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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 Yurii D. Tsvetkov, recipient of the Zavoisky Award 2013. It shows the structure of the trichogin peptide four-molecule aggregate in the nonpolar solution based on PELDOR data. The arrows indicate the positions of spin-labels at the distances of 23.5 and 26.0 Å.
Dear colleagues,

Yes, you guessed it right. Judging by the date that you read this editorial it could be nothing but a double issue of the EPR newsletter, and it is. Hopefully, you will find its content to be a proper reward for your patience. In fact, it is difficult to decide what material is the highlight of this issue. Probably we could call it the issue of highlights. I will comment only on some of them.

By now you must have read the flyer “Why should you become member of IES?” written by Klaus Möbius, President of the IES. We can never overdo our efforts to increase our visibility and attract new members, so here it is again on p. 4. Please do your best to contribute to these efforts and invite your colleagues to join our society. In co-authorship, Klaus and Anton Savitsky made an attempt to build bridges between EPR and NMR spectroscopies in their instructive and comprehensive article in the “Guest of the issue” column (pp. 5–13) demonstrating how EPR and NMR can greatly benefit from each other’s insights.

We join Rob Ammerlaan in congratulating George Watkins on his 90th birthday (pp. 16, 17) and send our warmest regards and heartfelt congratulations to George Feher who celebrated his 90th birthday on May 29th. According to the IES regulations for the “Anniversaries” column (to quote: “(iii) There is no need to cover the same person for 65, 70, 75, etc. anniversaries” (21/4, p. 2), we can only refer you to the article by Wolfgang Lubitz on the 80th birthday of George (14/3, pp. 10, 11). George Feher contributed a lot to the development of the EPR newsletter, starting with his “Playing Poker” article in 2003 (13/1-2, pp. 10–12) and generously sharing with us his knowledge and thoughts in many other publications in the following issues. It is also worth to note the EPR newsletter 16/2-3 (2006) dedicated to the 50th anniversary of ENDOR. We can never thank George enough for the continuing support and inspiration so once again: thank you, George!

Special thanks go to Harden McConnell who kindly allowed us to publish excerpts from his article to be found in full at the website http://hardenmcconnell.org (pp. 18, 19). Harden stated that this writing may serve a useful purpose for his students to learn the history of his research group, to connect, and to see the evolution of the scientific research in the McConnell laboratory. However, I feel it is a must read for the EPR community because it shows the grandeur of one of the newly elected Fellows of the IES better than any award citation.

Only two things made it possible for me to live with the news that Thomas Prisner decided to resign from being Associate Editor Europe: first, he continues to edit the “Pro & Contra” column and second, his successor is Sabine Van Doorslaer (p. 3) with whom we already collaborated on the newsletter. Vielen-vielen Dank, Thomas! Welcome, Sabine!

Presumably, you are looking for the information about the Bruker Prize 2014 awarded to Jörg Wrachtrup at the Dundee conference in April. Patience, patience, please wait for the forthcoming issue.

Now, welcome to the issue of highlights! Enjoy!

Laila Mosina
Let’s Jump Start Your Academic Journey with the International EPR Society

Are you interested in becoming a member of the International EPR Society? Please find the registration/information form for new/continuing members of the IES and non-credit-card payment instructions for individual members on this Web site: www.epr-newsletter.ethz.ch/contact.html

Is your company involved in magnetic resonance in any way? If so, consider advertising in the EPR newsletter. Your company will have its own advertising and information box in each issue. It will be seen by a targeted audience of thousands of specially selected scientists worldwide. Information on sponsoring the Society and advertising is shown on this Web site: www.epr-newsletter.ethz.ch/corporate_sponsors.html

Associate Editor Europe

Sabine Van Doorslaer studied both chemistry and physics at the University of Ghent (Belgium). She graduated in 1991 as licentiate in Chemistry with the thesis “Cluster computations of YBa2Cu3O7 superconductors using the relativistically parameterized extended Huckel method” prepared in the Laboratory for Inorganic Chemistry under the guidance of D. Van de Vondele. A year later, she graduated in Physics with the diploma thesis “EPR study of carbonate-derived radicals” in the Laboratory for Crystallography and Study of the Solid State (promoter E. Boesman).

She remained in the same group for her PhD work and in 1996 she obtained her PhD with the thesis “Structural analysis of paramagnetic chalcogenic defects in alkali halides and hydroxyapatites” performed under guidance of Freddy Callens. As the word “paramagnetic” already suggests, EPR and ENDOR formed the main techniques in this work. In April 1996, she became a postdoctoral fellow in the group of Arthur Schweiger in ETH Zurich (Switzerland), where she worked on the applications of pulsed EPR on several problems in (bio)inorganic chemistry till the end of 2001. In 2002, she returned to Belgium and became a lecturer at the University of Antwerp in the Department of Physics. She is now full professor at this University and guest professor at the University of Hasselt (Belgium).

Her research interests cover the use of combined spectroscopic (mainly EPR) and quantum-chemical (DFT) tools to study (i) the structure-function analysis of metal proteins and of metal-biomolecule interactions (studies on both model systems and the native systems), (ii) the structure-function analysis of synthetic (transition-metal containing) catalysts, and (iii) semi-conducting materials for photocatalysis or solar-cell applications.

Please send any Agenda items to the IES Secretary Prof. Sushil K. Misra (skmisra@alcor.concordia.ca) as soon as possible.

Dear members of the international EPR community:

I want to encourage you to join the membership of the International EPR (ESR) Society (IES). If you are already Member, please try to convince your colleagues and students to also become Members.

As you probably know, IES is the only international scientific organization that represents the whole range of the important research field of EPR spectroscopy and electron-magnetic resonance imaging (MRI). These methods are used as main research tools in a very wide range of fields including physics, chemistry, life sciences, materials research and medicine. IES is a world-wide association of scientists active in the fields of EPR and MRI and the development of related methodologies and technologies.

The Flyer “Why should you become member of IES ?” gives some good reasons to support the activities of IES to the benefit of the EPR community at large.

The 2014 Annual General Meeting (AGM) of the IES will be held in conjunction with APES-IES-SEST2014 (November 12–16, 2014) in Nara, Japan.

The 2014 awards will also be presented during this conference to the awardees attending it. The exact date and time for the AGM has yet to be confirmed.

Please send any Agenda items to the IES Secretary Prof. Sushil K. Misra (skmisra@alcor.concordia.ca) as soon as possible.

The success of the IES activities depends on the number and dedication of the IES Members. We hope to convince you to join IES and, thus, to contribute to its visibility and potentialities also in the future.

Sincerely,

Klaus Möbius, President, IES

The Editor in Chief
Dear Colleague:

IES is the only international scientific organization that represents the whole range of the important research field of electron paramagnetic resonance (EPR) spectroscopy and electron-magnetic resonance imaging (MRI). These methods are used as main research tools in a very wide range of fields including physics, chemistry, life sciences, materials research and medicine.

IES is a world-wide association of scientists active in the fields of EPR spectroscopy, medical applications of MRI and development of related methodologies and technologies. The IES mailing list serves the community to help spread EPR-related information (job, post-doc or PhD offers, conferences etc...). It provides public networking, but only IES members can post messages via the EPR Newsletter, the official IES publication organ. IES also provides information on opportunities for obtaining second-hand EPR instrumentation. Moreover, prominent manufacturers of EPR instrumentation disseminate their offers in dedicated advertisements in the EPR Newsletter issues.

The aims of IES are also to foster interactions among scientists in different fields of magnetic resonance; to encourage interdisciplinary explorations; to inform about dedicated schools, local and international symposia on EPR and related fields.

Today, IES has a large number of active members from many countries throughout the world. IES provides information about conferences, workshops, and schools in all fields of EPR with emphasis on encouraging young scientists to participate and to make use of existing exchange opportunities between recognized EPR laboratories.

IES also administers Prizes and Honors for outstanding contributions to EPR spectroscopy such as the prestigious IES Fellowships and the IES Gold and Silver Medals as well as the IES Young-Investigator Awards for excellent young people on the post-doctoral level and below 35 years of age. The newly created IES Poster Prizes honor excellent young scientists and PhD students for their contributions to international EPR conferences, their distinction is also reported on in the EPR Newsletter issues as are the other Prizes and Honors.

Members of IES have free access to the EPR Newsletter; four issues per year reach you either via their online editions or via mail to your affiliation address. They inform you about recent developments in EPR spectroscopy and important news from the EPR community at large. Furthermore, hot-topic subjects of EPR spectroscopy are adequately covered regularly by top-notch experts to update your knowledge and experience suitable to be used in your own research and teaching activities.

We cordially invite you to become Member of IES and, thus, become active in keeping IES alive and responsive to the ever young field of EPR spectroscopy. The member fees are encouragingly low (see www.ieprs.org).

Yours sincerely,

(President of the International EPR (ESR) Society, May 16, 2014)
Abstract. In this Essay on advanced EPR spectroscopy, emphasis is put on delineating the complementarity of solid-state NMR and EPR concerning the measurement of molecular interactions of large biomolecules. From these interactions detailed information can be revealed on structure and dynamics of macromolecules embedded in their specific matrix environments. Concerning detection sensitivity and interaction selectivity, spectral and time resolution, new developments in pulsed microwave and sweepable cryomagnet technology have pushed the limits of EPR spectroscopy and its multifrequency extensions to new horizons. One of the most important advances has been the extension of EPR to high magnetic fields and microwave frequencies, very much in analogy to what happens in NMR. This is exemplified by referring to ongoing efforts for signal enhancement in both NMR and EPR double-resonance techniques by exploiting dynamic nuclear and electronic spin polarization effects. Exchange of experiences between the EPR and NMR communities is frequently practiced and allows for optimizing polarization and resolution strategies. Unique structural and dynamic information is, thus, revealed that is hardly obtainable by any other analytical techniques. Micromolar quantites of sample molecules have become sufficient to characterize stable and transient reaction intermediates of complex molecular systems – offering highly interesting applications for (bio)chemists and molecular biologists. This is highlighted by reviewing a few representative examples of high-field PELDOR, ENDOR and ELDOR-detected NMR experiments for structure determination of functional ion radicals, radical pairs and transition-metal ions in bacterial and oxygenic photosynthetic reaction centers, as well as of nitroxide spin-labelled bacteriorhodopsin for structure-function studies.

1. Introduction

This Essay should be seen as an attempt to build bridges between EPR and NMR spectroscopics which can greatly benefit from each other’s insights. It is based on our recent review article High-field EPR on membrane proteins - Crossing the gap to NMR [1]. The title shall be reminiscent of the still ongoing discussion on C. P. Snow’s famous book The Two Cultures [2] from 1959 which provokingly addressed the existing gap of understanding and appreciation between the sciences and humanities. This academic dispute has left now its 50th anniversary behind, but still has not fundamentally changed the subject of concern. But stimulated The Third Culture [3] to arise at the horizon in which both sides of the gap try to enter a bridge where forces are united to help to solve important issues of common interest.

In the magnetic-resonance community the barrier of indifference, if not lack of interest, between the two cultures, NMR and EPR, is gradually dwindling because both sides have realized that there exist complementary strengths to employ to advantage particularly in the biosciences. They could be used as critical tools for responding to the most troubling problems in NMR or EPR, sensitivity and resolution. And more and more participants of the magnetic resonance community realize that there is just a lot to learn from each other, be it conceptually or technologically, to improve the analytical tools for high-quality information on molecular structure and dynamics.

