



Officers of the International EPR (ESR) Society

PRESIDENT

Jack H. Freed Department of Chemistry and Chemical Biology Director of ACERT B52 Baker Laboratory Cornell University, Ithaca, NY 14853, USA phone: 607-255-3647, fax: 607-255-0595 e-mail: jhf3@cornell.edu web: www.acert.cornell.edu

VICE PRESIDENTS

Americas

Michael Bowman Department of Chemistry, Box 870336 The University of Alabama Tuscaloosa, AL 35487-0336, USA phone: 205-348-7846, fax: 205-348-9104 e mail: mkbowman@as.ua.edu

Asia-Pacific

Michael Davies The Heart Research Institute 114 Pyrmont Bridge Road, Camperdown Sydney, NSW 2050, Australia phone: +61 2 8208 8900, fax: +61 2 9565 5584 e-mail: daviesm@hri.org.au

Europe

Thomas Prisner Institut für Physikalische und Theoretische Chemie J. W. Goethe-Universität Frankfurt Max-von-Laue-Str. 7 60438 Frankfurt am Main, Germany phone: 49 69 798 29 406, fax: 49 69 798 29 404 e-mail: prisner@chemie.uni-frankfurt.de web: www.prisner.de

SECRETARY

Sushil K. Misra Concordia University 1455 de Maisonneuve Boulevard West Montreal (Quebec), H3G 1M8, Canada phone: 514-848-2424 extension 3278 fax: 514-848-2828 e-mail: skmisra@alcor.concordia.ca web: physics.concordia.ca/faculty/misra.php

TREASURER

Tatyana I. Smirnova North Carolina State University Department of Chemistry Campus Box 8204, Raleigh, NC 27695-8204, USA phone: (919) 513-4375, fax: (919) 513-7353 e-mail: tatyana_smirnova@ncsu.edu

IMMEDIATE PAST PRESIDENT

Wolfgang Lubitz Max-Planck-Institut für Bioanorganische Chemie Stiftstr. 34-36, Mülheim an der Ruhr D-45470, Germany phone: 49 208 306 3614, fax: 49 208 306 3955 e-mail: lubitz@mpi-muelheim.mpg.de

FOUNDER PRESIDENT

Harold M. Swartz Dartmouth Medical School Department of Radiology & EPR Center 7785 Vail Room 702 Hanover, NH 03755-3863, USA phone: 1-603-650-1955 fax: 1-603-650-1717 e-mail: harold.swartz@dartmouth.edu

Fellows of the International EPR (ESR) Society

Anatole Abragam John Michael Baker Brebis Bleaney (1915-2006) James R. Bolton Harvey A. Buckmaster Anders Ehrenberg Gareth R. Eaton Sandra S. Eaton George Feher George Fraenkel Erwin Hahn Karl Hausser (1919-2001) Noboru Hirota Clyde A. Hutchison, Jr. (1913-2005) James S. Hyde Lowell Kispert Daniel Kivelson (1929–2003) Melvin P. Klein (1921-2000) Harry Kurreck August H. Maki (1930-2008)

Bruce R. McGarvey Keith A. McLauchlan Klaus Möbius Yuriy N. Molin James R. Norris John R. Pilbrow Charles P. Poole, Jr. Aleksandr M. Prokhorov (1916-2002) Tengiz I. Sanadze **Charles P. Slichter** Leslie H. Sutcliffe Harold M. Swartz Martyn C. R. Symons (1925-2002) Yuri D. Tsvetkov Joan H. van der Waals George D. Watkins John A. Weil (1929-2010) Samuel I. Weissman (1912-2007) David Whiffen (1922-2002) Hans C. Wolf



www.epr-newsletter.ethz.ch

The official publication of the International EPR (ESR) Society is supported by the Society, by corporate and other donors, the Zavoisky Physical-Technical Institute of the Russian Academy of Sciences, Kazan, Russian Federation, and the Swiss Federal Institute of Technology, Zürich, Switzerland.

EDITOR

Laila V. Mosina Zavoisky Physical-Technical Institute Russian Academy of Sciences Kazan, Russian Federation mosina@kfti.knc.ru

ASSOCIATE EDITORS Candice S. Klug Medical College of Wisconsin Milwaukee, WI, USA candice@mcw.edu Hitoshi Ohta Molecular Photoscience Research Center, Kobe University, Kobe, Japan hohta@kobe-u.ac.jp Thomas Prisner Institute of Physical Chemistry, Frankfurt, Germany prisner@chemie.uni-frankfurt.de

> TECHNICAL EDITOR Sergei M. Akhmin Zavoisky Physical-Technical Institute Russian Academy of Sciences Kazan, Russian Federation akhmin@kfti.knc.ru

FOUNDING EDITOR R. Linn Belford Illinois Research Center, University of Illinois at Urbana, Urbana, IL, USA rbelford@uiuc.edu

> EDITORIAL OFFICE Zavoisky Physical-Technical Institute Russian Academy of Sciences Sibirsky trakt 10/7, Kazan 420029 Russian Federation phone: 7-843-2319096 fax: 7-843-2725075

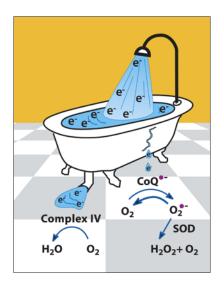
Please feel free to contact us with items (news, notices, technical notes, and comments) or ideas for the *EPR newsletter*.

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

ISSN 1094-5571



PRINTING: LaPlume and Sons Printing, Inc. One Farley Street, Lawrence MA 01843 USA phone: (978) 683-1009, fax: (978) 683-4594



The cover picture illustrates aspects of the research carried out by Garry R. Buettner, recipient of the 2009 IES Silver Medal for Biology/Medicine. His research focuses on the flow of electrons through chemical, biochemical, and biological systems and the consequences of changing the current in different biological circuits. This picture represents the flow of electrons through the electron transport chain; in the high-flux circuit, most of the electrons flow to dioxygen to form water, releasing the energy that sustains life. A small fraction flows through the low flux circuit producing superoxide and hydrogen peroxide, biological signaling molecules. Superoxide dismutase can "pull" electrons into the low flux circuit; SOD serves as a bifurcation point between one-electron and two-electron signaling cascades in cells and tissues. He has used EPR to understand the flow of electrons in a wide variety of issues in biology and medicine. (Adapted from Free Radic. Biol. Med. 41, 1338-1350, 2006.)



Eidgenössische Technische Hochschule Zürich Swiss Federal Institute of Technology Zurich



The Publication of the International EPR (ESR) Society

volume 21 number 1 2011

2	Editorial		
	by Laila Mosina		
	Guest of the issue		
2	Animal Detected Magnetic Resonance		
	by P. J. Hore		
	Another passion		
4	Birding as My Passion.		
	part 1: Representative Experimental Results		
	by Hal Swartz		
	Anniversaries		
6	70th Birthday of F. Ann Walker		
	by John H. Enemark		
7	70th Birthday of John H. Enemark		
	by Jon McMaster and C. David Garner		
	EPR newsletter anecdotes		
8	The First International Symposium on		
	Electron Spin Resonance in Chemistry in Greece		
	by Les Sutcliffe		
11	Present Day EPR Spectroscopy in Greece		
	by Yiannis Sanakis, George Mitrikas, Vassilios Petrouleas and Yiannis Deligiannakis		
14	Notices of meetings		
	Conference reports		
14	Magnetic Spectroscopy Community Celebrated the		
	70th Birthdays of John Enemark and Ann Walker at the 241st National Meeting of the		
	American Chemical Society in Anaheim		
	by Partha Basu and Mario Rivera		
10, 15	New books & journals		
15	Reader's corner		
16	Market place		

Editorial

Dear colleagues,

By now you must have received your copy of the *EPR newsletter* 20/4 (2011), the 50-years-of-Bruker special issue. I presume you could not believe your eyes when you saw that it is a full color issue. Yes, it is! You know, when I had a final look at it before it was put on the newsletter website, I had an inner feeling that we should have this issue in full color and that's it! I told Peter Höfer about this idea and he agreed that this issue is really special for Bruker, and promised to find extra money to have the full color version.

I cannot resist the temptation to share with you George Feher's comments on this issue: "As usual, your latest *EPR newsletter* was very interesting and well put together, with the exception, in my opinion, of an omission..." George meant that among all the accolades to Bruker, Jim Hyde's early important contribution of designing the well engineered VARIAN spectrometer was not mentioned. I could only respond to George that I would mention his comments in my next editorial and emphasized that we concentrated on Bruker equipment because it was a jubilee issue and we did not intend to give a comprehensive review of all EPR equipment available.

