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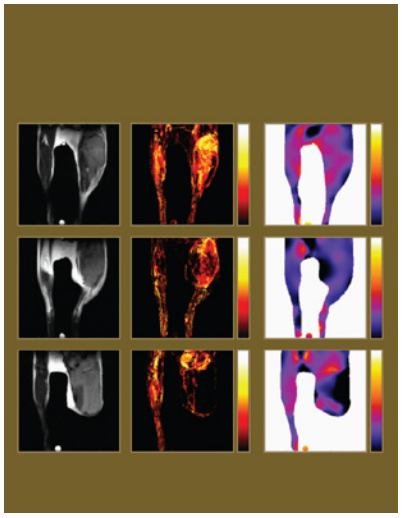

The cover picture illustrates aspects of research carried out by Murali K. Cherukuri, recipient of the IES Silver Medal for Biology/Medicine 2016. It shows anatomic images from ^{1}H MRI (left column), Blood vessel density images (middle column) from T_2^* weighted MRI using superparamagnetic iron oxide micro-particles which are restricted to blood vessels, and pO_2 images from EPR imaging (right column) from normal mouse legs (top row) and tumor bearing leg (middle and bottom rows) of mice. The tumor bearing leg is on the right. Using a 300 MHz resonant frequency for EPR and ^{1}H MRI, it is possible to co-register pO_2 images with anatomic images.

More details can be found in *J. Clinical Investigation* **118**, 1965–1973 (2008).

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ЛАБОРАТОРИЯ ФИЗИКО-ТЕХНИЧЕСКИХ ИЗМЕРЕНИЙ

ETH

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Editorial

Dear colleagues,

Lucky we! In the "Tips and Techniques" column Aharon Blank takes us on an exciting tour to his lab describing recent efforts at overcoming limitations of low sensitivity, coarse spatial resolution in imaging, and high instrumentation complexity and cost (pp. 13–17). The journey is extremely inspiring and instructive, the same as the column itself so nicely and efficiently edited by Keith Earle and appearing on a regular basis in the newsletter.

Another regular column is "Awards" and as usual, it is a meeting point for more experienced researchers and the younger generation: Murali K. Cherukuri (IES Silver Medal for Biology/Medicine 2015) for the former and Ilia Kaminker (IES Young Investigator Award 2015), Toshihide Yamasaki (APES Young Scientist Award 2014), Yuta Matsuoka (SEST Excellent Presentation Award 2014) and Shunsuke Furuya, Hideto Matsuoka, Hironori Yamaguchi, Hironobu Yasui (all SEST Young Investigator Award 2015) as the latter. Their articles demonstrate the wide variety of diverse applications of magnetic resonance (pp. 4–11). We also heartily congratulate "newly born" awardees (p. 3): Christoph Boehme, Michael Bowman, David Britt, Michael Lerch, Arnold Raitsimring, Charles Scholes, Claudia Tait, Takeji Takui and Sergey Veber to be featured in forthcoming issues of the *EPR newsletter*.

It is amazing how Wolfgang Lubitz manages to keep running the "EPR – Hot Science" column with a new set of advance research (pp. 22, 23).

I have to admit that for whatever reason the "Anniversaries" column is not as regular as it could be judging by the vast number of EPR researchers. This time I would like to remind you that 2016 marks the 60th anniversary of ENDOR. On June 15th, 1956 George Feher, father-founder of ENDOR, submitted his paper "Observation of Nuclear Magnetic Resonances via the Electron Spin Resonance Line" to *Physical Review* and it was published in vol. 103, 834–835 (1956). In 2006 we paid tribute to George Feher in connection with this seminal discovery by preparing an ENDOR-related issue of the *EPR newsletter* (double issue16/2-3).

To give several guidelines on this issue: even the cover picture was ENDOR-related illustrating research of Jos Disselhorst, the recipient of the IES Silver Medal for Instrumentation 2005. George Feher kindly gave an interview to the newsletter (also see Wolfgang Lubitz's article "80th Birthday of George Feher" in 14/3, p. 10). APS kindly permitted to reproduce George Feher's first ENDOR paper. John Pilbrow collected a selection of *EPR newsletter* anecdotes written by Michael Baker, Martin Spaeth, Jürgen Hütterman, Peter Höfer, Dieter Schmalbein, Klaus Möbius, Jim Hyde and Mikhail Falin. Erwin Hahn, a good and long-standing friend of George, contributed to the "Another Passion" column with an excellent semi-historical, semi-physical account of music. The "Pro&Contra" column, edited by Thomas Prisner, presented the comprehensive contribution on high-field pulsed ENDOR written by Daniella Goldfarb, a top expert in the field. In the "Anniversaries" column K.-Peter Dinse congratulated Klaus Möbius, an ENDOR-in-solution pioneer, on his 70th birthday (dear Klaus, our heartfelt congratulations on your recent 80th birthday!), Les Sutcliffe told about magnetic resonance spectroscopy in Britain in 1956 and Boris Kochelaev reviewed twenty years after the discovery of cuprate superconductors.

Dear IES members, welcome to traveling in time to 2006! You may download this issue from the newsletter website www.epr-newsletter.ethz.ch. Dear non-IES members! Join the society and enjoy back and current issues!

Laila Mosina

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IES Silver Medal in Physics/Materials 2016

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IES Young Investigator Award 2016

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International Tomography Center
Novosibirsk, Russia

John Weil Young Investigator Award 2016

Claudia E. Tait
University of Oxford, Oxford, UK

Zavoisky Award 2016

Michael K. Bowman
University of Alabama,
Tuscaloosa, Ala. USA

Arnold M. Raitsimring
University of Arizona
Tucson, AZ USA

From left to right: Peter Höfer (Director for EPR, Bruker), R. David Britt (University of California, Davis) and Graham Smith (St. Andrews). For details, see this newsletter, pp. 18, 19.

The Bruker Prize 2016 to R. David Britt

From left to right: Graham Smith (St. Andrews), Claudia E. Tait (University of Oxford) and Peter Höfer (Director for EPR, Bruker). For details, see this newsletter, pp. 18, 19.

The Bruker Thesis Prize 2016 to Claudia E. Tait

From left to right: Michael Lerch (University of California, Los Angeles) and Graham Smith (St. Andrews). For details, see this newsletter, pp. 18, 19.

The JEOL Student Lecture Prize 2016 to Michael Lerch

IES Silver Medal for Biology/Medicine 2015

Murali K. Cherukuri:

Transitioning from EPR spectroscopy of transition-metal in single crystals to mice and men

As a graduate student in the Physics Department of the Indian Institute of Technology, Madras (now Chennai) in 1979, I was introduced to EPR spectroscopy to study ferroelectric phase transitions in single crystals by my thesis professor Dr. BVR Chowdari, whose lab was strongly interested in material science. My interests in EPR continued even after Dr. Chowdari, in 1981, took another position in Singapore and I moved to the laboratory of Dr. Sankaran Subramanian (Subu) in IIT whose lab was active in the application of EPR and NMR spectroscopies to structural chemistry and structural biology. The years I spent in Subu's lab were formative in my transition from material science-based research to spectroscopy which I continue to this day. It was a productive time for me, that with the available resources, I was able to develop a single crystal system where I was able to monitor valence changes of Ni^{2+} in a Zn^{2+} host lattice upon γ-irradiation. We characterized five paramagnetic complexes exhibiting Jahn-Teller distortions (three Ni^{+} and two Ni^{3+} species) and further identification using the ^{61}Ni hyperfine interaction after isotope-substituted crystals were grown. As basic as this project was, it gave me working experience in not only EPR spectroscopy but in creating interest in the study of the effects of ionizing radiation to cause redox changes.

After getting my Ph. D I joined NIH in 1984. Dr. Peter Riesz, Senior Investigator, NCI/NIH, a renowned Radiation Chemist, took me in as a post-doctoral fellow to study chemical effects of ultrasound where free radicals were implicated and our task was to use EPR-Spin Trapping to detect and identify the intermediates. Along with sonochemistry, I got to also study free radical intermediates in photochemical, radiation-induced and enzymatic reactions. It was during this time that my horizons have expanded in terms of applying EPR spectroscopy to more applied topics. NIH is truly a unique place where a basic scientist can interact not only with other basic researchers, but also with those who are dedicated to translate their work to the clinic, and clinicians. After my post-doc period with Peter, which indeed was very useful and productive, in 1987 I joined the group of two incredible colleagues Dr. Angelo Russo, an Oncologist-Chemist and Dr. James Mitchell, a highly respected radiation biologist both of whom have translated several findings at the bench to clinic. These two people have had lasting impact on my future course of my career. Without their constant encouragement and guidance, I would not have been successful in continuing EPR research at NCI. During this time I was also fortunate to meet with Prof. Rami Samuni, who was on a sabbatical from Hebrew University, Jerusalem, Israel, with whom I learnt not only science but also how to be frugal at research. It was during this time that I was involved in work which started in the EPR cavity monitoring the redox reactions of Tempol and has seen its use as a radioprotector in the clinic. In the time period of 1987–1981, not only was I learning enzymology, xenobiotic metabolism, radiation biology, and pre-clinical radiation oncology and the use of EPR spectroscopy in all these studies, I was also having a very productive time. This stint at NIH positioned me as a strong candidate for the very few tenured positions in well-funded institutions in India. I succeeded in obtaining a position in 1991. But by this time the interest in EPR spectroscopy in the clinical branch was so strong that I eventually stayed back to assume tenured position at NIH and continued to work with Jim and Angelo, as well as with Rami during his frequent visits to NCI. However, a project I was encouraged to start upon receiving my tenure was to implement in vivo EPR imaging in small animals to map tumor oxygenation.

Tumor oxygen status being an important determinant in the outcomes of radiotherapy, and chemotherapy and prior work from Howard Halpern's group and Hal Swartz's group demonstrating the potential of EPR. Periannan Kuppusamy, my contemporary during my graduate student days and remains to be my good friend, who was at Johns Hopkins, helped us with our initial studies and guided us as we set to build our own scanner. We embarked on the development of a time-domain PER at 300 MHz, which was more challenging than we thought. Fortunately, Subu (my thesis mentor), who spent the whole of 1993 with us on sabbatical was interested to work on pulsed EPR development and worked tirelessly to get it to work in spite of some fundamental and many technical challenges. He also introduced Fourier imaging methods to obtain high spatial and temporal resolution. Nallathamby Devasahayam (Deva), with many innovations, took this rudimentary spectrometer and made significant improvements both in the hardware and in automation that made it user-friendly to a general purpose user. It was at this time that Nycomed Innovations led by Dr. Klaes Golman with Dr. Jan Henrik Ardenkjaer-Larsen introduced the trityl radical, which represents a significant milestone for in vivo EPR applications. With this probe, it is now possible to conduct EPR imaging in small animals in projects associated with testing chemotherapeutics in mouse models of human cancer. This same probe is the paramagnetic species used in DNP, which I consider a part of EPR. During this time several scientists joined the lab and used the scanner for in vivo studies. Drs. Ram Murugesan, Ken-Ichi Yamada, Ken-Ichiro Matsumoto, Fuminori Hyodo, Shingo Matsumoto, Hironobu Yasui, Yoichi Takakusagi, Masayuki Matsuo, Keita Saito, Shun Kishimoto, and Ayano Enomoto made use of the scanner and made several important findings related to tumor microenvironment and its influence on treatment response.

As we were pursuing in vivo EPR studies, we initiated hyperpolarized MRI using dissolution DNP. Here we saturating the EPR transition of the trityl radical in a mixture of ^{13}C-enriched pyruvate, an endogenous molecule participating in crucial cellular energetic pathways at ~1 K temperature. Upon rapid dissolution, the mixture at ambient temperature has the ^{13}C nucleus hyperpolarized to have enough signal for ^{13}C chemical-shift imaging

enabling us to monitor the metabolic conversion of pyruvate to various products depending on the cellular phenotype. Professor Albert Overhauser used to follow the progress in the few labs involved in this work including ours. After several pre-clinical studies, we are now prepared to do such studies in the clinic at NIH in patients.

I am honored to receive the 2015 Silver Medal from the International EPR Society. I owe my gratitude to all the people I mentioned in this letter without whose help and encouragement this would not have been possible. It is also gratifying to note that my mentor Subu has been recognized as a Fellow of the International EPR society the same year as I have received the Silver Medal.

IES Young Investigator Award 2015

Ilia Kaminker:

First, I would like to thank the members of the International EPR Society, in particular those who selected and nominated me for this prestigious prize. I am very proud and excited to receive such a distinction.

I still remember my first encounter with Electron Paramagnetic Resonance. The "EPR" abbreviation was mentioned in an undergraduate chemical physics course back in 2005. In the summer of the same year I could proudly say that I knew what stands behind the "EPR" abbreviation when I was interviewed by Prof. Daniella Goldfarb as part of the Emma and Oscar Getz summer program held in the Weizmann Institute of Science (WIS). I eventually joined Daniella's group and the choice of the research group for this summer program was one of the detrimental points in my career, and life, as I remained affiliated with this group for the next eight years, first as a summer student, next laboratory assistant and after graduating from Tel-Aviv University as a graduate student.

It is in the Goldfarb group I became fascinated with EPR and high field pulsed EPR in particular, as well as with the unique questions that the technique was capable of answering. At the time I joined the laboratory the unique W-band 95 GHz (3.3 T) pulsed EPR spectrometer was upgraded with a new, high power mw bridge which allowed the group to be at the top of the high field EPR developments opening new possibilities in high field pulsed EPR and ENDOR.

During my PhD I was involved in various projects ranging from methodological developments that resulted in higher sensitivity and resolution for high field pulsed EPR experiments to applications that in turn ranged from metalloenzymes to catalysis. For the former we used W-band ENDOR to study the local coordination of the Mn^{2+} ion in the active (ATP hydrolysis) site of the RNA helicase DbpA trapped in various states of its catalytic cycle. This project, that span the entire period of my PhD, exposed me to many techniques in molecular biology that were essential for the success of the study.

My collaboration with Dr. Hila Goldberg and Prof. Ronny Neumann from the department of Organic Chemistry at WIS was especially rewarding. Their interest in the polyoxometalate catalyst $[PV_2Mo_{10}O_{40}]^{6-}$ provided a rare opportunity to implement many techniques from the pulsed EPR repertoire such as W-band ^{17}O HYSCORE, ^{31}P Mims ENDOR, X-band ^{13}C and ^{51}V HYSCORE to name the few and see them reveal new information on the mechanism of the $[PV_2Mo_{10}O_{40}]^{6-}$ polyoxometalate catalysis.

Another interesting EPR adventure I've participated in during my PhD, was part of a much larger, concerted effort, concerned with developing and establishing of Gd^{3+}-based spin labels for high field distance measurements using Double Electron Electron Resonance (DEER). In particular, I was involved in developing selective nitroxide-nitroxide, nitroxide-Gd^{3+} and Gd^{3+}-Gd^{3+} distance measurements on a mixed sample carrying both types of spin labels. This development is especially exciting since it allows to tackle large and more complex biomolecular systems than it is possible with only homogeneous spin labeling. Subsequently, we could also demonstrate that high field DEER allows for obtaining the relative orientation between the nitroxide spin label and its Gd^{3+} counterpart. For this latter project the collaboration with the group of Prof. Dr. Marina Bennati and Dr. Igor Tkach who developed a unique dual mode 95 GHz resonator for W-band pulsed EPR was essential.

After finishing my PhD with Daniella Goldfarb I joined the group of Prof. Shimon Vega, again in the Weizmann Institute of Science. In Vega's group we further developed the basic theory of Dynamic Nuclear Polarization (DNP) at low temperatures for static (non spinning) samples. In particular, I was working on understanding of the complex system where both high spin (I = 1) low gamma deuterium and proton (I = 1/2) nuclei are polarized simultaneously. Even though this may seem remote from EPR, it was quickly obvious that this was not the case. Around the time I joined the Vega group we realized that Electron-Electron Double Resonance (ELDOR) pulsed EPR experiment can provide invaluable information on the electron polarization profile obtained after prolonged mw irradiation, typical for DNP experiments. This knowledge proved essential for understanding DNP and subsequently culminated in the development of the theory of the indirect cross effect (iCE) DNP mechanism.

