epr newsletter

2006
volume 16 number 2-3

The Publication of the International
EPR (ESR) Society

Officers of the International EPR (ESR) Society

Fellows of the International EPR (ESR) Society

Anatole Abragam
Brebis Bleaney
James R. Bolton
Harvey A. Buckmaster
Anders Ehrenberg
George Feher
George Fraenkel
Erwin Hahn
Karl Hausser (1919–2001)
Noboru Hirota
Clyde A. Hutchison, Jr.
James S. Hyde
Daniel Kivelson (1929–2003)
Melvin P. Klein (1921–2000)
Harry Kurreck
August H. Maki
Bruce R. McGarvey
Keith A. McLauchlan
Yuri N. Molin
John R. Pilbrow
Charles P. Poole, Jr.
Aleksandr M. Prokhorov (1916–2002)
Tengiz I. Sanadze
Charles P. Slichter
Harold M. Swartz
Martyn C. R. Symons (1925–2002)
Joan H. van der Waals
George D. Watkins
John A. Weil
Samuel I. Weissman
David Whiffen (1922–2002)
Hans C. Wolf

epr newsletter

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.

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 is based upon the probe head of the cw and pulsed 275 GHz EPR/ENDOR spectrometer, constructed at Leiden University by Harmen van der Meer and Jos Disselhorst, the recipient of the 2005 IES Silver Medal for Instrumentation. At its heart is a tunable single-mode cylindrical cavity (diameter 1.4 mm) with a loaded quality factor of about 1000. The detail shows this cavity with coupling hole and tuning plungers, and slits in the wall to allow the magnetic field produced by the current through the RF coils to reach the sample.

epr newsletter

The Publication of the International EPR (ESR) Society

volume 16 number 2-3 2006

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

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

Editorial

"Oh the road to En-dor is the oldest road
And the craziest road of all!"
Rudyard Kipling "En-Dor"

Dear colleagues,

As soon as I learned that Martina Huber and Klaus Möbius are working as Guest Editors on the preparation of a special issue of *Applied Magnetic Resonance* dedicated to the 50th anniversary of ENDOR, I realized that it is our lucky opportunity to pay tribute to George Feher in connection with this seminal discovery by preparing an ENDOR-related issue of the *EPR newsletter*.

We managed to collect the relevant material for most of the columns in this issue. Even the cover picture reflects the ENDOR research of Jos Disselhorst, the recipient of the IES Silver Medal for Instrumentation 2005. To start with, George kindly gave an interview to the *newsletter*. Flavored with his great sense of humor, it shows the infinite depth of this great man. (also read Wolfgang Lubitz's article "80th Birthday of George Feher" in 14/3, p. 10). We are grateful to APS for the permission to reproduce George Feher's first ENDOR paper. There are several other highlights of the issue. 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. I am happy to say that 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, presents the comprehensive contribution on high-field pulsed ENDOR written by Daniella Goldfarb, a top expert in the field and the 2007 Bruker Lecturer (awarded for "her contributions to the application and development of pulse EPR and ENDOR methodologies…"). We congratulate Klaus Möbius, an ENDOR-in-solution pioneer, on his recent 70th birthday.

As you might have already noticed, our patriarchs were nicely represented in the past issues of the *EPR newsletter*. The younger generation was not as active. To achieve a balance, we introduce a new column, 'IES Young Investigator Award Revisited' to be edited by Candice Klug. This column features past recipients of IES YIA and provides them an opportunity to explain their path, tell about their current lives, share the problems they face and solve, give advice to others, etc. but it also can be open to whatever they want to write. In this issue, Mark Newton, the recipient of this award in 2001, tells about his early days of ENDOR. Candice also collects material for the new column 'New EPR Faculty' with small highlights on newly hired Assistant Professors.

This issue is special squared. On the one hand, ENDOR runs all through this issue. On the other hand, George Feher, father-founder of ENDOR, is a very special man. Of course, every man is special but some people will always be more special than other people. What is it that makes George so special? Is it the boundless dimensions of his personality and wisdom?! His fascinating sense of humor?! His unaffected manners?! The story of his life being the reflection of the heaviest atrocities and the brightest challenges of the 20th century?! Be it told in a book, it would be a bestseller. Be it a movie, it would be a blockbuster.

I have a personal tenth anniversary to celebrate: I met with George for the first time in 1996 even though I knew about ENDOR from the University course on the theory of EPR dating back to 1970. I could hardly overestimate his contribution to the development and success of the *EPR newsletter* (see his previous articles: 13/1-2, p. 10; 14/4, p. 10; 15/2, p. 10).

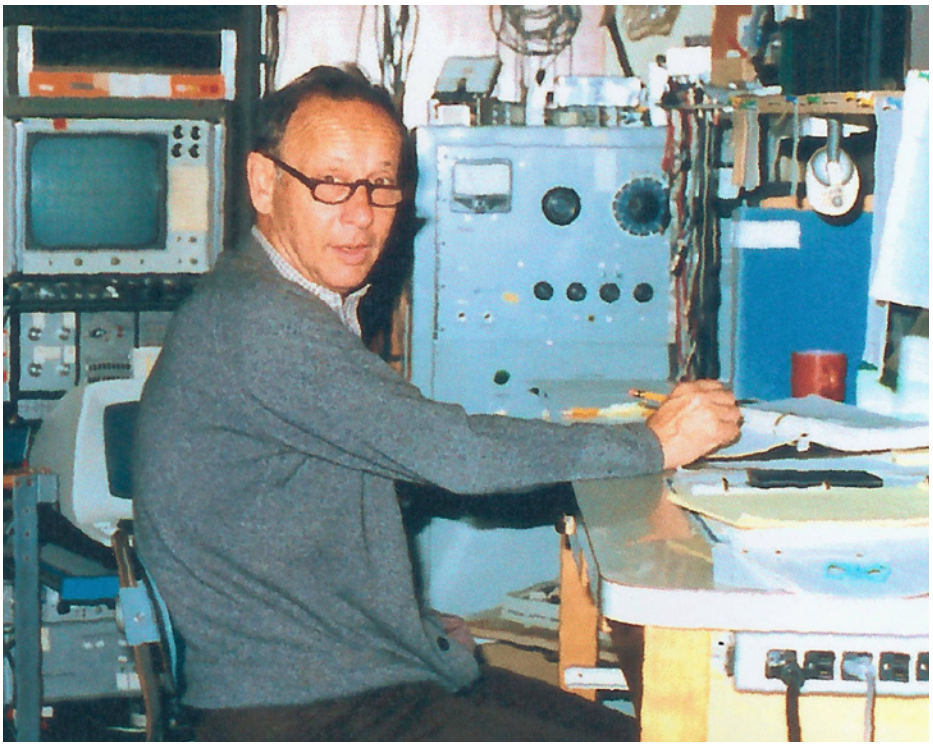
Dear George, thank you most gratefully for everything!

Laila Mosina

George Feher: An Interview to the EPR newsletter

ENDOR '50 dedicated

***EPR newsletter*:** Dear Professor Feher, on behalf of the readers of the *EPR newsletter* we congratulate you on the 50th anniversary of ENDOR and on your recent 82nd birthday. We are most appreciative that you agreed to answer the questions for this interview.



Q: What do you think about the role and place of ENDOR as a method of studying matter?

A: ENDOR is but one tool among several others that help to elucidate the electronic and spatial structure of molecules and matter.

I understand that later this year there will be a special issue of *Applied Magnetic Resonance* on ENDOR that should address your question more fully.

Q: Your earliest ENDOR experiments on P in silicon were carried out under 'passage' conditions. To what extent did you use passage conditions for your later ENDOR on biological systems? And what were the advantages of doing that?

A: The passage conditions encountered during our early experiments were due to the very long electron-spin relaxation times (T_1) of donor electrons in silicon. In most molecules the relaxation times are much shorter and passage effects become unimportant. I consider passage effects inherently not very interesting, but one needs on occasion to understand them in order to interpret and optimize EPR and ENDOR signals. I refer your readers to the article by Meir Weger (Bell System Tech. J. July 1960, 1013–1112) who worked out the many complicated passage conditions that can occur.

Q: Considering your life before going to the US, it was Slovakia and Palestine that represented your 'roots'. How important are your present links to Slovakia and Israel to you, both personally and scientifically?

A: I have very strong ties to Israel, both emotional and to some extent scientific. It was Palestine (now Israel) that I escaped to from the Holocaust in 1941. If it had not been for Palestine, I would most likely not be around to answer your questions. I frequently visit Israel. I have close friends and family there. I taught courses at the Hebrew University in Jerusalem on two occasions, I have been on the Board of Governors of the Technion in Haifa for some twenty years and on the Board of the Weizmann Institute for two terms. I have had many Israeli post-docs, with some of whom I keep in close contact. To summarize my feelings about Israel I quote Psalm 137 (1/α): "If I forget thee, Oh Jerusalem, may my right hand forget its cunning."

In contrast to Israel, I have no scientific ties with Slovakia or the Czech Republic (they used to be one country, Czechoslovakia). However, I still have family and friends in those countries whom I occasionally visit and with whom I keep in touch.

Q: In your article "The Development of ENDOR and Other Reminiscences of the 1950's"(Foundations of Modern EPR (Eaton G.R., Eaton S.S., Salikhov K.M., eds.), pp. 548–556. Singapore: World Scientific 1998.) you give a comprehensive story about the discovery of ENDOR. You also mention that C. S. Wu and T. D. Lee tried to convince you to measure the asymmetry of β-decay in a polarized sample of donor nuclei in silicon. You promised them that you would get to it as soon as you finished the experiments you were engaged in. However, when you could have carried out these measurements, it was too late. Did you ever regret not completing the experiments proposed by Wu and Lee? In general, is there something that you did or did not complete, that causes you regret?

A: In 1956 I was developing ENDOR and was involved, following Bloembergen's proposal, in building with Scovil and Seidel the first solid state maser, two exciting projects that I wanted to com-

plete before embarking on the parity experiment. I thought a few months' postponement wouldn't make a difference. I was wrong and got scooped by others. The importance of proving parity non-conservation exceeds by far the importance of ENDOR and the Maser. It was poor judgment on my part not to have dropped all other projects (including an extended ski trip) and concentrate on the parity experiment, which, of course, I regret.

Q: What is the driving force for you in your research?

A: The excitement of having a novel idea, of proving it right, of finding something new and the enjoyment of the process of experimentation (tinkering, really). The only thing that comes close to it is falling in love. What is the driving force for falling in love?

Incidentally, we have a 50-year-old running discussion with my colleague Bob Shulman about whether we would do research on an isolated island if we had no possibility of publishing or letting anybody know about our results. My resounding answer has always been: "Yes."

Q: In your fascinating story "Playing Poker" (13/1-2, pp. 10–12) you disclosed to us your secret passion and also the secrets of poker. Are there any other passions in your life?

A: Yes, but my answer was censored by my wife Elsa.

Let me describe instead something that comes close to passion. I have loved and enjoyed sports all my life: skiing, tennis and swimming. Unfortunately, I had to give up skiing a dozen years ago because of a heart condition and tennis last year because of poor vision. However, I still swim laps everyday and have participated the last ten years in the yearly Southern California Senior Olympics. I hope nobody will ask what my times are, suffice it to say that they are worse than when I competed 70 years ago as a 12 year old boy. As a matter of fact if I linearly extrapolate my deterioration, it seems that in a few years I will swim backwards.

Q: We all were charmed by your thrilling reminiscences of encounters with some of the pioneers of magnetic resonance (15/2, pp. 10–12): Wolfgang Pauli, Felix Bloch and Isidor Rabi. Felix Bloch advised the University Students "not to conform too soon and to resist the pressure of practical necessity" (14/1-2, p. 5). How does conformity affect a human being? Isidor Rabi emphasized the great need for a better understanding on the part of the scientist that he has a real responsibility for science (14/1-2, p. 5). What is your idea of responsibility as a scientist?

A: You raised several questions. Concerning conformity, I have written before that it has a detrimental effect on creative research as well as on human behavior. The 'herd instinct', which is a conse- ▶

ENDOR '50 dedicated

Observation of Nuclear Magnetic Resonances via the Electron Spin Resonance Line

G. Feher

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey

(Received June 15, 1956)

The double-frequency resonance method reported recently in connection with a nuclear polarization scheme [1] has been extended to observe nuclear transitions and thereby determine hyperfme interactions and nuclear g values.

The method is illustrated for the simple case $I = 1/2$, $J = 1/2$, in which the hyperfine structure is resolved. The transitions induced by the microwave field of frequency ν_e are indicated by arrows in Fig. 1. The amplitude of the signal due to these transitions is proportional to the difference in population in levels A and A' If we partially saturate this resonance the population difference will be diminished and the signal reduced. By inducing the nuclear transitions $h\nu_N$ (see Fig. 1), we may either equalize the populations in levels A and B (by saturating these transitions) or reverse the populations (by an adiabatic fast passage). In either case the population difference in levels A and A' has been increased and thereby the electron spin resonance signal enhanced.

The experimental setup and the phosphorus-doped silicon sample were similar to the one described earlier [2] with the exception that 100-cps magnetic field modulation was used. The magnetic field was adjusted to correspond to the resonance condition of the low-field line ($m_I = +1/2$). Figure 2 is the recorder tracing of the electron spin resonance signal. It

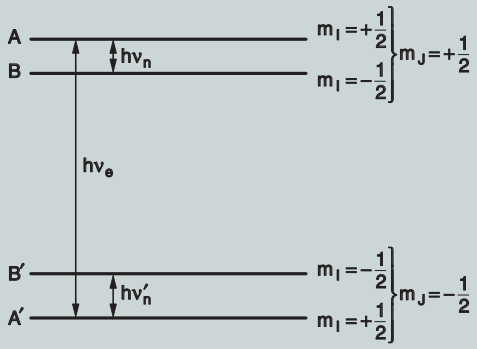


Fig. 1. Energy levels of a system with $I = 1/2$, $J = 1/2$. Arrows indicate transitions which were induced in the phosphorus-doped silicon sample.