As to the present issue, first of all I would like to thank most heartily Peter Hore, Hal Swartz, Les Sutcliffe, Ann Walker and John Enemark for their patience. Our latest issue somewhat delayed the publication of their material. Les Sutcliffe's story about the first International EPR conference in Greece (p. 8) is nicely supplemented by the overview of the present day EPR in Greece by Yiannis Sanakis et al. (p. 11). Interestingly, birds are the subject of the articles by Peter Hore (p. 2) and Hal Swartz (p. 4): bird's magnetic orientation and birding as a passion, respectively. By the way, do not be surprised that in contrast to the online version, in the printed version the terrific illustrations of birds from Hal's article move to the third cover page to keep their colorful beauty. Peter Höfer kindly agreed that the relevant Bruker ad be shifted to the body text. Pity, we cannot afford to have full color versions permanently... this would be just great ... or why not? If the IES members pay their dues and attract new members, then perhaps this dream could come true! In the long run, it depends only on us and our goodwill.

Last but not least: dear Ann and John, although delayed we very warmly congratulate you on your birthdays and wish you many happy returns of the day!

Laila Mosina



P. J. Hore

Department of Chemistry, University of Oxford

Agnetic resonance spectroscopists seem to be fond of acronyms: one you may not have come across before is ADMR, the title of this short article. It, or something similar, was coined by Thorsten Ritz of the University of California, Irvine to describe an unorthodox, very low frequency EPR technique in which magnetic resonance is manifested as a change in the behaviour of a bird. The experiment [1, 2], performed by Ritz in collaboration with Wolfgang and Roswitha Wiltschko at the University of Frankfurt, was designed to test the hypothesis that the magnetic compass used by migratory birds for the purpose of navigation relies on a magnetically sensitive photochemical reaction with free radicals as transient intermediates [3].

This mechanism of chemical magnetoreception was proposed by Klaus Schulten as long ago as 1978 in a remarkably far-sighted paper [4], but it was only in 2000 that it started to excite interest following the suggestion by Ritz and Schulten [5] that a photo-active protein called cryptochrome could be the source of the radicals, or to be more precise, radical pairs. Their proposal is that radical pairs are formed by photo-induced electron transfer

Animal Detected Magnetic Resonance

reactions in cryptochromes in birds' eyes and that the reaction yields depend on the orientation of the animal's head with respect to the Earth's magnetic field (~50 μ T). In 1978, the 'radical pair mechanism' was in its infancy but now, 30 years on, it is absolutely clear that applied magnetic fields can affect the rates and yields of radical pair reactions even though the relevant magnetic interaction energies are orders of magnitude smaller than the average thermal energy, $k_{\rm B}T$. The spin polarization patterns commonly observed in the EPR spectra of transient radicals have a similar origin. Although there are many examples of chemical magnetic field effects *in vitro*, few if any are known *in vivo*.

Radical pairs respond to weak magnetic interactions because their reactions conserve spin and because electron spin relaxation is often relatively slow. Typically formed in a highly non-equilibrium, non-stationary spin state, radical pairs coherently interconvert between their singlet (S) and triplet (T) states at frequencies determined by hyperfine interactions in the radicals. The extent and timing of these 'quantum beats' can be perturbed by weak Zeeman interactions, so changing the probabilities of spin-selective recombination from the S and T states.

The work of Christiane Timmel and others has shown that weak timedependent magnetic fields can greatly alter the responses of radical pairs to weak static fields [6, 7]. The thinking behind the ADMR experiment was that if exposure to an oscillating magnetic field were to modify a bird's magnetic orientation, this would be a strong indication of a radical pair compass. So, Ritz and the Wiltschkos and their colleagues intercepted migratory European robins en route between Scandinavia and the Mediterranean and tested them in funnel-shaped cages in wooden buildings in the Botanical Garden in

Guest of the issue

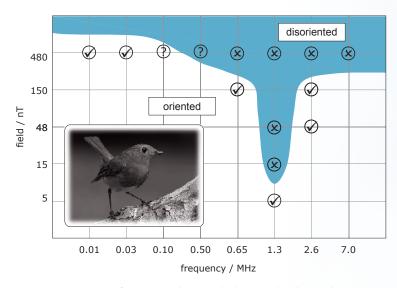


Fig. 1. 46 μ T ADMR spectrum of European robins [2]. The horizontal and vertical axes represent, respectively, the frequency and strength of the radiofrequency field to which the birds were subjected. The ticks indicate conditions under which the birds showed a statistically significant orientation in the correct migratory direction. The crosses are conditions in which the birds were disoriented by the radiofrequency field. The question marks indicate intermediate behaviour. The shaded area, corresponding to disoriented behaviour, has been added to emphasize the prominent resonance at 1.3 MHz, the Larmor frequency of a *g* = 2 radical in a 46 μ T field.

Frankfurt [1, 2]. The aim was to see whether the birds were still able to orient in the Earth's field when subject to electromagnetic fields at frequencies between 10 kHz and 7.0 MHz and intensities between 5 and 480 nT. Over a period of 4 years (these are not easy or quick experiments), they collected the data summarized in Fig. 1 [2]. Judged solely by its digital resolution, this is probably the worst spectrum you've ever seen. Nevertheless, the information it contains is truly remarkable. What these behavioural experiments show is that when subjected to a 15 nT, 1.3 MHz radiofrequency field, the birds are no longer able to orient in the Earth's field (46 μ T in Frankfurt). However, at half or at double that frequency, the field has to be as strong as 480 nT to have a similar disruptive effect on the magnetic compass. In addition, when the robins were tested in a 92 μ T static field (twice Earth-strength), the extraordinarily sensitive 15 nT response shifted to 2.6 MHz. The proportionality between static field strength and resonance frequency strongly suggests the EPR transitions of a radical with g-value close to 2. These ADMR results provide some of the most persuasive, if circumstantial, evidence so far that the avian compass really does rely on radical pair chemistry.

The only obvious way in which a radical in a 46 μ T static magnetic field could show a dominant EPR signal at 1.3 MHz would be if it had negligible hyperfine interactions. Otherwise any resonances would be spread over a wide frequency range, rather than being concentrated at the frequency of the much weaker Zeeman interaction. So, what could this radical be? It must satisfy a number of conditions in addition to $g \approx 2$. It should (a) have no hyperfine interaction larger than about 20 μ T (a value estimated from spectral simulations), (b) have spin relaxation slower than about 1 μ s (to allow time for weak fields to have a significant effect), (c) have appropriate radical pair chemistry, and (d) be biologically plausible. These criteria rule out most radicals, including the radical pair believed to be formed in cryptochrome, namely the reduced flavin adenine dinucleotide cofactor and an oxidised tryptophan residue. Both radicals have several large ¹H and ¹⁴N hyperfine interactions.

Reluctant to abandon cryptochrome altogether, Kiminori Maeda et al. [8] suggested that if one of the radicals was derived from the flavin, the other might be superoxide. Their argument was that O₂⁻ occurs biologically, has no magnetic nuclei, and is formed by the efficient oxidation of reduced flavins by dioxygen, O2. Although this idea is superficially attractive [9], Hannah Hogben has pointed out that there's a catch [10]. O_2^{-} has an orbitally degenerate ground state with an enormous spin-orbit coupling. As a consequence, a $O_2^{:-}$ radical tumbling in a liquid has very short relaxation times - probably less than 1 ns - which presumably accounts for the scarcity of EPR spectra of this radical in solution. However, if O₂⁻⁻ were tightly and asymmetrically bound to a cryptochrome,

its orbital angular momentum would be quenched, its g-value would be close to 2.0 and its relaxation could be as slow as 1 μ s. But, and here comes the catch, it is not clear that this would be compatible with insignificant hyperfine couplings. Whether or not O_2^- is bound to the protein by hydrogen bonds, it seems likely that some spin density in the radical would spill over onto protons or nitrogens in the binding site. For example, a DFT calculation performed by Ilya Kuprov indicates that O_2^- solvated by water has ¹H hyperfine interactiowns as large as 120 μ T [10]. Such couplings would be incompatible with the ADMR spectrum.

What next? The ADMR results are so remarkable (15 nT is an incredibly weak field) that they should be independently replicated in another laboratory to be sure that the 1.3 MHz resonance is genuine. One could test for the involvement of O_2^{-} in vitro by spintrapping or by looking for a ¹⁷O magnetic isotope effect on the radical pair spin dynamics. But maybe we're barking up the wrong tree. Is there another radical that satisfies the above conditions? Answers to peter.hore@ chem.ox.ac.uk, please.