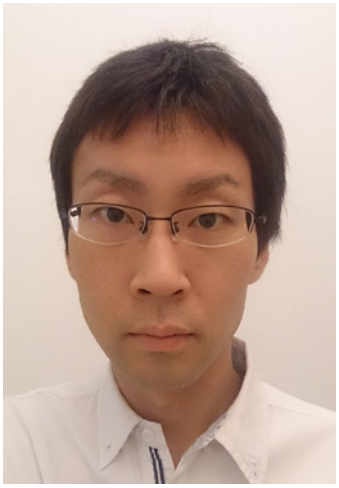
Since then, I moved to my second postdoctoral position in the group of Prof. Songi Han at the University of California, Santa Barbara (UCSB). Here I was provided with new opportunities to further develop my expertise in pulsed EPR and DNP. In my present position I am exposed to new developments allowing to further advance EPR progress, such as access to arbitrary waveform generator (AWG) pulsed EPR at X-band and since very recently 200 GHz (7 T) pulsed and CW EPR / DNP instrument. This spectrometer is now capable of routine operation in both EPR and DNP modes. Here I have to mention the help and advice received from long term collaborators of the Han group, the experts in high

frequency (Terahertz) operations, the group of Prof. Mark Sherwin at UCSB.

All the above is combined with mastering the signature technique developed in the Han laboratory – Overhauser DNP (ODNP) for studies of surface water dynamics. I had an honor to present, at the EPR symposium of the 57th Rocky Mountains Conference, the new EPR/ODNP results of the large collaborative project involving several research groups at UCSB. This project elucidated the chemistry and mechanics of the very efficient underwater adhesion of mussels, which to date current adhesive technology has yet to achieve. In this work the molecular level insights provided by EPR and ODNP proved invaluable in rationalizing the adhesive and rheological properties of the mussel-inspired adhesives.

I want to conclude by thanking all my supervisors: Profs. Daniella Goldfarb, Shimon Vega and Songi Han. It is their guidance, support and personal example that shaped me into a scientist I am now. To all members of their groups, many of whom became good friends of mine. To my collaborators, past and present, without whom all the science I've been doing would have been impossible. And last but not least, to my beloved family: my wife Dr. Revital Kaminker and daughter Abigail, without their continuous patience and support nothing would be possible.

APES Young Scientist Award 2014



Toshihide Yamasaki:

I am honored that the committee of APES (Asia-Pacific EPR/ESR Symposium) selected me for the APES2014 Young Scientist Award and I would like to thank the organizers of the Joint Conference of APES2014, IES and SEST2014 for the opportunity to present my current research at the conference in Nara.

My research is focused on the synthesis and biological application of nitroxides. Nitroxides have been widely used in the biological fields to serve as antioxidants, contrast agents, spin labels and spin probes. These usage are came from its paramagnetism. However in *in vivo*, nitroxides were immediately reduced to hydroxylamine by reaction with various substances. Among these substances, it is considered that ascorbate is well relevant to this reduction due to the high concentration within the cell [1]. And the reduction leads to the loss of the paramagnetism and its original function. To overcome this issue, nitroxides having ethyl groups at α-position of the N-O moiety have been reported and showed high resistance to reduction by ascorbate [2]. This motivated us to control the reactivity with the substituent near the N-O group. However there were no versatile synthetic method to introduce a variety of substituents near the N-O moiety. Then first, we aimed to develop the new synthetic approach to substitute the four methyl groups of 4-oxo-TEMPO (TEMPONE), which is well used for in vivo redox status monitoring.

Nitroxides can be obtained by oxidation of corresponding precursor secondary amine. So we used 4-oxo-2,2,6,6-tetramethylpiperidine as a starting material and expected the reactivity of methylene at 3 and 5 position due to the carbonyl functionality. Then we tried the aldol reaction with cyclohexanone as model substituent and we could obtain the desired 4-oxopiperidine compounds with cyclohexyl substituents by spiro-binding at 2 and 6 position after trying various conditions [3]. However the reaction yield was only 16%. Then we postulated the reaction mechanism as follows; aldol reaction, subsequent Grob's fragmentation and aza-Michael addition. From the viewpoint of this tentative mechanism, next I used N-methylated starting material to expect the promotion of the fragmentation. As a result, the yield was increased to 45% with modification of adding base and we could establish the synthetic route to substitute α-groups. And we could synthesize various nitroxides having heteroatom-containing cyclohexyl rings and alkyl groups.

Next we investigated the structure-reactivity relationship. The reactivity for reduction by ascorbate was measured by EPR. It was varied with the substituents proximal to N-O moiety. The alkyl groups had the tendency to resist the reduction [4], and heteroatom-containing groups were reactive to ascorbate. And to analyze the reactivity precisely, we measured the redox potential by cyclic voltammetry. The potentials were also altered with the type of substituents. The alkyl substituent showed lower redox potential than TEMPONE and heteroatom-containing cyclohexyl rings showed higher potential. And we plotted the pseudo-first order kinetics against Gibbs energy (ΔG) which is calculated from the redox potential of nitroxides and ascorbate. Interestingly, the plot showed good linearity in the negative range of ΔG. And in positive ΔG showed no reactivity to ascorbate [5]. Additionally we calculated the accessible surface area for heteroatom-containing cyclohexyl series, and there were no significant effect for the reactivity. From these results, the reactivity can be controlled also by electron withdrawing/donating effects as well as steric effect considered for tetraethyl substituents.

And next we conceived the application of ascorbate-reactive nitroxide for the sensitive detector of ascorbate. Ascorbate is physiologically important factor as coenzyme of collagen synthesis and antioxidant. Conventional methods are DCIP assay detected by UV or ECD followed by HPLC. UV detection lacks the sensitivity and ECD with HPLC is sometimes time-consuming method. To achieve the sensitivity and simple manipulation, we focused on the fluorescence detection. Moreover it is known that the fluorescence is quenched with nitroxide due to the paramagnetism and it recovers after reduction of nitroxide due to the loss of paramagnetism. Then we synthesized ascorbate-reactive nitroxide with naphthalene as a fluorescent moiety. This compound showed high sensitivity compared with tetramethyl derivatives and also high selectivity to ascorbate. And we compared this method with conventional HPLC-ECD using rat plasma sample, and it showed good correlation.

And another application is the detection of lipid-derived carbon-centered radical using ascorbate-resistive nitroxides. This radical species caused by ROS are known to be involved with the lipid peroxidation and finally cell damage. Moreover, it has reported that the end products of lipid peroxidation have mutagenicity [6]. So it is important to detect the

lipid-derived radical to clarify the pathogenesis and promotion mechanism. Among the developed nitoxides, alkyl group-substituted nitroxides had strong inhibition effect to lipid peroxidation. These nitroxides are suitable for this purpose because these have possibility to detect the target radical before loss of radial moiety due to the non-desired reaction such as reduction. Then we synthesized pro-fluorescent nitroxide with high fluorescent quantum yield under lipophilic condition. This probe showed high reactivity and selectivity to lipid-derived radical produced with fatty acid and lipoxygenase. Additionally this probe could visualized sensitively the production of lipid radical in cell by fluorescence microscopy.

Finally I would like to acknowledge my supervisor, Dr. Kenichi Yamada. I also would like to express my gratitude to supervisor, Dr. Kiyoshi Sakai for the discussion of synthetic experiment. And I would like to thank my colleagues for their support.

1. Saphier O., Silberstein T., Shames A.I., Likhtenshtein G.I., Maimon E., Mankuta D., Mazor M., Katz M., Meyerstein D., Meyerstein N.: *Free Radic. Res.* **2003**, 37, 301-8.
2. Bobko A., Kirilyuk I., Grigor'ev I., Zweier J., Khramtsov V.: *Free Radic. Biol. Med.* **2007**, 42, 404-12.
3. Sakai K., Yamada K., Yamasaki T., Kinoshita Y., Mito F., Utsumi H.: *Tetrahedron* **2010**, 66, 2311-5.
4. Yamasaki T., Ito Y., Mito F., Kitagawa K., Matsuoka Y., Yamato M., Yamada K.: *J. Org. Chem.* **2011**, 76, 4144-8.
5. Yamasaki T., Mito F., Ito Y., Pandian S., Kinoshita Y., Nakano K., Murugesan R., Sakai K., Utsumi H., Yamada K.: *J. Org. Chem.* **2011**, 76, 435-40.
6. Marnett L.J. : *Mut. Res.* **1999**, 424, 83–95.

SEST Excellent Presentation Award 2014

Yuta Matsuoka:

I am very honored to receive SEST Excellent Presentation Award and grateful to the organizers of Asia-Pacific EPR/ESR Symposium 2014 and International EPR (ESR) Society Symposium, the 53th SEST Anuual Meeting for the opportunity to share and discuss my research with pioneers and leaders in the field. I would also like to acknowledge Dr. Ken-ichi Yamada at Kyushu University for his support and guidance throughout my research career.

My presentation at the symposium involved the development of profluorescent nitroxide probe for the rapid and sensitive detection of ascorbic acid. Ascorbic acid is an essential biological antioxidant involved in many biological functions [1]. For instance, it acts as an enzymatic cofactor in the process of collagen synthesis, and a reducing agent in biochemical reactions. Moreover, in recent studies, ascorbic acid has also been attracted attention for its usefulness in anticancer therapy [2]. Hence, a rapid and simple detection method is highly required to understand the association between ascorbic acid concentration and disease development, and to facilitate anticancer treatments. To quantitate the level of ascorbic acid, various detection methods have been reported. For example, electrochemical detection of ascorbic acid using high performance liquid chromatography (HPLC) is widely employed sensitive method. However it requires a lot of time for a measurement. However, HPLC determination of ascorbic acid for a large number of samples is costly and complex. Therefore, a more convenient and selective method for detecting ascorbic acid is much desired, particularly for handling a large number of samples. On the other hand, Fluorophore linked nitroxides are one of most promising tools for detection of ascorbic acid and numerous profluorescent nitroxide probes with different types of fluorophores have been synthesized and demonstrated its utility [3]. However, the detection reactivity of nitroxide toward ascorbic acid is not so high, and because its reaction take place via equilibrium reaction, it needs an excess amount of ascorbic acid and takes time for the reaction. Additional to this, because fluorescent nitroxide also shows fluorescence response to toward reactive oxygen species as well as ascorbic acid, it have been required the improvement of its reactivity and response selectivity toward ascorbic acid. In almost case, these probes are synthesized using 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as a nitroxide moiety, which shows a relative weak reactivity toward ascorbic acid.

Hence, we developed the ascorbic acid selective and rapid detection probe, 15-(naphthyl-1-amino)-3,11-dioxa-7-azadispiro[5.1.5^8.3^6] hexadecan-7-oxyl (Naph-DiPy). Comparison to TEMPO type profluorescent nitroxide probe, Naph-DiPy showed higher reactivity and selectivity toward ascorbic acid because of the substitution effect which changed the electronic environment around the N-O radical moiety. To confirm the practical usefulness of the fluorophore-nitroxide probe, we demonstrated the use of Naph-DiPy for the measurement of ascorbic acid in the plasma of osteogenic disorder Shionogi rats when fed an ascorbic acid-deficient diet. More detailed results and discussion of this research were published in September 2012 in the Free Radical Biology and Medicine (Volume 53, Issue 11, Pages 2112-2118. DOI: 10.1016/j.freeradbiomed.2012.09.032). Although Naph-DiPy could rapidly and selectively detect ascorbic acid, it exhibits a small absorbance coefficient (ε_{absmax} = 6700) and short excitation and emission wavelengths at 313 and 430 nm respectively, where are overlapped with the other fluorescent substances in plasma, such as nicotinamide adenine dinucleotide (NADH). To overcome the undesirable optical property of Naph-DiPy, it is required to apply a bright and long wavelength fluorophore to profluorescent nitroxide.

Next, we have synthesized a long wavelength profluorescent nitroxide, 15-((9-(ethylimino)-10-methyl-9*H*-benzo[*a*]phenoxazin-5-yl) amino)-3,11-dioxa-7-azadispiro[5.1.5^8.3^6] hexadecan-7-yloxyl, (Nile-DiPy), which exhibits a larger absorption coefficients and longer absorption and emission than these of Naph-DiPy. The fluorescence emission of Nile-DiPy was efficiently quenched by its nitroxide moiety. To understand the quenching mechanism of Nile-DiPy, we measured its electrochemical property and intermediates in photo-induced event by using cyclic voltammetry (CV) and time-resolved spectroscopy, and it was revealed that the fluorophore moiety of Nile-DiPy can be quenched via the photo-induced electron transfer from the nitroxide radical moiety to the singlet excited state of the fluorophore moiety because it could occur thermodynamically due to the negative value of the Gibbs free energy of the photo-induced electron transfer. Upon the addition of ascor-

bic acid, the fluorescence emission of Nile-DiPy significantly increased and its limit of detection (LOD) of this fluorometric method was determined to be 9.72 nM, which is the lowest LOD in the detection method using profluorescent nitroxide probe. Furthermore, Nile-DiPy also showed high response selectivity toward ascorbic acid as well as Naph-DiPy, and the reactivity of nitroxide toward bio-reductants greatly depended on its bond dissociation free energy. Finally, we confirmed that Nile-DiPy could be used to measure the levels of ascorbic acid in the plasma of healthy and streptozotocin-induced diabetic rats. The fluorescence emission intensity of Nile-DiPy was not affected by the various substances present in the rat plasma. Moreover, compared with electrochemical detection method using HPLC, this fluorometric assay required less measurement time (20 min) and is more suited to processing multiple samples at the same time using a micro-plate reader.

Thank you to all who have taken an interest in my research. Please feel free to contact me with any questions or comments at: ymatsu1205@gmail.com

1. Eggersdorfer M., Laudert D., Letinois U., McClymont T., Medlock J., Netscher T., Bonrath W.: *Angew. Chem. Int. Ed.* **2012**, 51, 12960–12990.
2. Ma Y., Chapman J., Levine M., Polireddy K., Drisko J., Chen Q.: *Sci. Transl. Med.* **2014**, 6, 222ra218.
3. Blinco J.P., Fairfull-Smith K.E., Morrow B.J., Bottle S.E.: *Aust. J. Chem.* **2011**, 64, 373–389.

SEST Young Investigator Awards 2015

Shunsuke Furuya:

First of all I would like to thank the committee of the society of electron spin science and technology (SEST) for giving me the honor of the SEST young investigator award 2015. I am also grateful to the organizing committee of the 54th annual meeting of the society of electron spin science and technology (SEST2015) for providing me with the opportunity to present my researches. Finally I acknowledge Prof. Masaki Oshikawa for his support during my doctoral course at the university of Tokyo and for his continuous collaboration in my researches up to the present.

In SEST2015 I presented my theoretical studies on ESR in low-dimensional quantum magnets. ESR is well recognized as a very powerful probe to dynamics of electron spins inside matter. However, when electrons are strongly correlated with each other, analysis of ESR spectra becomes a highly nontrivial and challenging problem. Low-dimensional quantum magnets are a representative of such strongly correlated materials. Here I note that low-dimensional systems are embedded into three-dimensional crystal where its spatial anisotropy makes it possible to realize low-dimensional quantum magnets. Searching for new physics of strongly correlated electron spins, a lot of theoretical and experimental effort have been made into investigations of low-dimensional quantum magnets.

Theoretical studies of ESR in magnetic materials have a long history. Among them it will be worth mentioning the so-called Oshikawa-Affleck theory of ESR in $S = 1/2$ quantum antiferromagnetic spin chains with the uniaxially anisotropic exchange interaction and the staggered Dzyaloshinskii-Moriya interaction [1]. On the other hand synthetic studies of one-dimensional quantum magnets have been developed remarkably in the last decade and many ideally one-dimensional quantum magnets have been obtained, for example, quantum spin-ladder compounds called BPCB [2] and DIMPY [3]. Since the Oshikawa-Affleck theory is designed for the $S = 1/2$ single antiferromagnetic spin chain, the theory that can deal with a wider variety of one-dimensional quantum magnets was and still is strongly called for.