The two magnetic resonance sisters, EPR and NMR, are approaching now their 70th birthday, EPR – the elder one – in 2014, NMR a year later. EPR and NMR phenomena were originally observed in radiofrequency spectroscopy experiments employing continuous-wave (cw) electromagnetic fields, EPR in 1944 by E. K. Zavoisky at Kazan University, NMR in 1946 by E. M. Purcell, H. G. Torrey and R. V. Pound at Harvard and, independently, by F. Bloch, W. Hansen and M. E. Packard at Stanford. These classic NMR experiments were honored as early as 1952 by the Nobel Prize in Physics to Bloch and Purcell. Zavoisky’s discovery of EPR, however, was only inadequately recognized on the western side of the Iron Curtain – in contrast to the eastern side: In 1957, Zavoisky was awarded the Lenin Prize, the highest sign of recognition in the former USSR, for his discovery of the electron-paramagnetic-resonance phenomenon. It was as late as 1977, when finally Zavoisky was honored also internationally. Not by a Nobel Prize, though, but at least by the prestigious ISMAR Award of the International Society of Magnetic Resonance, presented at the ISMAR Conference in Banff, Canada, on May 21, 1977 – alas posthumously [4] as he had died October 9, 1976, in Moscow just after having been informed about the decision of the ISMAR Prize Committee.

At the occasion of this 70th birthday, time seems to be overdue for remembering the common family roots to strengthen each other. Like in many families, while growing up the two siblings have developed into quite different directions, the younger one becoming a famous celebrity honored by several Nobel Prizes and other high-rank distinctions, the elder one also blooming but always staying in the shade of the more charismatic NMR star. The existing disparity between mutual recognition of NMR and EPR is certainly not due to pretension of one side or insignificance of the other, but rather mirrors the sheer number of respective applications and publications [5] – and since NMR’s march through the medical institutions by means of MRI such a justification just leaps to the eye.

But in the last decade or so, one can observe a gradual move to a more balanced family sentiment in the magnetic resonance community, with an increasing recognition of also the EPR side leap, albeit the fan club of NMR remaining by orders of magnitude larger than that of EPR. The annual distributions of NMR and EPR publications show phases of stagnation followed by phases of strong growth reflecting active research periods and technological breakthroughs in instrumentation.

In NMR, the drastic increase of the number of publications on structure determinations since 1990 clearly correlates with the introduction of three-dimensional NMR spectroscopy in combination with selective isotope labelling. In EPR, at about the same years, also technological breakthroughs in terms of pulse EPR as well as high-field EPR gave rise to a strong increase of EPR publications. Interestingly, in these publications transient polarization effects of the electron spin system are often used for signal amplification or as source of unique information about details of reaction mechanisms – rather similar to what is being observed in the current NMR literature.
The family ties between NMR and EPR become even more visible when dealing with paramagnetic metal ions in proteins, and key words like NMR on paramagnetic systems, pseudocontact shifts, paramagnetic relaxation enhancements dominate the scene. Paramagnetic metal ions offer outstanding opportunities for protein studies by both NMR and EPR spectroscopy. The paramagnetic effects manifested in the NMR and EPR spectra provide powerful restraints for the determination of the three-dimensional structure of proteins, and open new possibilities for the analysis of protein-protein and protein-ligand interactions. Over the last decades, methods for site-specific tagging of proteins and oligonucleotides with paramagnetic molecules have been developed. Most often, the paramagnetic tags include nitroxide radicals and metal chelators. Site-directed double spin labelling with MTS nitroxide radicals are particularly promising [6–8] – as are tags suitable for site-specific and rigid attachment of lanthanide ions to bio-macromolecules [9, 10].

In the following we focus on aspects for which the distance from EPR to NMR spectroscopy across the moat is short, actually short enough to be inviting to cross the gap – be it because of related methodologies or because of similar molecular systems under study.

2. NMR versus EPR spectroscopy at high magnetic fields

It is only during the last two decades that the chemistry, biology and physics communities realize – and appreciate – a dramatic catching up of EPR with respect to NMR. The reasons for EPR’s Great Leap Forward rest on the remarkable technological breakthroughs in pulsed microwave technology, sweepable cryomagnet fabrication up to 14 T and ultra-fast data acquisition and handling instrumentation. Modern EPR is apparently booming now, rather similar to what had happened with NMR. 15 to 20 years earlier, and continues to do so, trading now under the brand name “Advanced EPR”. Why is there such a discrepancy between the technical requirements for pulsed NMR and pulsed EPR? The answer is related to the vastly different time scales of the NMR and EPR phenomena which, in turn, are a consequence of the vastly different magnetic moments of nuclei and electrons. Thus, the characteristic frequency separations in the respective spectra are Hz versus MHz, and the transverse relaxation times $T_2$ are ms versus ns. NMR rf pulses need not be shorter than 10 μs, which to generate and detect coherently does not pose any technical problems. The electronic $T_2$ times, however, are typically in the 10 ns range and, consequently, in EPR the mw pulses have to be as short as a few ns. To generate and detect them coherently poses great technical problems even today; likewise to handle the transient signals in the ns time scale. Modern developments in microwave technology and ultrafast electronics have pushed the limits of interaction selectivity, spectral and temporal resolution as well as detection sensitivity of advanced EPR spectroscopy and its multi-frequency pulse extensions to new horizons. Minute quantities of sample molecules have become sufficient to characterize stable and short-lived transient reaction intermediates of complex molecular systems – offering highly interesting applications for biochemists and molecular biologists. Particularly, the high detection sensitivity and short time scales of advanced EPR spectroscopy are advantageous – and in recent years modern NMR spectroscopy is fighting hard to boost its notoriously low detection sensitivity way up by taking advantage of higher spin polarization due to electron-nuclear interactions as in DNP-enhanced NMR experiments [11–13].

What a chance to join forces to provide powerful new methods for a better understanding the structure-dynamics-function relationships of large molecular complexes in the biosciences! Indeed, the DNP-enhanced NMR approach is currently very popular both in the NMR and EPR communities. A second “join forces” approach has become equally popular in the EPR community characterized, for example, by the acronyms ENDOR, PELDOR (or DEER) and ELDOR-detected NMR (see below).

The common link between the two magnetic resonance communities could be the striving for higher and higher external Zeeman fields with corresponding higher resonance frequencies. There are at least five important features, that are emerging from both EPR and NMR spectra with increasing Zeeman field: (i) enhanced spectral resolution; (ii) enhanced orientational selectivity in disordered samples; (iii) enhanced low-temperature spin polarization; (iv) enhanced detection sensitivity for restricted-volume samples, and (v) enhanced “snapshot” sensitivity for probing fast motional dynamics. For example, the strategy for spectral resolution enhancement is similar in EPR and NMR. With increasing external Zeeman field the field-dependent spin interactions in the spin Hamiltonian are separated from the field-independent ones. In high-field EPR, the g-factor resolution is increased in relation to the hyperfine couplings, in high-field NMR the chemical-shift resolution is increased in relation to the spin-spin couplings.

For low-symmetry systems, particularly in frozen solution samples, standard EPR suffers from low spectral resolution due to strong inhomogeneous line broadening. Such problems arise, for instance, because several radical species or different magnetic sites of rather similar g-values are present or the small g-tensor anisotropy of the paramagnetic system does not allow canonical orientations of the powder EPR spectrum to be observed. For improving the spectral resolution of delocalized spin systems, in which unresolved hyperfine interactions dominate the inhomogeneous EPR linewidth, a true high-field EPR experiment must fulfill the condition

$$\frac{(\Delta g_{iso})^2}{B_0} > \Delta B \quad (1)$$

i.e., the anisotropic electron Zeeman interaction, described by the difference $\Delta g$ of the principal g-tensor components, must exceed the EPR inhomogeneous linewidth $\Delta B$. On the other hand, when $\Delta B$ is reduced by isotope labeling, e.g., by perdeuteration of the nitroxide spin-label molecule and/or $^{14}$N-substitution by $^{15}$N, lower $B_0$ fields may be already sufficient to meet the condition for true high-field EPR, see Eqn. (1). In certain systems, the reduction of $\Delta B$ by isotope labeling may be the only way to enhance the spectral resolution when field dependent g-strain effects can become the linewidth-determining parameter at higher fields.

Enhanced orientational selectivity in disordered samples is another strength of high-field EPR, see Fig. 1. This feature becomes essential for frozen solutions of randomly oriented spin systems with only small g-anisotropy. Powder-type EPR spectra are obtained, and the canonical tensor orientations of the dominating interaction in the spin-Hamiltonian can be resolved leading to Pake-type spectral patterns that are so familiar from solid-state NMR spectroscopy. Similar arguments hold for the dipolar electron-electron spin interaction in a radical pair when studied by orientation-resolving high-field PELDOR (see below).

The complementarity of EPR and NMR methods becomes particularly evident when comparing the range of intermolecular distances between two spin entities in solid-state samples in which anisotropic spin-spin interactions are not averaged out as in fluid-solution samples. Typical short-range interproton distances, as derived from NOE spectra, have a cut-off limit of $\leq 5$ Å. This provides a very useful range
of distance restraints since in most proteins, there exits a significant number of residues far apart in the linear amino acid sequence that are close together in space. There are clearly instances, however, in which short-range distance restraints do not lead to unique solutions of a structure but, rather, long-range distance information extending over 15–25 Å would provide useful, if not critical, data. Normally, in such a situation, NMR spectroscopists would resort to paramagnetic relaxation effects on the NMR spectra. In the general case, this involves introducing a paramagnetic spin label at an appropriate site in the molecule, a strategy which is also familiar in EPR spectroscopy and used by a fast growing "spin-label EPR community." Thanks to its large magnetic moment the unpaired electron is a much more sensitive probe for the location of an interacting second spin, be it of nuclear or electron origin. Hence, the distance range, covered by anisotropic (dipolar) spin interactions that are accessible to EPR spectroscopy, covers distances from single bond lengths of about 1 Å up to transmembrane or inter-domain distances of 80 Å, separating weakly interacting radical pairs of cofactors or spin labels.

The inherent limitation of EPR – in contrast to NMR – to need paramagnetic samples is, in fact, not a very severe limitation because techniques have been developed during the last decades to introduce electron spin labels into diamagnetic molecules as "spy probes" to study the molecules by EPR without significantly disturbing their structure and function by the label. From the numerous overviews on advanced high-field EPR spectroscopy in the bio-sciences we mention here only a few recent books [14–17].

3. Advanced multifrequency EPR techniques, a chronological account

When comparing modern EPR and NMR one habit of the respective spectroscopists immediately catches one's eye: their apparent delight in creating handy acronyms for the specific variants of the magnetic resonance technique they use. NMR is still far ahead, and EPR has no GRASP to DANTE yet, but is catching up also in this respect.

TREPR (Transient EPR)
Concerning the detection of short-lived transient states or reaction intermediates, and studying their electron polarization mechanisms, besides pulsed EPR also specific cw EPR strategies can be used provided the time resolution of the EPR spectrometer is ensured to be fast enough. By employing field modulation at a frequency as high as 1 MHz the time resolution could be extended to the µs range. A decisive step forward to drastically higher time resolution was achieved for fast photoreactions by abandoning field modulation at all and generating the time-dependent EPR signal via wavelength-selective pulsed laser excitation. Subsequent direct, i.e., broad-band detection of the transient EPR signal at a fixed Zeeman-field value is accomplished by employing sufficiently fast data-acquisition systems. The Zeeman field is stepped through the spectrum. The pioneering experiment was performed by S. I. Weissman and co-workers at Washington University in 1979 [18]. The inherent loss of sensitivity for broadband detection of transient paramagnetic states can be compensated by accumulation of the spectra after each light flash. Moreover, an orders-of-magnitude signal enhancement via electron-spin polarization effects can be utilized which occur in many photoreactions with transient reaction intermediates, e.g., triplets, radicals, radical pairs, detected before spin-lattice relaxation can thermalize them. By now, the time resolution of TREPR has been pushed to the 10 ns range in a broad range of mw frequencies from S-band (4 GHz), X-band (9 GHz), K-band (24 GHz), Q-band (35 GHz) up to the high-field EPR frequencies 95, 120 and 240 GHz [14, 19–23].