References

- Ritz, T., Thalau, P., Phillips, J.B., Wiltschko, R. & Wiltschko, W.: Resonance effects indicate a radical-pair mechanism for avian magnetic compass. *Nature* 429, 177–180 (2004)
- 2 Ritz, T. *et al.*: Magnetic compass of birds is based on a molecule with optimal directional sensitivity. *Biophys. J.* 96, 3451–3457 (2009)
- 3 Rodgers, C.T. & Hore, P.J.: Chemical magnetoreception in birds: a radical pair mechanism. *Proc. Natl. Acad. Sci. USA* 106, 353–360 (2009)
- 4 Schulten, K., Swenberg, C.E. & Weller, A.: A biomagnetic sensory mechanism based on magnetic field modulated coherent electron spin motion. Z. *Phys. Chem. NF* 111, 1–5 (1978)
- 5 Ritz, T., Adem, S. & Schulten, K.: A model for photoreceptor-based magnetoreception in birds. *Biophys. J.* 78, 707–718 (2000)
- 6 Henbest, K.B., Kukura, P., Rodgers, C.T., Hore, P.J. & Timmel, C.R.: Radio frequency magnetic field effects on a radical recombination reaction: a diagnostic test for the radical pair mechanism. J. Am. Chem. Soc. 126, 8102–8103 (2004)
- 7 Rodgers, C.T., Henbest, K.B., Kukura, P., Timmel, C.R. & Hore, P.J.: Low-field optically detected EPR spectroscopy of transient photoinduced radical pairs. J. Phys. Chem. A 109, 5035–5041 (2005)
- 8 Maeda, K. *et al.*: Chemical compass model of avian magnetoreception. *Nature* **453**, 387–390 (2008)
- 9 Solov'yov, I.A. & Schulten, K.: Magnetoreception through cryptochrome may involve superoxide. *Biophys. J.* 96, 4804–4813 (2009)
- 10 Hogben, H.J., Efimova, O., Wagner-Rundell, N., Timmel, C.R. & Hore, P.J.: Possible involvement of superoxide and dioxygen with cryptochrome in avian magnetoreception: origin of Zeeman resonances observed by *in vivo* EPR spectroscopy. *Chem. Phys. Lett.* **480** 118–122 (2009)



Birding as My Passion Part 1: Representative Experimental Results

Hal Swartz

Director EPR Center for Viable Systems Dartmouth Medical School Hanover, NH, USA

I have been given the delightful task of contributing to the "My Passion" series, a very innovative and important part of the *EPR newsletter*. That birds and birding are my passion is not likely to be a surprise to those who have suffered through some of my talks, where amazing birds introduce new topics regardless of their relevance. Herein I will reveal why birds are always relevant to science discourse, using a two part series: first focusing on representative experimental results and second (to follow) on theoretical background.

The experimental results are given in Photos 1–7. These are derived from a study conducted in November, 2010 in Sri Lanka. Two scientific concerns dominated this site selection: first, Sri Lanka has a high level of interesting endemic birds (i.e., birds that are found nowhere else in the world) and, second, it is conveniently located near a scientific conference we attended just prior to the birding expedition. (In defense, I wish to point out that the expedition was scheduled after our attendance at the conference, in Chennai India, was confirmed.)

The photos are representative of several important methods behind my madness for birding. Necessarily (for my ultimate survival) the plans were made in collaboration with my lovely wife and scientific collaborator, Ann Flood, who enthusiastically endorsed collaborating in this study. The methods required use of a Canon 40D digital camera with an image stabilized 100-400 telephoto lens. The capabilities of the camera and the lens completely compensate for the limitations of the operator of the camera (HMS), even though the camera was handheld and a tripod was not used. As a matter of full disclosure, the photos have been enhanced by the use of Photoshop elements (version 7.0), but only to adjust the lighting and to crop the pictures.

The birds were completely unrestrained, consenting voluntarily to be photographed and admired for their beauty (particularly the males) and received no compensation for their participation. Because of the very close similarity among individuals of the same species, it was decided that the usual ethical rules about removing identifying characteristics of the individuals or blocking out the eyes were not followed. (Note: appropriate committees were not consulted for validation of this assumption, because a negative answer was not acceptable.)

Photos 1–4 illustrate the partial achievement of the purported goal of the expedition, to observe the endemic birds of Sri Lanka. Depending on the source, there are between 30 and 33 endemic species. Because of an insatiable urge to maximize the number of species seen, our default position is to agree with the authorities that maximize the number of unique species possible (although this strategy has the concomitant potential to reduce the percentage of such species I have personally observed)!

Photo 1, the Ceylon Magpie, illustrates an endemic bird that combines all of the desirable features most loved by passionate but occasional birders like me: it is beautiful; it is uniquely found in a very small geographic area on earth; and, although it is rare, it has the delightful habit of being commonly observable at a very specific site (in this case, a remote mountain inn named "Martin's Simple Inn" that was handbuilt by Martin in the heart of a mountain forest of great beauty in a national park that preserves a rain forest). The reason it is common at Martin's may be of scientific interest to methodologists: Martin discovered that, when he forgot to turn off the lights at night at the open dining/viewing area, moths congregated on the nearby trees and walls and at first light several of the rare Ceylon Magpies come to breakfast on (not with) the moths!

Photo 2 illustrates another endemic bird, the Brown Headed Barbet, that is quite common throughout Sri Lanka (another very desirable feature for endemics to have). Rather than beauty (well, in the eyes of the birders rather than the birds), it has an appearance of having been produced by a child who broke two different bird dolls and then put them together mixing them up.

Photo 3 illustrates an endemic bird whose weird appearance is truly outstanding. It is the Malabar Pied Hornbill. (By the way, 'big beaks' in my judgment are another very important feature for birds to have, and this species' behavior underscores some very important experimental findings.) That strange protuberance on his already sizable beak is, for this species, a real sex symbol that has led to selection of birds of both genders with the biggest protuberances. (Do take note of that finding!)

Photo 4 may look familiar but it is really an endemic bird, the Ceylon Jungle Fowl. The common chicken is derived from naturally occurring jungle fowl (there are several species throughout the orient), and our chickens are domesticated derivatives of these. Interestingly the habits of the Ceylon Jungle fowl closely resemble those of chickens – they love to scratch the dirt and are ready to crow at a moment's notice!

Photos 5–7 illustrate birds that never fail to fascinate even if they are not endemics. Photo 5 is a representative of a widespread genus of the old world, the bee-eaters. They do in fact eat bees (along with all sorts of other flying insects). This one, the Blue-Tailed Bee-Eater, like all bee-eaters is extremely attractive and has the happy habit of sitting out prominently on perches that give it a good view of passing insects (and us of a good view of them). They also have the nice habit of returning to the same perch frequently, so if you miss them the first time, they come back to give you another try. This is a pair, although the male and female in this species are quite similar.

Photo 6 illustrates another feature that often interests people addicted to watching birds: weirdness! This Crested Hawk-Eagle did not have a bad hair day – its hair looks like that every day. It is fairly common and often nicely sits in trees where it is quite visible.

Photo 7 illustrates that sometimes birds are aptly named: this is the Gray-Headed Fish Eagle. The photograph shows not only its gray head, but if you look carefully at its feet, there is a fish on which it is dining. You can even see bits of the fish in its mouth.

I suspect that you cannot wait until the next article where I will provide the underlying theory of why bird-watching can be a passion!

Another Passion

















70th Birthday of F. Ann Walker

In early June 2010, friends, relatives and former co-workers of Professor F. Ann Walker gathered in Tucson, Arizona in honor of her 70th birthday and her scientific career. Celebration of her internationally recognized scientific contributions continued in March 2011, with the symposium on "Magnetic Spectroscopic Approaches to the Study of Metals in Biology" at the National Meeting of the American Chemical Society in Anaheim, California.

F. Ann Walker was born in Adena, Ohio, USA, a small town located in the eastern part of the state. She received her B.A. in 1962 from The College of Wooster, with a major in chemistry. She did her graduate work at Brown University in physical inorganic chemistry with Richard L. Carlin and Philip H. Rieger on ESR studies of vanadyl complexes. After receiving her PhD in1966, she did further research on EPR spectroscopy with Professor Daniel Kivelson at UCLA as a NIH Postdoctoral Associate (1966-67). This period also marked the beginning of Professor Walker's interest in the magnetic spectroscopies of metalloporphyrin systems, which has continued throughout her academic career at Ithaca College (1967-70), San Francisco State University (1970-90), and the University of Arizona (1990-present). Her first independently authored research paper, "An Electron Spin Resonance Study of Coordination to the Fifth and Sixth Positions of $\alpha, \beta, \gamma, \delta$ -Tetra(p-methoxyphenyl-porphinatocobalt(II)", J. Am. Chem. Soc. 1970, 92, 4235-4244 is a seminal, widely cited paper that provided the first evidence for reversible binding of dioxygen to a cobalt(II) porphyrin and set the stage for kinetic, thermodynamic, structural and electronic studies of oxygen binding to cobalt(II) porphyrins in model compounds and modified



proteins by many laboratories. She next demonstrated that the concepts of electron donating or withdrawing properties of substituents on aromatic rings developed by physical organic chemists, can be applied to metalloporphyrins, and that such effects are exquisitely reflected in their spectroscopic properties. Her research papers in this area are classics that are characterized by carefully planned experiments, attention to experimental detail, thoughtful discussion, and comprehensive referencing, hallmarks of all of Professor Walker's research contributions, and which have set high standards for research in metalloporphyrin chemistry.