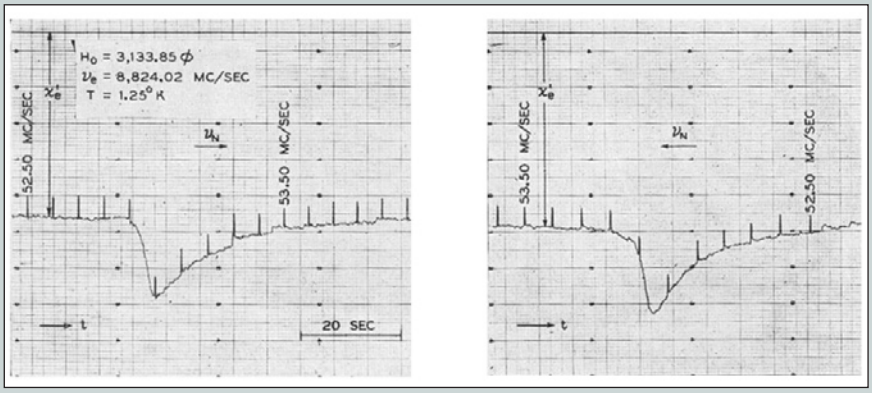


Fig. 2. Electron spin resonance signal in phosphorus-doped silicon. Small vertical lines on trace represent frequency markers of the rf field which is superimposed on the microwave field. A similar trace was obtained at a frequency 11.59 Mc/sec higher.

shows clearly the enhancement of the signal when the frequency corresponding to the nuclear transitions is being traversed. This enhancement decays with a characteristic time depending on the rate at which the levels A, A' are being saturated. This accounts for the observed asymmetry of the line. A similar line was observed at a frequency 11.59 ± 0.02 Mc/sec higher corresponding to nuclear transitions between levels A' and B' (see Fig. 1). From this frequency difference, one may easily calculate g_I for phosphorus [see ref. 1, Eq. (2)]. The value obtained is $g_I = 2.265 \pm 0.004$ which agrees with the accepted value [3] of 2.2632 ± 0.0004.

Since this method yields a value of g_I without having to know the wave function of the electron associated with the paramagnetic center, it may be used either to determine an unknown nuclear g_I or as an analytical tool to identify impurities.

The method is also applicable to uses in which the hyperfine interaction $a(\mathbf{I}\cdot\mathbf{J})$ is small in comparison to the electron line width and therefore no structure can be observed in a single-frequency spin resonance experiment. Such a case is, for example, lithium-doped silicon, in which Honig and Kip [4] first observed an unresolved electron spin resonance line. By performing the same experiment as in the phosphorus-doped silicon sample described before, we were able to observe an enhancement of the electron spin resonance line at the frequencies of 4.89 Mc/sec and 5.74 Mc/sec with an external magnetic field of 3217 oersteds. Since for this case $a(\mathbf{I}\cdot\mathbf{J}) < g_I\mu_0 H$, we expect the two frequencies $\nu_{1,2}$ to occur at

$$h\nu_{1,2} \cong g_I\mu_0 H \pm (1/2)a.$$

This yields for the hyperfine interaction constant $a = 0.85 \pm 0.01$ Mc/sec as compared with the theoretical estimate of Kohn and Luttinger [5] of 0.5 Mc/sec. We also obtained lines arising from the interaction of the electron with the Si^{29} nuclei. They are presently being analyzed in more detail and may prove to be a convenient way of getting the electron wave functions at different lattice points.

Another system to which the double-resonance method has been applied is F centers in KCl. An unresolved line was first observed by Hutchison [6] and investigated in greater detail by Kip *et al.* [7]. We were able to resolve different sets of lines which presumably arise from the interaction of the electron with the potassium and chlorine nuclei. A more detailed analysis is being prepared for publication.

I would like to thank Dr. P. W. Anderson, Dr. D. Pines, and Dr. W. Kohn for many helpful discussions, Dr. W. L. Brown and Mr. W. Augustyniak for bombarding the KCl with electrons, and Mr. E. A. Gere for his assistance in performing the experiments.

1. G. Feher: Phys. Rev. **103**, 500 (1956)
2. G. Feher and E. A. Gere: Phys. Rev. **103**, 501 (1956)
3. N. R. Ramsey: Nuclear Moments. New York: John Wiley and Sons, Inc. 1953.
4. A. Honig and A. F. Kip: Phys. Rev. **95**, 1686 (1954)
5. W. Kohn and J. M. Luttinger: Phys. Rev. **97**, 883 (1955)
6. C. A. Hutchison: Phys. Rev. **75**, 1769 (1949)
7. Kip, Kittel, Levy, and Portis: Phys. Rev. **91**, 1066 (1953)

George Feher: An Interview to the EPR newsletter (continuation)

quence of conformity, has contributed to horrible atrocities and suffering, the Holocaust being a prime example.

Concerning the responsibilities of scientist: Scientists have special technical and scientific knowledge that is required to arrive at meaningful conclusions on important social, economic, environmental and political issues. It is, therefore, the responsibility of scientists to speak up and inform and educate the public. However, being a scientist does not of itself bestow special moral authority. I think, therefore, that it is a mistake to look to scientists for guidance on moral values.

Q: If a fairy was willing to fulfill three of your wishes, what would they be?

A: My goodness, I haven't played that game since I was a kid. Here I go, 70 years later.

(1) Excision of aggressiveness and evil from the human genome; they may have had some survival value in eons past but now cause havoc and disasters. (Corollary: Peace on Earth.)

(2) Eternal youth, so I can watch and even contribute to the exciting advances in science, particularly the understanding of the brain. By the way Laila, do you think if our brain were simpler we would have an easier time understanding it?

(3) Grant me three more wishes. (I think I borrowed that one from my childhood.)

Q: People are greatly impressed by the breadth of your personality and also by your great sense of humor. I remember your wonderful way of telling jokes in a very soft voice with the faintest shadow of a smile on your poker face and a devilish look in your eyes. Could you please tell us the joke no. 7 from your and Anatole Abragam's collection of stories and jokes (14/4, p. 10)?

A: Oh dear, I forgot it. O tempora o memoria!! I must be getting old.

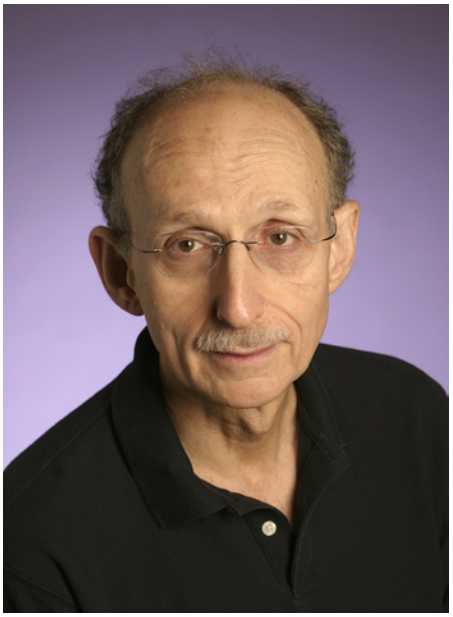
Q: You are one of the patriarchs of magnetic resonance. What would be your message to the younger generation and all the readers of the *EPR newsletter*?

A: Enjoy, carve out your own path and don't listen to us, old fogeys (this exempts me from giving you any advice).

Brian M. Hoffman Elected to the US National Academy of Sciences

On April 25, 2006 The National Academy of Sciences announced the election of 72 new members and 18 foreign associates in recognition of their distinguished and continuing achievements in original research. Election to the Academy is considered one of the highest honors that can be accorded a U.S. scientist or engineer. Those elected on April 25, 2006 bring the total number of active members to 2013.

The US National Academy of Sciences (www.nasonline.org) is a private organization of scientists and engineers dedicated to the furtherance of science and its use for the general welfare. It was established in 1863 by a congressional act of incorporation signed by Abraham Lincoln that calls on the Academy to act as an official adviser to the federal government, upon request, in any matter of science or technology.



Congratulation Letter to Brian Hoffman from the President of the IES

Dear Brian,

With great pleasure I have heard that you have been elected to the National Academy of Sciences of the USA. This is a great honor and I want to congratulate you to this election also in the name of the International EPR Society.

Your election is based on your excellent scientific work during the past decades that we all admire. This has very significantly advanced the field of magnetic resonance and EPR in particular.

I hope that due to your election to the National Academy of Sciences EPR will gain more visibility in the coming years.

With kindest regards and with best wishes for your future work I remain

Wolfgang Lubitz

★ IES BUSINESS ★ IES BUSINESS ★ IES BUSINESS ★ IES BUSINESS ★ IES BUSINESS ★ IES BUSINESS ★

International EPR (ESR) Society Awards 2007

Call for Nominations

Nominations are invited for: Silver Medal (Physics/Materials Science), Young Investigator Award and Fellowship of the Society.

Please see extract from by-laws below or visit ieprs.org for full constitution and by-laws).

All nominations must be accompanied by a 100–150 word citation in support of the nomination. No nomination can be considered without a citation. Additional supporting material may be included.

Nominations are to be sent in confidence to the President

– by email in word or pdf format to:
lubitz@mpi_muelheim.mpg.de
Please put the words: *Confidential IES Award Nomination* in the title
– or by mail to:
Prof. Dr. Wolfgang Lubitz,
IES President,
Max-Planck-Institut
für Bioanorganische Chemie,
Stiftstr. 34-36,
D-45470 Mülheim an der Ruhr,
GERMANY

The closing date for nominations for Awards in 2007 is 15th November 2006.

By-laws

A Silver Medal shall be awarded for significant contributions to EPR (ESR) Spectroscopy in the subject area of the Award.

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 judgment, represent the nominee's best work.

A Fellowship of the Society may be conferred on individuals who have made influential and distinguished contributions to the practice of EPR (ESR) Spectroscopy and its welfare over a long period.

The EPR community has available to it a list server. The address is epr-list@xenon.che.ilstu.edu.
To subscribe to the list, send the words SUBSCRIBE epr-list to majordomo@xenon.che.ilstu.edu.
That sends a message to Reef Morse who will then manually place you on the list. This honors only legitimate requests to join the list. Reef also moderates the list which keeps it spam-free.

The Zavoisky Award 2006

Jan Schmidt
Leiden University,
the Netherlands

in recognition of a lifetime's work in electron paramagnetic resonance, and, in particular, the laureate's contribution to the development of high-field/high-frequency pulsed EPR and ENDOR spectroscopies and their applications to semiconductor nanomaterials

The IES Silver Medal for Chemistry 2006

Kálmán Hideg
Institute of Organic and Medicinal Chemistry Pécs University,
Hungary

in recognition of his contribution to the design and synthesis of nitroxide compounds and their impact on the development of site directed spin labeling.

The IES Silver Medal for Biology/Medicine 2006

Jay Zweier and Periannan Kuppusamy
Davis Heart & Lung Research Institute,
Ohio State University,
USA

Joint award in recognition of their work in modern EPR imaging and in vivo EPR.

The Bruker Prize 2007

Daniella Goldfarb
Weizmann Instutute of Science,
Israel

in recognition of her contributions to the application and development of pulse EPR and ENDOR methodologies to obtain structural and dynamical information on porous materials and metalloenzymes.

Detailed information about these awards will be given in a future issue of the *EPR newsletter*.

The Bruker Prize 2006 to Yuri D. Tsvetkov

From left to right: Michael Bowman (PNL), Dieter Schmalbein (Bruker BioSpin), Yuri Tsvetkov (Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences) and Shirley Fairhurst (ESR Group).

For details, see this newsletter, p. 39.

The Jeol Young Investigator Prize to Janet Banham

From left to right: Peter Meadows (Jeol) with Riccardo Garzelli (University of York), Janet Banham (Oxford University) and Alexey Silakov (MPI Mülheim).

For details, see this newsletter, p. 39.

IES Young Investigator Award Revisited

This column features former recipients of the IES Young Investigator Award.

My early days of ENDOR in the Clarendon Laboratory

My postgraduate career started when I arrived in Oxford and was given two papers by Michael Baker, and told that I needed to build a X-band ENDOR cavity which could be used with an Oxford Instruments ESR 900 cryostat to study defects in diamond. Michael went on to explain that the TM_{110} ENDOR cavities described in the papers (R. Biehl, M. Plato, K. Mobius: J. Chem. Phys. **63**, 3515 (1975) and W. Mohl,w E. de Beoer: J. Phys. E: Sci. Instrum. **18**, 479 (1985)), looked like good designs and I should soon be able to come up with something to do the job. This was a pretty daunting start! Spurred on by the encouragement of Michael and invaluable advice from many (including Reinhart Biehl) things slowly began to come together. After many iterations on the basic design had been carried out by the terrific instrument makers in the Clarendon Laboratory workshop, a resonator was produced which worked really rather well! This process taught me many things but one of the most important was if you were trying to do an ENDOR experiment (and for that mater an EPR experiment), you should always endeavour to optimise your resonator for the sample you are trying to study. I still have fond memories of this resonator, which is now buried in a drawer, since it got me the data for my PhD and opened up a very interesting series of studies on nitrogen related defects in diamond using ^{14}N and natural abundance ^{15}N and ^{13}C ENDOR.

Today terrific ENDOR resonators are commercially available and for most experimenters the motivation to build resonators is not so great. However, at high microwave frequencies a number of researchers have reported on the design and implementation of innovative new ENDOR resonators which have terrific sensitivity, enabling a wide range of new experiments. One should not forget that excellent ENDOR sensitivity can often be achieved by simply winding a very small rf coil around the sample (which can even be a liquid sealed in a capillary), choosing a microwave resonator with a suitable mode and carefully positioning the coil + sample in the resonator. This rather intricate approach has the advantage that you can get away with using only a few watts of rf power. As a student when building the TM_{110} ENDOR resonator I worried about where all the power would go when we used the high power rf amplifier, and contemplated building a tuneable matching circuit, but seeing as most people simply managed by terminating the rf line with a 50 Ohm load I decided this was good enough for me. When running experiments I learned that if the 50 Ohm load was warm, then usually all was going well! The approach of using miniature ENDOR coils was used successfully by many in the Clarendon Laboratory, and today numerical simulations of resonator performance enables objective rather that intuitive design of new ENDOR resonators, and can explain why some of the old ENDOR resonators actually worked very well!

Today many regard continuous wave (cw) ENDOR as a black art. The versatility and sensitivity which is offered by the wide variety of pulsed ENDOR techniques means that this is usually the method of choice for investigating poorly resolved hyperfine structure. My first encounter with pulsed ENDOR was when I was given the job of disposing of a pulsed klystron power supply allegedly used by E. R. Davies in his pioneering experiments (Davies E.R.: Phys. Lett. A **47**, 1 (1974)). It had fallen into disrepair, and after electrocuting one technician twice nobody had dared switch it on for many, many years! I wished I had taken a picture before throwing it into the skip. Powerful as pulsed ENDOR is, for systems with long relaxation times (e.g. group IV semiconductors at low temperatures) a judicious choice of experimental conditions can often lead to near 100% cw-ENDOR enhancement. Hence although the balancing of different relaxation pathways maybe somewhat of a black art, cw-ENDOR still has something to offer.

At Warwick University we are just starting a new high field Dynamic Nuclear Polarisation (DNP) project. I am sure that my early training in ENDOR will be useful and that after 50 years ENDOR and other double resonance techniques still have much to offer!