ESR is an excellent in detecting anisotropic spin-spin interactions. It is of great importance to determine the anisotropy of spin-spin interaction in quantum many-body systems because the anisotropy, even if it is tiny, can seriously affect the low-temperature physics. The aforementioned spin ladder is one of such interesting systems. Besides in our paper [4] we investigated the EPR frequency of the spin-ladder compound BPCB. This work was the first theoretical study of ESR in spin-ladder compounds to propose a practical way to distinguish the location of the exchange anisotropy inside the spin ladder. In another paper [5], we showed with a collaboration of experimental, numerical and field-theoretical methods that the spin-ladder compound DIMPY has the Dzyaloshinskii-Moriya interaction uniform along the leg. We clarified that the uniform Dzyaloshinskii-Moriya interaction mixes the longitudinal susceptibility parallel to the magnetic field into the ESR spectrum even in the Faraday configuration. The longitudinal susceptibility turned out to be the source of a new resonance peak. The field-theoretical and the numerical analyses showed that the new peak exhibits quite an unusual magnetic-field dependence. That field dependence was experimentally confirmed with a quantitative agreement with the theories.

The main part of my presentation in SEST 2015 was devoted to introduction of our important work about the boundary resonance in $S = 1/2$ quantum antiferromagnetic spin chains under a staggered magnetic field [6]. The boundary resonance that we called is ESR of spin located at the boundary of magnetic and non-magnetic systems. Practically the spin chain is cut for many reasons. One reason is due to replacement of magnetic ions and non-magnetic ions in the magnetic crystal by accident or on purpose. An $S = 1/2$ antiferromagnetic spin chain compound $KCuGaF_6$ is a suitable material to see the cutting effect of the spin chain. Interestingly the electron spin of the Cu^{2+} ion of $KCuGaF_6$ feels a staggered magnetic field along the chain due to the crystal structure [7]. Let us imagine a spin chain of the semi-infinite length. Deep inside the spin chain far from the chain end, magnetic excitations can propagate freely as long as they are distant from each other. That is, the interaction effect of those magnetic excitations manifests itself in the scattering process of excitations. From this viewpoint we may regard magnetic excitations as "particles". We can also consider a reflection process of particles at the end of the spin chain. The reflection is similarly dealt with the scattering inside the spin chain. The precise analysis of the reflection process uncovered that new boundary resonance peaks emerges from the reflection. That is, when the "particle" hits the potential "wall" at the chain end, the "particle"

and the "wall" can form a bound state localized at the position of the boundary. In the paper [6] we demonstrated that the staggered magnetic field is crucial for the formation of the bound state at the boundary and that our theory of the boundary resonance beautifully explains the "unknown" peaks of $KCuGaF_6$ observed before [7].

Many issues still remain in the field of the theoretical study of ESR in low-dimensional quantum magnets. I firmly believe that further study of the theory of ESR will stimulate exciting development in the field of electron spin science and technology.

I am grateful to everyone who is interested in our works. Please contact me with your questions and comments at the following address: shunsuke.furuya@unige.ch.

1. M. Oshikawa and I. Affleck: Phys. Rev. Lett. **82**, 5136 (1999); Phys. Rev. B **65**, 134410 (2002)
2. M. Klanjšek et al.: Phys. Rev. Lett. **101**, 137207 (2008)
3. D. Schmidiger et al.: Phys. Rev. Lett. **108**, 167201 (2012)
4. S. C. Furuya, P. Bouillot, C. Kollath, M. Oshikawa, and T. Giamarchi: Phys. Rev. Lett. **108**, 037204 (2012)
5. M. Ozerov et al.: arXiv:1509.02056 (to be published in Phys. Rev. B)
6. S. C. Furuya and M. Oshikawa: Phys. Rev. Lett. **109**, 247603 (2012).
7. I. Umegaki et al.: Phys. Rev. B **79**, 184401 (2009)

Hideto Matsuoka:

I was honored that the Society of Electron Spin Science and Technology selected me for the SEST Young Investigator Award 2015. I was introduced to EPR when I joined Prof. Takeji Takui research group at Osaka City University, Japan, in spring 1997. Until I received my PhD degree in 2002, my major project was to develop a new methodology based on two-dimensional electron spin transient nutation spectroscopy for high-spin chemistry which has continued to be an important underlying theme in molecule-based magnetism. In this project, we demonstrated the advantage of using transition moments instead of resonance fields for the complete assignment of complicated hyperfine structures from a mixture of electronic and nuclear high-spin systems. As a model system, Eu(II) ions doped in a single crystal was employed, which is one of the rare earth elements widely used in photo-functional and magnetic materials around us. This experience has played an important role in my subsequent research projects mentioned below.

Following my PhD, I joined Prof. Tatsuhisa Kato research group at Institute for Molecular Science, Japan, as a JSPS research fellow. I first undertook high-frequency EPR in his group. I was initially involved into two major projects: (1) complete analysis of EPR spectra from long-lasting luminescent materials based on Eu(II) ions and identification of the local structures around the ions; (2) determination of electronic and molecular structures of europium metallofullerenes by EPR spectroscopy. Actually, these projects have already started in the group of Prof. Takui just before I received my PhD degree, in which I mainly employed X-band CW/pulse EPR spectroscopy. I continued the projects during my postdoctoral studies, which were successfully advanced by combining with high-frequency EPR spectroscopy. The accurate determination of ZFS was a crucial part of both projects. In general, only dominant interactions in the spin Hamiltonian are considered in spectral analyses of random-orientation EPR spectra. The higher-rank ZFS terms, which appear in the spin Hamiltonian for high-spin systems with $S \geq 2$ like the divalent europium ion ($S = 7/2$), have also been usually neglected. Under a perturbation theory, I derived a general expression for resonance fields of an $S = 7/2$ spin system, and applied it to our systems. It was clearly demonstrated that a spectral analysis neglecting the higher-rank terms does not reproduce the whole experimental spectra correctly, and the omission leads to the misevaluation of the E values. The precisely determined ZFS components were investigated with the help of the superposition model, and the local structures around the ions and the cage structures of the metallofullerenes could be determined. High-frequency EPR spectroscopy facilitated the derivation of the general expression.

As a JSPS research fellow, I also worked in another area – EPR detection of the oxygen-evolving Mn_4 cluster in single crystals of photosystem II at W-band. One of my research interests has been in EPR studies of biological systems since I was first introduced to EPR. I had a chance to extend my research area to biological science in 2003 when my collaborator, Prof. Jian-Ren Shen at Okayama University, obtained a high resolution crystal structure of photosystem II from *Thermosynechococcus vulcanus*. Around then, the other research groups (Berlin and Oxford groups) also reported the crystal structure from *Thermosynechococcus elongates*. In collaboration with Prof. Jian-Ren Shen and Prof. Asako Kawamori at Kwansei Gakuin University, we succeeded for the first time in observing the multiline signal from the cluster in single crystals, and clearly resolved the g anisotropy of the cluster. I continued EPR studies of photosynthetic proteins in Prof. Toshikazu Nakamura research group at Institute for Molecular Science, Japan, as a postdoctoral researcher, and in Prof. Seigo Yamauchi research group at Tohoku University, Japan, as an assistant professor. We could observe highly resolved W-band EPR spectra of a redox-active tyrosine residue Y_Z by using single-crystals of photosystem II. Because of the apparent proximity of Y_Z to the oxygen-evolving cluster and its redox activity, it is believed that Y_Z plays a significant role in water oxidation. With the help of density functional theory, our experimental data supported the proton-rocking mechanism, in which the proton of D1-His190 is transferred back to Y_Z upon rereduction. It is interesting to note that the EPR-derived molecular orientation of the tyrosine radical is identical to that obtained from the crystal structure at 1.9 Å resolution. The result demonstrates not only that the orientation of Y_Z is unchanged during photooxidation, but also that high-frequency EPR spectroscopy has a great potential to determine the molecular orientations of radicals in larger membrane proteins. I have also investigated photosystem I by high time resolution EPR at W-band, in collaboration with Prof. Gerd Kothe at University of Freiburg, Germany. By improving the time resolution of our W-band spectrometer, we succeeded in observing quantum beat oscillations at early times after light excitation of fully deuterated *Synechococcus lividus*. I have also continued EPR studies of photo-functional materials at Tohoku University. In collaboration with Prof. Elena G. Bagryanskaya at International Tomography Center, Russia, we observed light-induced spin dynamics on nanosecond timescales in the compound of molecular magnets family "breathing crystals" using W-band time-resolved EPR. Although

time-resolved EPR is widely used for studying photoinduced transient paramagnetic intermediates in liquid/frozen solutions, our study was the first application of the technique to solid-phase molecular magnets.

Finally, I would like to thank all those people I was not able to mention above, particularly Prof. Koichi Itoh, Prof. Kazunobu Sato, Prof. Daisuke Shiomi at Osaka City University, and Prof. Ko Furukawa at Niigata University, who taught me much about magnetism and EPR spectroscopy; Prof. Robert Bittl at Free University of Berlin for giving me an opportunity to work abroad and to learn the field of photosynthesis. In March 2013, I moved to Prof. Olav Schiemann research group at University of Bonn, Germany, as a senior scientist. My current research still focuses on EPR studies of photo-functional and photo-sensitive systems, but it will be extended to another area when a new high-frequency EPR spectrometer at 263 GHz is installed in our lab.

Hironori Yamaguchi:

I am honored that the Society of Electron Spin Science and Technology selected me for the SEST Young Investigator Award. I would like to thank the International EPR society for the opportunity to present my research here. I would also like to thank Prof. Masayuki Hagiwara at Osaka University, Prof. Yuko Hosokoshi at Osaka Prefecture University, and the other collaborators. All ESR measurements in my work were performed at Center for Advanced High Magnetic Field Science at Osaka University.

My research is focused on magnetic properties of quantum spin systems. Quantum spin systems provide a variety of unique many-body phenomena through strong quantum fluctuations. Haldane's prediction in 1983 has stimulated studies associated with the quantum magnetism. In recent years, the magnetic properties of frustrated systems have attracted much attention. In this newsletter, I would like to introduce our research on two-dimensional (2D) triangular lattice antiferromagnets (TAFMs), which have been intensively investigated in association with various noble states such as a spin liquid state. Moreover, considering recent discoveries of multiferroic materials, which have ferroelectricity related to the spiral spin structure caused by frustration, 2D TAFMs are also desired for the study of the multiferroics. We have studied focusing on three compounds forming 2D TAFM: $NiGa_2S_4$, $CuCrO_2$ and $Rb_4Mn(MoO_4)_3$, and performed multifrequency ESR and magnetization measurements in high magnetic fields up to about 68 T.

$NiGa_2S_4$ has attracted a substantial interest as a candidate of a spin liquid state [1]. The NMR studies evidenced the occurrence of a novel state where the spins do not freeze immediately, but keep fluctuating with the MHz frequency range. From the temperature evolution of the ESR absorption linewidth, we found a distinct disturbing of the development of the spin correlation by Z_2-vortices between 23 K and 8.5 K. Below T_v = 8.5 K, spin-wave calculations based on a spiral spin order, which was observed in a neutron scattering experiment, well explained the frequency dependence of the ESR resonance fields (ESR resonance mode) and high field magnetization curves. Furthermore, we explain the field independent specific heat with T^2-dependence by the same spin-wave calculation, but the magnitude of the specific heat is much less than the observed one. The relation between the value of the magnetic anisotropy and Z_2-vortex-induced topological transition derived by Kawamura and co-workers [2] is well satisfied by using the single ion anisotropy evaluated from the analysis of ESR resonance mode. Accordingly, our results suggested the occurrence of a Z_2 vortex-induced topological transition at T_v and clarified the quantum effects beyond the descriptions based on the classical spin models [3, 4].

$CuCrO_2$ has attracted a lot of attention as a new discovery of multiferroics which cannot be explained by a conventional microscopic origin [5]. Furthermore, the detail of the ground state spin structure associated with the ferroelectricity was not clarified. Our experimental results of ESR resonance modes and the magnetization curves are well explained by a spin-wave analysis considering the out-of-plane spiral spin structure, which was extracted from a neutron scattering experiment, on a distorted triangular-lattice model with two kinds of antiferromagnetic exchange interactions and rhombic anisotropy. We have quantitatively clarified not only the ground state spin structure associated with the ferroelectricity but also first-order magnetic phase transition associated with the flop of the electric polarization by applying magnetic field. Our results established the benefits of ESR measurements combined with spin-wave analyses to understand the origins of magnetoelectric effects in multiferroic materials, and also highlight the importance of lattice distortions for first-order magnetic phase transitions in frustrated triangular lattice antiferromagnets [6].

The 2D TAFM $Rb_4Mn(MoO_4)_3$ is reported to have a weak Ising anisotropy. This compound exhibits two successive phase transitions with decreasing temperature at zero-field. This behavior is considered to have its origin in a partial order of magnetic moment, where the specific components of the magnetic moment order in a stepwise fashion owing to the magnetic anisotropy and frustration. We have successfully explained the observed ESR resonance modes and the magnetization curves for both parallel and perpendicular to the easy-axis in the lower temperature phase by means of a spin-wave approximation and a classical Monte Carlo simulation assuming a spin Hamiltonian of 2D Heisenberg TAFM with Ising anisotropy. Thus, we evaluated the magnetic anisotropy and the exchange constants accurately. Consequently, we have confirmed that $Rb_4Mn(MoO_4)_3$ is a good example of a 2D Heisenberg TAFM with Ising anisotropy. Our ESR study is the first full observation of spin wave excitations and provides fundamental information on this spin system [7].

1. Nakatsuji, S.; Nambu, Y.; Tonomura, H.; Sakai, O.; Jonas, S.; Broholm, C.; Tsunetsugu, H.; Qiu, Y.; Maeno, Y.; *Science* **2005**, 309, 1696–1700.
2. Kawamura, H.; Yamamoto, A.; Okubo, T.; *J. Phys. Soc. Jpn*. **2010**, 79, 023701.
3. Yamaguchi, H.; Kimura, S.; Hagiwara, M.; Nambu, Y.; Nakatsuji, S.; Maeno, Y.; Kindo, K.; *Phys. Rev. B* **2008**, 78, 180404(R).
4. Yamaguchi, H.; Kimura, S.; Hagiwara, M.; Nambu, Y.; Nakatsuji, S.; Maeno, Y.; Matsuo, A.; Kindo, K.; *J. Phys. Soc. Jpn*. **2010**, 79, 054710.
5. Kimura, K.; Nakamura, H.; Kimura, S.; Hagiwara, M.; Kimura, T.; *Phys. Rev. Lett*. **2009**, 103, 107201.
6. Yamaguchi, H.; Ohtomo, S.; Kimura, S.; Hagiwara, M.; Kimura, K.; Kimura, T.; Okuda, T.; Kindo, K.; *Phys. Rev. B* **2010**, 81, 033104.
7. Yamaguchi, H.; Kimura, S.; Ishii, R.; Nakatsuji, S.; Hagiwara, M.; *J. Phys. Soc. Jpn*. **2011**, 80, 064705.

Hironobu Yasui:

I was honored to receive the young scientist award from the Society of Electron Spin Science and Technology (SEST) for my study, entitled "Biological study on cancer physiology and radioresponse using ESR techniques". I would like to thank the committees of SEST for this award and the organizers of the 54th annual meeting of SEST (SEST2015) for the opportunity to talk about my work. I would also like to acknowledge Prof. Osamu Inanami at Hokkaido University for the kind support and guidance throughout my graduate career and Dr. Murali Cherukuri Krishna at the National Cancer Institute/NIH for giving the exciting experience to establish in vivo ESR oxygen imaging when being at postdoctoral position there. Here, I would like to introduce a part of my research.