Since joining the faculty of the University of Arizona in 1990, Professor Walker has pioneered the imaginative application of a wide range of sophisticated spectroscopies to provide an integrated and detailed view of the electronic and molecular structures of heme centers in proteins and model compounds. The ultimate goal of these studies involving multidimensional NMR, pulsed EPR, ⁵⁷Fe NMR and Mössbauer spectroscopies is to understand the relationships between structure and function of the heme centers of proteins. These experiments, which are technically very difficult, provide information about dynamic processes in metalloporphyrin centers that is not available by any other technique. Her invited tutorial on "Advances in Single- and Multidimensional NMR Spectroscopy of Paramagnetic Metal Complexes" that was published by American Chemical Society Symposium Books in 1998 is essential reading for anyone doing experiments in this area. Another important and significant advance is her theoretical and experimental demonstration that the g-tensor of model heme complexes generally rotates counterclockwise about the heme normal as the planar axial ligands of the heme rotate clockwise. This result is extremely important for using NMR spectroscopy to determine the molecular structures of paramagnetic heme proteins; it provides an independent method for calculating the magnetic axis directions which are required to obtain the pseudocontact shifts that are used in refinement of the solution structure of paramagnetic proteins. A key component of these major contributions to metalloporphyrins and heme proteins is Professor Walker's ability to forge productive collaborations that provide essential auxiliary data that broaden the bases of the conclusions and enhance the impact of her creative work.

In recent years she has extended her research to nitrophorins, heme containing proteins from the saliva of the blood sucking insect *Rhodnius prolixus* (the kissing bug) that reversibly bind nitric oxide (NO). These studies have attracted wide attention because NO is an important messenger molecule in vasodilation and immune responses and because *R. prolixus* is the host for the parasite that causes Chagas' disease, a fatal incurable wasting of the muscles of the heart and the intestines. Following the determination of the crystal structure of a nitrophorin protein in collaboration with Professor William Montfort, she has embarked on an

JOHN WEIL YOUNG INVESTIGATOR AWARD

B

The family of late John Weil has established an award in his memory to be called **John Weil Young Investigator Award**, to be given each year, in addition to the regular Young Investigator Award.

The nominations are to be sent to the President of the International EPR Society by November 15. The requirements are the same as those for the regular award, as follows:

"A Young Investigator Award shall be made for outstanding contributions to EPR (ESR) Spectroscopy by a young scientist. Nominees should be under the age of 35 years on the 1st July of the year of the award. The date of birth of the nominee must be included in the nomination. The nominee will ordinarily be at the post-doctoral level. Only in exceptional circumstances will either doctoral candidates or junior faculty members be considered for this Award. In the case of the Young Investigator Award, please provide copies of two recently published papers which, in the nominator's judgement, represent the nominee's best work." extensive series of studies of these novel proteins and their reversible binding of NO using molecular biology, electrochemistry, pulsed EPR spectroscopy, and multi-dimensional NMR spectroscopy.

Professor Walker's contributions and leadership in magnetic resonance spectroscopies, especially of heme-containing systems, have been recognized by numerous awards, including: Fellow of the American Association for the Advancement of Science (1984); Garvan-Olin Medal, American Chemical Society (2000); Luigi Sacconi Medal, Inorganic Chemistry Division, Italian Chemical Society (September, 2001; awarded July 2002); Alexander von Humboldt Senior Research Awardee in Science (2003-05, Univ. of Lübeck, Prof. Alfred Trautwein); Alfred Bader Award in Bioinorganic Chemistry, American Chemical Society (2006).

Additionally, she has been active in service to the profession. A major contribution was

being an Associate Editor for the *Journal of the American Chemical Society* from 1998 to 2010, where she handled manuscripts dealing with magnetic resonance. She has also been Chair of Inorganic Chemistry Division of the American Chemical Society (2010), served on the ACS Presidential Commission on Women in Chemistry (2000–01), served on numerous review panels, and organized three symposia on Porphyrins, Metalloporphyrins and Heme Proteins at National Meetings of the American Chemical Society.

Currently she is a Regents Professor at the University of Arizona and a Fellow of the Galileo Circle of the College of Science.

Congratulations to Ann on her 70th birthday and for her many contributions to magnetic resonance spectroscopies. Best wishes for many productive years to come.

> John H. Enemark University of Arizona, Tucson, USA

70th Birthday of John H. Enemark

Dr John H. Enemark reached his 70th year on August 24th 2010 and celebrated this milestone at a surprise dinner in Tucson, Arizona on September 4th 2010 with family, friends, colleagues and collaborators.

John, who grew up in a Minnesotan farming community, gained his first degree in Chemistry at St. Olaf College, Northfield, Minnesota before moving to Harvard to gain his PhD under W. N. Lipscomb, Jr. He then took up a postdoctoral position in Professor J. A. Ibers' group at Northwestern before being appointed to Assistant Professor of Chemistry at The University of Arizona in 1968. He was appointed as Professor of Chemistry in 1977 and currently holds his Regents Professor Emeritus at The University of Arizona.

John is a bioinorganic chemist and an internationally recognised expert in the field of molybdenum-containing enzymes. Indeed, much of John's research has focussed on the chemistry and biochemistry of this family of metalloenzymes that catalyse key reactions in the metabolism of carbon, nitrogen and sulfur by bacteria, plants and animals, including humans. John's interdisciplinary approach has drawn on biochemistry to prepare and isolate these enzymes, synthetic inorganic chemistry to develop novel co-ordination complexes as analogues of their active sites and a battery of metal-centred physical and theoretical techniques to study both types of system. John's researches represent a considerable contribution to the field



and have greatly clarified our understanding of the geometric and electronic structures of the active sites of the enzymes.

A particular focus for the Enemark group has been sulfite oxidase (SOX), a prototype for one class of molybdenum-containing enzymes that, until the publication of an X-ray crystal structure of SOX from protein prepared in John's laboratories, had not been completely structurally defined.

Within the EPR community, John is best known for his development, with Ann Walker, Arnold Raitsimring and Andrei Astashkin, of a Variable Frequency Pulsed Electron Paramagnetic Resonance Spectroscopic Facility at The University of Arizona. This facility has brought powerful ESEEM and ENDOR methods to the determine the active site structures of SOX and DMSO reductases, that have been used to track the chemical nature of the catalytic cycles of these enzymes through measurement of the Mo^V couplings to ¹⁷O and ³³S. Also, John and his colleagues developed new pulsed EPR methods for studying key aspects of the nature and function of metalloproteins. Also, a truly international cast of researchers have benefitted from the information and insights provided by their collaborations with John and his colleagues and the facilities of the EPR Facility at The University of Arizona. John has also hosted many international visitors at Arizona. Frank Mabbs (University of Manchester) presented a graduate-level course in EPR spectroscopy that provided the genesis of the Mabbs and Collison book 'Electron Paramagnetic Resonance of d Transition Metal Compounds'.

John has received numerous honours and awards including a Fulbright Senior Scholar Award, Senior Alexander von Humboldt Awards and his election as Fellow of the American Association or the Advancement of Science in recognition of his contributions to science. John's infectious enthusiasm has also inspired undergraduate and graduate students and in recognition of his contributions to teaching he gained a Distinguished Career Teaching Award at The University of Arizona in 2005.

Our contact with John began in 1980 when Dave (then at Manchester University) met him at the Metals in Biology Gordon Conference in the Miramar Hotel, Santa Barbara. This led to many exchange visits between Manchester and Tucson, greatly assisted by a NATO Award. Both groups derived considerable scientific benefits from these information exchanges and led to Jon, after completing a PhD with Dave, moving to a Post-Doctoral position with John.

Outside of the laboratory, when John is not microwaving SOX, he can be found expanding his horizons with his wife Mary by cruising fjords of Scandinavia, snorkelling on the Great Barrier Reef, touring St. Petersburg or cycling around Europe. Every year we welcome the Christmas update from John and Mary providing interesting and amusing details of their many expeditions.