The next step forward was pulsed EPR for achieving fast time resolution. It was as early as 1950 when E. L. Hahn [24] at Urbana reported that he had applied rf pulses at NMR frequencies and invented the nuclear spin-echo detection. This, with the introduction of Fourier-transform (FT) NMR by R. R. Ernst at ETH Zurich [25, 26] and the availability of powerful computers for fast FT NMR in the late 70's, opened the arena for pulse NMR spectroscopy and with all its potential for recording multi-dimensional spectra of complex biosystems in the liquid and solid state and, of course, for applications in medical imaging. But it took almost a decade before R. J. Blume at Columbia [27] observed the first electron spin echoes analogous to Hahn's nuclear spin echoes. And it took many more years before electron spin echo-detected EPR (ESE) methodologies gained sufficient experimental and theoretical backing to revolutionize EPR spectroscopy in a way rather similar to what had happened in NMR spectroscopy decades earlier.

Pulse EPR spectroscopy has many founders, both from the theoretical and the experimental side. In the early 1970's, K. M. Salikhov at Novosibirsk [28] laid the theoretical foundation for several advanced pulse EPR methods. For example, he developed the theory of electron spin phase relaxation by stochastic modulation of the dipole-dipole interaction between paramagnetic centers and its effect on the ESE decay [29]. He suggested the first pulse ELDOR (PELDOR) protocol to observe the modulation of the ESE signal due to the electron-electron dipolar interaction of weakly coupled biradical systems in disordered solids [30]. The analogous NMR double-resonance...
ENDOR (Electron-nuclear double resonance)

Thorough accounts of multifrequency ENDOR, and its extension to electron-nuclear-nuclear TRIPLE resonance spectroscopy have been recently published, and we suggest them for further reading [34–36]. Conceptually, several different types of ENDOR spectroscopy have to be distinguished:

Local ENDOR

It was a milestone in the history of magnetic resonance spectroscopy when, in 1956, George Feher [37] at Bell Labs invented a reconciliatory “EPR meets NMR” experiment for which he coined the name ENDOR. This acronym seems to have been inspired by the Old Testament [1st Samuel 28:7-20], telling the story of the witch of Endor who made visible the invisible. Similar to an ENDOR experiment, when out of an unresolved inhomogeneously broadened EPR line well-resolved hyperfine lines appear – looking like an NMR spectrum (assuming no nuclear quadrupole interactions). They appear at

\[ \nu_{\text{ENDOR}} = \nu_n \pm A/2 \]  

with the nuclear Larmor frequency \( \nu_n \) = \( g_n \mu_B B_0 / h \) and the hyperfine coupling parameter \( A \), which contains isotropic and anisotropic contributions of the hyperfine tensor. The resolution enhancement becomes particularly drastic when nuclei with different magnetic moments are involved. Their ENDOR lines appear in different frequency ranges and, providing that their Larmor frequencies are separated at the chosen Zeeman field value \( B_0 \), the different nuclei can be immediately identified. In the case of an accidental overlap of ENDOR lines from the different nuclei at X-band (9.5 GHz, 0.34 T) the lines can be separated when working at higher Zeeman fields and mw frequencies, for instance at 3.4 T, 95 GHz [38] or even at 12.9 T, 360 GHz [39], see Fig. 2. In biological molecules with several non-proton magnetic nuclei this is extremely helpful for analyzing complex spin systems by means of their nuclear Zeeman and hyperfine interactions.

Distant ENDOR

In contrast to local-ENDOR techniques, in distant-ENDOR experiments the NMR resonances are induced on nuclei so far remote from the electron spin in a paramagnetic center that the nuclear-nuclear dipolar interactions become larger than the electron-nuclear hyperfine interaction. In other words: Distant nuclei are only weakly coupled to the electrons but are more strongly coupled to each other, for details, see [40]. Distant-ENDOR experiments, therefore, will produce typical wide-line NMR spectra – but with EPR sensitivity – and this from either disordered or single-crystal samples [40–42]. The distant-ENDOR polarization mechanisms in organic systems at \( T \leq 4 \) K, and the spin kinetics behind them, have been thoroughly studied for protons in copper Tutton salts [43] and for \(^1\)H, \(^2\)H, and \(^13\)C in partially deuterated succinic acid [41].

Pulse ENDOR

Actually, all ENDOR detection techniques (cw and pulsed) are sensitive to the nuclear (and electronic) relaxation rates. As a rule of thumb: “In most practical situations, cw ENDOR is the method of choice for the measurement of small hyperfine couplings in liquid solution, whereas in solids pulse ENDOR is often superior” [44]. For solid-state samples ESE-detected pulse ENDOR versions were introduced by W. B. Mims (1965) at Bell Labs [45] and E. R. Davies (1974) at Clarendon [46]. In a pulsed ENDOR experiment, the microwave pulses are used to generate an electron spin echo whose intensity is then recorded as a function of the pulsed rf frequency. If it hits a nuclear spin transition, the electron spin echo intensity will change, and the rf sweep over a certain frequency range results in the ENDOR spectrum.

Pulsed ENDOR spectroscopy offers several distinct advantages over the conventional cw technique: The ENDOR effect can be as large as the electron spin echo intensity itself (cw ENDOR reaches only about 1 to 10% of EPR); it requires no critical balance of rf power and relaxation times (a condition which has to be met in many cases of cw ENDOR); it is less susceptible to artifacts as there is neither an rf nor a microwave field applied during the detection period; it gives immediate access to all relaxation times of a spin system. Therefore, pulse ENDOR has been the commonly used technique in many laboratories in the last decades [47]. The Mims ENDOR technique is most suited for weakly coupled nuclei, i.e., nuclei with small hyperfine coupling constants. The Davies ENDOR technique is most suited to detect nuclei with large hyperfine couplings.
ESEEM (Electron spin echo envelope modulation)

Besides ENDOR there is another type of EPR-based hyperfine spectroscopy that is widely used: ESEEM. In both ENDOR and ESEEM experiments, the nuclear resonance transitions at NMR frequencies are monitored indirectly through EPR transitions. While in the pulsed ENDOR experiment the signal arises from the combined use of both mw and rf pulses, which directly excite the EPR and the NMR transitions sequentially, in the ESEEM experiment the NMR transitions are observed due to state mixing by dipolar hyperfine interaction resulting in semi-forbidden and allowed EPR transitions, respectively. These are coherently excited using short, intense microwave pulses. While ENDOR is a frequency-domain experiment, the ESEEM experiment is a time-domain experiment. Thus, to measure the electron-nuclear hyperfine and nuclear quadrupole interactions by EPR techniques, the nuclear transitions can be driven either directly by rf fields as in ENDOR or, as a more indirect alternative, by resonant microwave pulses as in ESEEM. This single-resonance technique was introduced by W. B. Mims in 1972 [48]. Efficient mixing of the nuclear and electron spin eigenfunctions by the dipolar hyperfine interaction is mandatory to obtain detectable echo modulations. Consequently, the strength of the external magnetic field has to be properly chosen to approximately balance the Zeeman splitting of the nuclear sublevels and the respective hyperfine splittings (“cancellation condition” [49]). For protons, the cancellation condition is often met in X-band (9.5 GHz) EPR, depending on the magnitude of their hyperfine couplings, but not at high Zeeman fields. The situation reverses, however, for nitrogen nuclei in W-band (95 GHz) EPR. First successful W-band high-field ESEEM measurements of $^{14}$N hyperfine and quadrupole interactions in disordered powder samples were performed in Berlin in 1998 [50]. Ten years later, this work was extended by elaborate W-band ESEEM studies on nitroxide spin-label molecules to explore the respective sensitivity of the g-, hyperfine- and quadrupole-tensors for probing polarity and proticity effects of the solvent matrix [51]. In some cases, also $^{15}$N hyperfine couplings have a favorable magnitude, which allows one to meet the cancellation condition even at X-band ESEEM [52].

HYSCORE (Hyperfine sublevel correlation spectroscopy)

A very powerful technique for measuring electron-nuclear hyperfine couplings of complex molecular systems is HYSCORE. It is essentially a two-dimensional ESEEM experiment in which correlation is transferred from one electron spin manifold $m_S$ (e.g., $m_S = +1/2$) to nuclear frequencies in the other $m_N$ manifold (e.g., $m_N = -1/2$). It is based upon the COSY (Correlation Spectroscopy) NMR experiment and was introduced by P. Höfer, M. Mehring and co-workers [53] at the University of Stuttgart in 1986. This 2D experiment improves the spectral resolution by spreading overlapping peaks over two dimensions and provides information which is difficult to obtain in a 1D ESEEM experiment. Hence, HYSCORE has become the standard experiment for the measurement of complex hyperfine and quadrupole spectra [44] and produces complimentary and comparable information to the ENDOR experiment. As in a standard ESEEM experiment, the peaks observed are essentially an NMR spectrum of nuclei that are coupled to the electron. HYSCORE on systems with many nuclei can make ESEEM spectra much more manageable to extract unambiguously the electron-nuclear spin interactions. Like in any other ESEEM variant, also HYSCORE is best to be performed close to the exact cancellation condition [44].

EDNMR (ELDOR-detected NMR)

As we have seen, several pulsed EPR techniques exist that are capable of probing nuclear transition frequencies of paramagnetic compounds, e.g., ESEEM-based techniques as well as ENDOR-based techniques. There is another technique to unravel congested nuclear spectra which has become very popular in recent years, and this is pulsed ELDOR-detected NMR [54]. The acronym ELDOR stands for electron-electron double resonance, i.e., two mw fields are involved. The EDNMR experiment was introduced by A. Schweiger and co-workers at the ETH Zurich in 1994 [54]; it excels by its potential to determine small hyperfine interactions in disordered systems. Polarization transfer in EDNMR involves allowed and forbidden transitions of the hyperfine-coupled electron and nuclear spins. The nuclear transitions of the spin manifold are probed indirectly by using a second strong and long microwave pulse (high-turning-angle (HTA) pulse), which drives forbidden electron transitions. $\Delta m_S = \pm 1; \Delta m_I = \pm 1$ that is, transitions where both the electron and nuclear spin change their projection direction. Such “forbidden” transitions in the spin manifold become weakly allowed in the presence of an anisotropic hyperfine interaction or a nuclear quadrupole interaction.

Compared to ENDOR, high-field EDNMR presents several advantages for the investigation of low-$\gamma$ nuclei coupled to the electron spin of metalloproteins. EDNMR is more robust against fast electron spin-lattice relaxation, $T_1$, and spectral diffusion than ENDOR.

Recently, the Goldfarb group at the Weizmann Institute in Rehovot has extended EDNMR to a correlation method with the acronym THYCOS (triple resonance hyperfine sublevel correlation spectroscopy) [55]. It combines ENDOR and EDNMR in a manner similar to the pulsed TRIPLE method [56, 57].