Even though multidisciplinary efforts to overcome cancer have been exerted globally, cancer remains one of fatal diseases. In order to improve survival rate of cancer patients, we need to make radiation therapy more efficient by prediction cancer-resistant factors and increasing tumor radiosensitivity. Especially, hypoxia has been known to be a feature associated with tumor radioresistance. So far, clinical strategies to overcome chronic hypoxia due to the limitation of the oxygen diffusion have been designed. However, intermittent or acute/cycling hypoxia, whose frequency can range between a few cycles per minutes to hours, is receiving increased attention recently, because this type of hypoxia has been reported to have an influence on tumor malignancy as well as treatment resistance via increased expression of pro-survival pathways. Therefore, a priori information on fluctuating hypoxia can be important in clinical treatment planning, but complicated dynamics makes it difficult to elucidate biological significance of intermittent hypoxia. We succeeded to directly monitor fluctuating oxygenation i.e. cycling hypoxia in transplanted tumors by using pulsed ESR imaging (ESRI) as a novel imaging method [1–3]. A common resonator platform for both ESRI and magnetic resonance imaging (MRI) provided pO_2 maps with anatomical guidance. Oxygen images every 3 min in pO_2 distinguished cycling hypoxia and chronic hypoxia, respectively. Furthermore, we have examined the vascular renormalization process by longitudinally pO_2 mapping during treatments with a multi-tyrosine kinase inhibitor sunitinib. Transient improvement in tumor oxygenation and the decrease of cycling tumor hypoxia were visualized by ESRI 2 to 4 days following antiangiogenic treatments. Radiation treatment during this time period of improved oxygenation by antiangiogenic therapy resulted in a synergistic delay in tumor growth [4]. Accordingly, this ESRI technique combined with MRI, may offer a powerful clinical tool to noninvasively detect variable hypoxic status in tumors and to identify a window of vascular renormalization to maximize the effects of combination therapy with antiangiogenic drugs.

Next, we focused on the effect of X-irradiation on the cellular energy metabolism, because adaptive response to radiation as ATP production is known to be responsible for cell survival. Especially, mitochondria are well-known to play a central role in the intrinsic pathway of X-ray-inducing apoptosis as well as cellular ATP production. We previously reported that the release of cytochrome c from mitochondria was regulated by intracellular ROS following X-irradiation [5]. Although the production of intracellular ROS is suggested to be linked with the upregulation of mitochondrial function, the detailed mechanism has not been fully elucidated. First, we attempted to detect the mitochondria-derived ROS and examine whether X-irradiation enhanced the ROS production from mitochondria. For this purpose, the ESR spectroscopy with spin-trapping technique using a DEPMPO-type nitrone spin trap, CYPMPO, was employed. When mitochondria isolated from tumor cells were incubated with respiration substrates and CYPMPO, ESR signal with the characteristic of hydroxyl radical (.OH) was observed only in the presence of a Complex III inhibitor, antimycin. The addition of SOD abolished this ESR signal, indicating that the CYPMPO-OH spin-adduct was derived from superoxide radical. Furthermore, the intensity of its EPR signal was enhanced by 10 Gy of X-irradiation [6]. Next, we analyzed the effect of X-irradiation on mitochondrial functions, particularly focusing on cellular oxygen consumption rate, using a LiNc-BuO-based ESR oxymetry. Six types of cells were irradiated with 10 Gy of X-rays and then were incubated for several hours. The suspended cells were mixed with LiNc-BuO as an oxygen probe. After this mixture in capillary tube was sealed, the oxygen concentration in culture medium was measured 15 times in 1 min interval at 37 °C by X-band ESR spectroscopy. It was demonstrated that X-irradiation enhanced the oxygen consumption rate in all cell lines tested, suggesting that the increase of mitochondrial respiration after X-irradiation was a universal phenomenon in mammalian cells [6].

In conclusion, our study suggested that X-irradiation caused the enhancement of cellular respiration due to the activation of mitochondrial electron transport chain, leading to mitochondrial ROS production.

Applying these methods as ESR oxymetry and spin-trapping to the study of cancer physiology after X-irradiation has produced interesting results. Currently, I am doing the further investigations for clarifying the molecular mechanism for X-ray-inducing cellular resistance. I will be grateful to report the novel findings about this topic to readers engaging in ESR science in the near future. Finally again, I really appreciate the award and encouragement by all the SEST members.

1. Yasui, H.; Matsumoto, S.; Devasahayam, N.; Munasinghe, J.P.; Choudhuri, R.; Saito, K.; Subramanian, S.; Mitchell, J.B.; Krishna M.C.; *Cancer Res.* **2010**, 70, 6427–6436.
2. Matsumoto, S.; Yasui, H.; Mitchell, J.B.; Krishna, M.C.; *Cancer Res.* **2010**, 70, 10019–10023.
3. Krishna, M.C.; Matsumoto, S.; Yasui, H.; Saito, K.; Devasahayam, N.; Subramanian, S.; Mitchell, J.B.; *Radiat. Res.* **2012**, 177, 376–386.
4. Matsumoto, S.; Batra, S.; Saito, K.; Yasui, H.; Choudhuri, R.; Gadisetti, C.; Subramanian, S.; Devasahayam, N.; Munasinghe, J.P.; Mitchell, J.B.; Krishna, M.C.; *Cancer Res.* **2011**, 71, 6350–6359.
5. Ogura, A.; Oowada, S.; Kon, Y.; Hirayama, A.; Yasui, H.; Meike, S.; Kobayashi, S.; Kuwabara, M.; Inanami, O.; *Cancer Lett.* **2009**, 277, 64–71.
6. Yamamori, T.; Yasui, H.; Yamazumi, M.; Wada, Y.; Nakamura, Y.; Nakamura, H.; Inanami, O.; *Free Radic. Biol. Med.* **2012**, 53,260–270.

New Methodologies and Applications in Electron Spin Resonance – from Wound Healing to Quantum Computing

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Electron spin resonance (ESR) is well-known in the world of physics and chemistry, with numerous applications ranging from structural biology to pre-clinical medicine. However, despite its wide commercial and scientific success, ESR still suffers from significant limitations of low sensitivity, coarse spatial resolution in imaging, and high instrumentation complexity and cost. In this short review, I will describe some of the recent efforts in my lab, aimed at overcoming these limitations, which have resulted in unique experimental capabilities, offering ultra-high sensitivity approaching the single electron spin level, as well as sub-micron imaging resolution. These capabilities enable one to address unique applications in materials- and life-sciences, ranging from oxygen measurements in cells to basic experiments in quantum computation. In addition, we are developing other systems that are far less complex and costly than conventional ones, aimed at specific medical applications. This direction, which is only in its infancy, may lead in the near future to a situation where ESR technology can serve as a basis for simple and affordable medical instruments, used by physicians and caregivers at the clinical level.

I. Introduction: the pro and cons of magnetic resonance

Magnetic resonance (MR) is one of the most fundamental scientific observation methods. MR is concerned mainly with nuclear magnetic resonance (NMR) and electron spin resonance (ESR). It has a broad range of applications from chemical structure determination to medical imaging and basic physics. From a scientific standpoint, MR has been at the center of at least seven Nobel prizes in physics [1–4], chemistry [5, 6], and medicine [7]. From an industrial standpoint, MR is a multibillion industry aimed primarily at a wide range of medical (magnetic resonance imaging, MRI) and chemical (NMR and ESR spectrometers) applications.

Despite the success of MR methodologies, their application is typically limited by sensitivity (the number of species that can be detected), by their coarse spatial resolution in imaging applications, and by the high cost and complexity of MR technology. *Overcoming these barriers will pave the way for transformative developments in the experimental sciences*. Our group is trying to address all of these issues, ranging over the whole field of magnetic resonance, although currently we are primarily focusing on methodologies and applications related to electron spin resonance. In this short review of activities, we picked some samples of our work related both to basic methodological developments in ESR, and how they can be applied to practical scientific, technological, and medical applications.

As noted above, the most fundamental limitation of magnetic resonance, including ESR, is the low sensitivity. The energy difference, ΔE, between the two states of a spin 1/2 system varies linearly with the strength of the external field ($\Delta E \sim 2\mu_B B_0$, where μ_B is a universal constant, the Bohr magneton), and is quite small, in the range of μeV to ~meV at most, for common static fields in the range of ~0.01–10 Tesla. This is one of the prime reasons why it is so hard to detect the presence of these unpaired spins, where in the most favorable case of a sample having a narrow ESR spectrum, commercial ESR systems require ~10^9 spins to achieve a measurable signal during 1 s of acquisition time.

II. Improving the sensitivity

In view of the above, the first challenge that our laboratory had to deal with is to significantly improve the spin sensitivity, aiming at the ultimate sensitivity of a single electron spin. Figure 1 summarizes the approach we took to achieve this goal. It is based on three main pillars. First and foremost, we developed a unique ultra-miniature resonator, which focuses the MW energy to a very small volume, on the μm scale (a highly challenging task since the wavelength of the frequency we work at is ~10 mm). This enables us to greatly enhance the response of the MW system to very small changes in the MW properties of a small sample in the resonator (when the resonance condition is satisfied). The second important point for achieving high sensitivity is that working with such a tiny resonator also enables the use of very low MW power for measuring the sample response, which means that the MW signal coming from the sample can be amplified by very sensitive cryogenic amplifiers that, otherwise, would be damaged by even moderate power MW radiation. This bring us to the last important point in our set up, which includes the use of a cryogenic probehead to enable measurements at low temperatures where the noise level is

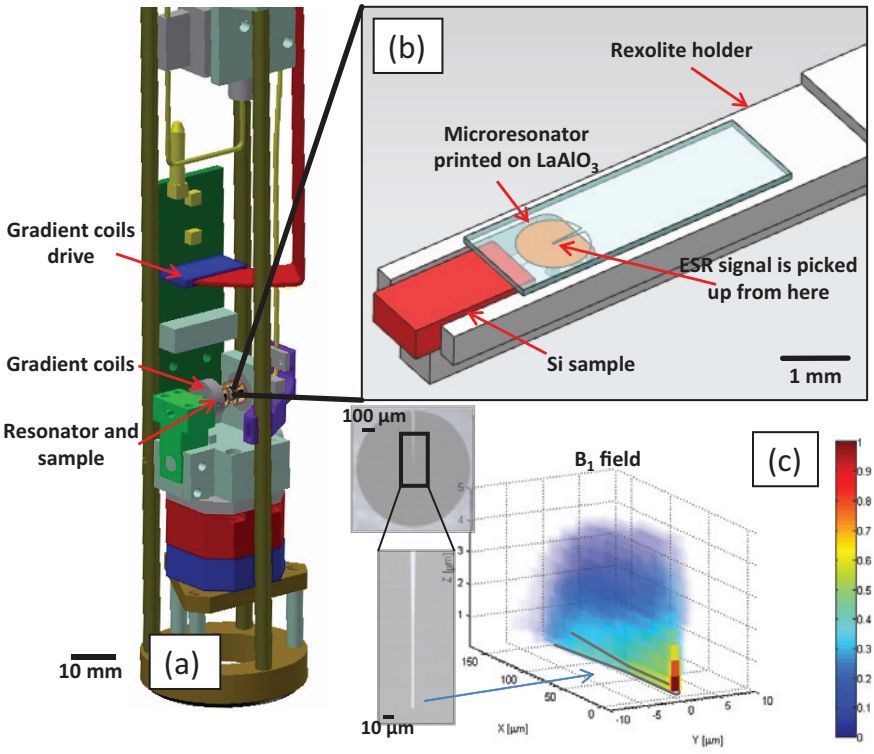


Figure 1: Experimental setup for ultra-high sensitivity and high spatial resolution ESR. (a) A drawing of an ESR detection probehead that operates at cryogenic temperatures, showing its main components. (b) Zoom-in to the center of the probehead, where a miniature ESR resonator (the "Pacman" shaped structure) is located near the sample. (c) Microscopic photos of the resonator, showing its details as well as the calculated microwave magnetic field at the center of the resonator, showing that the field is focused in a volume of a few μm^3.

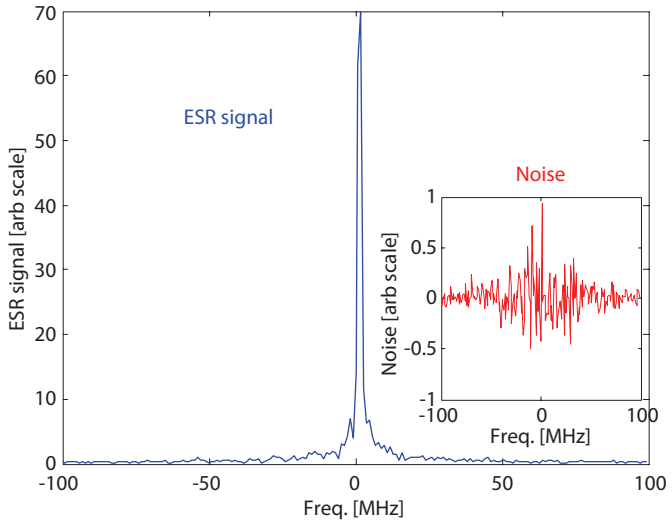


Figure 2: ESR signal and noise in the spectral domain for ^{28}Si:P sample at 10 K, for 1 second of acquisition time [8].

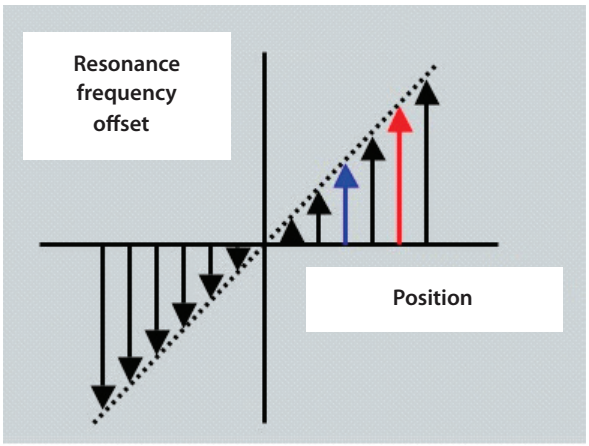


Figure 3: Schematic description of the method for spatial encoding of the sample in magnetic resonance. The resonance frequency of different parts in the sample can be either higher or lower than the resonance frequency of the center of the sample, when a small magnetic field gradient is added to the main static field.

reduced and is also important for facilitating the use of an ultra-low-noise cryogenic amplifier.

The capabilities of our systems were recently verified by achieving a sensitivity approaching a single electron spin when measuring unpaired spins in a phosphorus-doped silicon 28 (^{28}Si:P) wafer (Fig. 2). In this case the sample contained ~$2\cdot10^6$ spins, and analysis of the noise level reveals that a sensitivity of just a single spin can be achieved after a few hours of averaging time [8].

III. Improving the spatial resolution

The second limiting factor for magnetic resonance listed above is the coarse spatial resolution in imaging applications of heterogeneous samples. In order to understand the origins of this limitation, we must first provide a very brief explanation of how magnetic resonance can be used for imaging. The basic idea relies on the linear relation between the resonance frequency and the static field ($\nu = 2\mu_B B_0/h$). Thus, by placing the sample not in a homogeneous static magnetic field, but rather in a field that has a fixed gradient, each position in the sample is encoded by its resonance frequency (Fig. 3). Namely, different parts of the sample exhibit different resonance frequencies, thereby enabling creation of an image of the sample based on the ESR absorption signal at different frequencies.

Based on this explanation, it is evident that the image resolution depends on the strength of the field gradient employed, meaning the larger the gradient the better the resolution will be. However, as the pixels in the image become finer and finer, there are fewer and fewer spins in each pixel, meaning that at some point their number will be smaller than the minimal detectable number of spins of a given setup, resulting in a complete loss of image contrast in favor of noise. The setup shown in Fig. 1 is aimed at addressing both the gradient strength issue, as well as the sensitivity problem, at the same time. On one hand, it greatly improves the spin sensitivity – as explained above. On the other hand, since the resonator is so small, it enables one to employ miniature coils located around the resonator in very close proximity that generate very powerful magnetic field gradients and also can be switched on/off on a fast – nanosecond time scale (which is another important requirement for high resolution imaging in ESR). Figure 4 provides an example of a high-resolution (better than 1 μm) ESR image of a paramagnetic crystal acquired by our measurement system [9].