We join his many friends within the scientific community in congratulating John on attaining his Platinum (not molybdenum) anniversary. We send him our very best wishes for his continued scientific success, further developments of the EPR Facility at The University of Arizona, and new travelling adventures with Mary.

> Jon McMaster, C. David Garner The University of Nottingham



The First International Symposium on Electron Spin Resonance in Chemistry in Greece

Recalled by Les Sutcliffe (lesut@btinternet.com)

2009 saw the 30th anniversary of a historic conference on ESR in Thessaloniki, Greece organized by Professor Augustinos (Tinos) Anagnostopoulos and myself.

To begin at the beginning: I first met Tinos when he came from Greece as a young man to study for a PhD in Inorganic Chemistry at Liverpool University when we quickly became friends. After completing his degree, he returned to Greece and eventually became Professor of Chemistry at Thessaloniki University. Through the years he acquired a wife and two children and became a regular guest worker each summer in the Chemistry Department at Liverpool. His daughter, Maria so enjoyed Liverpool as a child on these visits that she returned as an adult to follow in her father's footsteps and to study Chemistry successfully. On his visits, Tinos became interested in the magnetic resonance research I was doing and suggested that I spend two weeks giving lectures in English on the subject to his undergraduates. Thus it was arranged that I should go in May 1978. Tinos and I went through each lecture before it was delivered to students so that he could expand on, in Greek, any points I was making. It was a delightful experience as the students were very enthusiastic and willing to learn. Although we worked hard, I was free to explore the region late in the day and I visited Meteora for a free weekend. During the two weeks, we thought it would be an excellent idea to give a boost to ESR in Greece by hosting an international symposium in Thessaloniki. This was to be the first such conference ever to be held in Greece. The city has had many earthquakes in its history and during my stay there was an earthquake of 6.3 on the Richter scale. However, Thessaloniki suffered a severe earthquake soon after my departure of 6.6 on the Richter scale when 40 people were killed: despite this it was decided to go ahead with the conference to demonstrate the resilience of the city. Tinos's apartment was badly damaged and he and his family had to move out until it was repaired. Thessaloniki is Greece's second city and has an important University; it has had an eventful history over more than two thousand years and is a World Heritage site. It also has many interesting features including ramparts, a citadel, Roman remains and the iconic White Tower.

The prime aim of the conference was to provide a series of reviews on ESR given by invited experts of international repute and covering a wide range of topics. Fortunately, there were only a handful of such people who were unable to accept our invitation. The symposium was organized along the lines of a workshop: each plenary lecturer was to be given a rather long period 90 minutes in order to provide the basic theory of their area of interest followed by a section on their recent researches. In the event, speakers kept to this brief so that the 90 minutes allocated didn't prove to be too taxing on the audience. In addition to the main talks there were to be short contributions. My job was to set up the scientific programme while Tinos was to take on the vital job of organizing

Beganovinch



Shirley Fairhurst, Cairine & Keith Ingold and others at Lunch.

the finance and making all the local arrangements. Although participants were to be housed in different hotels it was hoped that, for most of the time, they would be together in the true spirit of a Greek symposium.

Keith McLauchlan arrived a few days before the meeting began in order to assist Tinos with the final preparations and, indeed, all went very smoothly for the whole conference. Tinos was helped locally with Professors A. Galinos (Patra) and P. Bekiaroglou. Bruce Gilbert had brought his Greek postdoctoral fellow Chryssostomos (Chrys) Chatgilialoglu to the meeting and this proved to



be of tremendous benefit to our transport arrangements because we needed someone who spoke the language to help, since Tinos and his helpers couldn't be everywhere.

The plenary lecturers and the titles of their talks are given below:

Keith Ingold (Canada) "Conformational and Kinetic Applications of ESR to Organic Chemistry",

Bruce Gilbert (UK) "ESR Studies of the Structures of Organic Radicals",

Hanns Fischer (Switzerland) "ESR in Photochemistry and Photochemical Free Radical Kinetics",

Keith McLauchlan (UK) "Electron Polarisation (CIDEP) and it Application to Chemistry",

Lodovico Lunazzi (Italy) "Conformational Analysis of Neutral and Charged Organic Free Radicals",

Massimo Simonetta (Italy) "Ion Pairs in Solution",

Ed Janzen (Canada) "Detection of Free Radicals by Spin Trapping",

Alex Forrester (UK) "Use of Complementary NMR and ESR Measurements in the Determination of Electron Distribution in Nitrogen Free Radicals",

André Rassat (France) "Recent Results with Nitroxide Free Radicals",

Mitsuyoshi Matsuo (Japan) "Some Radical Scavenging Reactions of Tocopherols and Their Model Compounds",

Ivano Bertini (Italy) "ESR of Copper(II): Information and Pitfalls in the Spectral



Keith Ingold, Les Sutcliffe and Bruce Gilbert at the Conference Dinner.

Tinos at the Conference Dinner.

Interpretation of Diluted and Undiluted Systems",

Neil Atherton (UK) "Ligand Proton ENDOR of Transition Metal Complexes",

John Ammeter (Switzerland) "EPR of Orbitally Degenerate Sandwich Compounds", Leo Burlamacchi (Italy) "ESR Lineshape Stud-

ies of Paramagnetic Probes in Liquids", Anna Segre (Italy) "ESR of Living Cells

Grown "in vitro",

Phil Barker/Alwyn Davies (UK) "The ESR Spectra and Structure of Cyclopentadienyl Radicals".

The meeting began on the evening of Saturday 22nd September 1979 with an informal reception. The following morning, before the lectures began, there was a sumptuous buffet followed by welcoming speeches which were televised and shown on Greek national TV at 6 and 9 pm on the same evening.

There followed a full scientific programme with a short break for lunch. In the evening a truly memorable reception was given: many Greek delicacies were provided along with a wide selection of fruit and wine. This reception proved to be a glittering occasion as it allowed the 80 conference participants to meet around 100 local civic and business dignitaries, including:

N. Martis, Minister for Northern Greece; D. Nianias, Minister of Culture and Science;

A. Tsakonas, Administrator of the Thessaloniki region;

M. Papadopoulos, Mayor of Thessaloniki; N. Konomis, Rector of Thessaloniki University;

N. Panayiotopoulos, Dean of the Faculty of Technology, Thessaloniki University.

On three days, the meeting was split into morning and evening sessions. At mid-day coaches took participants 24 km to the beach at Agia Triada for lunch and the afternoon at leisure.

All the lectures were of a very high standard but that of John Ammeter deserves special mention. He had just begun his highly theoretical talk when the projector failed but John decided to carry on as a TV crew was present. He still gave a superb lecture even though he was only able to show his slides at the very end.

All good conferences provide relaxation by taking delegates to nearby places of interest

EPR newsletter Anecdotes



and this one was no exception. There was an afternoon excursion to Veria and Pella, founded by Archelaus (413 – 399 BC). The tomb of Philip (II) (the father of Alexander the Great) had been identified recently at Pella. The site has some beautiful mosaics.

On Thursday 27th September there was a full day cruise to view the monasteries on Mount Athos. We were taken by coach to Vourvourou to meet our boat. However, on arrival, the crew would not sail because the sea was far too rough but they thought that if we waited for an hour or so the storm would abate. They were right and so we went on board and put to sea. The sea was extremely rough and it looked at one time that the boat would sink and our conference would be responsible for obliterating a significant fraction of the then world's ESR experts! Although the conditions were bad, we did get to sail past the spectacular monasteries on Mount Athos (no females are allowed to land!) and we travelled on to Ouranopolis where we landed. The weather suddenly improved and we were able to enjoy a picnic on the delightful beach in sunshine. The return boat trip was amazing – the sea was calm and we were treated to a glorious sunset.

On the final evening we had the conference dinner at the Kapsis hotel. After the meal a group of Greek dancers entertained us with some traditional dances. Tinos kept up his role of host by joining in the dancing at one point.

I have attended many international conferences but this one has a special place for me for both for the science and the general enjoyment. Despite the big efforts he had to

From left to right: Tinos, Shirley and Les: reunion of friends after some thirty years.

make, Tinos has equally fond memories of the occasion: as have other delegates.

What has happened to the plenary speakers? Sadly, some are no longer with us, these include Hanns Fischer, André Rassat, John Ammeter and Anna Segre. Most of the rest have retired.