Mark Newton
Department of Physics,
University of Warwick

Another Passion

A BRIEF HISTORY OF THE PHYSICS OF MUSIC*

Erwin L. Hahn

The history of the ancient world tells us that astronomy and music were considered to be basic sciences, although many of the observations were couched in terms of dogma and mysticism. The naked eye could readily perceive positions of the planets and the sun, enabling observers to record and anticipate periodicities in their orbits. In response to the harmonious vibrations of stretched strings the Pythagoreans (600–500 B.C.) of ancient Greece cultivated a religion of numbers arising from their discovery that integer (whole number) ratios correspond to the soundings of vibrating strings of varying lengths. A string under constant tension when doubled or halved in length produces sounds an octave below or above the sound with the original length. The ratio of string lengths of 2 to 1 (written 2:1, or 2/1) gives an octave; ratios of 3/2 (fifth), 4/3 (fourth), 5/4 (major third), and 6/5 (minor third) have pleasing effects ('concordant') when sounded together, while lengths not having such simple ratios are less pleasant ('discordant').

These ratios provided a basis for devising the Pythagorean scale, which later led to the construction of the other musical scales we know and use today. Sounds from the vibrations of strings, the striking of drums and gourds, the blowing of horns, and even the whistling of the wind across strings (Aeolian tones) and sharp objects inclined the ancients to regard music as a paramount part of man's existence and connection with the universe. In ancient Greece the complete man acquired his full education by the study of music for the soul, philosophy and poetry for the mind, and gymnastics for the body. The perception of harmony in music by the ancients led them to conceive of a universe governed by a similar harmony. Because of the harmonious sounds of musical intervals, the ordering of integer ('whole') numbers served as an example for modeling the ordering of objects in the universe. The ideal simplicity of the circle and the sphere, which seemed to the naked eye to be the form of the paths of the heavenly bodies, was combined with the use of ratios of whole numbers to define the radii of circular concentric orbits of the moon, the sun, and the five known planets. Although now known to be far from correct, this concept of orbital motion constituted an oversimplified but important precedent, adopted much later, in modern times, for the picture of electrons circling an atomic nucleus. The notion of ratios of orbital radii might even be viewed as a precursor to the Bohr theory of the atom.

"The Music of the Spheres" developed as a fanciful representation of the harmony of the universe. A specific tone corresponding to a note in the sequence of a Pythagorean musical scale was attributed to each of seven heavenly bodies on rotating concentric spheres. Only Heavenly Angels residing on the outermost sphere of the fixed stars could hear the chorus of sounds, not heard by sin-ridden earthlings located at the center of the universe.This picture was condemned as utter nonsense by Johannes Kepler (1571–1630) who made the revolutionary step forward with his three laws of elliptical planetary motion. Yet he could not free himself completely from the grip of ancient Pythagorean dogma. He thought he could confirm in some manner or form that the ratios of major and minor axes of his newly discovered elliptical trajectories would be identical to Pythagorean musical intervals, or at least to some other set of rational intervals. Actually, this was not a bad idea considering the fact that a few centuries later the wavelengths of atomic spectra were also found not to obey the laws of vibrating strings.

Because music in ancient times became connected with universal harmony, the mysticism of numbers became a religion that imposed its quota of bigotry. In the school of Pythagoras the sanctity of integer numbers (such as 5 and 13) and rational fractions (such as 7/5 and 4/3) was so revered that the existence of irrational numbers (such as $2^{1/2}$, the square root of two, and $5^{1/3}$, the cube root of five) was held secret until Hippasos exposed them to the public. He thus put himself in a position like that of Galileo (1564–1642) who dared to promulgate the Copernican theory that the earth revolved around the sun. However, instead of being put on trial for his sacrilegious revelation (as was Galileo), Hippasos was summarily drowned by his fellow Pythagoreans. Because of this 'information leakage' of the irrational numbers to the public, we have both profited and suffered from its implications down through the ages. The mysticism of numbers became so overbearing that it came to be considered quite vulgar, and practically illegal, to generate or play music near the end of the first century A.D. and beyond through the age of Ptolemy (90–168 A.D.). Because of the accumulated contributions of such post-Pythagoreans as Euclid (300 B.C.), Plato (427–374 B.C.), Eudoxos (322 B.C.), Varro (116–28 B.C.), and others, ending with Ptolemy, the theory of numbers became so highbrow that only an inner circle of 'number priests' were supposed to be capable of dealing with numbers. The vulgar lay public was forbidden to corrupt the orderly existence of holy numbers by uncontrolled soundings of instruments. During the early days of quantum mechanics and relativity, when these subjects were new highbrow disciplines, only a few theoretical-physicist 'priests' at first had access to the ▶

* This essay was issued as a supplement to an elementary Physics of Music course initiated and taught at UC Berkeley by the author. It promotes the idea, often not given enough attention, that the physics of music is important in science history. Informative physics of music discussions with the late E. T. Jaynes are gratefully acknowledged.

holy shrines of sacred knowledge. Today we seem to have a similar resurgence of priesthood- like 'string theorists' of a multidimensional universe, incapable of being tested by experiment. Enough said.

After the fall of the Roman Empire the authority of the church took hold; all knowledge and practical development of music was within the confines of the church. It is therefore not surprising that some of the most important physical principles of vibration physics were discovered, if not completely understood, by church appointed musicians, composers, and other clerical-music personages. The impetus causing Galileo to take up the study of science came from his father, Vinzenzo Galilei (1533–1591) who was a baroque and church music theorist. It was

he who chose the number 18/17 = 1.0588 (which is very close to the twelfth root of two = $2^{1/12}$ = 1.0594) for the positioning of the frets on a lute or guitar. (An octave on a modern piano is divided into twelve 'half-step' keys tuned so that the ratio of the frequency of any key to the one below it is $2^{1/12}$, giving a total frequency increase after twelve steps by a factor two, the octave ratio. This is the basis of the 'well-tempered' scale.) Frets are placed on a guitar at distances of about $(17/18)^n L_0$ where L_0 is the string length. The frets correspond, in order, to $n = 1, 2, ..., 12$, with $n = 1$ assigned to the first fret. Hence the octave occurs at $(17/18)^{12} L_0$, very close to $(1/2)L_0$, and the frets for decreasing values of n correspond closely to the well-tempered half-steps.

Concurrent with the introdution of opera by composers Palestrina and Monteverdi, the contributions of Galileo followed by Newton began the era of modern science. Music as the 'ancient science' became decoupled more and more from the church and taken over by the practitioners of music, who had their own 'physics demonstration equipment' in their instruments. The Italian composer and violinist Guiseppi Tartini (1692–1770) discovered difference tones on the violin, presaging the idea of the Bohr principle of 'eigenfrequency' differences among the different energy levels of electrons in their atomic orbits. Jean Phillipe Rameau (1683–1764), a very able French composer, and founder of the theory of harmony in western music, put to use the existence of overtones without knowing why they were produced or understanding their physical interpretation. He established the fundamental relations of the principles of harmony as we know them today. In some respects these principles have analogues in the optical spectra of atomic vibrations. Mersenne, a Friar, independently discovered the laws of vibrating strings. Galileo also found them in connection with his discovery of the periodic motions of pendulums, but Mersenne is given the credit. Galileo recorded that he generated mechanically two notes in the ratio of a musical fifth, which have a frequency ratio of 3 to 2. To confirm his observations he forced a chisel to screech or chatter on a block of metal, once producing a sound of corresponding frequency 3 (in some units) and again with a sound of frequency 2, a fifth below the first. He then counted out the chatter marks, and found them to be in the ratio of 3 to 2.

Newton is often regarded as the founder of modern science; his many activities included carrying out measurements of the speed of sound. As science continued to develop, a remarkable number of famous scientists and mathematicians did some dabbling in the physics of acoustics and musical sounds. Here we will refer only to a few. Ohm's Law pertaining to electrical resistance is familiar to a great many people, but it is little known that Ohm (1787–1854) first spelled out the fact that the ear 'Fourier analyzes' sound, whereas the eye does not do the same with light. Although there are a number of psycho-acoustic violations and departures from this simple superposition, the observation by Ohm was fundamentally correct. Ludwig Boltzmann (1844–1906), one of the founders of statistical thermodynamics, who developed the concept of kT (with k Boltzmann's constant and T the temperature) as the fundamental measure of thermal energy, investigated the hearing threshold of the human ear. A young child is sensitive to a power as small as 10^{-16} Watts/cm^2 at a frequency of 3500 cycles per second; just below that power, noise power (such as that from circulation of the blood) is present which, fortunately, the ear and brain do not register.

From scanning the list of scientific theoretical and physical investigations of mechanical vibration phenomena one can see that the choice of problems was confined to special cases involving mathematical analysis. The one great exception was the comprehensive work of Herman von Helmholtz (1821–1894), who wrote a profound treatise that put physical sense into the interpretation of physical sounds and how they are generated in musical practice. However, physical theories and mathematics of vibrations added very little to the actual improvement of instruments, and certainly contributed nothing to the quality of musical performances. Vibrating musical instruments were interpreted long after they were established. Theorists were exercising their newly found mathematical powers in order to explain the vibration patterns of objects, mainly strings, horns and drumheads.

From all this we can state that science owes more to music than music owes to science. The development of musical instruments has been based primarily on the process of trial

and error. The violin represents the most efficient and flexible sounding instrument yet arrived at by the taste and demand of the art, and not by conscious physical analysis. After the final formulation of the violin by da Salo and by Amati around 1530–1550, and of adaptations and improvements in the sound and power of horns, brass, and the piano, it is remarkable how little the form of musical instruments has changed over the last few hundred years. Among the exceptions are the Steinway piano, made possible (around 1850) by use of a cast iron frame, and the modern flute, reconstructed in a revolutionary way by Boehm. There have been certain improvements in metals and alloys, string materials, valves, and other fixtures, but the tastes of tradition have kept the physical nature of musical instruments relatively static.

Finally we come to this question: does a knowledge of the physics of music have benefits aside from its historical interest? Some have argued that objective knowledge destroys the lyricism and beauty of art, the stability of religion, and even the joy of love. However, these are views held by half-baked romanticists and fundamentalists. Real artists will concede their eagerness to know to what extent their art can be freely developed on the basis of their own invention, and to what extent bounds are imposed by physical law. A little knowledge of physics can erase many misconceptions and erroneous superstitions among musicians. For examples, in the old days of opera it was thought that the sympathetic vibrations of an array of broken wine bottles spread beneath the stage floor would enhance the rendition of opera performances. Glib erroneous notions still exist: that the lowest note of an eight foot piano sounds the same pitch as that of an eight foot organ pipe; that the purpose of the two F-holes of the violin is to let the sound come out from the top; (and this next one by people who learn music only with a piano): D sharp, for example, is always the same as E flat in music written for any instrument. Among non-musicians it took a long time to figure out the proper interpretation of sound and how it is propagated. Aristotle (384–322 B.C.) had a vague notion that air was a medium for conducting sound. He claimed erroneously that high notes moved faster through the air than low notes. During the time of Galileo, the French philosopher Gassendi (1592–1655) postulated that sound was caused by emission from the source of invisible particles which struck the ear. Otto von Guericke (1602–1686) claimed that sound could be transmitted in the absence of air. Finally Robert Boyle (1627–1691) proved that air was necessary for sound transmission by carrying out a proper experiment with a sound source in a bell jar from which the air could be evacuated.

Anniversaries

70th Birthday of Klaus Möbius

Visiting Klaus Möbius these days in Berlin, one can hardly imagine that he is soon celebrating his 70th birthday. Apparently not inhibited in his research activities by any rigid retirement rule, he 'resides' in his office, the door open to a constant 'come and go' of people. Judging from the pile of papers related to various scientific organizations, his advice on personal issues and problems of general science management is highly appreciated, and therefore he has the difficult job of allocating enough time to 'real science'.

Many reasons can be quoted for this situation, the most important, however, is based on his outreaching personality, combined with a high sensibility for new exciting developments in science. This enabled him to establish a reliable network, consisting of leading scientist in EPR. Because of his success in establishing an outstanding EPR centre at Berlin, this inevitably led to a constant influx of highly motivated post-docs and visiting scholars from all over the world. Looking at the impressive list of long term visitors, it is obvious that in addition to well established ties to scientist in the western world, Klaus tried in particular to activate collaboration with groups from the former Soviet Union and countries under her control. He thus established a lasting connection to highly motivated researchers from countries especially strong in magnetic resonance. Exposing himself to the highest level of competition, persisting success on the international stage was only possible not only by keeping up with the latest developments in technology but even more important by targeting hot topics in science.

What are the ingredients for such a successful scientific carrier? Looking back into the mid 60's, Klaus started as a group leader with 2 empty rooms, which soon after hosted the first AEG EPR spectrometer. I don't know how he succeeded in allocating funds for the instrument, but I guess that his optimistic personality combined with a clear vision was important for this first important step. Such a new and 'shiny' instrument was not common in these days in German universities and was therefore attractive for many graduate students. (I admit that I was also attracted by this sight, even when finding out shortly after that my initial duty was caring for a vacuum pump system.) Because of his previous experience in the AEG research lab in Frankfurt, he knew how to handle a competing group of students without allowing disintegration. All problems were defined as 'group problems' and discussed in a very open way. A solution finally had to be stated on the famous white board in his office in the cosy barracks in Helmhotzsstreet, before leaving for a break. This method culminated in the generally adapted procedure of co-phrasing sentence by sentence the

upcoming publications in the presence of all active coworkers. Although seemingly difficult for the young group members to develop an own personal scientific profile under these conditions, this drawback was more than compensated by a sound knowledge in 'adjacent' research topics, and most important, by Klaus's method to urge all students to give presentations not only on national but also on international conferences. At these days, special government funds for instance allowed to send graduate students to big conferences like ISMAR meetings in Israel and India. He also took care to send his students as post docs to high-level research groups to gain international visibility. Group life was also intensified by 'after talk meetings' in his house in Dahlem, which from the very beginning hosted an impressive collection of scientific instruments and contemporary art. Such an intensity in scientific and social life was certainly only possible because of constant support from his wife Uta.

In the first decade of his carrier, Klaus focussed on instrument developments, signalling to the international community that outstanding results can be obtained most efficiently by coming to Berlin. It is fair to say that at the end of the 70's, liquid state ENDOR and TRIPLE resonance facilities were unique in Klaus's lab. However, the search for new directions in EPR continued, and culminated in building a 360 GHz spectrometer. As can be expected, not all projects started were successful. But this can be taken as evidence for his effort always riding on the 'cutting edge' of experimental techniques.