PELDOR (Pulsed electron-electron double resonance)

In EPR spectroscopy, practically all its sub-disciplines, such as cw, time-resolved and pulsed EPR, ENDOR and ELDOR techniques, show distinct virtues at high magnetic fields and microwave frequencies as compared to standard X-band spectroscopy with its much lower Zeeman fields [14, 15]. Recently, it has also been demonstrated that distance measurements between paramagnetic centers by PELDOR, a technique which often is also called DEER (double electron-electron resonance), can be performed at high Zeeman fields [58–61] and that by doing so important additional information concerning the three-dimensional molecular structure – beyond distances – can be obtained. Measurements of distances between spin labels in large molecules by PELDOR methods have become very popular in the last few years; usually they are carried out at X-band frequencies (for overviews, see for instance [62–66]). The measurements at high field additionally reveal the relative orientations of the g-tensors of the two coupled paramagnetic centers and, thereby, of the electron spin-carrying molecular domains [58–61, 67].

Long-range distance measurements on chemical and biological systems with the scale of a few nm up to almost 10 nm are an important area of application for pulse EPR spectroscopy [68]. Pulsed EPR methods exploiting the electron-electron dipolar interaction between two spin centers have been used in the past to yield spatial distributions in solids. Several methods of practical importance have emerged and, although their acronyms are often not too informative about their task specificity, they all are based on modifying the local dipolar field seen by one electron spin when manipulating a dipole-dipole coupled second electron spin – thereby modulating the spin-echo intensity. Hence, the common generic name is Pulsed Dipolar EPR Spectroscopy.
copy. The electron dipolar echo modulation is produced by a 2- or 3-pulse sequence with a pulse at either the same frequency [69] or at a different frequency [70, 71]. It is the different-frequency variant, using selective microwave pulses, which became the most popular one under the names PELDOR or DEER. Like many other inventions in pulsed EPR, it originates from NMR analogues, here from a concept in solid-state NMR [31].

The goal of PELDOR is the selective measurements of the electron-electron dipolar coupling between two spin-carrying domains, which is a function of their interspin distance and relative orientation. The main advantage of pulse versus cw EPR techniques in this endeavor is the ability to separate the electron-electron coupling from other interactions, such as electron-nuclear hyperfine interactions, and to reduce inhomogeneous line broadening. Thereby, the distance range that can be probed is extended to about 8 nm. Yu. D. Tsvetkov and his co-workers in Novosibirsk [30, 72] established the 3-pulse electron-electron double resonance technique (PELDOR or DEER) in 1981. Later it was extended to a 4-pulse sequence for dead-time free detection [44, 66, 73]. Other powerful pulse sequences for measuring electron-electron frequencies and, thereby, distances have been invented, for example the single-frequency 6-pulse techniques DQC (double-quantum-coherence) by J. H. Freed and co-workers at Cornell [63, 74] and RIDME (relaxation-induced dipolar modulation enhancement) by Kulik and co-workers in Novosibirsk [75].

In 2006/2007 pulsed high-field electron dipolar spectroscopy, specifically PELDOR, was introduced for resolving the relative orientation of weakly coupled radical-pair partners in a frozen-solution sample in addition to measuring their distance. This extension of electron dipolar spectroscopy to high microwave frequencies and Zeeman fields was accomplished independently by the groups of T. F. Prisner (Frankfurt (Main)) [59, 76, 77] at 180 GHz, G. Jeschke (Konstanz/Zurich) [61] at 95 GHz and K. Möbius (Berlin/Mülheim) at 180 GHz, independently by the groups of T. F. Prisner and K. Möbius (Berlin/Mülheim) [59, 76, 77] at 180 GHz, G. Jeschke (Konstanz/Zurich) [61] at 95 GHz and K. Möbius (Berlin/Mülheim) at 95 GHz [60] at about the same time.

In Fig. 3 typical advanced EPR experiments at high fields on laser-pulse created radicals and radical pairs are summarized showing the mw and rf irradiation schemes of a variety of cw and pulse techniques. We take the view that the arsenal of modern EPR techniques in general, and of high-field EPR in particular, provides powerful and versatile tools desperately needed for elucidating structure and dynamics of complex biosystems in both stable and transient states of action. These tools can provide details of molecular information complementary to information from other biophysical techniques established in the field, specifically NMR spectroscopy or X-ray crystallography.

4. Applications of high-field EPR techniques on frozen-solution systems

For typical applications of this arsenal of advanced multi-frequency EPR techniques in biochemistry and molecular biology, we refer to our recent review article [1] and the original references therein. To considerable detail, three case studies are described to give an impression of the power of the spectroscopic techniques and the molecular information obtained by them. Here, only short summaries will be given.

4.1. Case Study I: High-field PELDOR and ENDOR structure determination of cation- and anion radical pairs in reaction centers from photosynthetic purple bacteria and cyanobacteria

Photosynthesis is the most important process that enables life on Earth by converting the energy of sunlight into electrochemical energy, which is needed by higher organisms for synthesis, growth and replication. The so-called primary processes of photosynthesis are those in which the incoming light quanta, after being harvested by “antenna” pigment/protein complexes and channelled to the reaction-center (RC) complexes by ultra-fast energy transfer, initiate electron-transfer (ET) reactions between protein-bound donor and acceptor pigments across the cytoplasmic membrane. Thereby, a charge-separated radical pair is created which, in the case of the photosynthetic purple bacterium *Rhodobacter (Rh.) sphaeroides*, is formed from the “special pair” donor and quinone acceptor, $P_{680}$Q$_A^-$. The cascade of charge-separating ET steps of primary photosynthesis competes extremely favorably with wasteful charge-recombination ET steps thereby providing almost 100% quantum yield. Fast optical experiments have indicated that, to ensure the high efficiency of solar-energy conversion, conformational changes of the protein cofactors in their binding sites might occur during light-induced ET.

The flexibility of the Q$_A$ quinone binding site has initiated speculations about its functional role in the charge-separation/charge-recombination electron-transfer cycle. Such speculations related to potential structural changes associated with Q$_A$ reduction were fostered by an early observation by D. Kleinfeld, M. Y. Okamura and G. Feher [78] who showed by optical spectroscopy that the rate of recombination from the transient radical-pair state $P_{680}^-Q_A^+$ to the ground state $P_{680}Q_A^+$ differs in RCs cooled to cryogenic temperatures in the dark (dark-adapted RCs) compared to RCs cooled under continuous illumination (light-adapted RCs). The slower recombination kinetics in the light-adapted sample

![Figure 3. Microwave (mw) and radio-frequency (rf) cw and pulse irradiation schemes of various time-resolved EPR techniques. In the case of photochemical EPR applications, the initial laser excitation pulse $h\nu$ starts the photo-reaction with paramagnetic intermediates. In the case of EPR applications on stable paramagnetic systems, the laser pulse is, of course, omitted. Abbreviations: TREPR (transient EPR), ENDOR (electron-nuclear double resonance), TRIPLE (electron-nuclear-nuclear triple resonance), ESE (electron spin echo), HYSCORE (hyperfine sublevel correlation spectroscopy), PELDOR (pulsed electron-electron double resonance), EDNMR (ELDOR-detected NMR), HTA (high turning angle).](image)
was explained by suggesting changes of the donor-acceptor average distance (by ≈1 Å) and of its distribution. At variance with this model, Savitsky et al. [60] and Flores et al. [79] concluded from their orientation-resolving W-band high-field dipolar EPR studies (at T = 90 K) of the transient P_{865}Q_{A} in dark- and light-adapted RCs that no substantial rearrangement at the QA site occurs under illumination, see Fig. 4.

The parameters ν_{||} and B_{Q||}, which are highly specific for the radical-pair structure (ν_{||} for the distance, B_{Q||} for the orientation, see ref. [60]), can be directly read off from the PELDOR spectra. The values for the dark-adapted sample fully agree with those for the light-adapted sample. Also the angular distribution width, ΔB_{1/2}, is the same within experimental error.

In other words, from PELDOR we learn that there is no conformational redistribution of QA under light-driven reduction.

4.2. Case Study II: High-field ENDOR and ELDOR-detected NMR spectroscopy on the oxygen-evolving complex of Photosystem II

Among the main fields of EPR applications is the investigation of transition metal ions, which often have one or more unpaired electrons in their d-orbitals [81]. Many proteins carry more than one metal ion or even combinations of metals to fulfill certain tasks in their complicated catalytic cycles. Illustrative example are the two photosystems of oxyphotgenic photosynthesis, Photosystem I and Photosystem II. They contain Mg-complexes (chlorophylls), non-heme iron, cytochromes and iron-sulfur centers for light harvesting, charge separation and electron transfer – as well as a tetranuclear manganese/calcium cluster for catalytic water oxidation, the famous “oxygen-evolving complex” (OEC). The OEC is one of the most interesting biocatalytic metal centers, it is directly related to the topfield of solar-energy research [82–84].

It contains a protein-bound Mn_{4}O_{5}Ca cluster and is located in PS II of all organisms performing oxygenic photosynthesis. According to B. Kok [85] the OEC passes various Mn oxidation states with electron spin states S = 5/2, 4/2, and 3/2 for its function, called the S-state cycle S_{0} to S_{4}. The subscripts indicate the number of stored oxidizing equivalents in the Mn cluster. An accurate picture of the electronic structure of the OEC is critical to an understanding of the mechanism of water oxidation. It has been shown that all S-states display paramagnetism [86] with S_{0} and S_{2} possessing an effective half-integer spin ground states, S_{eff} = 1/2. These two states are readily accessible by cw and pulse EPR techniques, and detailed information has been collected on the electronic structure of them.

High-field EPR spectroscopy turned out to be particularly powerful for determining the identity (H_{2}O/OH\(^{-}/O_{2}^{-}\)) and location of water-derived species bound at or in the vicinity of the Mn_{4}O_{5}Ca cluster. This can be achieved via the detection of the coupling of magnetic nuclei, \(^{1}\text{H}/^{2}\text{H}(I = 1/2, 1)\) or \(^{17}\text{O}(I = 5/2)\), to the S_{eff} = 1/2 states. Recently, we have addressed this question using high-field \(^{17}\text{O}-\text{EDNMR}\) observing exchangeable \(^{17}\text{O}\) “water” signals [87]. The \(^{17}\text{O}\) EDNMR at 94 GHz is shown in Fig. 5a. Both single- and double-quantum transitions were observed and analyzed yielding three different \(^{17}\text{O}\) hyperfine couplings. They were assigned (Fig. 5b) by comparison with \(^{17}\text{O}\) labelled model complexes [87]; the result is consistent with the recent high-resolution X-ray structure [88]. We note that EPR techniques have contributed strongly to the understanding of the electronic structure of the complex in different states of the S cycle, as well as to the binding of water, proton release and O_{2} formation.

Figure 4. W-band PELDOR spectra of the spin-correlated radical pair P_{865}Q_{A} in Zn-substituted RCs from Rb. sphaeroides at 90 K. (a) in the sample frozen in the dark, (b) frozen under continuous illumination. Only those PELDOR responses are shown that were used to probe the spectral position, B_{Q||} within the Q_{A} EPR spectrum corresponding to the parallel dipolar frequency, ν_{||}. The observer microwave frequency is fixed at the value corresponding to the field value B', while the pump microwave is swept through the field region B'. Upper part: The individual EPR spectra of P_{865} and Q_{A} are shown for referring to the spectral positions. Middle part: Contour plot of the positive Fourier amplitudes of the PELDOR echo decays. Lower part: The contour-plot amplitude (at the slice position) vs. magnetic field 17O-EDNMR observing exchangeable 17O “water” signals [87]. The 17O EDNMR at 94 GHz is shown in Fig. 5a. Both single- and double-quantum transitions were observed and analyzed yielding three different 17O hyperfine couplings. They were assigned (Fig. 5b) by comparison with 17O labelled model complexes [87]; the result is consistent with the recent high-resolution X-ray structure [88]. We note that EPR techniques have contributed strongly to the understanding of the electronic structure of the complex in different states of the S cycle, as well as to the binding of water, proton release and O_{2} formation.