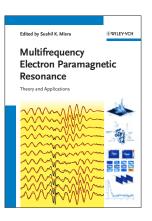
What has happened to the younger speakers? Phil Barker is Senior Scientist at Coatings Research, BlueScope Steel, Australia; Chrys Chatgilialoglu is a Professor at the Consiglio Nazionale delle Ricerche at Bologna; Shirley Fairhurst (John Innes Centre, Norwich) is the first woman to be Chairman of the ESR Group of the Royal Society of Chemistry and she has been Secretary of the International EPR/ESR Society; Ken White is Magnetic Resonance Program Manager, Philips Healthcare, USA.

What has happened to the progress of ESR in Greece since the meeting? Following this article is a review of the present status of EPR in Greece written by Y. Sanakis, G. Mitrikas, V. Petrouleas and Y. Deligiannakis.

I wish to thank Tinos, Maria and Costas Anagnostopoulos for their help in preparing this article. Thanks are also due to Professor I. Gerothanassis of Ioannina University for providing information on the Greek EPR Group.

Finally, in September 2010 Shirley Fairhurst (now my wife) and I have returned to Thessaloniki where we received a fantastic welcome by Tinos and his family

New Books & Journals



Multifrequency Electron Paramagnetic Resonance. Theory and Applications

Misra, S. K. (ed.)

Publisher: Wiley-VCH Releases on 20 April 2011 ISBN: 978-3-527-40779-8 Approx XVI, 1056 pages with approx 200 figures Hardcover Price: appr. € 387.- Filling the gap for a systematic, authoritative, and up-to-date review of this cutting-edge technique, this book covers both low and high frequency EPR, emphasizing the importance of adopting the multifrequency approach to study paramagnetic systems in full detail by using the EPR method. In so doing, it discusses not only the underlying theory and applications, but also all recent advances – with a final section devoted to future perspectives.

For more information contact Sushil Misra (skmisra@alcor.concordia.ca)

S. K. Misra, Concordia University, Montreal, Canada

Present Day EPR Spectroscopy in Greece

Yiannis Sanakis¹, George Mitrikas¹, Vassilios Petrouleas¹ and Yiannis Deligiannakis²

EPR spectroscopy was introduced into Greek research institutes and academic foundations some 30-35 years ago, rather late in comparison with other European countries. Since then, EPR spectroscopy has become one of the main scientific interests of some research groups. It is five years since the Greek EPR community joined the European Federation of EPR Groups. During this time, the Greek EPR community has devoted much effort, with emphasis on the training of young researchers, and in stressing the significance of the EPR technique through the Greek scientific community. The Greek EPR groups have also participated in major EPR international meetings and workshops. Of special importance was the participation in the European COST network "Advanced Paramagnetic Resonance Methods in Molecular Biophysics".

Currently, EPR groups are located at the Institute of Materials Science (IMS) of National Center for Scientific Research, Demokritos (D), in Athens, the Department of Environmental and Natural Resources Management, University of Ioannina (Laboratory of Physical Chemistry of Materials and Environment, LPCME), the National Hellenic Research Foundation in Athens and at the University of Athens. It is not possible to cover all aspects of EPR spectroscopy in Greece and below we outline the activities from IMS, Demokritos, and the University of Ioannina.

EPR at Demokritos

EPR spectroscopy in the IMS, "D" was established in 1984 with the installation of an ER-200D Bruker CW X-band EPR spectrometer operating in dual mode. Since then, this unit has been extensively modified and upgraded. The pulsed EPR laboratory was established in 1993 with the installation of an X-band



The group of Dr Vassilios Petrouleas at the Institute of Materials Science, NCSR Demokritos in mid nineties. Upright (from left to right): Yiannis Sanakis, Vassilios Petrouleas, Yiannis Deligiannakis. Seated (from left to right): Haris Goussias, Panayiotis Vassilopoulos.

Bruker ESP 380E instrument. The spectrometer operates in both CW and pulse modes and includes a DICE unit together with an ENI amplifier (radio frequencies up to 35 MHz) for pulsed ENDOR experiments. Recently, a CW Q-band EPR spectrometer was assembled and installed. All spectrometers are equipped with cryostats for measurements at liquid helium temperatures. Experiments at cryogenic temperatures are supported by the helium liquefier that operates within IMS "D". The following research activities of IMS strongly depend on EPR spectroscopy:

Bioinorganic Catalyst Centers and Mixed Valence Multinuclear Complexes (Dr Vassilios Petrouleas and Dr Yiannis Sanakis)

The research activities of the group aim at (a) the understanding and synthetic simulation of the function of active centers in biological systems, which catalyze important processes (conversion of light energy to electric charge separation, water oxidation, electron/proton transfer etc), and (b) the study of the electronic and magnetic properties of synthetic multinuclear complexes of transition metals. Emphasis is given to the study of the tetranuclear Mn complex, which oxidizes water and constitutes part of the so-called Photosystem II (PSII).

A few examples of the work carried out are given below:

- Identification of components of the acceptor site of PS II.
- Binding of exogenous ligands (carboxylate ions, nitric oxide, cyanide) at the non-heme iron of PSII.
- The transformation of the tyrosine radical YD of PSII to an iminoxyl radical upon interactions with nitric oxide.
- Trapping of the Mn_4Ca in the super-reduced S_{-2} oxidation state featuring a Mn^{2+} dimer.
- Trapping of the Mn₄Ca cluster of PSII in a modified S₂ state characterized by an S = 7/2 state.
- EPR characterization of the S_3 oxidation state of the Mn_4Ca cluster.

¹ Institute of Materials Science, NCSR Demokritos, 15310 Ag. Paraskevi, Attiki, Greece

² Department of Environmental and Natural Resources Management, University of Ioannina, 2 Seferi st., 30100 Agrinion, Greece

EPR newsletter Anecdotes

 Metallo-radical interactions of the tyrosine radical YZ of PSII with the Mn₄Ca cluster in various oxidation states and their implications in proton and electron transfer during water oxidation.

Many synthetic multinuclear complexes of transition metals exhibit interesting properties which render them candidates for technological applications in the field of magnetic data storage, magnetic cooling, quantum computing, or in their use as magnetic resonance contrast agents. EPR spectroscopy in combination with other techniques such as Mössbauer spectroscopy and magnetic susceptibility studies are applied in order to determine the electronic and magnetic properties of such compounds.

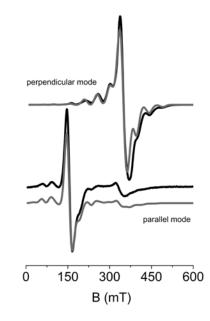
Sol-gel Pulsed EPR-group (Dr. George Kordas and Dr. George Mitrikas)

Early fields of interest included application of EPR spectroscopy for studying the structure of glasses (boron oxide anomaly, mixed alkali effect, phosphate glass structure) and quantum size effects in metallic nanoparticles. On-going research is focused on the structure of glasses with bio-compatible properties and on the electronic structure of molecular magnets and transition metal complexes. Recently, the development of advanced pulsed EPR methods and the characterization of relevant materials for applications in quantum computing have also become two long-term activities of the laboratory. Examples of applications include:

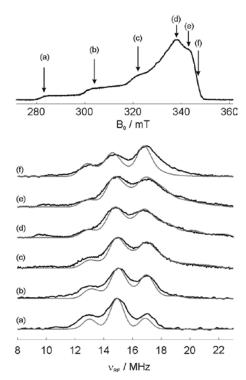
- Estimation of the ionic character of the Li-O bond in lithium silicate glasses using HYSCORE spectroscopy.
- Study of the electronic structure of paramagnetic silver nanoparticles by measuring their spin-lattice relaxation times.
- Electronic structure of B₂O₃ glass studied by one-, two-dimensional ESEEM and EN-DOR spectroscopy.
- Elucidation of the electronic structure of the trinuclear oxo-centered iron(III) complex $Fe_3(\mu_3-O)(O_2CPh)_5(salox)(EtOH)(H_2O)$ by utilizing the temperature dependence of the spin-lattice relaxation rate.
- Demonstration of fast nuclear spin control in hybrid electron-nuclear spin systems using only microwave pulses.

Archaeometry (Dr Yiannis Maniatis)

EPR spectroscopy has been proved to be a powerful tool for characterization of the marble of which ancient monuments, sculptures and artefacts are made and the determination of their provenance. The paramagnetic Mn^{2+} and



Experimental (black) and theoretical (gray) dual mode X-band EPR spectra from a Gd^{2+} (S = 7/2) monomer at 4.2 K [Yiannis Sanakis, unpubl.].



X-band ¹⁴N Davies ENDOR spectra of a monomer Cu²⁺ compound measured at different observer positions. Black traces: experiments. Gray traces: simulations. Top trace: X-band FID-detected EPR spectrum (T = 30 K). [G. Kordas and G. Mitrikas, unpubl.]