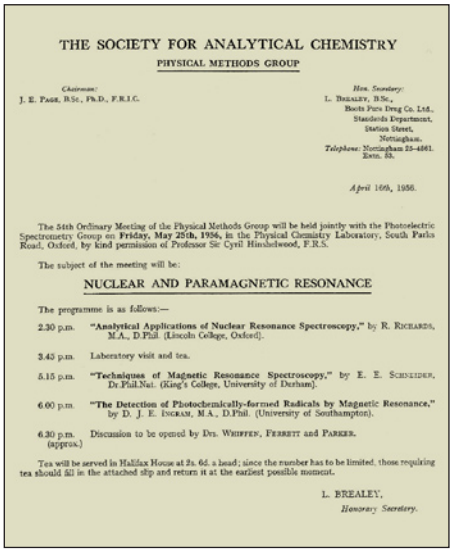
In a smooth transition, he changed his focus from 'instrumentation' to 'application', and having established an impressive 'zoo' of spectrometers, he could enter the highly competitive area of photosynthesis research. We all are aware of his outstanding contributions in this field, which were recognized by prestigious awards like the IES Gold Medal, the AMPERE Prize, the Zavoisky Award, and the Philip-Morris Prize, just to name a few.

I think we all wish Klaus Möbius ongoing fun by playing on the molecular scale, and may I add as personal note: thanks a lot, Klaus, for your support!

K.-Peter Dinse
Darmstadt University of Technology

Magnetic Resonance Spectroscopy in Britain in 1956

We are celebrating the 50th anniversary of what is probably the first public meeting on magnetic resonance which was held at the Physical Laboratory, Oxford University on 16th April 1956 – about 50 people attended, including the writer. The conference was organised jointly by the Physical Methods Group of The Society for Analytical Chemistry and the Photoelectric Spectrometry Group: the latter group was mainly concerned with optical spectroscopy. Both these groups had recognised that some new techniques were arriving on the scene and needed to be understood. It is interesting that at this time, a half-day meeting was sufficient to encompass both electron and nuclear magnetic resonance! Also, the cost of the meeting (to cover tea and biscuits) was a mere 2s 6d (12.5p or 0.15€). At time of the meeting there were no commercial magnetic resonance spectrometers in Britain, hence the equipment in use was home-built. Some of the magnetic resonance pioneers are Rex Richards (Oxford) and Raymond Andrew (Bangor) who built NMR spectrometers and David Ingram (Southampton) and E. E. Schneider (Durham) who constructed EMR spectrometers. It is interesting that the latter researcher preferred to call the technique "paramagnetic resonance", but clearly this wasn't adopted. At this time there was no settled nomenclature with nuclear resonance being called NMR or NSR, while electron resonance was (and still is today) referred to as ESR or EPR – with a few dissenters, like the writer, preferring EMR – to be consistent with NMR. It can be seen from the meeting programme that three of the above pioneers gave talks: during his talk Rex Richards gave a demonstration using a gyroscope to illustrate the phenomenon of nutation. Soon after the meeting, three ▶



THE SOCIETY FOR ANALYTICAL CHEMISTRY

PHYSICAL METHODS GROUP

Chairman:
J. E. Page, B.Sc., Ph.D., F.R.I.C.

Hon. Secretary:
L. Brealey, B.Sc.,
Boots Pure Drug Co. Ltd.,
Standards Department,
Station Street,
Nottingham.
Telephone: Nottingham 25-4061.
Ext. 53.

April 16th, 1956.

The 54th Ordinary Meeting of the Physical Methods Group will be held jointly with the Photoelectric Spectrometry Group on **Friday, May 25th, 1956**, in the Physical Chemistry Laboratory, South Parks Road, Oxford, by kind permission of Professor Sir Cyril Hinshelwood, F.R.S.

The subject of the meeting will be:

NUCLEAR AND PARAMAGNETIC RESONANCE

The programme is as follows:—

2.30 p.m. **"Analytical Applications of Nuclear Resonance Spectroscopy,"** by R. Richards, M.A., D.Phil. (Lincoln College, Oxford).

3.45 p.m. Laboratory visit and tea.

5.15 p.m. **"Techniques of Magnetic Resonance Spectroscopy,"** by E. E. Schneider, Dr.Phil.Nat. (King's College, University of Durham).

6.00 p.m. **"The Detection of Photochemically-formed Radicals by Magnetic Resonance,"** by D. J. E. Ingram, M.A., D.Phil. (University of Southampton).

6.30 p.m. (approx.) Discussion to be opened by Drs. Whiffen, Ferrett and Parker.

Tea will be served in Halifax House at 2s. 6d. a head; since the number has to be limited, those requiring tea should fill in the attached slip and return it at the earliest possible moment.

L. BREALEY,
Honorary Secretary.

Announcement about the 54th Ordinary Meeting of the Physical Methods Group to be held jointly with the Photoelectric Spectrometry Group on May 25th, 1956.

Photo from the conference on free radical research at Cirencester in 1965.

Varian 40 MHz high-resolution NMR spectrometers were delivered to Cambridge and Liverpool Universities and to ICI Blackley. These were followed some time later by Varian V4500 EPR X-band spectrometers. In the early 1960's both areas of magnetic had blossomed sufficiently to warrant a split into the two major fields: an independent NMR Discussion Group was formed and there was a large conference on free radical research at Cirencester in 1965. (see picture). These groups were largely for Chemists while Physicists founded the British Radiofrequency Spectroscopy Group which embraced all forms of magnetic resonance. Eventually, the two Chemistry-orientated groups separately joined the then Chemical Society (now the Royal Society of Chemistry) as NMR and ESR subject groups. Although the emphasis has shifted towards international groups, the original organisations still continue to flourish and there seems to be no end to the speed of development of magnetic resonance.

Les Sutcliffe

Alex Müller (left) and Boris Kochelaev (right).

Anniversaries

20 Years after the Discovery of Cuprate Superconductors

In September 1986, the paper "Possible High T_c Superconductivity in the Ba-La-Cu-O System" by J. G. Bednorz and K. A. Müller [1] was published, and one year later the authors were awarded the Nobel prize in Physics. The unprecedented fast reaction of the Swedish Academy reflected a general confidence that we are witnesses of a breakthrough in the physics of condensed matter. I remember a great enthusiasm at that time among students and professors in the Kazan University: the main lecture hall of the Physics Faculty was overcrowded (people were sitting and standing everywhere including the space in front of, behind, and between desks) during my presentation about this discovery with demonstrations of a levitated sample of YBCO in a magnetic field at liquid-nitrogen temperatures. I was told that at the Kapitza Institute of Physical Problems in Moscow people were listening to the lecture about the discovery even via speakers outside the lecture hall. The discovery of high-temperature superconductivity (HTSC) stimulated an avalanche of experimental and theoretical works on the nature, fascinating properties, and applications of superconducting cuprates, as well as on strongly correlated systems in general. Every year national and international conferences dedicated to problems of HTSC take place.

Recently, from March 27th to March 29th, 2006, the International Symposium in Honor of J. G. Bednorz and K. A. Müller and celebrating 20 years of HTSC was organized by Hugo Keller, Annette Bussmann-Holder and Davor Pavuna in Zurich. In his lecture, Georg Bednorz recalled the situation in superconductivity research in the mid-80s and described the role of the environment and decisive circumstances leading up to this discovery. Considerable attention was given to applications of superconducting cuprates and other oxide perovskites. The lecture of Alex Müller was dedicated to recent experiments and ideas concerning the nature of HTSC. The analysis of local properties with a different space-time scale resolution and the isotope effect indicate the presence of two kinds of quasi-particles of the Fermi and vibronic character. The agglomerations of bipolarons in clusters or stripes with metallic character even at very low doping and temperatures were discussed. C. W. Chu described the present status and the future of the first liquid-nitrogen-temperature YBCO superconductors, including small-current and large-current applications. The problems of competing or cooperating spin-charge-lattice degrees of freedom to produce remarkable phenomena on very different space-time scales were discussed by T. Egami, A. Bishop, Z. X. Shen, A. Lanzara, J. C. S. Davis, D. Mihailovich, J. Haase, A. Shengelaya, the author of this contribution, and others on the basis of the neutron inelastic scattering, X-ray spectroscopy, angle-resolved photoemission, tunneling spectroscopy, optical picosecond excitations, NMR and EPR measurements. During the symposium a total of 22 talks was presented and a lot of illuminating and free discussions took place.

I think that the readers of the *EPR newsletter* would be interested and pleased to realize that ideas that led to the high-temperature superconductors were created during a long and very successful EPR study of perovskite-type oxides by Alex Müller. Here I would like to call the reader's attention to the philosophical-psychological work of Alex Müller "Approaching fire" [2], in which we can find some very personal impulses, motivations and symbols of his scientific activity. In 1952, Alex Müller had a final exam on the four-semester lecture course taught by Wolfgang Pauli on Theoretical Physics at ETH Zurich. After graduation, during his doctoral work on the newest crystal $SrTiO_3$ with the perovskite-type structure, Alex Müller had a colorful dream in 1957: Wolfgang Pauli, looking like Buddha in a deep meditation, had in his right hand the cubic lattice of $SrTiO_3$, which transformed a white beam of light in a

colorful spectrum. It seems now that it was a symbolic sign of a great variety of properties hidden in perovskites. The next step was related to the EPR study of the Jahn-Teller effect of the Ni^{3+} ion in $SrTiO_3$ with his first PhD student U. Höchli in the mid-60s. Analysis of the dynamic features of this effect was published later [3]. The possibility of a structural phase transition in similar crystals due to the cooperative Jahn-Teller effect was investigated in collaboration with Harry Thomas [4]. This name I heard from Alex Müller at the Conference on Polarons in Erice (Sicily, 1998) in connection with the appearance of an idea on high-temperature superconductivity in perovskite-like systems. We enjoyed a beautiful view of the Mediterranean Sea from the Monastery hill, where the conference took place. Alex was in a serene mood and told me that exactly at this place in 1983 he got the idea after a talk by Harry Thomas at the workshop on anharmonic behavior of crystals near the structural phase transitions. Professor Thomas suggested a polaron created by an electron due to the local Jahn-Teller anharmonic distortions of the lattice, which can move through the lattice because of the quantum tunneling. Since the classical superconductivity appears due to the coupling of electrons via harmonic vibrations of the lattice, strongly anharmonic behavior of the Jahn-Teller polarons allowed proposing superconductivity at higher temperatures.

After his return from Sicily, Alex Müller suggested working on this project to his colleague in the IBM laboratory J. Georg Bednorz, who accepted it with enthusiasm. They have chosen layered cuprates consisting of CuO_2 planes organized in the perovskite-like lattice! It seems, it was predetermined from above. The result is well known. At this point I would like to quote Alex Müller from [2]: "This lattice had for me a special meaning, as I have already explained. Crystals of this structure, besides the structural phase transformations, also gave me in other fields of solid-state physics like photochromie and ferroelectrics before 1983 much joy, satisfaction and recognition. Only in an important field of superconductivity I did not make any attempt till this time point. However, the decomposed by the perovskite-lattice light spectra in the dream 1957 could probably include an aspect of superconductivity too." (translation from German – B. K.) It seems to me, having in mind all steps of this story, that Alex Müller and Georg Bednorz were led from above and could not avoid their discovery.

Returning to special interests of the EPR community I would like to mention that the EPR method continues to give important information on fascinating properties of high temperature superconductors and their parent compounds. In particular, the plenary lecture given by Alex Müller at the International conference on nanoscale properties of condensed matter probed by resonance phenomena (August 2004, Kazan) was entitled "Electron Paramagnetic Resonance and High Temperature Superconductivity". Many results can be found, also, in a review [5].

1. Bednorz J.G., Müller K.A.: Possible High T_c Superconductivity in the Ba-La-Cu-O System. Z. Phys. B **64**, 189 (1986)
2. Müller K.A.: Annäherungen ans Feuer. In a volume "Jung und Jünger" (Thomas Arzt, K. Alex Müller und Maria Hippius-Gräfin Dürckheim (Hrsg.), eds.), pp. 37–50. Zurich: Königshausen & Neumann 1999.
3. Slonczewski J.C., Müller K.A., Berlinger W.: Dynamic Jahn-Teller Effect of an Impurity in a Spontaneously Distorted Crystal. Phys. Rev. B **1**, 3545 (1970)
4. Thomas H., Müller K.A.: Theory of a Structural Phase Transition Induced by the Jahn-Teller Effect. Phys. Rev. Lett. **28**, 820 (1972)
5. Kochelaev B.I., Teitel'baum G.B.: "Nanoscale Properties of Superconducting Cuprates Probed by the Electron Paramagnetic Resonance." in: Superconductivity in Complex Systems (Müller K.A., Bussmann-Holder A., eds.), pp. 203–266. Berlin: Springer 2005.

Boris I. Kochelaev
Kazan State University, Kazan, Russia

ENDOR, discovered by George Feher in 1956, was the first high-resolution method to find its way into EPR Spectroscopy and was achieved through the simultaneous irradiation of a sample at both microwave and radio frequencies.

I am perhaps not the best person to address this subject as I have to confess to being a failed ENDOR experimenter! Throughout much of 1963 I looked for ligand ENDOR in Fe^{3+}:AgCl, working at 20K, the temperature of liquid hydrogen that was more readily available in the Clarendon Laboratory than liquid helium! In parallel, J. C. Garth, a student of Charles Slichter at the University of Illinois, succeeded by working at ~4K. So we were defeated by a poor choice of temperature. My ENDOR education was completed when in 1966, one of the contributors, Martin Spaeth, whose doctorate in Stuttgart involved the ENDOR of hydrogen atoms in KCl, spent about 10 months at Monash University. Although we did not undertake ENDOR, our collaboration led Martin to add transition metal ions to his ENDOR repertoire when he returned to Germany.

The feature articles and reminiscences that appear in this issue of the EPR Newsletter are representative of the many directions ENDOR has taken. Technical developments have permitted cw-ENDOR to be replaced by pulsed-ENDOR In what follows once can sense something of the breadth of applications from solid-state physics, through chemistry, to biology. These reminiscences and the insights into the history of ENDOR remind us that ENDOR is often the only way to obtain particular hyperfine and structural information.

Special thanks are due to Michael Baker, Martin Spaeth, Jürgen Hütterman, Peter Höfer, Dieter Schmalbein, Klaus Möbius, Jim Hyde and Mikhail Falin for providing these contributions.

John Pilbrow
Monash University

ENDOR '50 dedicated

New Heights of EPR Resolution or Beating the 'Wizard of ENDOR'

The beginnings of ENDOR in Oxford

Michael Baker
Clarendon Laboratory, Oxford

I have mentioned in an earlier article* that the stage was set for ENDOR in Oxford by the various enterprises Brebis Bleaney was pursuing in the 1950s on aspects of the hyperfine interaction (HFI). The latter was first observed in EPR in 'high' magnetic field, where electron spin S and nuclear spin I are decoupled, so the strong transitions are $\Delta M = \pm 1$, $\Delta m = 0$. HFI admixtures led to weak transitions where $\Delta m \neq 0$, revealing nuclear quadrupole interaction (NQI) and nuclear Zeeman interaction. As some of the HFI were large (several hundred MHz) and some measuring frequencies were low (~1500 MHz) some HFI measurements were made in zero magnetic field.