Figure 5. a High-field ELDOR-detected NMR spectrum at W-band (94 GHz) obtained at center field in the W-band EPR spectrum of the S2 state of the OEC (spinach PS II), in which the water has been exchanged 3x with H_{2}^{17}O (90% 17O enrichment). 14N and 17O resonances are detected. The 14N lines stem from the histidine bound to Mn_{4}. Three types of 17O hyperfine couplings were analyzed (shown in green, orange and purple) using both the single- (SQ) and double-quantum (DQ) transitions. The assignments to the oxygens of the OEC are shown in panel b. For further details, see [87].
5. Concluding remarks

Modern multifrequency EPR methods, in particular at high magnetic fields and microwave frequencies, provide unique information on structure and dynamics of stable and transient radicals and radical pairs participating in chemical and biological processes. This specifically applies to the elucidation of mechanisms for fine-tuning electronic properties of donors and acceptors in electron- and proton-transfer reactions in proteins via weak interactions with the matrix environment, such as hydrogen bonding to specific amino-acid residues and unbound water molecules.

Coming back to the title question of our Essay, “will solid-state EPR and NMR converge at high magnetic fields?”, it seems to us that the analogue of C. P. Snow’s grievance, the gap between the two cultures, is continuing to exist – but is in the process of being bridged. More and more scientists realize that a “Third Culture” of convergence is taking over in the magnetic-resonance community – instead of continuing to bemoan the gap between EPR and NMR. The core notion of this convergence is that as the EPR and NMR communities achieve similar levels of scientific and technological development they will become more alike in terms of mutual understanding and recognition. This convergence involves more than the simple movement from diversity to uniformity. Coming from different directions, it involves movement toward a common point by an increase of abilities for some cases. This convergence calls for a willingness for the crossing of thresholds rather than changes in absolute differences which, of course, will remain.

Indeed, both EPR and NMR cultures are driven by the same motivation – to understand the spin interactions in complex molecular systems for the purpose of revealing their structure and dynamics – be it from the viewpoint of material sciences, biological or medical sciences. For example, both EPR and NMR are indispensable as screening tools for structure-determination protocols for structural but not yet crystallizable proteins. The big issues in the natural and life sciences – Health and Disease, Environment, Sustainable Energy and Learning from Nature – ask for the best of all methodologies to apply. This will work best only by collaboration between scientists from many different fields of education and expertise. It’s high time to join forces and turn down artificial borders between the NMR and EPR communities!

Acknowledgments

Over the years, numerous co-workers – students, postdocs, and colleagues – have contributed to our high-field EPR work on proteins. To all of them we want to express our gratitude and appreciation. Our laboratories have enjoyed generous financial support primarily by the Deutsche Forschungsgemeinschaft, for example in the frame of the Priority Program SPP 1051 “High-field EPR in Biology, Chemistry and Physics”, the Collaborative Research Center SFB 498 “Protein-Cofactor Interactions in Biological Processes” and the Group Project MO 132/19-2 “Protein Action Observed by Advanced EPR”.

We gratefully acknowledge continued support by the Max Planck Society and the Free University Berlin.
Britt R. David grew up in a farming community in rural North Carolina, before attending NC State University as a Physics major. He then began the Physics Ph.D program at UC Berkeley, where he joined the laboratory of Melvin P. Klein (IES Fellow, 1999). He worked with Mel’s group (along with Professor Ken Sauer of UCB Chemistry) doing X-ray spectroscopy of the Photosystem II Manganese Oxygen Evolving Complex (OEC), but decided that in the long run EPR held more interest to him. This led to his writing a grant proposal to the US Department of Agriculture in order to obtain needed components to build an X-band pulse EPR spectrometer to be applied to OEC studies. This being successful, he put together the pulse spectrometer using the new parts (TWT, preamps, timing circuits, etc) along with a lot of components already in the Klein/Sauer labs. He designed a waveguide coupled loop gap resonator probe that was stable in bubbling liquid He in the quartz immersion dewar that was available in the lab. The “multiline” Mn EPR signal from the S2 state of the Kok cycle had recently been reported by Siderer and Dismukes, so with the pulse machine finished this was deemed a good target for study, along with a set of mixed valence Mn model complexes that Mel Klein had previously worked on with Steve Cooper and Melvin Calvin. David carried out the first pulse EPR studies of the Mn multiline signal, and reported in JACS ESEEM evidence for a nitrogen protein ligand to the Mn cluster, along with ammonia binding studies (with Jean-Luc Zimmermann) that pointed to direct ammonia ligation to Mn in such-treated PSII membranes.

With his Physics Ph.D dissertation completed in 1988 Dr. Britt looked for an independent faculty position, and was happy to begin as an Assistant Professor of Chemistry at the nearby University of California, Davis (1989). One big plus at Davis was the presence of August Maki (IES Fellow, 2000), along with other strong research groups in magnetic resonance and bioinorganic chemistry. Dr. Britt and one of his first students, Brad Sturgeon, built a wideband 8–18 GHz pulse EPR with a microwave synthesizer source. They made a push to implement pulse ENDOR capabilities with this new instrument, adding this important pulse EPR technique, complementary to the ESEEM method he had previously used. The other new student, Lane Gilchrist, mostly focused on PSII, and his paper assigning a recently discovered EPR signal in Ca-depleted PSII to a diradical center involving the Mn cluster and the tyrosine radical \( Y_z \) remains one of the lab’s most cited papers. Another new...
Interview with Yurii Tsvetkov on the occasion of His Zavoisky Award 2013

Dear Professor Tsvetkov, on behalf of the readers of the EPR newsletter we congratulate you on your Zavoisky Award 2013. We are most appreciative that you agreed to answer the questions of this interview. Why did you start towards your career in science?

I was born in 1933 in a family of an engineer-architect and I belong to the generation whose childhood dates to the years of WWII. In the beginning of the 1950s I finished studies at school, and my parents’ dream was that I become, like my father, an architect. As often happens, I took my own path. At that time, youngsters were mainly attracted by two professions: as a nuclear physicist or as a diplomat. The popularity of the first profession was determined by the first successes of our country in its nuclear project. These successes were covered by a veil of secrecy that added a certain romance to the profession of a physicist. The career of a diplomat had the allure under the conditions of the Iron Curtain of journeys and the life abroad. It was necessary to choose resolutely between these two professions. After some hesitations, I chose the first and entered the Faculty of Chemical Physics of the Moscow Physical Technical Institute. And although I did not manage to be associated with nuclear physics, I do not regret my education at this famous institute. Thus, my career in science is a matter of chance. I never felt sorry about this and do not know what sort of diplomat I would have been.

Who introduced you into magnetic resonance?

It was mainly by chance as well. As two- and three-year students we had to examine and read scientific journals in order to practice English and get acquainted with publications close to our specialization. When examining the literature on spectroscopy, by chance I used several articles of the Oxford school of paramagnetic resonance for reading and translating. This spectroscopy seemed interesting to me and I had an idea to construct a simple EPR spectrometer for my laboratory pracitcum work. I implemented this idea together with my fellow student Yu. N. Molin. We got EPR signals from coals and demonstrated them to our tutors. Professor V. V. Voevodsky was especially interested in this work. Probably, he was the first to evaluate the possibilities of EPR in physical-chemical studies, particularly in the studies of free radicals. He offered us to work in his laboratory at the Institute of Chemical Physics, to make a more sensitive spectrometer and perform EPR studies as our degree work. My career in EPR spectroscopy began in this manner.

What is the driving force for you in your research?

The driving force for any researcher is curiosity and doubt; the desire to understand why something happens in this way and not otherwise in the field of science where he works. This is an eternal pursuit for truth that is never attainable in its absolute meaning.

What part of your research is most dear to your heart and why?

You cannot love scientific research with all your heart like you can a girl. Each research project is dear as a step to understanding. With age you begin to understand that the most important of your many published works are those that opened the way for other researchers and that became popular among colleagues working in the field of EPR spectroscopy and its applications. For example, I consider as such our work...
with V. N. Panfilov, in which we demonstrated for the first time the possibility of using EPR to study flames and other radical reactions in the gas phase. The development and creation of pulsed EPR spectroscopy methods opened a variety of new directions for EPR applications in chemistry and biophysics for me and my students and colleagues. I note that we performed almost all these studies together with the theorists K. M. Salikhov and A. G. Maryasov. We managed to find the radical tracks in irradiated organic materials (A. M. Raitsimring) that turned out to be important for the theory of radiation chemistry, to obtain new data about the magnetic relaxation of free radicals and atoms in the solid phase (A. D. Milov), to find and study weak electron-nuclear interactions in randomly oriented media, the so-called ESEEM effects (V. F. Yudanov, S. A. Dikanov). Important works on the molecular dynamics were performed together with S. A. Dzuba. But, probably, it was the development and applications of PELDOR spectroscopy where A. D. Milov and I achieved the most success. This work opened new horizons and applications in chemistry and, especially, in biology, for the EPR world.

In spite of the current problems in Russian science, our EPR results warm my heart. In a total of sixty years in EPR, there is no work of mine that I am ashamed of. I am deeply grateful to all my coauthors.

What is your message to the younger generation of the EPR researchers?

EPR is a powerful tool for the studies with a sound theoretical and experimental basis. It should be used to solve the diverse array of current problems in physics, chemistry and biology. My experience showed that this is one of most interesting occupations in science.

Search for and find new applications of EPR, develop the theoretical and experimental methods. I am sure that you will find deep satisfaction on this path and be filled with the desire to learn more and more. I wish you success!

Awards

On April 28 of this year (2014), George D(aniels) Watkins reached the age of 90 years. It is highly appropriate to present a brief summary of a career dedicated to EPR research in semiconductor physics.

George was born in Evanston, Illinois, USA. He started his studies in physics at Randolph Macon College (Ashland, Virginia) where he obtained the bachelor’s degree in 1943. After military service as a Radar Officer in World War II, he went to Harvard where he obtained his Ph.D. on NMR studies in 1952, with Robert Pound as his thesis advisor. He then joined the General Electric Research and Development Center in Schenectady, New York, where he stayed until 1975. During this period he served in part-time professorships at Rensselaer Polytechnic Institute (Troy, 1962–1965) and at the State University of New York at Albany (Albany, 1969–1973). In 1975 he moved to Lehigh University in Bethlehem, Pennsylvania, to become the first Sherman Fairchild Professor of Physics. His official retirement followed in 1996 at the age of 72, but the true end of his active involvement in research was some nine years later.

In these years at General Electric and Lehigh University, George was intensely involved in his field of research, which concerned point defects (radiation-produced defects, crystal lattice defects, impurities) in various semiconductors. Through the relevance and depth of his research he naturally became the most prominent researcher in this field. His eminence was recognized by several major awards. To mention a few: in 1978 he received the Oliver E. Buckley Condensed Matter Physics Prize of the American Physical Society, in 1988 he was elected to the U. S. National Academy of Sciences, and in 1999 he received the Silver Medal Award for Physics and Materials Science of the International ESR/EPR Society, of which Society he was elected Fellow in 2005.