Fe³⁺ ions, replacing Ca sites in the carbonate structure of marble, as well as the impurities and point defects are studied. All the above depend on the geological conditions prevailing during formation of marble deposits and their history since then and hence are used to discriminate one marble origin from another. An extended database with the EPR parameters of the marble from all the known ancient marble quarries all over the Mediterranean has been created in the Laboratory of Archaeometry at IMS "D".

The origins of the marble of a very large number of ancient monuments and works of art in Greece and Italy have been determined. These include famous statues, such as the Nike of Samothrace and the statue of Augustus in Prima Porta of Vatican, a series of important monuments from the Sanctuary of the Great Gods of Samothrace, a series of statues and monuments from Ancient Olympia, the Hekatombedon metopes from the Acropolis, the Roman Sarcophagi of Thessaloniki, several archaic Kouroi, and hundreds of prehistoric Cycladic figurines and vessels.

EPR at the University of Ioannina

LPCME (Prof. Yiannis Deligiannakis)

The infrastructure of EPR spectroscopy at LPCME of the University of Ioannina includes EPR200D Bruker, equipped with an Oriel UV-Vis irradiation system, 10 ms transient signals detection. An S-Band spectrometer is under construction.

The group uses EPR spectroscopy in the study of (a) catalytic intermediates in oxidation-catalysts, (b) soil organic matter and (c) hybrid functionalized materials. Some recent representative results are:

- Heme and non-heme Fe catalysts evolve through high oxidation states Fe⁴⁺, Fe⁵⁺ involving Fe⁴⁺-Por⁺⁺ states in heme systems.
- High to Low-Spin state transitions of Fe³⁺ determine the catalytic path.
- Cu²⁺-Catecholase Biomimetic Catalysts can be stabilized on SiO₂ forming dinuclear Cu centers.
- Humic acids contain indigenous stable radicals which are involved in many biogeochemical cycles in nature.
- Radical centers can be stabilized by covalent grafting or intercalation in clays.

Concluding remarks

Since the Greek EPR Society was formed remarkable progress has been made. There is a strong will among the members of the Greek EPR Society to propagate the technique in Greece. It is their firm belief that close collaboration with colleagues from abroad will continue to be a priority.

Serving the scientific community for special and one-of-a-kind jobs

We have experience in designing computer interfaces for older scientific instruments, spectral analysis and image reconstruction as well as mapping and graphic layouts. Contact us for your specific needs.

Installation services

 Parts replacement service contracts Consulting and programming
Consulting, training, and

modification servicesExperience in a number of computer languages including

computer languages including C, C++, FORTRAN, BASIC and assembly

S³ Products for Spectroscopists

EWWIN - EPRWare for Windows EPR data acquisition, manipulation and line shape analysis software for Windows.

SpecMan4EPR Software for control of pulse spectrometers.

See what we can do for you, download trial versions of our software. Visit our website for details



Magnetic Test and Measurement Equipment

- Fluxgate Nanoteslameters for measurement of environmental fields with 1 nT (10 µG) resolution.
- Hall effect Teslameters for magnet field measurement and control with resolution to 0.1 µT (1 mG)
- NMR Teslameters with field measurement from as low as $1.4 \,\mu\text{T}$ (14 mG) up to 23.4 T.
- Digital Voltage Integrators for flux change measurements.
- Precision Current Transducers and Electromagnet Power Supplies.
- Laboratory Electromagnet & Helmholtz Coil Systems for spectroscopy and imaging.

GMW

955 Industrial Road, San Carlos, CA 94070 Tel: (650) 802-8292 Fax: (650) 802-8298 E-mail: sales@gmw.com Web: www.gmw.com

Wilmad-LabGlass A Name You can Trust EPR Sample Tubes and Accessories





Molecular Specialties, Inc. TPX Capillary (Catalog No. TPX-2) Compatible with most resonators Accepts liquid and solid samples Ideal for oxygen-control studies Easily cleaned Address: 10437 Innovation Drive, Suite 301, Milwaukee, WI 53226 Phone: 414-258-6724 **Richard J. Stevens** Contact: E-Mail: rich.stevens@molspec.com Web: www.molspec.com Contributor to the International EPR Society



Notices of Meetings

Conference reports



Magnetic Spectroscopy Community Celebrated the 70th Birthdays of John Enemark and Ann Walker at the 241st National Meeting of the American Chemical Society in Anaheim

Ann Walker and John Enemark 70th birthdays were celebrated by colleagues and friends attending the Magnetic Spectroscopic Approaches to the Study of Metals in Biology Symposium (March 28-30, 2011) at the 241st National Meeting of the American Chemical Society in Anaheim, CA. The symposium was organized by Partha Basu and Mario Rivera who obtained their postdoctoral training in the 90s in the Enemark and Walker laboratories, respectively. Ann's and John's birthdays were celebrated in Tucson, AZ in the company of a large number alumni, friends, and family. While planning these celebrations, Basu and Rivera thought that it would be nice to also celebrate the field to which Ann and John have contributed so much, by bringing together as many scientists as possible who share a passion with Ann and John for utilizing magnetic spectroscopic methods to learn about the role played by metal ions in life processes. The symposium was approved and generously supported by the INOR and BIOL divisions of the American Chemical Society. The community's enthusiasm resulted in a three day symposium with 29 oral contributions and a poster session from participants residing in Argentina, Australia, France, Germany, Japan, Italy, Israel, and the U.S. and a program that included lectures covering applications and methods development in the areas of EPR, NMR, nuclear resonance vibrational spectroscopy, circular dichroism spectroscopy, magnetic circular dichroism spectroscopy and imaging, as well as theory. John and Ann hosted all the speakers to a dinner party, where the group enjoyed the company of old and new friends, and wished John and Ann many more years of enjoyment pursuing their passion for understanding the roles played by metal in biological systems.

Happy 70th birthday John and Ann! We look forward to many more years of your science and friendship.

Mario Rivera

Partha Basu

The dates of the ISESS-SEST2011 meeting (a joint conference of the 2nd International Symposium on Electron Spin Science (ISESS) & SEST2011) has been changed as follows due to a delay in the preparation after the terrible earthquake and related accidents. This year, the meeting is held as the domestic meeting & a joint international workshop with Institute for Material Research, Tohoku University. The ISESS meeting will be held on July 23–25, 2012 at Matsushima, Japan. Those who are interested in this meeting please contact Dr. Seigo Yamauchi, chairman of the Conference. e-mail: yamauchi@tagen.tohoku.ac.jp

The 53rd Rocky Mountain Conference Snowmass, Colorado, USA, July 24-28, 2011 www.rockychem.com

The 11th International Conference on Magnetic Resonance Microscopy Beijing, China, August 14-18, 2011 web: icmrm11.cup.edu.cn

EUROMAR 2011

Frankfurt (Main), Germany, August 21-25, 2011

www.euromar2011.org

Presentations of this unique conference will thus cover all aspects of magnetic resonance spectroscopy such as methodological and technical advancements as well as new areas of application in material and life sciences, physics, chemistry and biology.

International conference "Spin Physics, Spin Chemistry, and Spin Technology" Kazan, Russia, November 1-6, 2011 www.kazan spin2011.kfti.knc.ru

The 40th Southeastern Magnetic Resonance Conference (SEMRC 2011) Atlanta, Georgia, USA, November 4–6, 2011 web: chemistry.gsu.edu/SEMRC

The 50th Annual Meeting of the Society of Electron Spin Science and Technology: SEST2011

Sendai International Center, Sendai, Japan, November 16–18, 2011

web: res.tagen.tohoku.ac.jp/SEST2011/ domestic/, e-mail: sest2011@res.tagen. tohoku.ac.jp

Model 8400 ESR/EPR Spectrometer Sales and Service by

Resonance Instruments, Inc.

Portable • High Performance • Reliable • Versatile Competitively Priced • PC Control Via COM Port Accessories and Upgrades

9054 Terminal Avenue, Skokie, Illinois 60077 1-847-583-1000, FAX 1-847-583-1021

E-mail: 8400@ResonanceInstruments.com www.resonanceinstruments.com

RELAXATION TIMES REVIEW

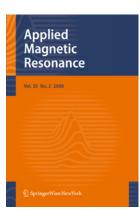
Extensive reviews of electron spin relaxation times are in:

- K. J. Standley and R. A. Vaughan: Electron Spin Relaxation Phenomena in Solids. Plenum Press 1969.
- I. Bertini, G. Martini, and C. Luchinat: Relaxation data Tabulation, chapt. IV in Handbook of Electron Spin Resonance (C. P. Poole, Jr. and H. A. Farach, eds.) AIP Press 1994.
- S. S. Eaton and G. R. Eaton: Relaxation Times of Organic Radicals and Transition Metal Ions. Biol. Magn. Reson. 19, 29–154 (2000)

We are gathering relaxation times to update these prior reviews. Many electron spin relaxation times are buried in papers deeply enough that they are not found by computer searches. Sometimes we find them only serendipitously. Some papers contain information that suggest to us that the lab might have measured relaxation times but did not actually put a numerical result in the published paper. We will appreciate having relaxation time values brought to our attention, so that our review can be more complete than in the past.