IV. Applications of High Sensitivity/High resolution ESR

The new capabilities described above can be implemented in a variety of scientific and technological applications. For example, in the field of semiconductor devices, high-resolution ESR imaging enables one to observe diffusion and migration phenomena of point defects in amorphous oxides [10]. Amorphous oxides are key ingredients in electronic and optical devices. Such oxides include a variety of point defects that greatly affect their electrical and optical properties. Many of these defects are paramagnetic and, as such, the best tool to identify them and characterize their structure is ESR. However, due to its limited sensitivity and spatial resolution, traditional ESR could not provide information about the defects' migration properties, which are of crucial importance for device fabrication. Ultra-high-resolution imaging modalities such as transmission electron microscope (TEM), as well as theoretical calculations, are severely limited in amorphous media, resulting in a wide knowledge gap in this field. Our ESR microimaging technique was applied to examine unique samples that are prepared using e-beam irradiation and have well-defined point defect patterns. This provides the capability to unambiguously identify the defects and at the same time track their migration with high spatial resolution, revealing new information about their properties. Figure 5 shows a typical example of ESR imaging results of amorphous SiO_2 piece on which a rectangular pattern of point defects was created by e-beam irradiation. The piece was imaged immediately after preparation and then following a 3 h heat cycle at 400 °C. Changes in the image were analyzed to obtain valuable information about atomic level potentials and forces between point defects in SiO_2 [10].

Another example, taken from a completely different field, is focused on the use of ESR micro-imaging for mapping oxygen in sub-mm sized tissues. Oxygen (O_2) plays a central role in most living organisms. The concentration of O_2 is important in physiology and pathology. Despite the importance of accurate knowledge of O_2 levels, there is very limited capability to measure its distribution in millimeter-scale live biological samples with micron scale spatial resolution. Many of the current oximetric methods, such as oxygen microelectrodes and fluorescence lifetime imaging, are compromised by O_2 consumption, sample destruction, invasiveness, and difficulty of calibration. In the case of biological samples, ESR imaging requires the incorporation of a suitable stable and inert paramagnetic spin probe into the desired

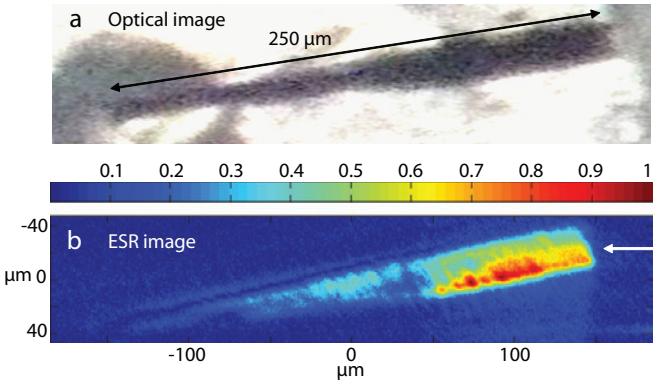


Figure 4: Optical (a) and two-dimensional ESR image (b) of a single paramagnetic Lithium Phthalocyanine crystal. The crystal was positioned with its long axis in the XY plane of the ESR image.

object. In our work, we used microcrystals of a paramagnetic spin probe in a new crystallographic matrix (denoted tg-LiNc-BuO). These paramagnetic species interact with the paramagnetic oxygen molecules, causing spectral line broadening that is linearly proportional to the oxygen concentration. This new oximetry microimaging method addresses all the problems mentioned above. It is noninvasive, sensitive to physiological oxygen levels, and easy to calibrate. Furthermore, in principle, it can be used for repetitive measurements without causing cell damage. The tissue model used in this research was spheroids of Human Colorectal carcinoma cell line (HCT-116) with a typical diameter of ~600 microns. Most studies of the microenvironmental O_2 conditions inside such viable spheroids carried out in the past used microelectrodes, which require invasive puncturing of the spheroid and are also not applicable to 3D O_2 imaging. High-resolution 3D oxygen maps could make it possible to evaluate the relationship between morphological and physiological alterations in the spheroids, which would help in understanding the oxygen metabolism in solid tumors and its correlation with the susceptibility of tumors to various oncologic treatments. Figure 6 shows a typical example of an oxygen map measured for one of the spheroids. It indicates that there is more oxygen on the exterior parts than in the inner parts, as one would expect for such tissues. It also shows the significant heterogeneity such spheroids may possess with respect to their oxygen concentration.

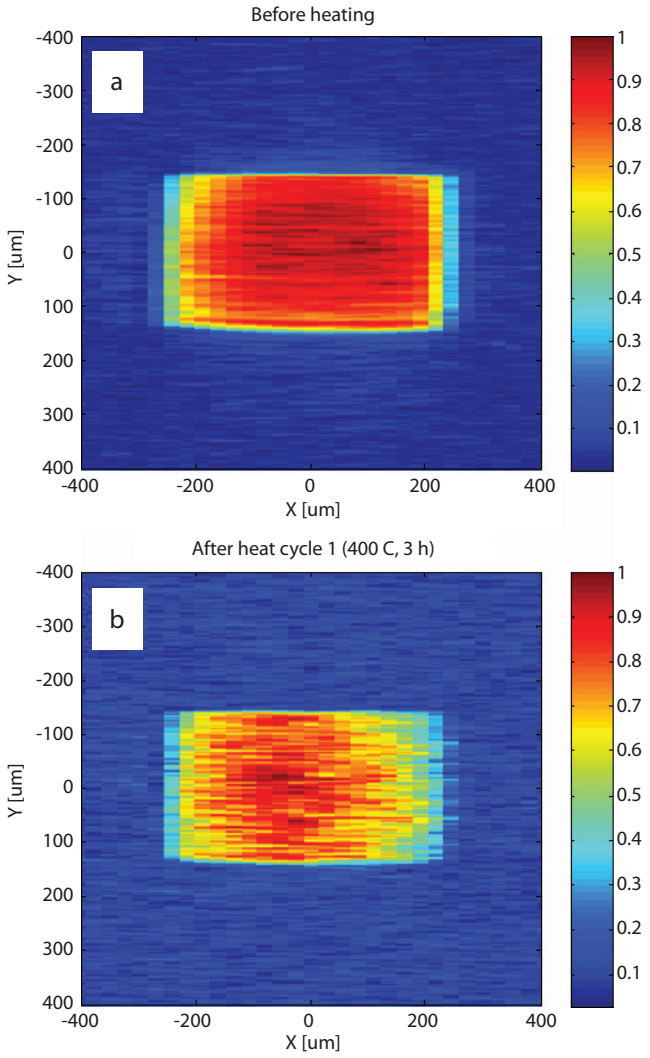


Figure 5: Pulsed ESR 2D images of the irradiated SiO_2 sample before (a) and after (b) heating cycle at 400 °C for 3 hours. The heat cycle causes some changes in the spatial pattern that can be analyzed to provide information about forces acting on the defects in the SiO_2 and processes they undergo.

A third emerging application of high resolution/high sensitivity ESR comes from the regime of basic physics, where ESR can be used as a basis for a quantum computer [11]. Quantum computing (QC) is a relatively new concept that aims at significantly improving the capability to calculate some types of high complexity problems by making use of unique hardware and algorithms from the regime of quantum physics. Unlike regular computers that make use of binary bits that can be either 0 or 1, QC employs quantum bits that can be either 0, or 1, or in a superposition of states, being both 0 and 1 at the same time, with some probability. The latter situation is of course only possible for a quantum system and thus electron spins, which can exist in this strange superposition of states, were found to be one of the leading candidates to be used as such quantum bits. However, beyond the basic concept, much practical work is still needed. For example, one must enable the selective manipulation of these qubits, creating controlled interaction between them to perform calculations, and at the end read out the solution by processing the state of the electron spins, ideally with single-spin sensitivity and nano-scale spatial resolution. Here is where our high sensitivity/high resolution methodologies come into play in the construction of such unique QC hardware. The basic concept (currently only theoretical) is described in Fig. 7 [11]. It makes use of an array of multiple identical "computer" vectors of phosphorus-doped silicon where the nuclei serve as logical qubits and the electrons as working qubits. The spins are addressed by a combination of electron spin resonance and nuclear magnetic resonance techniques operating at a field of ~3.3 T and cryogenic temperatures with an ultra-sensitive surface microresonator. Spin initialization to the ground (0) state is invoked by a combination of strong pre-polarization fields and laser pulses. The set of universal quantum gates for this system includes an arbitrary rotation of single qubits and controlled-NOT operation with two qubits. The efficient parallel readout of all the spins in the system is performed by high-sensitivity induction detection of the electron spin resonance signals with one-dimensional imaging.

V. Simple, affordable, and transportable ESR systems

As noted above, the third aspect of magnetic resonance that severely limits its widescale use, is related to the complexity of the instrumentation, their excessive cost and their limited portability. Addressing these issues is one of the focal interests of our laboratory, which develops

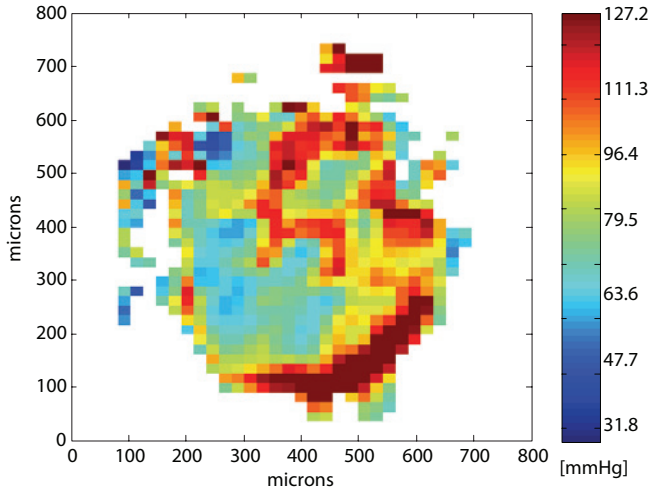


Figure 6: Oxygen map of a spheroid containing LiNc-BuO. The map shows the oxygen concentration in various parts of the spheroid, as derived from their measured spatially-resolved ESR spectrum.

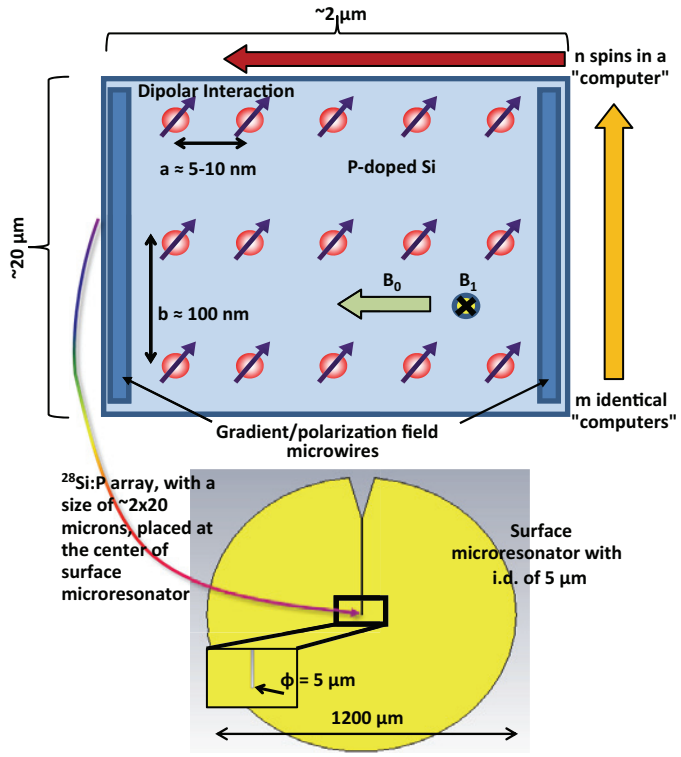


Figure 7: The suggested QC scheme to be used in conjunction with ultra-high sensitivity/high-resolution induction detection [11]. A two-dimensional array of phosphorus atoms is produced inside a pure ^{28}Si single crystal. The crystal is placed upside down on the center of our ultrasensitive surface resonator [16–18], and operated at cryogenic temperatures. Each phosphorus nucleus in the crystal serves as a logical quantum bit (qubit), while its adjacent electron is the working qubit. The array has two lattice constants: a short one (a) that enables electron spins to interact through dipolar couplings along this linear vector (similar to the manner described in [19]), and a long one (b) that separates many identical copies of the same individual vector computers. Individual spins can be addressed by applying a large magnetic field gradient with DC current into microwires (separating the spins in the frequency domain), and the state of all spins can be read out in parallel via a one-dimensional image along the crystal's x-axis. All parallel identical computer vectors should give the same vector of spin states, thereby increasing the measured signal and also greatly minimizing the need for quantum error correction due to random spin flips, since the measured result averages over ~10^2–10^3 spins per qubit. Information can be swapped between working electron spins and logical nuclear spins through combined radiofrequency (RF) and microwave (MW) pulse sequences, as described in [20].

miniature self-contained ESR probes for specific applications, mainly in medicine. However, unlike the cases of sensitivity and resolution improvements, we will not go into the details of the technology behind these devices and simply provide two representative examples that show the scope of our activities in this field.

The first example is a miniature ESR probehead that includes a static field source and a microwave resonator for *in-vivo* measurement of paramagnetic defects in tooth enamel [12]. These defects are known to be a good marker for quantifying the ionizing radiation dose absorbed in teeth. The probehead has a typical length of just 30 mm and total weight of 220 g. The patient "bites" into the probehead while the measurement procedure is being carried out (Fig. 8). Experimental results with irradiated incisor teeth validated the probehead's sensitivity, being able to detect signals in tooth irradiated by only 2 Gy. Such probe is of importance for fast triage of mass populations that were potentially exposed to ionizing radiation, where a 2 Gy dose serves as a threshold for administrating medical care.

A second example for a compact, simple, and affordable ESR-based measurement system is shown in Fig. 9, which describes a sensor for measuring oxygen content in the skin [13]. Oxygen concentration in the skin is an important clinical indicator for monitoring pathological conditions such as chronic wounds, skin cancer, and peripheral vascular disease. Currently, the only clinically-approved method for acquiring these oxygen levels is based on electrochemical measurements that employ Clarke-type electrodes attached to the skin. This technique has many drawbacks and limitations, making it unattractive for standard medical practice and care. ESR can obtain the oxygen concentration through measurements of the relaxation time (T_2) of paramagnetic species interacting with molecular oxygen and thus provides a possible alternative. However, a traditional ESR setup requires a large homogeneous static magnetic field source with a limited gap between the poles and complicated equipment, making it unattractive for clinical use. Our miniature ESR probehead, which is composed of a specially-designed permanent magnet and a small microwave resonator, can be used for these measurements. The small size of the probehead (36 mm diameter cylinder with a height of 24 mm) enables measurements from virtually any part of the skin. Compared to the electrochemical method, this ESR-based approach may provide faster and more accurate readings of oxygen concentration in the skin, making it highly attractive for future clinical use.

VI. Summary and conclusions

The field of magnetic resonance has enjoyed enormous success, but still suffers from some major limitations in terms of sensitivity, imaging resolution, and affordability, which, if solved could boost its impact even further. Our recent work on ESR, which is an indispensable branch of magnetic resonance, has resulted in significant improvement in spin sensitivity (4–6 orders of magnitude) and image resolution (~2 orders of magnitude), as well as showing how compact, simple, and affordable ESR probes can be constructed to address specific applications (mainly in medicine). These new capabilities have already opened the door to unique applications in wide areas of science and technology. Further work along these lines, which include yet additional improvements in sensitivity, image resolution, and simplification of system architectures, are being pursed in our lab. Some of these efforts make use of conventional resonator-based ESR detection approaches, as discussed in this paper, while others look into advanced and alternative techniques such as electrical and optical detection, which may be useful for additional future applications [14, 15].