So, it was a natural extension for Brebis to suggest that we should attempt to detect $\Delta M = 0$, $\Delta m = \pm 1$ transitions directly, and I have rued the fact that I did not take his suggestion seriously when he first made it around 1954*. Brebis realised that this could give much narrower lines than EPR and consequently greater precision in HFI measurements, as well as direct access to NQI and nuclear moment measurement.

Our principal interest was in paramagnetic transition ions, which had short T_1, so for ENDOR a different steady state saturation method was needed at low temperatures from that which was used by George Feher for donors in silicon. Unlike George, who used a thin walled microwave cavity and an external r.f. coil, we put a single r.f. loop inside the cavity: in either case it was important to introduce the r.f field for inducing the nuclear transitions without compromising the sensitivity of the EPR spectrometer. It fell to F. I. B. (Tito) Williams, one of my first graduate students, to be successful in making these tricky ENDOR measurements work. Tito, a native of Bermuda, came to the UK in mid 1958 and found the British weather so irksome that he started a chart on the lab's blackboard early in 1959 of rainy and sunny days, to convince the natives of our dreadful climate. 1959 was one of the sunniest summers of the century! Fortunately, Tito's work was as sunny as his first summer.

Our EPR had moved from hydrated salts to anhydrous fluorides grown from the melt, where substituted paramagnetic ions had a nice regular environment of 100% abundant ^{19}F nuclei as close neighbours. So it was a natural extension for John Hurrell, my next graduate student, to make a success of ligand ENDOR.

Curiously, both of these pioneers of ENDOR in Oxford married girls working in my lab. Although ENDOR produced doctorates for many more of my graduate students, it was never again so good a marriage broker.

I gave an invited talk at a conference in Clermond-Ferrand in 1962, to mark the 300th anniversary of the death of Blaise Pascal, to try to spread the gospel of ENDOR to the rest of Europe. Sadly, although I had worked hard to make my presentation in French, the one person who really wanted to understand me was a German, Horst Seidel, who spoke no French!

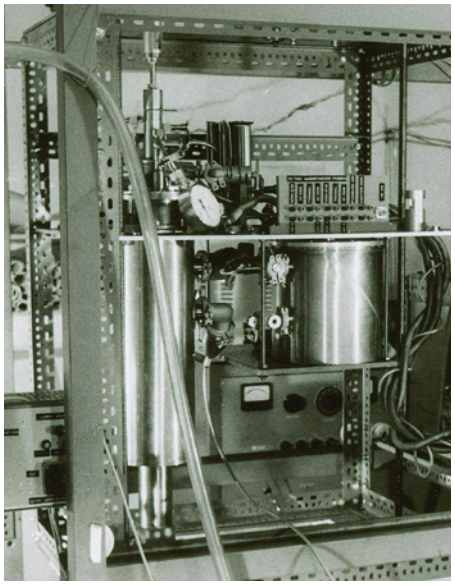
Another innovation in ENDOR at Oxford was made by Roy Davies. He had been ▶

* 90th Birthday of Brebis Bleaney, EPR newsletter, vol. 15, no. 2, 2005.

a graduate student of mine working on ligand ENDOR of defects in alkaline earth fluorides. During a subsequent period as a postdoc in my group around 1969 he modified the pulse-ENDOR techniques, which had been developed by Mims in 1965, by using a different pulse sequence. The r.f. was turned on for a while after an initial hole-burning EPR pulse, and then the system was interrogated by a $\pi/2, \pi$ EPR-pulse sequence giving the advantages of greater sensitivity and lack of 'blind spots'. Sadly this technique was not subsequently pursued far by either its inventor or by me. I am grateful to Michael Mehring for acknowledging Davies's early invention of this pulse method when it was later re-invented, by calling it "Davies-ENDOR".

When I used the spectrometer to study atomic hydrogen in KCl I had to illuminate the OH^--containing crystals with a potent Al arc at low temperature and while doing this I noted that radio direction finding cars of the broadcasting authorities were eagerly searching the jamming station around the physics building! I thus completed my measurements mainly during the night.

The development of the first computer controlled ENDOR in Germany in my group in Paderborn starting 1976 was necessary to handle the hundreds of lines of semiconductor defects and profited from the cooperation of the computer freak Horst Ziegler who already as a high school kid had built a sizable computer by filling his desk with hundreds of relays then used by telephone switch boards!



Early ENDOR in Germany

Johann-Martin Spaeth
Emeritus Professor of Physics
University of Paderborn

The first ENDOR spectrometer in Germany was built by Horst Seidel at the University of Stuttgart around 1958.

Horst Seidel's university training was electrical engineering. To work for his PhD he originally wanted to join the group of Prof. Kopfermann in Heidelberg known for the determination of nuclear moments. However, for whatever reason, he was not accepted. Horst Seidel then joined the group of Prof. Pick at the University of Stuttgart which was studying colour centres in alkali halides and had just started EPR. Horst Seidel's engineering background was ideally suited for his given task to build an ENDOR spectrometer, with which a 'normal' physics graduate would have had difficulties. Thus Kopfermann's refusal was most fortunate for the development of ENDOR in Germany. Horst Seidel built an X-band superheterodyne spectrometer and a helium cryostat in which a crystalline sample was cooled inside a quartz finger which stayed warm and which could be illuminated. The quartz finger was inserted into a RT cylindrical ENDOR cavity. Horst Seidel developed the 'stationary' ENDOR, now standard for solid state defects, in which the rf is slowly swept and the ENDOR signal is recorded as a stationary change of the EPR signal. He died far too young in 1974, aged 42.

ENDOR Notes

James S. Hyde
Department of Biophysics,
Medical College of Wisconsin,
Milwaukee, Wisconsin

George Feher's famous paper on ENDOR of donors in Silicon appeared in the June 1, 1959 issue of the Physical Review [1]. My MIT PhD dissertation "Magnetic Resonance, Relaxation and Rapid Passage Phenomena in LiF F Centers" also carries a June 1959 date. When I read George's paper I came upon Appendix A: "Behavior of an Inhomogenously Broadened Line Under Adiabatic Fast Passage Conditions." It got my attention! Unknown to each other, in some degree he and I were in the same scientific space. His pioneering ENDOR experiment had been performed by irradiating the sample with an NMR radio frequency while observing a dispersion EPR signal that had been obtained using field modulation with the reference phase of the phase-sensitive detector shifted by 90° from the field modulation phase. The biblical story of the Saul's visit to the Witch at ENDOR [2], to which Feher once called my attention, is subtle and complex, like the ENDOR experiment.

Gus Maki and I decided to make an all-out effort to detect ENDOR in free radicals in solution working together in Palo Alto in the late summer of 1963. Finally we thought we saw signals – always between 5 and 6 PM. And then came a very good week. The signal-to-noise ratio improved by a factor of two each day for five successive days. We could publish [3]! George Feher coined a phrase: "people's ENDOR." These are ENDOR-like signals correlated with human movement that modulates ground loops, microwave leakage, and RF. People's ENDOR was the source of noise, and we finally had it under control.

One day as I studied the ENDOR line shape from the four most strongly coupled protons of the tetracene positive ion under conditions of slow rotational diffusion, the idea occurred to me that ENDOR in the limit of no motion such as powders or frozen solution should be possible. The concept was to select molecules that are similarly oriented by observing a turning point with EPR and sweeping the RF to obtain single-crystal-like ENDOR spectra. And it worked [4, 5]! Today there may be as many ENDOR experiments performed in powders as in single crystals.

Nearly half a century since the publication of Feher's seminal paper that influenced me so much, the Witch at ENDOR continues to cast her spell over me from time-to-time and I see new visions of truth. For example, Feher taught that any T_1-dependent EPR display was a suitable candidate for ENDOR. This perspective led to our paper on ENDOR using a Multiquantum EPR display [6].

References

1. Feher G.: Phys. Rev. **114**, 1219 (1959)
2. I Sam. 28.
3. Hyde J.S., Maki A.H.: J. Chem. Phys. **40**, 3117 (1964)
4. Hyde J.S., Rist G.H., Eriksson L.E.G.: J. Phys. Chem. **72**, 4269 (1968)
5. Rist G.H., Hyde J.S.: J. Chem. Phys. **52**, 4633 (1970)
6. Mchaourab H.S., Christidis T.C., Hyde J.S.: J. Chem. Phys. **99**, 4975 (1993)

ENDOR in Solution – a Look Back upon Exciting Experiments

Klaus Möbius*
Department of Physics,
Free University Berlin

Introduction

The 50th birthday of ENDOR: There are many good reasons for physicists, chemists and biologists to celebrate the 1956 offspring of this happy liaison between EPR and NMR with George Feher as the matrimonial agent. The main motivation for extending single resonance EPR to double resonance ENDOR techniques is twofold: 1) to enhance the sensitivity of detection by 'quantum transformation' from the low-frequency NMR domain, where the radiofrequency (rf) transitions to be measured occur, are transformed to the high-frequency EPR domain, where spectral changes due to the absorbed microwave (mw) energy are detected, and 2) to enhance the resolution of the spectrum, i.e., to reduce the number of spectral lines in a given frequency range by imposing additional 'selection rules' on the induced transitions thereby eliminating redundant hyperfine lines in the inhomogeneously broadened spectrum. As a result, the line density in an ENDOR spectrum increases only in an additive way with increasing number of groups of equivalent nuclei, whereas in an EPR spectrum it increases in a multiplicative way.

Under continuous wave (cw) mw and rf irradiation (to this situation common for liquid samples I want to restrict myself) ENDOR signals are obtained by monitoring the changes of the amplitude of a saturated EPR line when sweeping through the nuclear (NMR) frequency region. The first successful ENDOR experiment by G. Feher [1] was performed on a solid-state sample – phosphorus-doped silicon at low temperature – where the relaxation times are sufficiently long to easily obtain saturation. For doublet state radicals in liquid solution, however, the relaxation times are much shorter – in the order of 10^{-5} to 10^{-7} s – and, consequently, much larger saturating mw and rf fields are needed. This probably explains why it took another eight years before the first ENDOR-in-solution experiments on organic radicals could be successfully performed 1964 by J. S. Hyde and A. H. Maki [2].

To learn from the experience Gus Maki had accumulated already on ENDOR in solution at UC Riverside and to benefit from it for our own, still new high-power ENDOR efforts, I spent a postdoctoral year 1969/70 in his laboratory. There I met Hans van Willigen, a postdoc from the University of Nijmegen. We shared the fun and frustration to rebuild the dismantled ENDOR spectrometer which had been cannibalized after Robert Allendoerfer had left the Maki group. Ultimately, we found a solution to the problem of high rf power to be impedance matched to the ENDOR coil by incorporating an (empty) California wine bottle wrapped with a few turns of heavy copper wire (see A. H. Maki in *EPR newsletter* 2004, vol. 14, no. 3, p. 13). This resort to empty (and full) California wine bottles enabled us to perform an ENDOR study on the lifting of orbital degeneracy in high-symmetry large molecules by weak perturbations. We chose pentaphenylcyclopentadienyl (PPCPD) successively methyl-substituted at the para positions [3]. The samples were a generous gift by Harry Kurreck from FU Berlin.

For several years thereafter, only a few groups invested the time (and money) to build their own ENDOR-in-solution spectrometers with high-power rf capability. The development and understanding of ENDOR-in-solution spectroscopy was highly stimulated by J. H. Freed [4–6] whose general theory of saturation and double-resonance proved to be adequate in describing amplitude, width and shape of ENDOR lines in great detail, including subtle coherence effects due to the strong mw and rf fields. When commercial ENDOR spectrometers became available around the mid 70s [7, 8] the field exploded by applications from chemistry, biochemistry and molecular physics (for overviews, see [9–20]).

For doublet state radicals in isotropic solution, each group of equivalent nuclei contributes, to first order, only two ENDOR lines to the spectrum:

$$\nu^{\pm}_{\mathrm{ENDOR}} = |\nu_n \pm a/2| \qquad (1)$$

with the nuclear Larmor frequency $\nu_n = (g_n \mu_K/h)B_0$ and the isotropic hyperfine coupling constant (hfc) a. The gain in resolution becomes particularly pronounced when nuclei with different magnetic moments are involved with their ENDOR lines to appear in different Larmor frequency ranges. If this is not the case at X-band ENDOR, the lines can be disentangled by performing ENDOR at higher Zeeman fields and correspondingly higher mw frequencies [21].

From many applications in chemistry, biology and physics it became clear that steady-state cw ENDOR in solution, though extremely powerful in resolving complex hyperfine structures of low-symmetry radicals, suffers from sensitivity problems: Only less than 10% of the EPR intensity is normally observable as the ENDOR effect which has to be maximized by carefully controlling temperature and viscosity of the solvents, thereby optimizing the delicate interplay between electron and nuclear relaxation rates. Cw ENDOR suffers also from problems of assigning the measured hyperfine couplings to molecular positions: The ENDOR line intensities are determined primarily by electron and nuclear relaxation and not by the multiplicity of the NMR transitions. These drawbacks motivated us at FU Berlin in 1974/75 to extend ENDOR in liquid solution to electron-nuclear-nuclear TRIPLE resonance experiments [22, 23] in which two high-power rf sources are connected to the NMR coil inside the EPR cavity. It was primarily the enthusiasm of Reinhard Biehl and Peter Dinse which enabled us to solve the experimental problems when setting up high-power ENDOR and TRIPLE instrumentation at X-band. And it was primarily the enthusiasm of Martina Huber, Friedhelm Lendzian, Wolfgang Lubitz and Martin Plato as well as that of our friends Harry Kurreck from the Chemistry Department of FU Berlin, Hugo Scheer from the Botanical Institute of the University of Munich, and Haim Levanon from the Department of Physical Chemistry of the Hebrew University of Jerusalem which enabled us to apply EPR/ENDOR/TRIPLE to complex and novel chemical as well as biological systems in fluid solution to elucidate their molecular and electronic structure.

At this point it is appropriate to remember late Arnold Hoff (University of Leiden) whom I first met during an EPR symposium in Nijmegen, August 1976. Over a glass of beer or two Arnold introduced me to the beauties of photosynthesis, and we discussed joint ENDOR-in-solution experiments on the electron transfer cofactors in bacterial photosynthesis. During his first – unforgettable – visit, nitrogen ENDOR and proton TRIPLE spectra of the bacteriochlorophyll *a* cation radicals in fluid organic solvents could be recorded, and most of the hfcs (including their signs) were measured [24]. It is very sad that both Reinhard Biehl and Arnold Hoff ▶

* Author's address: Department of Physics, Free University Berlin, Arnimallee 14, D-14195 Berlin, Germany. E-mail: moebius@physik.fu-berlin.de

died so early, Reinhard in 1987 at the age of 43, Arnold in 2002 at the age of 63.