Gareth R. Eaton (geaton@du.edu)

New Books & Journals



Discount AMR subscription rate for IES members

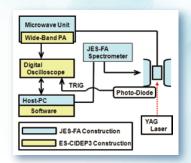
Springer offers the journal *Applied Magnetic Resonance* at a special subscription rate for the members of the IES. In 2011, it is EUR 209,- (excl. VAT and carriages charges) for volumes 40 and 41 (4 issues each) (regular list price EUR 2215,- plus postage). Orders must be sent directly to:

Springer-Verlag Wien, Sachsenplatz 4-6, P.O. Box 89, A-1201 Wien, Austria phone: +43 1 330 24 15 227, fax: +43 1 330 24 26 62 e-mail: journals@springer.at

ES-CIDEP3 for JES-FA Series ESR

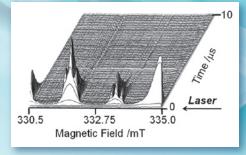
Chemically Induced Dynamic Electron Polarisation (CIDEP) facilitates sub-microsecond detection of spinpolarized paramagnetic intermediates as produced by laser excitation. This can yield unrivalled information on the spin dynamics and the chemical reaction.

The high sensitivity and high speed of the JEOL FA series ESR spectrometers fitted with a CIDEP attachment ensures simple and reliable measurements.



Block diagram of CIDEP attachment





JES-FA200

2D TR-ESR of photo-polymerization process

JEOL Ltd. http://www.jeol.com/ 1-2 Musashino 3-Chome Akishima Tokyo 196-8558 Japan Sales Division Telephone:+81-42-528-3381 Facsimile:+81-42-528-3386





POSITIONS

Positions available immediately at Dartmouth

Job description: The Electron Paramagnetic Resonance (EPR) Center for the Study of Viable Systems at the Dartmouth Medical School is developing instrumentation and methodology to enable after-the-fact characterization of individual personal radiation exposures following a large-scale radiation accident or attack. This research is supported by several major grants from federal agencies. Our approach focuses on the use of EPR spectroscopy to detect radiation induced radical species in tooth enamel and keratin in nails.

Requirements for the instrumentation include high sensitivity to radicals present in the tissues, full automation of measurement procedures, compatibility for use with human subjects, ease of transport, and reliability and robustness under field conditions.

Activities within our engineering lab include the development of surface-loop and other novel resonators for detection of in vivo EPR signals, the design and fabrication of RF bridges, and the incorporation of these components into optimized systems capable of automatic tuning, coupling, and phase adjustment.

We are seeking several well-prepared, highly motivated individuals to join our international team pursuing this research. The persons hired for this position will assist in the design and construction of the instrumentation for EPR spectroscopy and will service the prototype instruments being evaluated within clinical studies. More specifically, they will be working with a team of local RF engineers, as well as national and international collaborators, to design, fabricate, and optimize RF bridges and resonators and to incorporate them into fully functional and automated instrumentation, to enable EPR techniques to address an important national security concern.

The candidate should have experience in the design and manufacture of RF systems for frequency conversion and signal demodulation. The candidate should have practical knowledge in digital electronics systems and proficiency in Matlab based analyses. Familiarity with simulation software such as HFSS, ADS, and/or Pspice is desirable. Prior experience with EPR is desirable but not essential. An advanced degree in engineering is desirable. A strong work ethic and willingness to work hard and learn new areas is essential.

Qualifications: BS or more advanced degree in RF engineering or Physics. Experience with at least one and preferably several of the following: (1) EPR experience, (2) microwave circuit and/or system design experience, (3) modeling experience with either HFSS, ADS, Pspice or other circuit software design packages, (4) knowledge of Matlab, (5) digital electronics experience.

Contact:

Harold M. Swartz, MD, PhD Dartmouth Medical School 704 Vail, HB7785 phone: (603) 650-1784 fax: (603) 650-1717 e-mail: epr@dartmouth.edu

Multiple positions available – will consider varying degrees of expertise.

Postdoctoral position at Physics Department, National Dong Hwa University, Taiwan

A postdoctoral position is available in the laboratory of Prof. Shyue-Chu Ke at the Physics Department, National Dong Hwa University, Taiwan.

The research will involve the application of EPR and pulsed EPR spectroscopy to understand the fundamental questions related to adenosylcobalamin-dependent enzymatic reactions.

Additional information about the laboratory is available at: www.phys.ndhu.edu.tw/teachers/

ke/ke.htm.

Applicants should

have experience in

analytical techniques

and continuous or

pulsed EPR methods

and data analysis. Ex-

perimental physical

chemists with expe-

rience in cell culture

or synthesis would be

beneficial, but is not

essential.

L&M EPR Supplies, Inc.				
4152 W. Lisbon Ave., Milwaukee, WI 53208				

Phone: (414) 324-1052; Fax: (262) 889-2368 www.lmepr.com sales@lmepr.com

ິ	TPX Capillaries	EPR Sampling Tubes
с ПС	Quantity 1–19	Price/Part (\$US) 60.00
Б	20–99 100+	50.00 40.00
-	100+	40.00

The position is available this summer and appointments are for up to 3 years.

If interested, please send a CV and summary of previous research experience to ke@mail.ndhu.edu.tw.

EQUIPMENT

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

For sale: Varian and ESR equipment

Resonance Instruments has available: (1) Replacement klystrons for Varian EPR bridges and some Bruker bridges (at reduced prices) and other klystrons; (2) Resonance Instrument's Model 8320A is a general purpose Hall-effect based magnetic field controller that provides direct control and precise regulation of the magnetic field between the pole pieces of an electromatnet. Its high resolution permits precise adjustment of the magnet's field either though the front panel keyboard or though an RS232 serial interface with your PC.

Please contact: Clarence Arnow, President, email: 8400sales@resonanceinstruments.com, phone: 1-847-583-1000, fax: 1-847-583-1021.

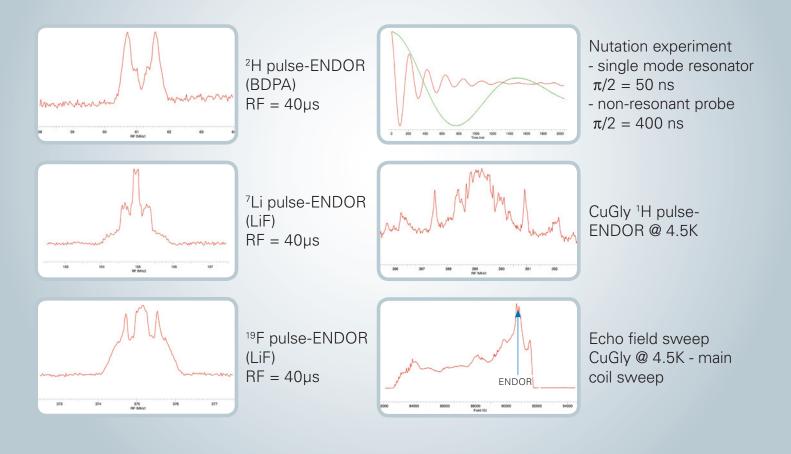
Available: Used Varian EPR equipment

(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



E780 Latest experimental examples



- Variable temperature from 3.8 to 300 K
- Pulse-ENDOR from 1 to 650 MHz with single mode resonator
- RF pulse of 40 µs with 125 W amplifier
- Single mode resonator with $\pi/2$ mw-pulse of 50 ns
- Non resonant probe with $\pi/2$ mw-pulse of 400 ns

Contact us for more details: www.bruker.com/epr

Innovation with Integrity



mm-wave EPR E780 quasi optical spectrometer BRUKER Non-resonant probe Magnet System Cryogen Free EPR | Single mode VT resonator Quasi-optical front-end

- ELEXSYS based single door console
- Bruker IF-concept
- Quasi-optical front-end
- 263 GHz EPR
- g = 2 @ 9.4 T

- 12T Cryo-Free superconducting magnet (main and sweep coil operation)
- Single mode VT resonator TE011
- Non resonant large sample VT probe
- Operation modes: CW & Pulse / ENDOR / ELDOR

Contact us for more details: www.bruker.com/epr

Innovation with Integrity