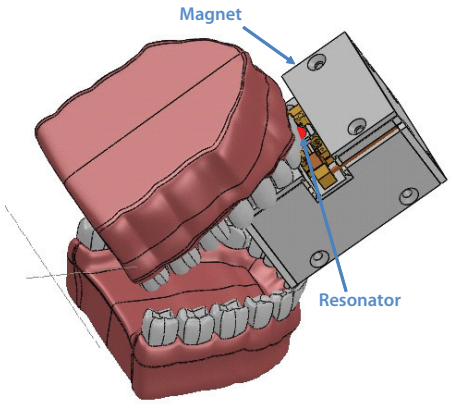


Figure 8: General overview of the compact ESR probehead for ESR measurements of incisor tooth during a projected measurement.

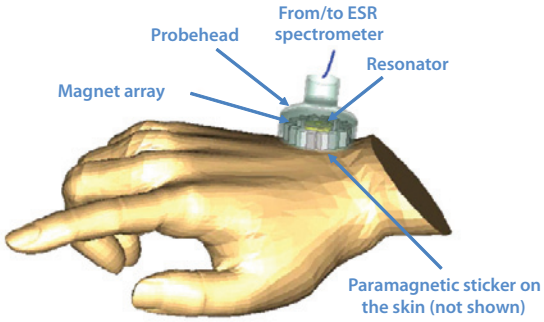


Figure 9: Drawing of the compact skin O_2 ESR probehead, showing the permanent magnet and resonator assembly during a projected *in-vivo* measurement of skin oxygen level. A special paramagnetic sticker is placed on the skin and the measurement of the relaxation time (T_2) of the particles in this sticker provides the oxygen concentration in the skin.

VII. Acknowledgments

I would like to thank current and past group members that were involved in the construction of our ESR systems and in the application work described in this manuscript: Anton Algin, Yaron Artzi, Ekaterina Dikarov, Dr. Revital Halevy (Herman), Mada Hashem, Shlomo Ish Shalom, Alexander Katchkis, Itai Katz, Sergei Kovel, Michael Levit, Rami Maymon, Michael Nachkovsky, Alon Plattner, Dr. Lazar Shtirberg, Ksenia Sirota, Dr. Yael Talmon, Dr. Ygal Twig, Dr. Nasim Warwar, Helen Wolfson, and Ran Yehiely.

References

1. I. Rabi, Nuclear magnetic resonance using atomic beam methods (Noble prize lecture, 1944)
2. F. Bloch, and E. M. Purcell, Nuclear Magnetic Resonance (Noble prize lecture, 1952)
3. C. H. Townes, N. G. Basov, and A. M. Prokhorov, Maser and laser amplifiers (some of which are based on ESR) (Noble prize lecture, 1964)
4. N. Bloembergen and A. Schawlow, The three level maser (Noble prize lecture, 1981)
5. R. R. Ernst, Development of the methodology of high resolution nuclear magnetic resonance (NMR) spectroscopy (Noble prize lecture, 1991)
6. K. Wuthrich, Nuclear magnetic resonance spectroscopy for determining the three-dimensional structure of biological macromolecules in solution (Noble prize lecture, 2002)
7. P. C. Lauterbur and P. Mansfield, Discoveries concerning magnetic resonance imaging (Noble prize lecture, 2003)
8. Y. Artzi, Y. Twig, and A. Blank, Induction-detection electron spin resonance with spin sensitivity of a few tens of spins. Appl. Phys. Lett. 106 (2015)
9. L. Shtirberg, Y. Twig, E. Dikarov, R. Halevy, M. Levit, and A. Blank, High-sensitivity Q-band electron spin resonance imaging system with submicron resolution. Rev. Sci. Instrum. 82, 043708 (2011)
10. E. Dikarov, R. Shklyar, and A. Blank, New approach for measuring migration properties of point defects in amorphous oxides. physica status solidi (a). 211, 2177–2183 (2014)
11. A. Blank, Scheme for a spin-based quantum computer employing induction detection and imaging. Quantum Information Processing 12, 2993–3006 (2013)
12. H. Wolfson, R. Ahmad, Y. Twig, B. Williams, and A. Blank, A magnetic resonance probehead for evaluating the level of ionizing radiation absorbed in human teeth. Health Phys. 108, 326-35 (2015)
13. H. Wolfson, R. Ahmad, Y. Twig, P. Kuppusamy, and A. Blank, A miniature electron spin resonance probehead for transcutaneous oxygen monitoring. Appl Magn. Reson. 45, 955–967 (2014)
14. I. Katz, M. Fehr, A. Schnegg, K. Lips, and A. Blank, High resolution microimaging with pulsed electrically-detected magnetic resonance. J. Magn. Reson. 25, 26–35 (2015)
15. A. Blank, G. Shapiro, R. Fischer, P. London, and D. Gershoni, Optically detected magnetic resonance imaging. Appl. Phys. Lett. 106, 034102 (2015)
16. A. Blank, E. Dikarov, R. Shklyar, and Y. Twig, Induction-detection electron spin resonance with sensitivity of 1000 spins: En route to scalable quantum computations. Phys. Lett. A 377, 1937–1942 (2013)
17. Y. Twig, E. Dikarov, and A. Blank, Cryogenic electron spin resonance microimaging probe. J. Magn. Reson. 218, 22–29 (2012)
18. Y. Twig, E. Dikarov, W. D. Hutchison, and A. Blank, Note: High sensitivity pulsed electron spin resonance spectroscopy with induction detection. Rev. Sci. Instrum. 82, 076105 (2011)
19. W. Harneit, C. Meyer, A. Weidinger, D. Suter, and J. Twamley, Architectures for a spin quantum computer based on endohedral fullerenes. physica status solidi (b) 233, 453–461 (2002)
20. J. J. L. Morton, A. M. Tyryshkin, R. M. Brown, S. Shankar, B. W. Lovett, A. Ardavan, T. Schenkel, E. E. Haller, J. W. Ager, and S. A. Lyon, Solid-state quantum memory using the ^{31}P nuclear spin. Nature 455, 1085–1088 (2008)

49th RSC Meeting, Colchester (April 3rd – 7th, 2016)

The 49th annual international Royal Society of Chemistry EPR Meeting was held in Colchester, in the South East of England, and was organized by Dr Dimitri Svistunenko from the University of Essex. This was a meeting replete with history. The RSC meeting is perhaps the oldest continuously running annual EPR in the world. Colchester is famous for being the oldest recorded town in Britain, dating from well before Roman times. The majority of attendees stayed in restored coach houses – some dating from the 15th century – hotels replete with oak beams and olde world charm, and the meeting itself was held in the 19th century plush surroundings of Wivenhoe House, part of the University of Essex.

The 2016 meeting continued the tradition of bringing together researchers across Physics, Chemistry and Biology to discuss the latest theoretical, computational, methodological, instrumental and experimental work in EPR. The program, as usual, consisted of ten invited talks, including four plenaries, eight student talks and the award of the prestigious Bruker prize, Bruker Thesis prize and Jeol student prizes. The conference is interspersed with numerous coffee breaks, wine receptions and poster sessions designed to maximize interaction between all the participants.

Each day the conference started with a plenary talk. Prof Gunnar Jeschke (ETH Zurich) started the conference with a visionary talk on "A new era in pulsed EPR" followed by plenaries from Enrica Bordignon (Berlin), Christiane Timmel (Oxford) and Ah-Lim Tsai (Texas). Other invited speakers included Mario Chiesa (Turin), Aharon Blank (Technion), Daniel Klose (ETH Zurich), Janet Lovett (St Andrews), Till Biskup (Freiberg) and Anatoly Vanin (Moscow).

One of the highlights of the meeting is the award of prestigious Bruker prize, awarded every year, by the RSC EPR committee, to a scientist with an outstanding academic record, who has provided leadership in their field and whose work has had wide and clear international scientific impact, and who are also wonderful communicators. The 30 previous winners represent many of the most well known names in EPR. This year, the 31st winner of the prize was Prof David Britt from UC Davis who gave an outstanding and entertaining Bruker lecture entitled "Exploiting radical based catalysis in enzymes".

The now annual Bruker thesis prize offers slightly less history but the hope is that in time it will become just as prestigious as its more well established partner, and help lead to academic careers. This year the 2nd Bruker thesis prize was won by Dr Claudia Tait (Oxford) for a thesis and talk entitled "Uncrossing wires: EPR reveals spin delocalization in porphyrin nanoassemblies". There were many extremely high quality submissions, but the committee awarded the prize for a beautifully written and detailed thesis that was highly praised by the external examiners and all reviewers. As part of the prize, the winner is invited to give a lecture at the meeting and Claudia has now firmly established the tradition of wonderful Bruker thesis prize-winning talks. Details on how to enter the Bruker thesis prize can be found on the RSC EPR website.

Each year JEOL also awards a series of prizes for the best student talk with the winner being awarded the JEOL medal. Many past winners have now gone on to senior postdoctoral and academic positions, and each year the quality of the talks increase. This year the prize was won by Michael Lerch (UCLA) for an exemplary and beautiful talk entitled "Exploring protein conformational landscapes with SDSL and pressure resolved DEER". Runners-up included Matthew Dale (Warwick), Dimitry Akhmetzyanov (Frankfurt) and Satoru Yamamoto (Osaka City).

This year the student poster prize was sponsored by the International EPR Society and was won by Claire Motion (St Andrews) for a poster entitled "DEER Sensitivity between iron centres and nitroxides improves dramatically using broadband, high field EPR".

Best joke of the meeting was from Prof Sarah Raven (Leicester) who was concerned that not everyone present would know exactly where Leicester was. Top of the Premier League she reminded everybody!

The annual RSC meeting is run for the benefit of the EPR community and a prime aim is to make the meeting as interesting and accessible as possible. Registration costs are comparable to some other major conferences but include all food and accommodation, wine receptions, conference trip and the conference dinner. Conference costs are largely kept low by the local organizer aided by the RSC committee, taking on the administration duties and arranging subsidies with local hotels. Every year this represents a serious amount of work and the RSC committee would like to express its sincerest thanks to Dimitri and

the rest of his team who were tireless in their efforts to ensure the smooth and successful running of the meeting.

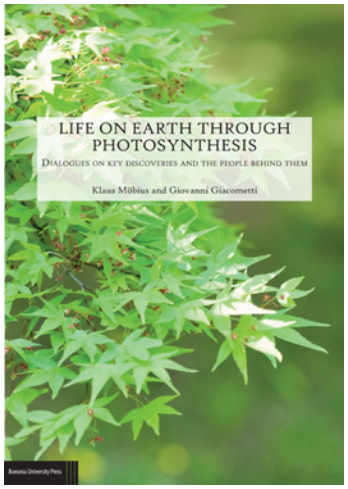
This certainly extended to the conference dinner, which was a grand and highly enjoyable affair held in Colchester Town Hall, and was accompanied with much wine, music, and magicians who entertained at every table followed by a highly entertaining and instructive talk from Prof Gert Denninger (Stuttgart) on the amazing science and acoustics of wine glasses.

The RSC group also welcomed a new Chair – Prof Eric McInnes (Manchester), a new secretary – Dr Ilya Kuprov (Southampton) and a new web-master – Dr Chris Wedge (Warwick) and three new Ordinary committee members – Dr David Norman (Dundee), Dr Alice Bowen (Oxford/Frankfurt) and Dr Bela Bode (St Andrews). They join Fraser McMillan (UEA) as Treasurer, Dr Maxi Roessler (QMC London), the outgoing Chair Dr Graham Smith (St Andrews), outgoing conference organizer Dr Dimitri Svistunenko, and incoming conference organisers Profs Christiane Timmel and Arzhand Ardevan on the committee. Prof Chris Kay and Dr Janet Lovett were terrific outgoing ordinary members.

The 50th anniversary RSC EPR meeting will be held in the "Harry Potteresque" Keble College, Oxford and will be organized by Christiane Timmel and Arzhang Ardavan. This is an amazing venue and promises to be an extremely special and memorable event, and so the dates of 2nd – 7th April 2017 should be firmly written in your diaries. Travel bursaries will be available to RSC student members.

Graham Smith

Timothy Cunningham became an Assistant Professor of Chemistry at Hanover College in Hanover, IN in August of 2016. Tim began his career by obtaining his B.S. in Chemistry from Mercyhurst College in Erie, PA. In his time at Mercyhurst, he performed computational modeling research investigating the structure of crystalline cellulose using Monte Carlo methods. The research inspired him to continue his education, specifically seeking his Ph.D. in Chemistry and thus in the Fall of 2008, Tim began graduate school at the University of Pittsburgh. Due to his interest in the field of Biophysical Chemistry, Tim joined the lab of Prof. Sunil Saxena to use ESR as a means to better understand biological systems. Tim's early work focused on using a variety of methods in an attempt to understand the behavior of the common R1 nitroxide spin label within the β-sheet protein environment. Further into his graduate career, Tim became interested in site-specific placement of Cu^{2+} within proteins using chelating tags and engineered binding sites generated through mutagenesis. After finishing graduate school in the summer of 2015, Tim accepted a Visiting Professor of Chemistry position at Hanover College. After one year in this role, Tim subsequently was selected for his current role as Assistant Professor. In his new position, Tim plans to further his work of developing metal binding motifs for the site specific placement of spins within protein systems.



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Summary

Photosynthesis is the most important process for Life on Earth. It provides all the oxygen we breathe, all the food we eat and all the fossil fuels we burn for our civilization. Understanding the underlying physical, chemical and biological principles of photosynthetic solar-energy conversion and sustainable storage – and ultimately copying them for "artificial" photosynthesis devices – is among the grand challenges of the cultural world under the threat of global climate change. The book describes milestone discoveries in photosynthesis research, ranging from the times of alchemy to present-day molecular biology, biophysics and biochemistry. It is written in the format of "Science-on-Stage" with dialogues between different characters related to research achievements in their historical and political context. It is composed of 13 Scenes, a Prologue, an Intermezzo and an Epilogue.

The Prologue is setting the stage for the follow-up Scenes with their discussions about essential discoveries, interspersing them with memoirs of the scientists involved, history of the ground-breaking work done in the respective time periods, their specific politics and consequences for society at large. Those social aspects are even more accented in the Intermezzo and Epilogue with reflections on how to bridge the gap between the two cultures, science and humanities. Whenever felt necessary, some technicalities of the photosynthetic processes are also given within the Scenes for a better understanding of the discussions. This is further supported by a Glossary and a Bibliography that is recommended for further reading. Each Scene stages "The Chorus", as in classical Greek theater and in many contemporary plays. It summarizes accepted scientific background knowledge, voices general ideas on progress and responsibility in science, and reminds of most important contributions of a multitude of researchers in the field. The Chorus consists of seven members, all experts in contemporary photosynthesis research: George Feher, Giovanni Giacometti, Klaus Möbius, Wolfgang Lubitz, Kev Salikhov, Harry Kurreck, and Giovanni Venturoli. More than 40 characters are involved in the dialogues.

Dialogues as the format of writing about controversial topics in science and humanities have been the traditional way of Renaissance Europe to express new ideas – and to defend them against traditional views. But this tradition practically disappeared from the scientific literature since the Age of Enlightenment. It was, however, reanimated after World War II, leading to a modern generation of Science-on-stage plays, often well received by a broad public.

The book describes not only eminent discoveries but also tells illuminating stories on the people behind them. Complicated characters are involved in intense competition; extremes of euphoria in case of success alternate with bottomless disappointment in case of failure. Stories are told of the researchers' greatest strength and – in not so rare cases – of their human weakness. They are told to experts and laymen alike, to teachers and students, to undergraduates, postdoctoral researchers and professors, in short to anybody from the educated public. The hope is that even if the details of photosynthesis may be obscure to many readers and audiences, the life stories of the protagonists and the implications of their discoveries and ideas become accessible.