Realistic sensitivity estimates for successful steady-state ENDOR/TRIPLE in solution show that a minimum of 10^{13} radicals in the cavity during the detection period is needed. As a consequence, steady-state ENDOR on short-lived radicals in solution is restricted to lifetimes longer than ms, even when using fast-flow systems to supply fresh sample to the cavity. To extend the applicability to transient radical intermediates with lifetimes as short as sub-µs, a goal we found appealing for elucidating complex reaction mechanisms, we took advantage of chemically or photolytically induced electron spin polarization effects as signal boosters, and invented 'CIDEP-enhanced ENDOR' (CIDEP = Chemically Induced Dynamic Electron Polarization). This experiment was developed in 1983–85, first together with Renad Sagdeev as visiting scientist from Novosibirsk in the cw detection mode [25], and somewhat later extended by Friedhelm Lendzian and Petra Jaegermann to time-resolved direct-detection mode [26].

Time-resolved detection techniques of multifrequency EPR and ENDOR were heavily used in subsequent years to study photoinduced transient radicals and radical pairs of donor-acceptor complexes in photosynthetic reaction centers and their biomimetic model systems as well as in DNA photolyases. Our high-field EPR and ENDOR activities started in the early 80s [27, 28].

In the course of these activities it was again the enthusiasm and tanacity of students and postdocs which allowed us to solve the instrumental problems and to apply 95 GHz and 360 GHz EPR and ENDOR to novel molecular systems from biochemistry and biology. In this respect I want to mention especially Olaf Burghaus, Edmund Haindl, Martin Fuchs, Michael Fuhs, Thomas Prisner, Martin Rohrer, Anton Savitsky, Alexander Schnegg and Jens Törring. I also want to mention our cooperation partners at this point, because practically all our application work of multifrequency EPR/ENDOR/TRIPLE was performed in cooperation with many groups from around the world (see Acknowledgments).

After this brief historical survey, some key experiments of ENDOR in solution at FU Berlin will be described. The selection of examples reflects my personal liking, and is certainly not meant as a review of ENDOR in solution in general. Hence, indulgence is being asked for from those esteemed colleagues whose important contributions have inspired our work and that of the whole community, but had to be omitted because of the very limited space for this report.

Selected ENDOR-in-Solution Experiments at FU Berlin

Liquid Phase ENDOR Intensities and Lineshapes

As has been pointed out in the Introduction, the most detailed theoretical treatment of steady-state multi-resonance experiments in the liquid phase has been carried out by J. H. Freed and coworkers in a series of papers [4–6] using the density matrix formalism and Redfield's approximate treatment of relaxation. In one of these papers [6], subtle line shape effects – broadenings and splittings – were described that are due to the coherent nature of the applied strong rf and mw fields. A specific coherence effect is particularly interesting because it can be exploited to assign ENDOR lines to molecular positions, i.e., when applying ENDOR as an analytical tool. It requires nuclear spins $I > 1/2$ or a set of at least two equivalent nuclei of $I = 1/2$. The magnitude of the coherence splitting is dependent on the hyperfine transitions being mw saturated and on the rf field strength.

This coherence effect was optimized by K.P. Dinse *et al.* [29, 30] to assign hyperfine splittings in ENDOR-in-solution spectra of various low-symmetry radicals by counting the number of protons contributing to a specific ENDOR line. A cylindrical ENDOR cavity (TE_{011} mode) was constructed to achieve cw rf fields up to 30 G (rotating frame). The internal NMR coil was part of the power stage of a 1 kW cw rf transmitter station. To secure thermal stability of the cavity frequency, effective water cooling was employed both for the cavity body and the two-loop NMR coil [30].

On the basis of Freed's relaxation theory for radicals in fluid solution, M. Plato *et al.* [31] carried out a systematic investigation of the ENDOR sensitivity of various hetero-nuclei, i.e., nuclei other than protons, in organic radicals. Optimum ENDOR conditions, such as temperature and viscosity of the solvent, mw and rf field strengths, were formulated as a function of a few nuclear and molecular properties. They include relaxation from fluctuating spin-rotation interaction, electron-nuclear dipolar and nuclear quadrupolar couplings and Heisenberg spin exchange. The theoretical results were found to be in good agreement with experimental

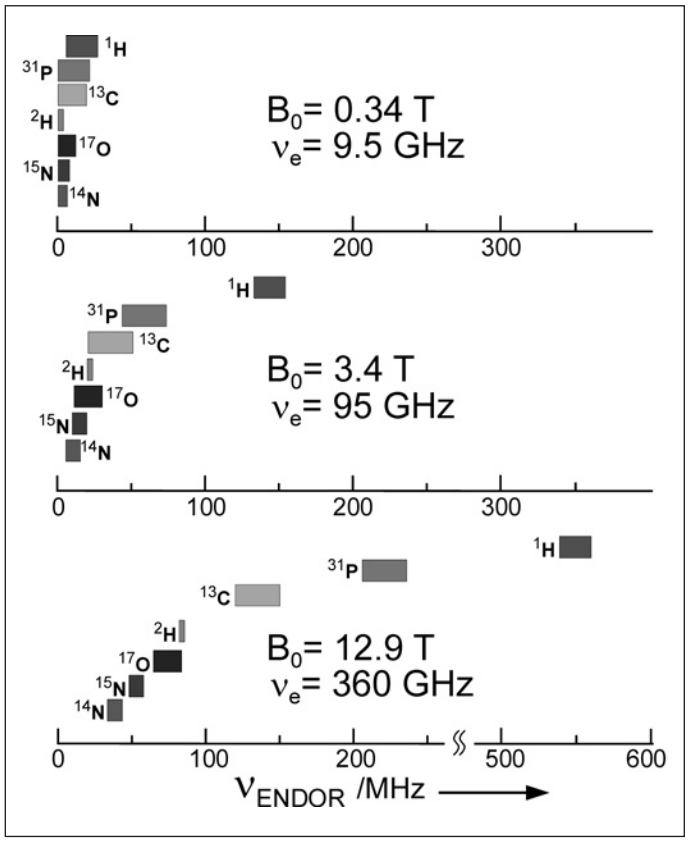


Fig. 1. Improved ENDOR resolution for different nuclei in doublet state systems ($S = 1/2$, $g = 2$) with increasing mw frequencies and Zeeman fields. Adapted from ref. 21.

observations on ^{2}H, ^{13}C, $^{14/15}$N, ^{19}F, ^{31}P and alkali nuclei in different molecular systems, thus allowing predictions to be made on the ENDOR detectability of other chemically interesting nuclei, such as $^{10/11}$B, ^{17}O, ^{27}Al, ^{29}Si, ^{33}S and $^{35/37}$Cl. In the meantime, most of these nuclei have indeed been detected by ENDOR in solution [13, 20]. In biological molecules, often several magnetic non-proton nuclei are present, and at X-band (9.5 GHz, 0.34 T) their ENDOR lines may overlap accidentally. As can be seen in Fig. 1, they become separated by working at higher mw frequencies and corresponding Zeeman fields, for instance at 95 GHz, 3.4 T or even at 360 GHz, 12.9 T.

ENDOR in Liquid Crystals

Evidently, magnetic resonance spectroscopy in liquids excels by narrow lines, but sacrifices information on anisotropic interactions as long as isotropic solvents are used. This is because the anisotropic parts of tensor interactions are averaged out by rapid Brownian tumbling. However, by using liquid crystals as anisotropic solvents, valuable information about anisotropic interactions can be retrieved from line positions while retaining narrow hyperfine lines typical for liquid-solution spectra. In the nematic mesophase of a liquid crystal, solute molecules can be partially aligned in the external Zeeman field of an EPR spectrometer. This results, for axial symmetry of either the interaction or ordering tensor, in a shift of the measured interaction parameter relative to its isotropic value, $F - F_{iso} = O_{33}F'_{33}$. Here O_{33} is the temperature-dependent ordering parameter, and F'_{33} is the principal component of the traceless interaction tensor that refers to the axis of highest symmetry of the solute molecule. F stands for any second-rank interaction tensor, for example the g-, hyperfine or quadrupole tensors.

The most striking aspect of ENDOR in liquid crystals is the possibility to directly determine, for nuclei with $I > 1/2$, components of the quadrupole interaction tensor of radicals in fluid solution from their ENDOR line positions. EPR in liquid crystals is not suitable in this respect because, to first order, the quadrupole interaction shifts all EPR-connected levels equally. The first determination of ^{14}N quadrupole couplings in an organic radical was achieved by ENDOR in liquid crystals by K. P. Dinse *et al.* [32]. When cooling the liquid crystal from its isotropic to its nematic phase one observes shifts or even splittings of the ENDOR lines of the quadrupole nucleus (e.g., $I = 1$), depending on which EPR line ($m_I = +1, 0, -1$) is saturated. The quadrupole splitting is given by

$$\delta\nu_Q = (3/2)\, O_{zz} e^2 q_{zz} Q/h \qquad (2)$$

from which $e^2 q_{zz} Q$ can be deduced when the ordering parameter O_{zz} is known. Even the small deuterium quadrupole coupling along the C-D bond of the aromatic radical perinaphthenyl (PNT), $e^2 q_{CD} Q/h = +188$ kHz, could be measured with this technique by R. Biehl *et al.* [33]. For small quadrupole couplings of radicals in an anisotropic matrix, ENDOR is probably the only method of choice. As an illustrative example, the ^{2}H ENDOR spectra of the partially deuterated PNT radical in isotropic and nematic solution (33) are presented in Fig. 2. A TM_{110} cylindrical cavity was designed to perform the double and triple resonance experiments with high rf power.

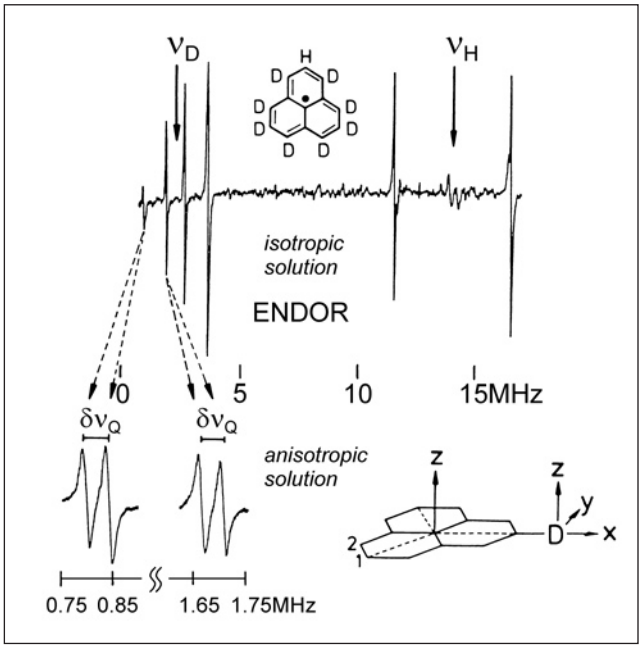


Fig. 2. Proton and deuterium ENDOR lines of the partially deuterated perinaphthenyl radical in isotropic and anisotropic phases of a liquid crystal. In the nematic mesophase, quadrupole splittings of the deuterons, $\delta\nu_Q$, are resolved. For both lines $\delta\nu_Q = 42.2$ kHz at 20°C. From $\delta\nu_Q = (3/2)\, O_{zz} e^2 q_{zz} Q/h$ with $O_{zz} = -0.300$ at 20°C, $e^2 q_{zz} Q/h = -94$ kHz (corresponding to $e^2 q_{CD} Q/h = +188$ kHz) was determined. Adapted from ref. 33.

TRIPLE Resonance as an Extension of ENDOR in Solution

In cases where electron-nuclear cross-relaxation (flip-flop rate W_{x1} and flop-flop rate W_{x2}) does not operate , e.g. at lower temperatures, and thus cannot increase the ENDOR enhancement, maximum ENDOR-in-solution signals are obtained when the 'matching condition' for the electron and nuclear relaxation rates, $W_e = W_n$, is fulfilled [31]. This condition is often difficult to meet for specific systems when trying to select the proper temperature and solvent. This is particularly true for biological systems for which $W_n \ll W_e$ is the common situation. As a consequence, for $W_{x1} = W_{x2} = 0$, the slow W_n acts like a bottle-neck for the rf-induced EPR desaturation, thereby drastically reducing the ENDOR signal intensity.

There is an obvious solution to this problem by 'short-circuiting' the W_n bottle-neck, i.e., by applying two rf fields tuned to drive both NMR transitions, ν^+ and ν^-, of the same nucleus. Such an electron-nuclear-nuclear triple resonance was proposed by G. Feher [34] and J. H. Freed [35], but was first experimentally realized for a radical in liquid solution by K. P. Dinse *et al.* [22] ('Special TRIPLE' [10]). As was demonstrated by R. Biehl *et al.* [23], additional information about relative signs of hyperfine couplings of radicals in solution can be obtained by generalizing the triple resonance experiment to include NMR transitions of different nuclei in the radical ('General TRIPLE' [10]). The analogue of this experiment for solid-state samples at low temperature was performed earlier by R. J. Cook and D. H. Whiffen [36]. The advantages of TRIPLE over ENDOR – enhanced sensitivity and resolution, information about multiplicity and relative signs of hyperfine couplings from line intensity variations – become apparent from Fig. 3a where the TRIPLE am-

plification factors are plotted versus W_e/W_n. In the case $W_e/W_n \gg 1$, Special TRIPLE can approach 100% EPR sensitivity, and different relative signs of hfcs are reflected by amplitude changes of the General TRIPLE lines. Fig. 3b gives an experimental verification of this analysis.

Porphyrinoid and Chlorophyll Ions

Since the mid 70s a growing interest in chlorophylls and structural variants of porphyrins is noticed, one reason is their potential to model photosynthetic chromophores. As examples of such ionic porphyrinoid systems, porphycene radical anions [37] and bacteriopurpurin radical cations [38] have been studied by liquid-phase EPR, ENDOR and TRIPLE (see Fig.4). The determination of the spatial and electronic structures of (bacterio) chlorophyll ion radicals in vitro, i.e., the isolated chromophores in non-aqueous solvents, is considered to be a prerequisite for understanding their role in the photoinduced electron transfer chain of in vivo systems, i.e., the photosynthetic chromophore-protein complexes. ENDOR-in-solution techniques in conjunction with elaborate MO methods turned out to be extremely powerful for resolving and analyzing the complex hyperfine structures of these chromophores [39, 40].