Several times George stayed in Europe for joint research with prominent colleagues in their laboratories. As an NSF Senior Fellow he spent 1966–1967 in the Clarendon Laboratory of Oxford University as the guest of Brebis Bleaney. In the years 1983–1984 he went to Germany to work with Hans Queisser in the Institut für Festkörperforschung of the Max Planck Institute in Stuttgart, and with Martin Spaeth in the Hochschule in Paderborn. Another visit to Europe took place in 1990–1991 to Hermann Grimmeiss in Lund University, Sweden, Ed Lightowlers in King’s College London, and Jürgen Schneider in Freiburg, Germany. In addition he made lecture trips to the Soviet Union (1973, 1984, 1988), China (1977, 1987), Brazil (1985), Poland (1992), South Africa (1995), and Pakistan (1998).

There are a few topics, among his wide research, that must be put into the spotlight here. It all started in the sixties in the General Electric period with the studies of radiation-produced defects. This was in the age that space capsules were sent in orbit into environments with heavy radiation background, and had to stay there for years without an option to replace a damaged component. The standard procedure of introducing primary defects for

 Daniella Goldfarb – President of ISMAR

Daniella Goldfarb (Weizmann Institute of Science, Rehovot, Israel) was elected President of ISMAR for the period 2014–2018. Elena Bagryanskaya (Institute of Organic Chemistry, Russian Academy of Sciences, Novosibirsk, Russia), Wayne Hubbell (Jules...
study by heat treatment and quenching was not appropriate for silicon because of its extreme sensitivity to contamination. Therefore, the clean method of MeV electron irradiation was adopted for producing native defects. It appeared immediately that in room temperature experiments only defect structures with some complexity were observed. This led to the exemplary papers on the oxygen-vacancy complex, the phosphorus-vacancy pair, and divacancies, with the corresponding EPR spectra B1, G8, G6 and G7, following the notation introduced by Watkins. This was the era of the productive collaboration between George and Jim Corbett (SUNY, †1981). An important discovery by this team was the high mobility of vacancies and interstitials in silicon. To observe the primary defects, therefore, Watkins had to devise a method for MeV electron irradiation of the EPR samples in situ at cryogenic temperatures. The EPR spectra G1 and G2 of positively and negatively charged paramagnetic vacancies were observed and studied in detail, supplemented by theoretical interpretations within molecular orbital schemes.

Another striking result was the unambiguous demonstration of the negative-U electronic properties of the vacancy and interstitial boron in silicon. These defects change their charge states at once by two units, a second electron or hole being effectively attracted by a first one. This required sophisticated experimental procedures, also involving the popular technique of Deep Level Transient Spectroscopy (DLTS). The negative-U phenomenon, reminiscent of superconductivity, had not been experimentally observed prior to this study in any material.

Some of the newly discovered phenomena were so uniquely revealed, confirmed and understood by Watkins that his name was attached to them. In this category there is the Watkins replacement mechanism accounting for the creation of interstitial impurities by knock out by self-interstitials, and also the Watkins vacancy model for late transition metal impurities. Watkins showed that for heavier transition metal elements, such as gold and platinum, the known structure of the negative vacancy provided a better starting point, for instance directly accounting for the orthorhombic symmetry, rather than by the model of Ludwig and Woodbury (1980). Among GE colleagues, the learned theoretician Frank Ham (†2002) should never be forgotten; George could sharpen his understanding by critical (lunch time) discussions with him. Together they published an impressive paper on the shallow interstitial donor lithium in silicon. Frank later joined George at Lehigh.

The unique experimental laboratory established by George at Lehigh served him well throughout his research career, allowing him to determine also the properties of native defects in the wide band gap semiconductors of the II-VI and III-V families that continue to advance electronics technology.

The world-wide reputation established by George attracted many researchers to collaborate with him at Lehigh to make defect studies under his guidance. I joined George for the second half of 1970, at the GE laboratory. My wife and I have an indelible memory of our stay in upstate New York. At Lehigh, his collaborators used the spectrometers for EPR and ENDOR, supplemented by a variety of optical techniques, such as photoluminescence or more sophisticated optically-detected magnetic resonance (ODMR), to develop theoretical models for a thorough understanding. Some of these eminent scholars were Joerg Weber from Stuttgart or Dresden, Yuri Goreliksky from Almavy, Leonid Vlasenko from St. Petersburg, Haflidi Gislason from Reykjavik, John Donegan from Dublin, Le Si Dang from Grenoble, Helena Nazaré from Aveiro, Kevin O’Donnell from Strathclyde, Bernd Itermann from Marburg, Kim Chow from Alberta, Yasunori Mochizuki from Tsukuba.

George celebrated his birthday in his present domicile, Richmond, Virginia, in the presence of his wife Carolyn, his children Bobbie, Paul and Ann, his six grandchildren and (at the time of writing) one great-grandchild. We wish him many more years to come in the circle of his family.

Rob Ammerlaan
Research Studies of Harden M. McConnell: Together with Graduate Students, Postdocs and Colleagues *

EPR newsletter Anecdotes

Harden M. McConnell

Physical chemistry of the future

Historically physical chemistry was the interface between physics and chemistry, where discoveries in physics were applied to the solution of chemical problems. Today of course physical chemists are also involved in the application and development of physical tools for the solution of biological and even medical problems. Since biology promises a nearly infinite reservoir of interesting problems to be solved, we can anticipate increasing activity in that direction. For physical chemists such as myself, this presents a conundrum. Biological problems are often problems of great complexity and interrelationships with other problems. One solution leads to another problem, and so on. A complete solution of a single problem can involve a lifetime of effort. So the physical chemist is best advised to collaborate with an established biologist, or MD, even though this has not been my style. With few exceptions, my collaborations have been largely confined to graduate students and postdocs. In my case the important exceptions have been Mark Davis in the Stanford Medical School, and Phillippa Marrack of the National Jewish Hospital who have provided cell lines that have been essential for our work in immunology.

Physical chemistry promises a continuing source of new techniques such as single molecule tracking and functional magnetic resonance imaging, both of which have become mature sciences in recent years. And of course, in my own areas of interest, there remain some subjects, such as critical phenomena, lipid membranes, molecular electronic structure theory, and protein folding that remain challenging in themselves without regard to specific applications. Continuous advances in computing power strengthen many techniques in current use and are likely to make new methods possible.

The young scientist – my experiences

When I say young scientist I am referring to an individual starting or seeking to do research, no matter his or her age.

My interest in science, particularly chemistry began when I discovered a box of copper sulfate crystals in the basement of my home in Washington D. C. I was perhaps 12 years old. One chemical quickly led to another. ‘Through out my life there was zero interference in my work (play) by my parents.’ I obtained a part-time job at a local grocery store on Saturday mornings, and on Saturday afternoons spent my earnings at Gilman’s chemical store (then on Constitution Ave) buying chemicals such as sulfuric acid, sodium, white phosphorus, and of course, perchlorates, sulfur and carbon. I built my own laboratory in the basement. I had no supervision whatsoever in my experiments. If I did many dumb things, never intended to harm anyone, which are best not described.

Regrets: I spent too little time working with electronics. During one summer and on Saturdays I worked as an analytical chemist, analyzing cooking gas for CO₂, H₂, CO, CH₄, and O₃, using a rather old fashioned apparatus where this gas mixture was passed through various liquid mixtures that would selectively absorb O₃ or another gas. The sourcing of the samples was sometimes dangerous I thought. The experiments were taken directly from the side of a blast furnace, whose top would alternately open and close. In between these two states the sample top would be bathed in flames when the top of the furnace was periodically closed. As a prank the operator of one blast furnace thought he would frighten me while I was taking a sample, and he almost fried me. Being surrounded by fumes two or three stories up in the air next to a blast furnace is a memorable event. Again, modern safety regulations and labor laws would doubtless prevent this activity. Now days many universities and medical schools do offer research internships for high school students.

My high school work was completed in three years, and I was offered a scholarship to George Washington University, which I gratefully accepted. The effort to spend only three years in high school and three years in college was to get as much education as possible before being drafted into the army. (At some point during this period I did try to enlist in the Naval Air Force but was turned down because of color blindness). I finished up at Cal Tech in 1950 and received an NRC postdoctoral fellowship.
for the physics Department at the University of Chicago. In normal times I think it is a mistake to speed through undergraduate school and graduate school. It is better to spend as much time as possible listening to seminars in different areas of science and obtaining experience in laboratories dealing with a variety of subjects.

Now, with respect to advice: For me, science and creativity tend to flourish when there is peace, social, political and economic stability. Throughout most of my lifetime I have been witness to war: WWII, the Korean war, the “cold” war, the war in Vietnam, and most recently the debacles in Iraq and Afghanistan. In my case I sought a pure science career, and my choice of the Spectroscopy Department at Shell was the perfect choice at the time. It was ideal in terms of independence, subject matter, and a supportive environment. At the time there was economic and job security at Shell. (The Korean War was still in progress.) I had no ambition with respect to earning a lot of money. The AT&T Bell labs at that time would have been another good choice. At the time I did not consider it likely that I could obtain a good academic job, as my graduate and postdoc work was good, but not spectacular, and the likelihood of my contributing anything really significant to electronic structure theory was remote. As I look back on my own history, I cannot avoid thinking of Adam Smith’s “invisible hand”, in my case guiding not commerce but scientific choices. Some of my choices were not only scientific, the constant threat of being drafted, the limited financial resources of my parents, and the realization that there were many young people who were smarter and better informed than I was. My main blunder throughout my career was a kind of scientific introversion – not paying attention to the scientific work of others. As a stellar example, Clyde Hutchison was starting up research on paramagnetic resonance not many steps away from where I sat in the Eckhardt Physics building of the University of Chicago. It’s never too late to look over your shoulder and see what others are doing, and talk to them.

At present a limited national commitment to scientific research again reduces the attractiveness and availability of academic positions. There seems to be an abundance of job openings in venture backed start-up companies, which provide ample opportunities for those suitable to the subject matter and the financial risk/reward opportunities. (However, one of my most talented mathematical physics students wound up working for AIG, which must have been nice while it lasted.) My own recommendations are to young scientists is to pick a job in which offers the greatest interest, and the most independence, and one where the “boss” is an established scientist, or at least has knowledge of what science is all about. Avoid start-ups run by newly minted MBAs. My own flirtation with the NSA arose partly from a latent interest in cryptography, but I doubt that would have been satisfying over the long hall. On the other hand a year or two working on quantum cryptography would be very attractive to me today. My student Don Chesnut joined DuPont, did good work there, then became a Professor at Duke. Another student, Seiji Ogawa joined the AT&T Bell labs, and discovered functional magnetic resonance imaging. He is now a professor in Japan. Most of my students have wound up in academic positions in universities or medical schools. A lower percentage are in industry or the NIH. Very few have left science or related technologies altogether. My impression is that today there are relatively few large stable companies where one can focus on fundamental scientific problems. Start-ups as a group probably offer the greatest opportunity where discovery matches the commercial objectives. My advice – count on guidance from common sense and Adam Smith’s “invisible hand”.

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In Memoriam

George Fraenkel
(1921–2009)

On April 16th, 2014 a special reception took place at Columbia University, NYC, to proffer the first George K. Fraenkel Fund Award to a Young Physical Chemist. The award went to Wei Min, Assistant Professor, Department of Chemistry, Columbia University for his developments in Stimulated Raman Scattering.

This award is in memory of George Fraenkel (July 27, 1921 – June 10, 2009), who joined the Department of Chemistry at Columbia in 1949. It was attended by many of his former Columbia University colleagues, as well as me, a former graduate student of his from 1958–1962.