The book appears at the right time for the United Nations "International Year of Light and Light-based Technologies, 2015", this observance "that aims to raise awareness of the achievements of light science, its applications, and its importance to humankind to provide solutions to worldwide challenges in energy, education, agriculture, communications and health."

EPR => Hot Science

Detecting weak spin-spin coupling in triplet-exciton polaron complexes 16

Title: Using coherent dynamics to quantify spin coupling within triplet-exciton/polaron complexes in organic diodes
Authors: W. J. Baker, T. L. Keevers, C. Boehme, D. R. McCamey
Journal/Publication date: Phys. Rev. B, 2 July 2015: Vol. 92, no. 4, pp. 041201, DOI: http://dx.doi.org/10.1103/PhysRevB.92.041201

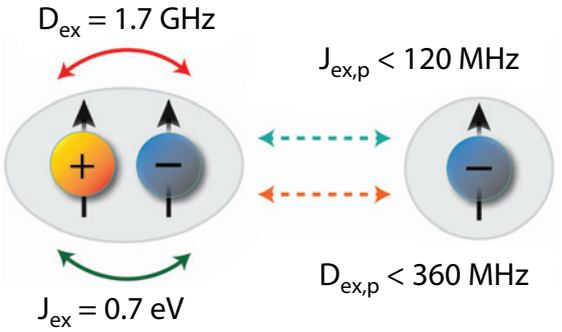


Figure: We used electrically-detected ESR to measure the zero-field splitting found in exciton-polaron complexes.

Spin is essential to the performance of organic (carbon-based) electronics. External magnetic fields can induce conductivity changes of more than 4000% in light-emitting devices [1]. These kinds of effects provide unique insight into the microscopic structure of organic devices and can be used to improve their performance.

Organic magnetic field effects are driven by the spin-dependent annihilation of spin pairs. Identifying and characterizing these processes is an outstanding problem. We investigated the annihilation of a triplet-exciton by a trapped electron using electrically-detected spin resonance [2]. Electronic transitions within the spin-1/2 polaron or spin-1 exciton change the overall permutation-symmetry of the pair, leading to a change in the sample conductivity.

Rabi oscillations were seen from the polaron transitions at full field and the exciton transitions at half-field. Our analytic and numerical calculations showed that these transition frequencies were sensitive to the spin-spin coupling within the pair. By correlating the observed Rabi frequencies we were able to accurately estimate the spin-spin coupling, as shown in the figure. These experiments clarify the origin of magnetic field effects in organic polymers by clearly establishing the role of weakly-coupled triplet-exciton polaron complexes.

1. Wang, Yifei, et al. "Immense magnetic response of exciplex light emission due to correlated spin-charge dynamics." arXiv preprint arXiv:1601.03621 (2016).
2. Boehme, Christoph, and Klaus Lips. "Theory of time-domain measurement of spin-dependent recombination with pulsed electrically detected magnetic resonance." Physical Review B 68.24 (2003): 245105.

Enhancing coherence in molecular spin qubits 17

Title: Enhancing coherence in molecular spin qubits via atomic clock transitions
Authors: Muhandis Shiddiq, Dorsa Komijani, Yan Duan, Alejandro Gaita-Ariño, Eugenio Coronado and Stephen Hill
Journal/Publication date: Nature, 17 March 2016: Vol. 531, pp. 348–351, DOI: 10.1038/nature16984

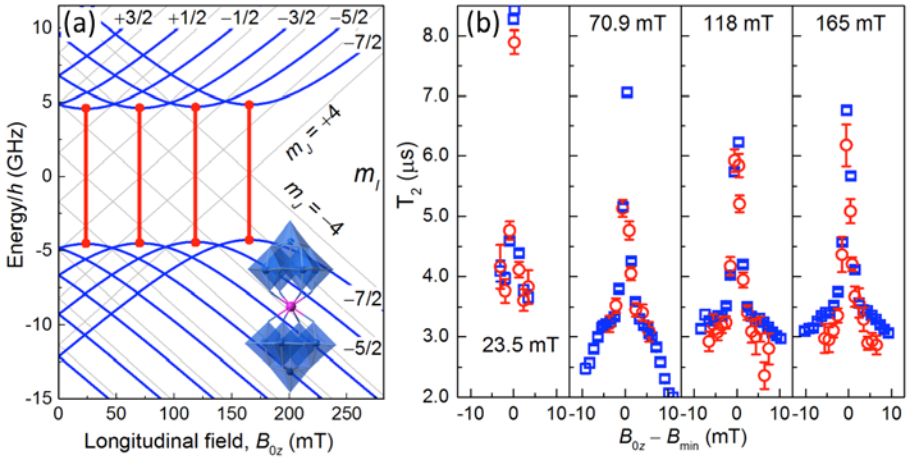


Figure: (a) A slight axial asymmetry of the $Ho(W_5O_{18})_2$ molecule (inset) generates avoided level crossings (blue curves) between hyperfine levels with the same nuclear projection, m_I; the hyperfine levels for the unperturbed axial case are shown in gray. Transitions that connect the gap minima (red lines) are the clock transitions. (b) 5 K coherence times (T_2) deduced 9.1 (red) and 9.2 GHz (blue) at the four clock transitions in (a).

Electron and nuclear spin states associated with molecular nanomagnets are among the many systems being explored as potential building blocks for a quantum computer. All such systems are challenged by decoherence – the destructive interaction of the quantum unit of information, or qubit, with its environment. When dealing with spin qubits, the strongest source of decoherence is the magnetic dipolar interaction. To minimize it, spins are typically diluted in a diamagnetic matrix. For example, this dilution can be taken to the extreme of a single phosphorus atom in silicon, while in molecular matrices a typical ratio is one magnetic molecule per 10,000. However, there is a fundamental contradiction between reducing decoherence by dilution, and allowing quantum operations via the interaction between spin qubits. To solve this apparent paradox, the design and engineering of quantum hardware can benefit from a "bottom-up" approach whereby the electronic structure of magnetic molecules is chemically tailored to give the desired physical behavior. This publication reports a very effective way of eliminating decoherence in solid-state molecular spin qubits without resorting to extreme dilution [1]. It is based on the design of molecular structures with crystal field ground states possessing large tunneling gaps that give rise to optimal operating points, or "atomic clock transitions",

at which the quantum spin dynamics become protected against dipolar decoherence. This approach is illustrated with a holmium molecular nanomagnet in which long coherence times (up to 8.4 μs at 5 K) can be obtained at unusually high concentrations. This finding opens new avenues for quantum computing based on molecular spin qubits. See also [2].

1. Shiddiq, M. et al., Nature 2016 531, 348–351.
2. B. Goss Levi, Physics Today 2016 69, 17–21. DOI: 10.1063/PT.3.3157

In situ EPR reveals the catalytic mechanisms for the preferential CO oxidation in hydrogen using $CuO–CeO_2$ catalysts 18

Title: *In situ* EPR study of the redox properties of $CuO–CeO_2$ catalysts for the preferential CO oxidation (PROX)
Authors: Feng Wang, Robert Büchel, Anton Savitsky, Michal Zalibera, Daniel Widmann, Sotiris E. Pratsinis, Wolfgang Lubitz, Ferdi Schüth
Journal/Publication date: ACS Catalysis, 18 April 2016: Vol. 6, 3520–3530, DOI: 10.1021/acscatal.6b00589

Understanding the redox properties of metal oxide based catalysts is a major task in catalysis research. *In situ* EPR spectroscopy is capable of monitoring the change of metal ion valences and formation of active sites during redox reactions, allowing for the identification of ongoing redox pathways.

We have applied *in situ* cw EPR spectroscopy combined with online gas analysis, supported by *ex situ* multifrequency pulsed EPR and X-ray photoelectron spectroscopies, X-ray diffraction, X-ray absorption near edge structure, temporal analysis of product, and mass spectrometry to study the catalytic mechanisms of $CuO–CeO_2$ catalysts for preferential oxidation of carbon monoxide in hydrogen (PROX).

We find that two redox mechanisms are responsible for CO oxidation: (i) a *synergetic mechanism* that involves the redox pair Ce^{4+}/Ce^{3+} during oxidation of Cu^0/Cu^+ species to Cu^{2+}, and (ii) a *direct mechanism* that bypasses the redox pair Ce^{4+}/Ce^{3+}. In addition, EPR experiments with isotopically enriched $^{17}O_2$ established the *synergetic mechanism* as the major redox reaction pathway. These results emphasize the importance of the interactions between Cu and Ce atoms for catalyst performance. Guided by these results an optimized $CuO–CeO_2$ catalyst could be designed. A rather wide temperature operation window of 11 degrees (from 377 K to 388 K), with 99% conversion efficiency and 99% selectivity was achieved for the preferential oxidation of CO in a H_2 feed.

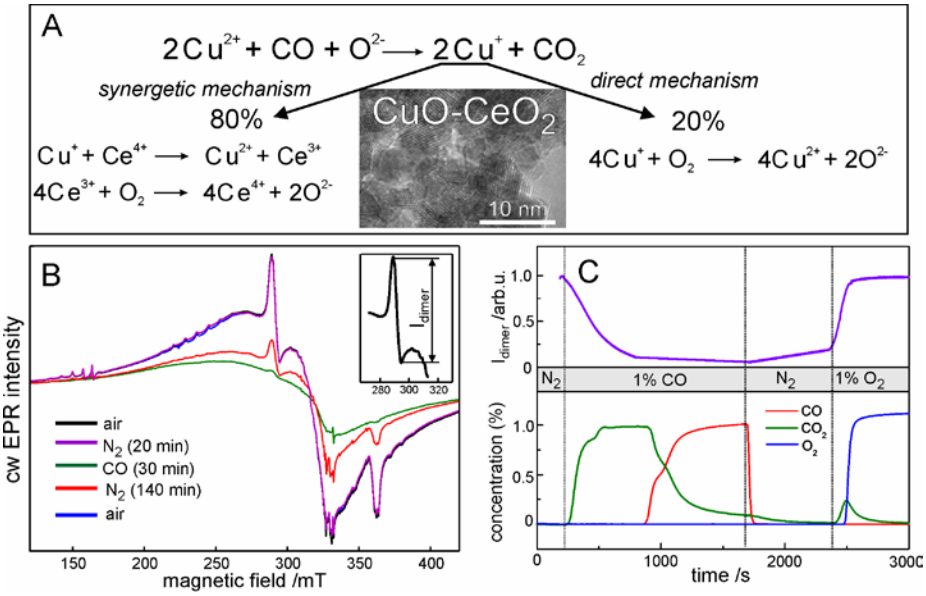


Figure: (A) Reaction schemes demonstrating the elucidation of synergetic and direct CO oxidation mechanisms for $CuO–CeO_2$ catalyst. (B) X-band cw EPR spectra of 20 wt% $CuO–CeO_2$ recorded at 453 K during the treatment with air/N_2/CO/N_2/air. The durations of the particular gas treatments are indicated. The insert shows the dimer EPR signal used for kinetic measurements. (C) Upper trace: Time dependence of Cu^{2+} dimer EPR signal intensity at 289 mT during the N_2/CO/N_2/air cycle at 453 K. Lower traces: Corresponding CO, CO_2 and O_2 concentrations simultaneously recorded by the gas analysis system.

Virginia Diodes, Inc.
virginiadiodes.com

Transmit and Receive Systems Covering the 70GHz-3THz Spectrum

VDI offers a wide variety of transmit and receive systems covering the 70GHz-3THz spectrum. These systems incorporate VDI's frequency extension and mixer components coupled with commercially available microwave oscillators and amplifiers.

For transmit systems, VDI can configure them with or without a drive oscillator. A VDI Amplifier / Multiplier Chain (AMC) requires a customer supplied low frequency source (typically <20GHz, 10dBm nominal). A VDI Transmitter (Tx) integrates a source (oscillator or synthesizer) with the VDI AMC. A VDI Mixer / Amplifier / Multiplier Chain (MixAMC) requires a customer low frequency local oscillator. A VDI Receiver (Rx) integrates the LO drive oscillator with the Mixer and LO Chain for turn-key operation.

Standard AMCs and MixAMCs have been developed to provide high performance RF drive multiplication and downconversion for full waveguide band coverage. These systems can be used to extend traditional spectrum analyzers and signal generators into the THz and mm-wave ranges. VDI's standard AMC and MixAMCs offer various modes of operation. VDI AMCs can be operated in standard frequency mode (<20GHz, 10dBm nominal) or high frequency RF drive mode (<45GHz, 0dBm nominal). VDI MixAMCs can also operate in standard and high frequency LO drive modes. Customers also have the option to operate MixAMCs for block-downconversion (<20GHz IF) or as a spectrum analyzer extender. Standard AMCs and MixAMCs are available from WR15 (50-75GHz) to WR1.0 (750-1,100GHz).

VDI offers both narrow-band high-power and broadband low-power systems. High power systems use VDI's D-series X2 multipliers to achieve maximum multiplier efficiency and power handling. VDI has developed many high power systems for special customer applications, such as a novel multiplier based source with output power of 160mW at 200GHz.

Reconfigurable / modular AMCs are also available upon request.

How to retire and still make a difference in the world with EPR

Chapter One

At 71, I'm on the bleeding edge of the baby boom. There are a bunch of us who are hitting retirement age. There are scores of newly minted PhD students clambering for our university positions. Likely, sticking around in our current jobs will not bring in more retirement salary. In fact, retiring past 65 will cost us money. But we love our labs, our work, our students, our potential. What are we to do?

There is lots of advice about how we can help schools, teach science to their students, teach science to their teachers, and so forth. But this is not what we have spent our lives training ourselves to do. I shudder to think how a group of middle or high school students would take to my lecturing them on critical thinking, experimental design, data analysis, and writing. I guarantee I could put them all to sleep in under an hour because, honestly, none of this matters to them. Science has been taught as a 4 (or 5, or 6, or 7, or 8...) step process that you have to follow or you get graded down. And, besides, the scientific experiments these students will be doing have all been done before. Indeed, they have been done so many times before that the teachers have written answers and can grade the students on how close they come. Why should the kids listen to me? I can tell them nothing that will give them a better grade.

If you watch a two-year old play, they are already fantastic scientists. They do experiments, they learn from their mistakes, they improve, they widen their horizons every moment of every day. But, by the time they hit middle school or high school, most of this curiosity has been beaten out of them by the daily grind of being told they are doing it wrong.

This is where we can make a difference. Students (at least the bright ones) crave something real, something that is much closer to the science we do as professionals rather than the science they are taught by educators. In the subsequent paragraphs, I propose a way to expose students to science that is real enough to interest them, difficult enough to challenge them, and interesting enough to capture their imagination and bring back the sense of wonder they were born with.

The Steppingstone MAgnetic Resonance Training Center was founded on this principle – create an environment that was real, challenging, and interesting for students who wanted to taste science the way scientists do it. Electron Spin Resonance offers a unique opportunity for this environment because they have never heard of it and, therefore, have no preconceived notions of what they should or should not know about it. A big Bruker-BioSpin ESP 300 certainly looks impressive – it's got a huge magnet, lots of knobs and buttons, dials and switches, and make a satisfying amount of noise. The students are drawn to it like moths to a flame and they can pretty much learn to use it in a couple of hours (even middle school students although it helps to have bright ones). A brief discussion of free radicals (the kids have heard of these) and how omnipresent they are in our environment brings forth lots of questions of the type "Does this have free radicals in it?" Now it's easy to show them the difference between something that doesn't have free radicals (all you see is a baseline although they will think the noise means something at this point) and something that does (a big squiggly line on the chart). Have some samples available – tea (great for manganese if you choose lousy tea), coffee, hair samples (I'm old enough to be the control), pine needles, nail polish, for them to play with. My hair has a small signal, the hair from someone with dark or black hair will be much larger. Now you have the beginnings of a scientific experiment – students will ask about blonds and redheads, natural or dyed hair, and you can answer "I don't know, how would you find out?" This gives them the context for listening to your lecture about scientific design. Obvious questions to ask them are "Are you all using the same amount of hair? Why might that matter? What kinds of experiments could you do to answer your question? How do you interpret the results (what do you measure)?" They are off and running.