Primary Donor in Bacterial Photosynthesis

Photosynthesis is the most important process that enables life on Earth by converting the energy of sunlight into electrochemical energy needed by higher organisms for synthesis, growth and replication. The so-called primary processes of photosynthesis are those in which the incoming light quanta, after being harvested by 'antenna' pigment-protein complexes and channelled to the reaction center (RC) complexes by ultra-fast energy transfer, initiate electron-transfer (ET) reactions between protein-bound donor and acceptor pigments across the cytoplasmic membrane. The successive charge-separating ET steps between the various redox partners in the transmembrane RC have very different reaction rates, ranging from ps to ms. The cascade of charge-separating ET steps of primary photosynthesis competes favourably with wasteful charge-recombination ET steps, thereby providing almost 100 % quantum yield. Three billion years before green plants evolved, photosynthetic energy conversion could be achieved by certain bacteria, for instance the purple bacteria *Rhodobacter* (*Rb.*) *sphaeroides* and *Rhodopseudomonas* (*Rps.*) *viridis*. The ET cofactors are embedded in the L, M, H protein domains forming two ET branches, A and B. The RC of *Rb. sphaeroides* contains as ET cofactors the primary donor P_{865} 'special pair' (a bacterio-chlorophyll *a* (BChl) dimer), two accessory BChls, two bacteriopheophytins *a*, two ubiquinones (QA, QB), one non-heme iron (Fe^{2+}).

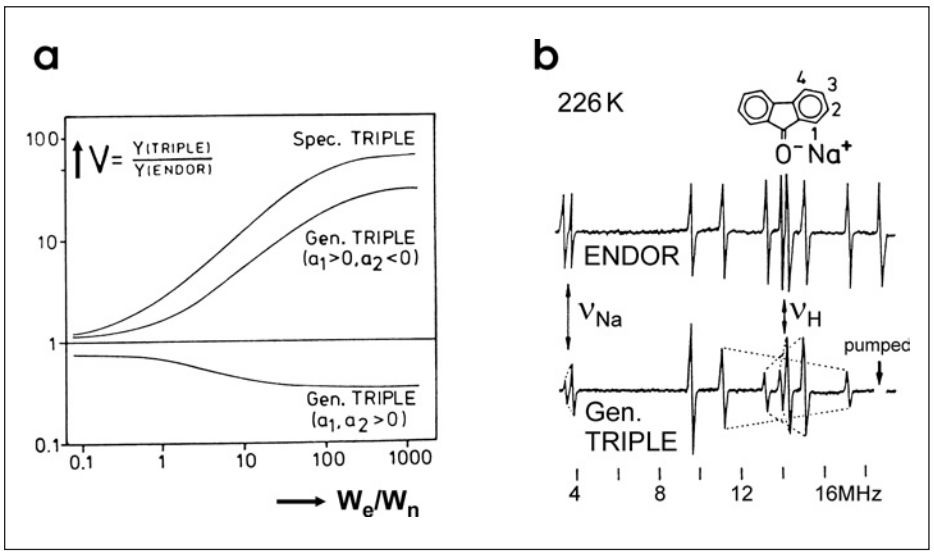


Fig. 3. a TRIPLE amplification factor (ratio of TRIPLE and ENDOR line amplitudes) as function of W_e/W_n, **b** ENDOR and General TRIPLE spectra of the radical anion fluorenone$^{-\bullet}$ (solvent: tetrahydrofuran, counter ion: Na^+, $T = 226$ K). Adapted from ref. 10.

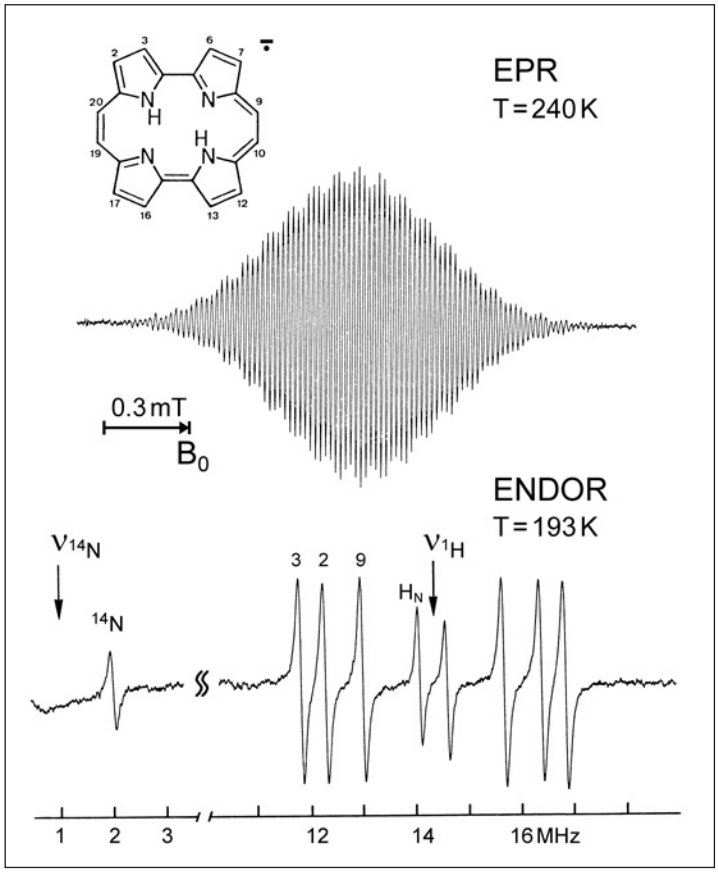


Fig. 4. EPR and ^{14}N and ^{1}H ENDOR spectra from free-base porphycene radical anion in tetrahydrofuran. The signs of the hfcs are from General TRIPLE, the assignment to molecular positions is based on MO calculations. Adapted from ref. 37.

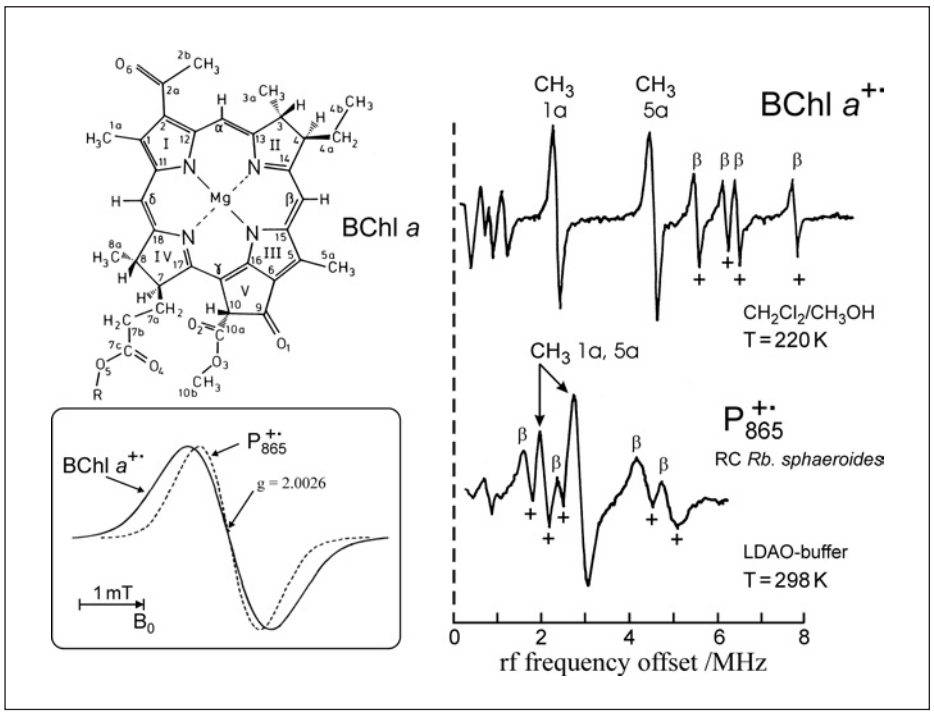


Fig. 5. EPR and Special TRIPLE spectra of the monomeric BChl $a^{+\bullet}$ and the dimeric primary donor $P_{865}{}^{+\bullet}$ cation radicals at room temperature. The signs of the hfcs (indicated at the resonance lines) are from General TRIPLE. Adapted from ref. 43.

As a dominant motif in the evolution of photosynthetic bacteria, an approximate C_2 symmetry of the cofactor arrangement in the RC prevails. It is intriguing that, despite the apparent two-fold local symmetry of the cofactor arrangement, the primary ET pathway is one-sided along the A branch. The origin of this 'unidirectionality' enigma of bacterial ET is not yet fully understood despite the numerous elaborate studies, both experimentally and theoretically, performed over the last decades. As a matter of fact, the high-resolution X-ray structure already reveals that C_2 symmetry does not hold for the protein environment of the cofactors, but is broken by different amino acids along the two ET branches. Thereby, the relative energetics and H-bond properties of the cofactors along the two branches will be different. They control the participation of cofactors as intermediate states in the ET cascade. The unidirectional nature of the primary ET route is probably not determined by a single structural feature, but rather by the concerted effects of small contributions of several different optimized factors. Examples are the energetics of the various intermediate states as well as the coupling scheme of the cofactor wavefunctions (theoretical concepts invoke 'overlap' and 'superexchange' coupling mechanisms). Both contributions can be systematically modified by selectively exchanging amino-acid residues of the protein environment by means of site-specific mutation. From numerous genetic engineering experiments it turned out that the 'unidirectionality switch' in the RC system is very robust against point mutations of the amino-acid environment of the cofactors. It was only recently demonstrated that specific double-site mutations in the vicinity of the primary donor and an accessory BChl can significantly change the partition of ET between the A and B branches [41].

Despite all the progress made in the last two decades in understanding bacterial photosynthesis on the molecular level, the puzzle of unidirectional ET is still unsolved. In order to contribute to a solution of this enigma, the electronic structure of the primary donor cation radicals, the dimeric $P_{865}{}^{+\bullet}$ in *Rb. sphaeroides* and $P_{960}{}^{+\bullet}$ in *Rps. viridis*, and their monomeric constituents, BChl $a^{+\bullet}$ and BChl $b^{+\bullet}$, respectively, have been studied in great detail by EPR/ENDOR/TRIPLE. This was done in liquid and frozen solutions as well as in single crystals of RCs (for a chronological account, see [42], for reviews, see [39, 40]). Lendzian *et al.* [43–45], for example, performed ENDOR/ TRIPLE investigations on the cation radicals in fluid solution under physiological conditions (see Fig. 5). From the highly resolved hyperfine spectra of the monomers and dimers and their analysis by all-valence electron MO methods (RHF-INDO/SP, see [40]) it was concluded (i) that for both organisms the primary donor dimer has to be viewed as a supermolecule with the wavefunction extending over both dimer halves, (ii) that the symmetry in the electron spin density distribution over the two dimer halves is broken favouring the L half, on the average, by 2:1, (iii) that this asymmetry ratio is primarily caused by subtle details of the dimer structure with some 'fine-tuning' from neighboring amino acid residues. These results have been fully confirmed by ENDOR/TRIPLE experiments on $P_{865}{}^{+\bullet}$ in RC single crystals of *Rb. sphaeroides* near room temperature [46]. The single-crystal work at physiological temperatures, performed independently by three groups, Feher at UC San Diego, Lubitz at TU Berlin, Möbius at FU Berlin, but ultimately published jointly, represents a culmination of two decades of ENDOR work on the primary donor in bacterial RCs. For the first time it was possible to assign ENDOR lines unambigously to the individual dimer halves. An important – and comforting – aspect was the result that the experimental isotropic hfcs, as determined from the traces of the single-crystal hyperfine data, agree well the hfcs from liquid-solution ENDOR. This shows that there is no significant change of the spatial structure of $P_{865}{}^{+\bullet}$ and its immediate protein environment upon crystallization of the RC.

The ENDOR-in-solution experiments described above have been extended to other BChl *a* containing organisms [47], to various mutants with specifically changed amino acids in the vicinity of P [48, 49], and to RCs of *Rb. sphaeroides* reconstituted with chemically modified bacteriochlorophylls [50].

Quinone Acceptors in Bacterial Photosynthesis

In the light-driven ET processes of *Rb. sphaeroides* the primary and secondary quinones, Q_A and Q_B, are the same ubiquinones-10. They act as one- and two-electron gates, respectively. Obviously, their different function in the ET processes is induced by different interactions with the amino-acid environment in their binding sites. To learn about these interactions within the binding pocket, for example the specific H-bonding patterns, EPR and ENDOR on quinone anion radicals in bacterial RCs (with Fe^{2+} replaced by Zn^{2+} to avoid fast spin relaxation) and in organic solvents have been performed at several mw frequencies by various groups, both in fluid and frozen solution. For example, in the Möbius

group W-band high-field EPR and ENDOR experiments on a series of quinones related to photosynthesis were performed and their intramolecular and intermolecular proton hyperfine interactions were discerned [51, 52]. As another example, in the Feher group ^{2}H ENDOR at Q-band frequencies was used to detect both the electron-nuclear hyperfine and the nuclear quadrupole couplings of the H-bonded deuterons [20, 53].

High-field ENDOR on frozen-solution samples has the additional advantage of providing single-crystal like hyperfine information in the reference frame of the *g*-tensor, even from disordered samples with very small *g*-anisotropy [52]. As an example, the Zeeman magnetoselection of W-band EPR and ENDOR on the radical anions of ubiquinone-10 in frozen perdeuterated propan-2-ol at $T = 115$ K turned out to provide pronounced orientational selectivity of the *g*-tensor components. This would remain inaccessible at X- and Q-bands. The orientational selectivity was exploited by performing W-band Davies-type pulsed ENDOR at the well-separated field values corresponding to the canonical *g*-tensor peaks in order to obtain the dominant proton hfcs. At least for the g_{xx} and g_{zz} canonical field positions, the ENDOR spectra are single-crystal like with narrow lines. When varying the solvent (protic and aprotic, with and without perdeuteration) characteristic changes of hyperfine- (predominantly along the y-direction) and *g*-tensor components (predominantly along the x-direction) could be discerned. They were attributed to hydrogen-bond formation at the lone-pair orbitals of the oxygens of the quinone.

Outlook

ENDOR at 50 – this reminiscence is not a "Look Back in Anger" (John Osborne, 1956) but quite the contrary: It is a look forward to new exciting ENDOR experiments! Nevertheless, Osborne's famous play shows some parallels to Feher's famous ENDOR – beyond the same year of first publication: The play represented a revolution in modern theater with far-reaching consequences in literature, very similar to what ENDOR represented in modern EPR spectroscopy. There can be no doubt that ENDOR and its extension to TRIPLE will continue to play an important role as analytical tool in biology, chemistry and physics for determining the spatial and electronic characteristics of complex systems. Also dynamic processes, such as ion pairing, hindered rotation, electron and/or proton transfer reactions, can be characterized in great detail, down to the sub-μs time scale, even for low-symmetry systems. In photochemistry and biology time-resolved ENDOR, for instance with cw mw irradiation and direct-detection techniques of spin-polarized transient radicals in solution is anticipated to become equally important as steady-state ENDOR of stable radicals. Furthermore, the potentials of high-field ENDOR, for instance at 95 GHz and 360 GHz mw frequencies, for separating overlapping ENDOR lines of various nuclei, for disentangling ENDOR spectra of mixtures of radicals with only small *g*-factor differences, or for providing orientation selection with single-crystal like ENDOR spectra even in disordered systems with small hyperfine and Zeeman anisotropies. For frozen solutions of organic molecules, these potentials have just started to be realized by the magnetic resonance community. They are particularly promising for multifrequency bio-ENDOR: By combining the specific strengths of EPR and NMR as analytical tools and applying them to complex new materials from biochemistry and molecular biology, significant steps forward are anticipated towards 'synthetic biology' with all its consequences for basic and applied science.

