentration
- Hindered Molecular Motion
- Relaxation Mechanisms
- Everyday Radicals

Active Spectrum's Benchtop X-band ESR Spectrometers

- Requires no costly setup or maintenance
- User friendly software for both data acquisition and processing
- User control of all important parameters
- The Micro-ESR is only 30.5 x 30.5 x30.5 cm^3 and 10 kg
- Excellent Resolution and Signal to Noise

Perylene Radical Cation

Protein analysis via spin labeling

Contact us for more details:
sales@activespectrum.com *or* +1 650-212-2625

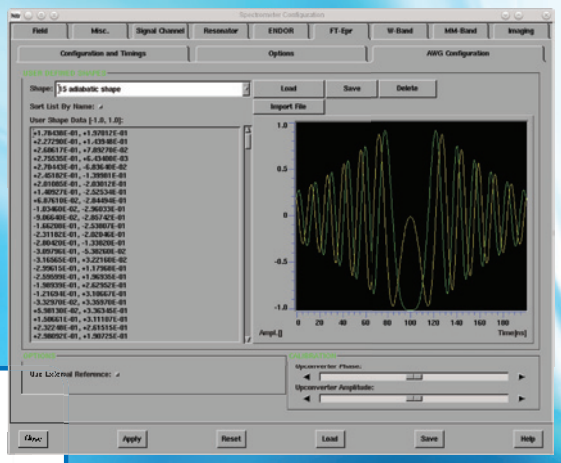
Read our white papers, posters and application notes:
www.activespectrum.com/about-us.shtml

ACTIVE SPECTRUM

Innovation in Magnetic Resonance

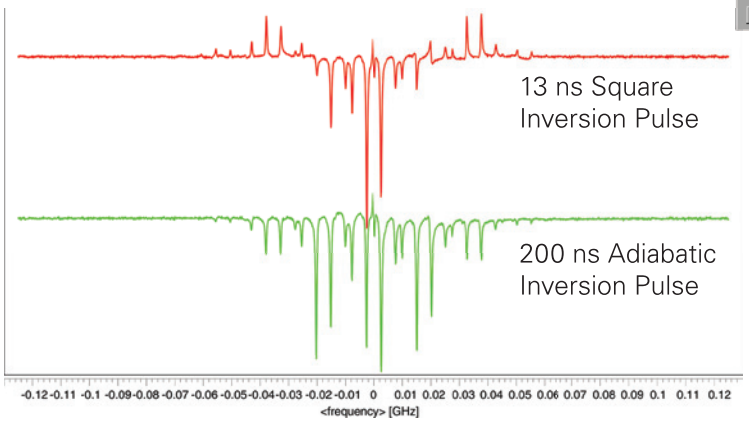
Optimum Pulse Control with SpinJet-AWG

Improved Results



Easy to Define Shapes

PNT Sample



Angew. Chem. , P. E. Spindler, S. J. Glaser, T. E. Skinner, T. F. Prisner, v52, p3425, 2013

User Optimization with SpinJet-AWG

User-defined pulse shapes within SpinJet-AWG allow a wide variety of experimental opportunities, for all available frequency bands from L-band to 263 GHz:

- Uniform spectrum inversion
- Optimized excitation
- Resonator compensation
- Frequency correction

Includes predefined shapes:

- Square
- Gaussian
- Ramp up and down
- Sine bell

Discover more about the new era in pulse EPR: www.bruker.com/epr

The EMXnano

Bringing EPR to the Wider World

The EMXnano is a compact, state-of-the-art bench top instrument designed to give the power and flexibility needed for a range of analysis and teaching applications. With the latest digital and microwave technologies, the EMXnano provides superior sensitivity and stability.

Experimental flexibility

- Adjustable internal marker
- Liquid nitrogen VT system
- UV/Vis irradiation system

Software Features

- SpinCount for Quantitative EPR
- SpinFit for Fitting of EPR spectra
- Python interface for flexibility

For more information please visit: www.bruker.com/emxnano