Let me summarize George Fraenkel’s extensive and varied career. He received his B.A. from Harvard in 1942, Magna Cum Laude. His graduate studies at Harvard were interrupted by his involvement in a scientific research project under the direction of Professor E. Bright Wilson for the National Defense Research Committee, which shortly thereafter (1943) was moved to the Woods Hole Oceanographic Institute. He was in charge of developing sophisticated electronic equipment for the measurement of the explosive power of bombs, and conducted numerous field expeditions, including some to determine the optimum height to drop the atom bomb over Japan, and he received the Army-Navy Certificate of Appreciation in 1948. He returned to graduate school at Cornell University, after the war in 1946. After initial studies with Professor John G. Kirkwood, he wrote his dissertation under Nobel Laureate Peter J. W. Debye on visco-elastic effects and dielectric constants of solutions, and received his Ph.D. in 1949.

George then joined the Columbia chemistry department in 1949. Early on he became involved in the then new technique, especially for chemists, of electron spin resonance. He was one of the first chemists in this field. He and his early students developed unique high sensitivity, high resolution ESR spectrometers. His research group was the first to detect the ESR spectra of the free radicals of quinones, of the free radicals in molten sulfur, and of thermochromic compounds. By the time I joined his lab as a young graduate student, his was a very active and a leading ESR lab with focus in two major areas. First was the focus on the electronic structure of aromatic anion radicals in solution via observations of their proton, nitrogen-14, and carbon-13 hyperfine splittings. Second was the study of their electron-spin relaxation both by linewidth and line shape analysis (e.g. $T_2$), and by their saturation behavior (e.g. $T_1$). Numerous radical anions could readily be generated by electrochemical methods. My own activities centered upon the second, when unusual and surprising linewidth behavior was observed in some cases, e.g. para-dinitrodurene. This necessitated an extensive revision of the theory of linewidths in ESR, that we successfully carried out.

In 1965 he became chairman of the Columbia chemistry department, and then became Dean of the Graduate School in 1968 till 1983. It is the number three position in the Columbia University administration. He initially planned to continue his ESR lab half time with the other half time devoted to the Administrative Duties of his Deanship. But a few months after his accepting the deanship, Columbia University was thrust into major student uprisings, largely against the Vietnam War, and George was directly involved in the administrative challenges. As a consequence, by that summer he was forced to conclude that it would be necessary to devote all of his energies to the problems of the University, therefore giving up completely his active career as a research scientist. Through the skillful efforts of Dean Fraenkel, the Arts and Sciences at Columbia survived major crises and today are much stronger centers of scholarship. From 1983–1986, he held the position of Vice President of Special Projects, whereupon he returned to the Chemistry Department, retiring in 1991.

George was a Fellow of the American Physical Society, the American Association for the Advancement of Science, and the International EPR (ESR) Society. He was awarded the Harold C. Urey Award of the Gamma Chapter of Phi Lambda Upsilon (1972) and was elected to the Title of Officer dans l’Ordre des Palmes Académiques (1981), and served as Director and Treasurer of the Atran Foundation in New York City.

When I started as a graduate student at Columbia in 1958, I was very impressed with George as a teacher of Advanced Chemical Physics and Quantum Mechanics. I found his brand of Chemical Physics exciting and decided to join his ESR lab. My graduate work with him has been a great influence on my ensuing career at Cornell. George was a very wise and thoughtful man even when we extensively discussed/argued about a key point in the relaxation theory that George and earlier co-workers had not gotten quite right. He ultimately allowed his lowly graduate student to convince him of the fact. My interaction with George continued over many years, and was a constant source of advice and support for me.

Jack Freed
Etienne Boesman (1932–2014)

Een uniek mens is van ons heengegaan...

Etienne Boesman graduated both in mathematics and physics at Ghent University. He was the pioneer of EPR in Belgium, together with Dirk Schoemaker, who further developed his career at the University of Antwerp. They obtained their PhD degree in Physics at Ghent University in 1962, on the same day and both on solid state EPR. Etienne Boesman introduced the first EPR spectrometer (VARIAN) in Belgium, at Ghent University after it had been demonstrated at the Brussels World’s Fair (EXPO 58). The spectrometer became one of the highlights of the Laboratory for Crystallography and Study of the Solid State (now “Department of Solid State Sciences”), founded by Prof. Dr. Willy Dekeyser in Gent. The main topics of research were defect centers in alkali halides, kaolinite, V₂O₅, etc. In the early sixties Etienne Boesman spent one postdoc year at the laboratory of Prof. Stapleton in the US (Urbana) where he developed a strong interest in spin-lattice relaxation.

Over 3-4 decades (he retired in 1998), supervising many PhD students, including the later professors P. Matthys, F. Callens, S. Van Doorslaer and H. Vrielinck, he extended his research by introducing new techniques and topics. In the 70’s mainly chalcogen defects were studied by spin-lattice relaxation and EPR. In the same period he also became a professor at Ghent University (full professor in 1977), teaching mathematics, atomic and molecular physics, optics and quantum electronics and group theory. In the 80’s the research topics became more diverse, including also semiconductors (Ge), biological (tooth enamel) and synthetic apatites. More advanced spectrum analysis became necessary to study powders and the second VARIAN spectrometer was automated long before commercial spectrometers offered similar possibilities. The first Bruker spectrometer (ESP300) was installed and several new collaborations originated with e.g. the dentistry, chemistry, geology and nuclear physics departments. Also the quantitative trumps of EPR were explored studying dosimeter materials like alanine and sugars, taking advantage of the implementation of advanced statistical decomposition techniques in EPR (MLCFA). In 1992 the first (X-band) ENDOR in Belgium was installed and at the end of his career he witnessed the arrival of the Q-band ENDOR equipment. Using ENDOR the defect characterization was strongly improved and attracted also industrial interest (defects in silver halides in collaboration with AGFA). Also important results for EPR applications in dating and detection of irradiation in foodstuffs have been acquired. His work resulted in about 75 peer-reviewed publications.

We will remember Etienne Boesman as an enthusiastic researcher, combining excellent experimental and theoretical skills. As a professor, he was very much appreciated by his students and colleagues. He was a highly cultivated person, music-lover (mainly opera) and always “aimable”.

Freddy Callens, Ghent University

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<td>5 x 10⁻⁴ spins/T</td>
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<td>Operating Frequency</td>
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Freddy Callens, Ghent University

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**ADANI from ideas to solutions**

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The third edition of this column introduces non-adiabatic rapid sweep as an approach for improving EPR sensitivity and its utilisation at L-band frequencies for identifying a Cu(II) ions’ coordination sphere and two reports of highly unusual radicals characterised by EPR and computational chemistry.

I look forward to receiving contributions that showcase the very best research carried out primarily by IES members and has been published in high impact journals, typically the best journals in the appropriate field of research. IES members are invited and encouraged to contribute general summaries (word document) of no more than 200 words, together with a colour image to Graeme Hanson (Graeme.Hanson@cai.uq.edu.au).

Graeme Hanson
Centre for Advanced Imaging
The University of Queensland
Australia

**EPR => Hot Science**

Non-adiabatic rapid sweep (NARS) of a spin-label was introduced by A. A. Kittell et al. (*J. Magn. Reson.* 2011, 211, 228–233). In NARS, the spectrum is divided into segments, each of which is scanned repetitively about a million times at a rate of 10,000 sweeps per second and time-averaged. Averaged spectral segments are aligned to produce a complete pure absorption spectrum. NARS has been applied at L-band to doubly labelled proteins (Kittell, A. A.; et al., *ibid*, 2012, 221, 51–56), and to a frozen solution of Cu-imidazole at 1.9 GHz, (Hyde, J. S.; et al., *ibid*, 2013, 236, 15–25). The upper spectrum shows the pure absorption of Cu(II). Hyperfine and Zeeman interactions are very evident in this display. Application of a moving difference (MDIFF) filter, which is defined in the figure, results in the middle spectrum. Further application of a moving ”difference-of-differences” digital filter results in the lower spectrum. Both low frequency noise and broad spectral features are filtered by these transformations, and the nitrogen ligand superhyperfine features are elegantly revealed. The middle spectrum was found to have higher SNR by a factor of about 6 compared with field-modulation EPR for equal acquisition times.

Electron Transfer via Stable MX$_2$ radicals (M = Ga, In, Tl)

The chemistry of the Group 13 metals is dominated by the +1 and +3 oxidation states, and simple monomeric M(II) species are typically short-lived, highly reactive species. In a manuscript published in Nature Chemistry (Protchenko, A.V.; Deepak Dange, D.; Harmer, J.R.; Tang, C.Y.; Schwarz, A.D.; Kelly, M.J.; Phillips, N.; Birjkumar, K.H.; Jones, C.; Kaltsoyannis, N.; Mountford, P.; Aldridge, S. *Nature Chem.*, 2014, 6, 315–319) the authors report on the first thermally robust monomeric MX$_2$ radicals of gallium, indium and thallium. By making use of sterically demanding boryl substituents, compounds of the type M(II)(boryl)$_2$ (M = Ga, In, Tl) were synthesized. These decompose above 130 °C and are amenable to structural characterization in the solid state by X-ray crystallography. Electron paramagnetic resonance and computational studies reveal a dominant metal-centred character for all three radicals (>70% spin density at the metal). The Tl compound is of particularly interest from a purely EPR measurement perspective, with principal g-values of [1.23, 0.7, 0.6], and a Tl hyperfine coupling exceeding 10,000 MHz! M(II) species have been invoked as key short-lived intermediates in well-known electron-transfer processes; consistently, the chemical behaviour of these novel isolated species reveals facile one-electron shuttling processes at the metal centre.

X-band and W-band EPR spectra of the radicals M(II)(boryl)$_2$ (M = Ga, In, Tl) (black) and the simulations (red).
Sodium phosphaaethynolate, Na(OCP), reacts as a P− transfer reagent with the imidazolium salt \([\text{DippNHC-H}]^+\) \([\text{Cl}]^-\) \([\text{DippNHC} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}]\) to give the parent phosphinidene-carbene adduct, DippNHC=PH, with the loss of CO. In a less atom economic reaction, the cage compound, \(\text{P}_7(\text{TMS})_3\) (TMS = SiMe\(_3\)) reacts likewise with the imidazolium salt to yield DippNHC=PH thereby giving two entry points into parent phosphinidene based chemistry.

The authors report (Tondreau, A.M.; Benkő, Z.; Harmer, J.R.; Grützmacher, H. Chem. Sci., 2014, 5, 1545–1554.) that from the building block DippNHC=PH, the carbene supported \(\text{P}_3\) cation \([\text{DippNHC}(\mu-\text{P}_3)]\) can be rationally synthesized using half an equivalent of PCl\(_3\) in the presence of DABCO (1,4-diazabicyclo[2.2.2] octane). The corresponding arsenic analogue, \([\text{DippNHC}(\mu-\text{PAsP})]\)\([\text{Cl}]^-\), was synthesized in the same manner using AsCl\(_3\). The reduction of both \([\text{DippNHC}](\mu-\text{P}_3)]\) and \([\text{DippNHC}](\mu-\text{PAsP})]\)\([\text{Cl}]^-\) into their corresponding neutral radical species was achieved simply by reducing the compounds with an excess of magnesium. This allowed the electronic structures of the compounds to be investigated using a combination of NMR and EPR spectroscopy, X-ray crystallography, and computational studies. The findings of the investigation into \([\text{DippNHC}](\mu-\text{P}_3)]\) and \([\text{DippNHC}](\mu-\text{PAsP})\) reveal the central pnictogen atom in both cases as the main carrier of the spin density (~60%), and that they are best described as the P3 or PAsP analogues of the elusive allyl radical dianion. The phosphorus radical was also able to undergo a cycloaddition with an activated acetylene, followed by an electron transfer to give the ion pair \([\text{DippNHC}](\mu-\text{P}_3)]\)\([\text{P}_3\text{C(COOMe)}]\).
Zavoisky Week 2013
Kazan, Russia, September 24–28, 2013

Zavoisky Physical-Technical Institute, Russian Academy of Sciences and the Academy of Sciences of the Republic of Tatarstan organized the Zavoisky Week 2013 in the period from 24 to 28 September 2013, which included the annual International Conference “Modern Development of Magnetic Resonance 2013” and the Zavoisky Award 2013 ceremony. The conference was organized under the auspices of the Groupement AMPERE.