Dr. Reef (Philip D., II) Morse, Director
Steppingstone MAgnetic Resonance
Training Center
30250 Grand River Ave.
Farmington Hills, MI 48336

The International Conference Modern Development of Magnetic Resonance (MDMR2016)

Kazan, Russian Federation,
October 31 – November 4, 2016
www.kfti.knc.ru/mdmr/2016

The Zavoisky Physical-Technical Institute of the Russian Academy of Sciences organizes the Week of Science "Horizons of Magnetic Resonance" including the International Conference "MDMR2016" and the Zavoisky Award 2016 ceremony. The celebration of the 80th birthday of Prof. Kev M. Salikhov is planned within the Week of Science.

The online registration is open at www.kfti.knc.ru/mdmr/2016

Contact: Dr. Violeta K. Voronkova
mdmr@kfti.knc.ru

The 55th Annual Meeting of the Society of Electron Spin Science and Technology (SEST2016)

Osaka City University, Osaka, Japan,
November 10–12, 2016
www.sci.osaka-cu.ac.jp/~sest2016

Chair: Kazunobu Sato
Vice Chair: Daisuke Shiomi
Local Organizing Committee: Ikuko Akimoto, Toshiaki Arata, Hideo Iwahashi, Katsuichi Kanemoto, Yoshio Teki, Yuko Hosokoshi, Hiroyuki Yasui, Chihiro Yamanaka.
Secretariat: Shigeaki Nakazawa, Kazuo Toyota, Kenji Sugisaki
Contact: sest2016@sci.osaka-cu.ac.jp

XXVII International EPR Seminar

Center of Spectroelectrochemistry, Leibniz Institute for Solid State and Materials Research, Dresden, Germany, April 3–5, 2017
www.ifw-dresden.de/de/institute/institut-fuer-festkoerperforschung/events/xxvii-international-epr-seminar

Contact: Dr. Evgenia Dmitrieva and Dr. Alexey Popov epr27@ifw-dresden.de

EPR2017 – The International Conference on Biomedical Electron Paramagnetic Resonance Spectroscopy and Imaging

In Vivo Multifunctional Magnetic Resonance center, Health Sciences Center at West Virginia University, Morgantown, West Virginia, USA, July 16–22, 2017
www.hsc.wvu.edu/epr2017

Contact: oxana.tseytlin@hsc.wvu.edu

POSITIONS

EPR sales position

Bruker Biospin GmbH, Germany, is seeking a candidate for an EPR sales position covering Central and Eastern EU. The candidate should have a PhD degree in natural science, a deep knowledge of EPR and a high technical competence to be able to help potential customers making the right choice. The successful candidate will work in close interaction with the EPR application group, the Bruker marketing division and be part of the international Bruker Biospin sales team.

The position requires the willingness and ability for frequent domestic and international traveling. Strong communication skills are essential as well as fluent English. Knowledge of German is an advantage.

Bruker Biospin GmbH is located in the Karlsruhe area. From here the Black Forrest and France are within easy reach and offer many attractive activities. Karlsruhe is also located at main rail way line connecting to the international airports in Frankfurt and Stuttgart and all major cities in Germany and neighboring countries.

Interested applicants should send their cover letter and resume to Dr Peter Hoefer (peter.hoefer@bruker.com) or Dr Ruediger Weisemann (ruediger.weisemann@bruker.com)

Postdoc in optical nuclear magnetic resonance, joint Los Alamos/UNM, USA

The quantum nanophotonics and biosensing lab at U. of New Mexico (PI: Victor Acosta) and the atomic magnetometer/NMR/MRI labs at Los Alamos National Lab (PI: Igor Savukov) seek a motivated postdoctoral candidate for a joint UNM/LANL project. The successful candidate will work on a highly multidisciplinary project that combines new techniques in optical nuclear polarization using NV centers in diamond nanostructures with low-field and optically-detected NMR/MRI. The goal is to develop a microfluidic platform operating at room temperature and low magnetic field which can deliver biochemical analytes with a nuclear polarization exceeding that possible using large superconducting magnets and/or cryogenic temperatures.

While working on the project, the postdoc will:

- Apply quantum mechanics, nanophotonics, and biochemistry to emerging new fields.
- Learn semiconductor nanofabrication techniques in world-class cleanrooms (CHTM, CINT).
- Work with partners in academia, national labs (LANL, Sandia), and industry (ODMR Tech).

The position will initially be based in Albuquerque, NM at the UNM lab. There the work will be focused on developing the NV hyperpolarization apparatus. Then the postdoc will transition to conducting NMR/MRI experiments at LANL to characterize and optimize its performance.

A PhD in Physics, Chemistry, Optical/Electrical/Chemical/Biomedical Engineering, or a related field is required. Experience in spin physics, biophysics tool development, and/or quantum optics is desired. Experience in magnetometry, semiconductor nanofabrication, and/or solid-state color centers is also helpful. Compensation is commensurate with experience and is expected to increase when work transitions to LANL. Candidates with very strong publication records will have an opportunity to apply to highly competitive

LANL fellowship programs. More information is available on our webpage. Interested candidates, please send Cover letter (describing research interests and career goals) and CV (with complete publication record) to Victor Acosta (vmacosta@unm.edu) and Igor Savukov (isavukov@lanl.gov). UNM and LANL are equal opportunity employers.

Postdoctoral Fellow

The Magnetic Resonance Spectroscopy group at Rensselaer Polytechnic Institute (RPI) is conducting cuttingedge research in the fields of solar energy transduction in natural and artificial systems and the development of novel materials and solar technologies. By performing fundamental and applied research, we work on sustainable solutions for major challenges facing energy and the environment. RPI is committed to the training of future scientists and engineers and is one of the oldest science and engineering universities in the United States.

We are looking for a Postdoctoral Fellow for advanced multi-frequency pulsed electron paramagnetic resonance (EPR) spectroscopy of natural and artificial systems.

Your tasks

– Operation and further development of pulsed EPR spectroscopy experiments (including ENDOR, HYSCORE and transient EPR spectroscopy)
– Performance of experiments on redox proteins, metal oxides and thin films
– Analysis and numerical simulation of experimental data
– Presentation of scientific results at national and international conferences
– Publication of scientific results in international journals
– Scientific collaboration with graduate and undergraduate researchers at RPI

Your profile

You are a flexible team member able to work independently on different projects. You have completed your PhD in chemistry or physics and have experience with pulsed EPR spectroscopy. A good command of various software tools enables you to analyze pulsed EPR spectra readily. You have active interest in experimental work with good practical skills and enjoy working in an interdisciplinary team. Your broad knowledge in physical chemistry and spin physics is a valuable asset to understanding the results of complex experiments. Good communication skills in English are required.

For further information please contact:
Prof. K. V. Lakshmi
Department of Chemistry and Chemical Biology and The Baruch '60 Center for Biochemical Solar Energy Research Rensselaer Polytechnic Institute
Troy, NY 12180
e-mail: lakshk@rpi.edu
lakshmi@baruch60center.org
phone: (518) 698 7976

Please send your application materials to Prof. K. V. Lakshmi through e-mail correspondence.

Cryogenic EPR Postdoctoral Position

A postdoctoral position is available immediately for a collaborative project between Professor Cory's lab at The Institute for Quantum Computing (IQC) and a local startup. The project uses superconducting resonators and Optimal Control Theory (OCT) to increase the sensitivity of pulsed electron spin resonance at cryogenic temperatures. The goal of the project is to also demonstrate applications to molecularly thin samples. This program is expected to reveal new and interesting results of EPR of biochemical processes.

The successful applicant should have an advanced degree (PhD) in chemistry, biochemistry or physics with significant experience in EPR of biomolecules.

The appointment will be for two years with the possibility of renewal. The salary is competitive and commensurate with experience, ranging from $55,000 to $70,000. Women and minorities are encouraged to apply.

Apply to grum.teklemariam@highqlp.com.

Research Scientist (Postdoctoral associate)

The Institute of Macromolecular Chemistry AS CR, v.v.i. seeks a postdoctoral associate / research scientist to join the Laboratory of electron paramagnetic resonance of polymer systems (EPR)

Requirements: University degree and PhD in the field of chemistry, physical chemistry or physics / Practical experience with the method of electron paramagnetic resonance (EPR) / Knowledge of and working experience with polymers and EPR imaging will be an advantage / Stays abroad will be an advantage / Good knowledge of English language / Good publication activity / Independence, reliability.

Details about research work can be obtained from RNDr. Petr Štěpánek, DrSc., stepanek@imc.cas.cz

Candidates should submit a structured CV emphasizing experience relevant to the advertised position, a motivation letter and a list of publications and other results to e-mail: fencl@umch.cz HR department tel. (420) 296 809 385.

Available: Used EPR Spectroscopist

Old, but well maintained EPR Spectroscopist, with wide application experience, seeks opportunity to support active research group. EPR- based publications over 5 decades, most recently 2011, mass spectrometry publications to 2014. Experience in the study of transient organic and organometallic free-radicals; transition metal complexes; spin-trapping; spin probe; radical ions; matrix isolation and γ-radiolysis techniques; photocatalysis; polymer degradation and stabilisation etc. Has Bruker, Varian and JEOL operating experience, plus track record in NMR and mass spectrometry techniques. Would prefer to ▶

work in biochem/biological area, but would consider anything interesting. Opportunity arises due to restructure of Research Department in Australian steel company after 26 years faithful service. Excellent grant writing skills, 100% success rate. Speaks English, German and some French.

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

Postdoctoral Associateships in Magnetics at NIST

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

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

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

EPR Specialist Position at Johns Hopkins

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

Bruker BioSpin Corp

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

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

EQUIPMENT

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

EPR parts, electronics and hardware

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

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

Design and construction of EPR electronics

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

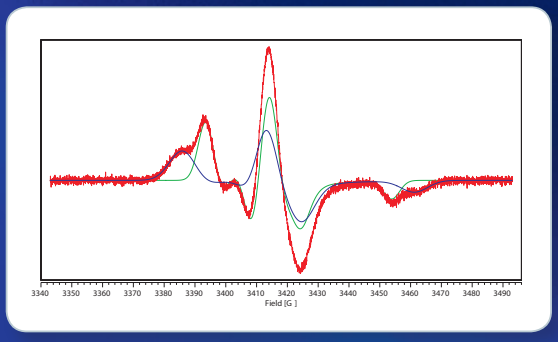
Available: Used Varian EPR equipment

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

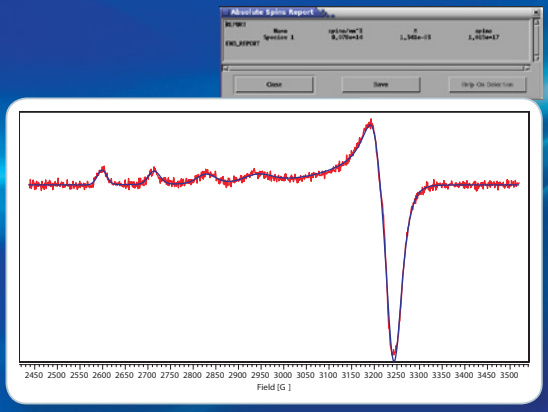
Please contact: James Anderson, Research Specialties, 1030 S. Main St., Cedar Grove, WI 53013, USA. phone/fax: 1-920-668-9905, e-mail: janderson36@wi.rr.com

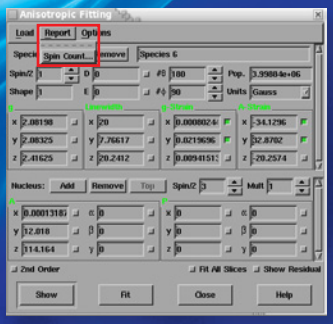
Anisotropic SpinFit

Now available in Xepr and Xenon



Fitting and quantifying multiple species



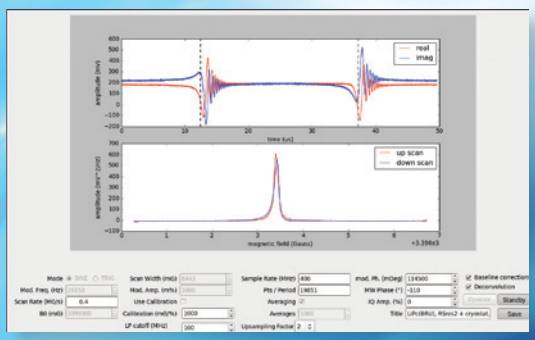


Direct link to SpinCount

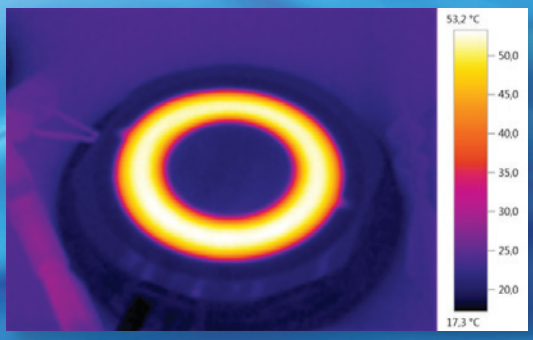
- Fast perturbation simulation
- Fitting of anisotropic spectra
- Quantification via SpinCount (with transition moments)
- Disentangling of multiple species
- Library of common EPR species

Discover more at: www.bruker.com/epr

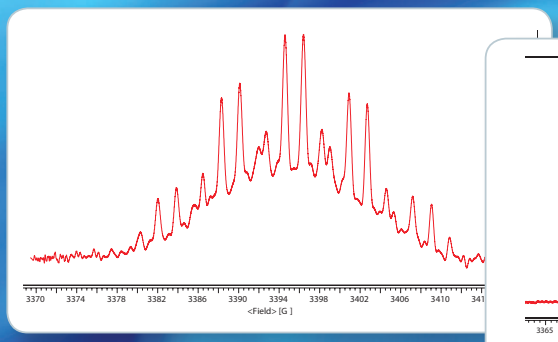
Towards a Commercial Rapid Scan Unit



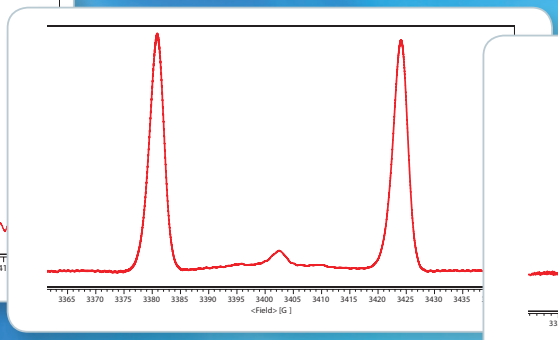
Real-time monitoring of time domain and reconstructed signal



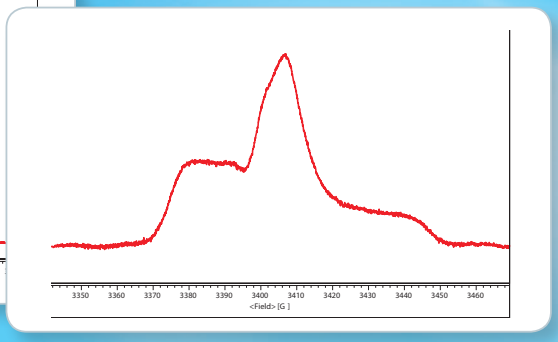
Infrared picture of rapid scan coil at 4.5 A with water cooling of 2l/m



PNT solution (50 G/ 20 kHz)



31P doped Si at 10 K (100G, 30 kHz)



TEMPO/TMP at RT (130 G, 20 kHz)

First Performance Data

- Scan width up to 170 G
- Scan frequency range 10 – 100 kHz
- Real time reconstruction
- Compatible with variable temperature units

Discover more at: www.bruker.com/epr