There were three plenary sessions with a total of ten talks. The conference included eight sections: chemical and biological systems; strongly correlated electron systems; electron spin based methods for electronic and spatial structure determination in physics, chemistry and biology; spin-based information processing; theory of magnetic resonance and modern methods of magnetic resonance; low-dimensional systems and nanosystems, and a session devoted to the memory of the late Yurii V. Yablokov. There were presented 41 oral and invited talks, and 47 posters. Presentations were made by the scientists from China, Czech Republic, Germany, Israel, Japan, Kazakhstan, Moldova, Poland, Russia, Switzerland, Turkey and USA.

To give a short overview of plenary talks, first we mention Wolfgang Lubitz (Mülheim-an-der-Ruhr), who presented the mechanistic model for water oxidation in photosynthesis and Klaus Möbius (Berlin), who discussed probing of conformational changes in photosynthetic protein complexes using high-field dipolar EPR spectroscopy. The lecture of Aleksei Semenov (Moscow) was devoted to studies of the asymmetry of electron transfer in photosystem I using femtosecond pump-probe flash spectrometry and high-field W-band transient EPR spectroscopy. Valery Khramtsov (Columbus) gave a talk about multifunctional in vivo EPR spectroscopy and imaging using advanced nitroxide and trityl paramagnetic probes. Development and applications of multi-extreme THz and high-field ESR were presented by Hitoshi Ohta (Kobe) and Vladislav Kataev (Dresden). Sergei Demishev (Moscow) reported about high-frequency EPR for studying strong correlated system. The plenary lecture of Michael Bowman (Tuscaloosa) was concerned with the problems of the dynamic nuclear polarization. EPR methods including PELDOR of spin-labeled molecules were discussed by Gunnar Jeschke (Zurich), Yurii Tsvetkov (Novosibirsk) and Kev Salikhov (Kazan). Oral and invited talks covered all aspects of the scope of the conference. The poster session reflected different aspects of the application EPR and NMR spectroscopy.

A reception at the Academy of Sciences of the Republic of Tatarstan on September 25th, 2013 was dedicated to new foreign members of the Academy, Klaus Möbius (Berlin) and Wolfgang Lubitz (Mülheim-an-der-Ruhr).
The Zavoisky Award 2013 ceremony took place on September 27th. The Zavoisky Award 2013 Yuriy Tsvetkov (Novosibirsk) was distinguished for his contribution to the application of pulse EPR methods to studying structure of disordered systems. The decision of the Zavoisky Award Committee was announced by Kev M. Salikhov, Chairman of the Zavoisky Award Committee, Zavoisky Award 2004. The award was presented by Rimma A. Ratnikova, Deputy Chairman of State Council of the Republic of Tatarstan.

Hitoshi Ohta, Vice President of the International EPR Society, Gunnar Jeschke, Secretary of the Groupement AMPERE, Wolfgang Lubitz, member of the ISMAR Committee, Zavoisky Award 2002, were among those who warmly congratulated Yuriy Tsvetkov. Special congratulations from Springer were forwarded to him as well. The laureate gave a plenary talk “Pulsed EPR Dipolar Spectroscopy and Its Applications”.

We are grateful to the participants of the Zavoisky Week and to everybody who contributed to its organization. The support of the Government of the Republic of Tatarstan, Russian Academy of Sciences, Russian Foundation for Basic Research, Academy of Sciences of the Republic of Tatarstan, and Bruker BioSpin is gratefully acknowledged.

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Kev M. Salikhov
Chairman of the Local Committee
Valery Tarasov

The IXth International Workshop
EPR(ESR) in Biology and Medicine
Krakow, Poland, October 7–10, 2013
www.eprworkshop.mol.uj.edu.pl

The IXth International Workshop on EPR(ESR) in Biology and Medicine was jointly organized by the Faculty of Biochemistry, Biophysics and Biotechnology, Jagiellonian University, the Department of Biophysics, Medical College of Wisconsin, the Max Planck Institute for Chemical Energy Conversion, and the Committee of Biochemistry and Biophysics, Polish Academy of Sciences. Traditionally, such workshops are organized every three years in Krakow, Poland with the last one taking place from October 7–10, 2013. The workshop was co-chaired by: Professors Tadeusz Sarna, Balaraman Kalyanaraman, Wolfgang Lubitz and Tadeusz Sarna.

The meeting gathered some 130 participants from USA, Germany, France, Russia, Israel, Australia, Japan, Sweden, Austria, Croatia and, of course, Poland. During three and half days of the meeting, 56 oral presentations, including plenary and invited lectures and short communications, were delivered in 11 sessions. The sessions focused on recent developments in EPR instrumentation and methodology, metals in biology, advances in lipids and membrane biophysics, distance measurements by site-directed spin labelling, detection of reactive oxygen and nitrogen species by new spin straps, spin probes and fluorescent probes, hyperpolarized MRI and metabolomics, in vivo EPR imaging and EPR oximetry, oxidative stress – modification of proteins and other biomolecules, free radicals and excited states in photobiology and photomedicine. In addition, there were 31 poster presentations, which were briefly discussed during a special session.

Despite a growing number of scientific meetings organized all over the world on related topics, the workshop in Krakow continues to serve its purpose by stimulating vivid discussion among participants, facilitating information exchange, sharing research experience, and helping to establish new contacts and possible collaboration. All friends and colleagues were invited to come to Krakow in 2016 to participate in the Xth EPR Workshop.

Tadeusz Sarna

Conference Program
W. Froncisz at the Opening

A. Nalepa & A. Adamska at Poster Session
T. Sarna & J. Hyde at Banquet

Photos courtesy of Wolfgang Lubitz
The 42nd SEMRC was hosted by the National High Magnetic Field Laboratory and held on the campus of Florida State University in Tallahassee. The 2013 meeting continued the tradition of bringing together a diverse group of researchers studying topics involving magnetic resonance in three major areas: EPR, MRI and NMR. SEMRC traditionally provides a venue for discussing new scientific ideas and advancements in an informal setting, with a special emphasis on the participation of young scientists (students and postdocs). Emphasis is placed on recent progress in magnetic resonance research, including new applications and technique development. This year’s session topics included “New Methodology & Applications”, “Solid Materials and Molecular Complexes”, “Metabolism and Dynamics”, “Proteins and Peptides”, “Drugs and Diseases”, and “Metals in Materials and Biology”.

The conference included three keynote lectures, six invited talks, 26 contributed talks by students, postdocs and more senior researchers, and over 50 poster presentations. More than 120 participants attended the meeting. Eight graduate students won travel awards for their research accomplishments. The plenary lectures given by keynote speakers discussed the latest developments in magnetic resonance: Graham Smith (University of St. Andrews) reported on the development of HiPER - a high-power 94 GHz pulsed EPR spectrometer; Joshua Wand (University of Pennsylvania) described recent developments in NMR spectroscopy of proteins and DNAs in reversed micelles; and Robert Gillies (Moffitt Cancer Center, Tampa, FL) talked about hyperpolarized MRI and pH determination in cancer.

Especially noteworthy for the EPR community was Graham Smith’s talk on the development of HiPER, with increased sensitivity and resolution in pulsed EPR. To quote Graham’s abstract: “In this talk we will describe the HiPER system, which is a low loss high power, high bandwidth, 94 GHz spectrometer developed at St. Andrews over many years. We will demonstrate, using the design mantra of “High Frequency, High Power and High Volume”, that it is possible to obtain dramatic increases in concentration sensitivity of between one and two orders of magnitude, for common pulsed EPR experiments. This allows, for example, PELDOR measurements to be made in minutes rather than days, or permits measurements at micromolar concentrations, or gives experimental access to longer distances in challenging biomolecular systems.”

The conference was sponsored by a number of public and private institutions. As in the past, a major supporter was the National High Magnetic Field Laboratory, with contributions from the NMR and EMR programs, as well as the Director’s office. Various departments at Florida State University also contributed, including: Chemical & Biomedical Engineering, Physics, Chemistry, the Institute of Molecular Biophysics, and the Office of the Vice President for Research. The following companies also contributed: Avanti Polar Lipids, Bruker Biospin, Cambridge Isotopes Labs, Doty Scientific, Isocet-Sigma Aldrich, Philips, Siemens Medical, Tecmag, and the Leon County Tourist Development Council.

SEMRC is held every year and rotates among various locations in the Southeastern United States. This year’s SEMRC will be held at the University of Alabama, Tuscaloosa, AL, from October 24–26. The University of Florida will host the SEMRC in 2015 in Gainesville, FL.

Steve Hill

Jennifer Klein became an Assistant Professor of Biology at the University of Wisconsin - La Crosse in August 2012. Jenny received her undergraduate degree in 2004 from the College of Saint Benedict and Saint John’s University (Minnesota) and her PhD in Biochemistry, Molecular Biology and Biophysics from the University of Minnesota in 2008. Her doctoral work was carried out in the laboratory of David Thomas and focused on the structural dynamics of the muscle protein myosin using state of the art protein labeling technologies in combination with innovative magnetic resonance techniques. Jenny’s postdoctoral work focused on the functional proteomics of aging and was also carried out in the Thomas lab. Prior to starting at UW-La Crosse, she was a Visiting Assistant Professor of Chemistry at St. Olaf College (Minnesota).

Her current research focuses on oxidation stress and muscle protein structure and function. The goals of her lab are to understand how molecules sense, respond, and are eventually damaged by oxidative stress. The lab examines how post-translational protein modifications associated with oxidative stress trigger functional and structural changes in the proteins involved in muscle contraction and tests the role of antioxidant systems in recovering protein function after oxidative modification. She uses a variety of techniques as part of this research, including molecular biology to create proteins for site-directed spectroscopy, cell culture and protein expression, carrying out biochemical assays, and biophysical spectroscopy. Right now she splits her time between research and teaching in the molecular biosciences, where she is heavily invested in mentoring undergraduate research. Each fall she organizes an annual Midwest Biophysical Society Networking Event that brings together educators, scientists and clinicians from the region to initiate and sustain collaborative work in biophysics.
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**Post-doctoral position in structural studies of kinesins**
A post-doctoral position is available immediately for a multi-disciplinary research project investigating the regulation of kinesin activity from the cellular to the molecular level. The group comprises the laboratories of Gary Gerfen, Ao Ma, David Sharp and Hernando Sosa in the Department of Physiology and Biophysics of the Albert Einstein College of Medicine, New York, USA. A strong interest in cell and structural biology is required for this position. A major component of the structure/function characterization will involve site directed spin label EPR (SDSL-EPR) spectroscopy, with contributions from Cryo-electron microscopy, X-ray crystallography, fluorescence spectroscopy and molecular modeling.

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EPR Specialist Position at Johns Hopkins

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