Acknowledgments

Over the years many coworkers – students, postdocs, colleagues – have contributed to the work presented. To all of them I want to express my gratitude. Most of our work was, and still is, performed in the frame of happy cooperations with numerous groups from chemistry, biology and physics around the world – and many cooperations are still functioning. In particular I want to mention (in alphabetical order) our cooperations with the groups of Adelbert Bacher (TU Munich), Robert Bittl (FU Berlin), Alexander Doubinskii (Moscow), Martin Engelhard (Dortmund), Jack Fajer (Brookhaven), George Feher (UC San Diego), Jack Freed (Ithaca), Maurice van Gastel (Mülheim), Fabian Gerson (Basel), Giovanni Giacometti (Padova), Daniella Goldfarb (Rehovot), Yuri Grishin (Novosibirsk), Edgar Groenen (Leiden), Arnold Hoff (Leiden), Martina Huber (Leiden), Jim Hyde (Palo Alto; Milwaukee), Harry Kurreck (FU Berlin), Haim Levanon (Jerusalem), Wolfgang Lubitz (TU Berlin; Stuttgart; Mülheim), Gus Maki (UC Riverside; UC Davis), Alexei Osintsev (Kemerovo), Thomas Prisner (Frankfurt/M), Günther Rist (Basel), Kev Salikhov (Kazan), Hugo Scheer (TU Munich), Jan Schmidt (Leiden), Andrzej Sczyczewsky (Poznan), Jonathan Sessler (Austin), Dietmar Stehlik (FU Berlin), Heinz-Jürgen Steinhoff (Osnabrück), Giovanni Venturoli (Bologna), Emanuel Vogel (Cologne), Hans van Willigen (Boston), Seigo Yamauchi (Sendai) and Herbert Zimmermann (Heidelberg).

From our group the following Diploma or PhD students and postdocs were, and some of them still are, particularly involved in such cooperation projects, doing ENDOR experiments from zero field to high fields, from helium to room temperatures, using cw or pulsed detection schemes: (i) the Diploma and/or PhD students since 1967 (in chronological order) Peter Dinse, Reinhard Biehl, Edwin Boroske, Lothar Mayas, Christian von Borczyskowski, Werner Fröhling, Wolfgang Lubitz, Friedhelm Lendzian, Wolfgang Möhl, Martina Huber, Petra Jaegermann, Olaf Burghaus, Anna Toth-Kischkat, Vera Hamacher, Jörg Wrachtrup, Jenny Schlüpmann, Robert Klette, Martin Rohrer, Jens Törring, Burkhard Endeward, Andreas Saniter, Jakob Lopez, Andreas Kuppig, Volker Weis, Gordon Elger, Michael Fuhs, Martin Fuchs and Alexander Schnegg, (ii) the senior scientists (in alphabetical order) Fosca Conti, Edmund Haindl, Chris Kay, Martin Plato, Thomas Prisner, Anton Savitsky, Marilena Di Valentin, Stefan Weber and Chris Winscom. All of them I want to thank for their essential contributions over many years of exciting ENDOR experiments.

It is a tragedy that both Reinhard Biehl and Arnold Hoff, who were an inspiration to all who worked in the field of modern EPR in (bio)chemistry and (bio)physics, died so early, Reinhard in 1987, Arnold in 2002. Their contributions to the field as well as their friendship will remain unforgotten.

I am indebted to Laila Mosina for her encouragement to write a look back upon our ENDOR-in-solution experiments to be included in the special issue of the *EPR newsletter* dedicated to the 50th anniversary of ENDOR. Congratulations to George Feher!

The work described was supported by the Deutsche Forschungsgemeinschaft in the frame of a variety of priority and normal programs including SFBs 161, 337, 498, SPP 1051 and MO 132/19-2, by the Volkswagenstiftung priority program "Intra-and Intermolecular Electron Transfer", and by HCM and TMR programs of the European Union.

References

1. Feher G.; Phys. Rev. **103**, 834 (1956)
2. Hyde J.S., Maki A.H.: J. Chem. Phys. **40**, 3117 (1964)
3. Möbius K., van Willigen H., Maki A.H.: Mol. Phys. **20**, 289 (1971)
4. Freed J.H.: J. Chem. Phys. **43**, 2312 (1965)
5. Freed J.H.: J. Phys. Chem. **71**, 38 (1967)
6. Freed J.H., Leniart D.S., Connor H.D.: J. Chem. Phys. **58**, 3089 (1973)
7. Hyde J.S. in: "Foundations of Modern EPR" (Eaton G.R., Eaton S.S., Salikhov K.M., eds.), p. 695. Singapore:World Scientific 1998.
8. Schmalbein D. in "Foundations of Modern EPR" (Eaton G.R., Eaton S.S., Salikhov K.M., eds.), p. 717. Singapore:World Scientific 1998.
9. Dorio M.M., Freed J.H. (eds.): "Multiple Electron Resonance Spectroscopy"., New York: Plenum 1979.
10. Möbius K., Biehl R. in: "Multiple Electron Resonance Spectroscopy" (Dorio M.M., Freed J.H., eds.), chpt. 14. New York: Plenum 1979.
11. Möbius K., Plato M., Lubitz W.: Phys. Reports **87**, 171 (1982)
12. Möbius K., Lubitz W.: Biol. Magn. Reson. **7**, 129 (1987)
13. Kurreck H., Kirste B., Lubitz W.: "Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution". New York: VCH Publishers 1988.
14. Hoff A.J. (ed.): "Advanced EPR". Amsterdam: Elsevier 1989.
15. Lubitz W., Lendzian F. in: "Biolphysical Techniques in Photosynthesis". (Amesz J., Hoff A.J., eds.), chpt. 16. Dordrecht: Kluwer 1996.
16. Hoff A.J., Deisenhofer J.: Phys. Reports **287**, 1 (1997)
17. Levanon H., Möbius K.: Annu. Rev. Biophys. Biomol. Struct. **26**, 495 (1997)
18. Möbius K.: Chem. Soc. Rev. **29**, 129 (2000)
19. Weber S. in: "Electron Paramagnetic Resonance", Specialist Periodical Reports. (Gilbert B.C., Davies M.J., McLauchlan K.A., eds.), vol. 17, p. 43. Cambridge: The Royal Society of Chemistry 2000.
20. Lubitz W. in: "Electron Paramagnetic Resonance", Specialist Periodical Reports. (Gilbert B.C., Davies M.J., Murphy D.M., eds.), vol. 19, p. 174, Cambridge: The Royal Society of Chemistry 2004.
21. Möbius K., Savitsky A., Schnegg A., Plato M., Fuchs M.: Phys. Chem. Chem. Phys. **7**, 19 (2005)
22. Dinse K.P., Biehl R., Möbius K.: J. Chem. Phys. **61**, 4335 (1974)
23. Biehl R., Plato M., Möbius K.: J. Chem. Phys. **63**, 3515 (1975)
24. Hoff A.J., Möbius K.: Proc. Natl. Acad. Sci. USA **75**, 2296 (1978)
25. Sagdeev R.Z., Möhl W., Möbius K.: J. Phys. Chem. **87**, 3183 (1983)
26. Lendzian F., Jaegermann P., Möbius K.: Chem. Phys. Lett. **120**, 195 (1985)
27. Haindl E., Möbius K., Oloff H.: Z. Naturforsch. **40**a, 169 (1985)
28. Burghaus O., Toth-Kischkat A., Klette R., Möbius K.: J. Magn. Reson. **80**, 383 (1988)
29. Dinse K.P., Biehl R., Möbius K., Plato M.: J. Magn. Reson. **6**, 444 (1972)
30. Dinse K.P., Möbius K., Biehl R.: Z. Naturforsch. **28**a, 1069 (1973)
31. Plato M., Lubitz W., Möbius K.: J. Phys. Chem. **85**, 1202 (1981)
32. Dinse K.P., Möbius K., Plato M., Biehl R., Haustein H.: Chem. Phys. Lett. **14**, 196 (1972)
33. Biehl R., Lubitz W., Möbius K., Plato M.: J. Chem. Phys. **66**, 2074 (1977)
34. Feher G.: Physica **XXIV**, 80 (1958)
35. Freed J.H.: J. Chem. Phys. **50**, 2271 (1969)
36. Cook R.J., Whiffen D.H.: Proc. Phys. Soc. London **84**, 845 (1964)
37. Schlüpmann J., Huber M., Toporowicz M., Plato M., Köcher M., Vogel E., Levanon H., Möbius K.: J. Am. Chem. Soc. **112**, 6463 (1990)
38. Kay C.W.M., Conti F., Fuhs M., Plato M., Weber S., Bordignon E., Carbonera D., Robinson B.C., Renner M.W., Fajer J., J. Phys. Chem. B **106**, 2769 (2002)
39. Lubitz W. in: "Chlorophylls" (Scheer H., ed.), p. 903. Boca Raton: CRC Press 1991.
40. Plato M., Möbius K., Lubitz W. in: "Chlorophylls" (Scheer H., ed.), p. 1015. Boca Raton: CRC Press 1991.
41. Haffa A.L.M., Lin S., Williams J.C., Bowen B.P., Taguchi A.K.W., Allen J.P., Woodbury N.W.: J. Phys. Chem. B **108**, 4 (2004)
42. Feher G.: J. Chem. Soc. Perkin Trans. **2**, 1861 (1992)
43. Lendzian F., Lubitz W., Scheer H., Bubenzer C., Möbius K.: J. Am. Chem. Soc. **103**, 4635 (1981)
44. Lendzian F., Lubitz W., Steiner R., Tränkle E., Plato M., Scheer H., Möbius K.: Chem. Phys. Lett. **126**, 290 (1986)
45. Lendzian F., Lubitz W., Scheer H., Hoff A.J., Plato M., Tränkle E., Möbius K.: Chem. Phys. Lett. **148**, 377 (1988)
46. Lendzian F., Huber M., Isaacson R.A., Endeward B., Plato M., Bönigk B., Möbius K., Lubitz W., Feher G.: Biochim. Biophys. Acta **1183**, 139 (1993)
47. Rautter J., Lendzian F., Lubitz W., Wang S., Allen J.P.: Biochemistry **33**, 12077 (1994)
48. Huber M., Lous E.J., Isaacson R.A., Feher G., Gaul D., Schenck C.C. in: "Reaction Centers of Photosynthetic Bacteria" (Michel-Beyerle M.E., ed.), p. 219. Berlin: Springer-Verlag 1990.
49. Rautter J., Geßner Ch., Lendzian F., Lubitz W., Williams J.C., Murchison H.A., Wang S., Woodbury N.W., Allen J.P. in: "The Photosynthetic Bacterial Reaction Center II" (Breton J., Verméglio A., eds.), p. 99. New York: Plenum Press 1992.
50. Käss H., Rautter J., Zweygart W., Struck A., Scheer H., Lubitz W.: J. Phys. Chem. **98**, 354 (1994)
51. Burghaus O., Plato M., Rohrer M., Möbius K., MacMillan F., Lubitz W.: J. Phys. Chem. **97**, 7639 (1993)
52. Rohrer M., Plato M., MacMillan F., Grishin Y., Lubitz W., Möbius K.: J. Magn. Reson. **116**, 59 (1995)
53. Flores M., Isaacson R., Abresch E., Calvo R., Lubitz W., Feher G.: Biophys. J. **90**, 3356 (2006).

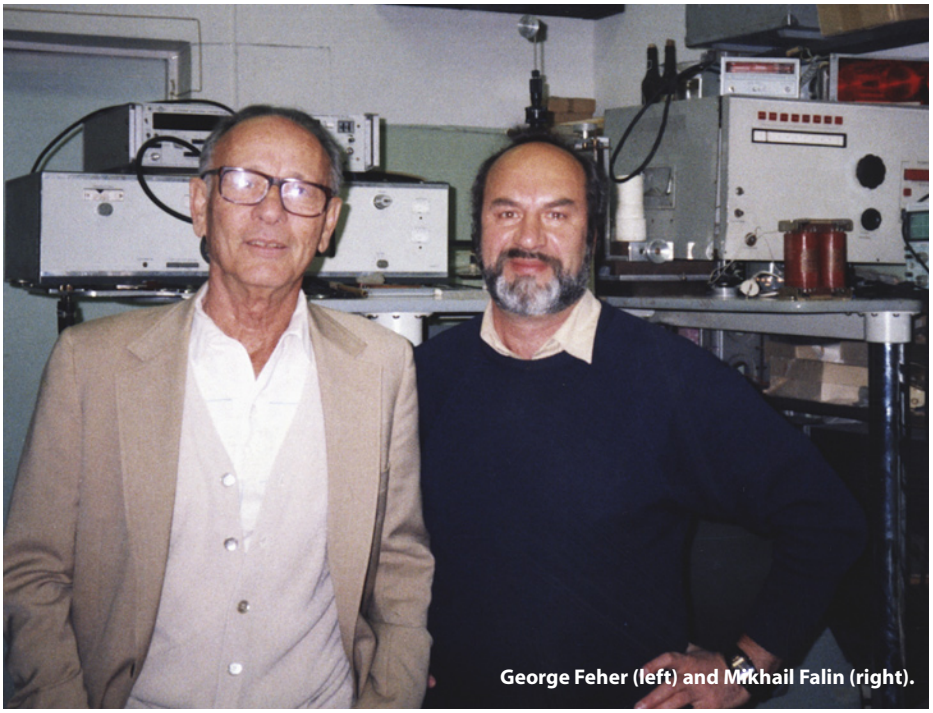
ENDOR Recollections

Jürgen Hütterman
University of Saarland, Germany

My recollections concerning ENDOR go back to 1970, the time when I decided to aim at working with this technique. I just had spend a post-doc year in Los Angeles (UCLA) doing DNA radiation-chemistry with Prof. L. Myers, Jr.. Before, during my PhD-work at the Technische Hochschule Karlsruhe (Prof. K.-G. Zimmer), I had been studying, by EPR, free radicals in single crystals from irradiated DNA constituents. Basically, it was my naïve hope, that the enhanced resolution of ENDOR would allow to unravel EPR spectra from DNA itself. Back from the US, on my first university position (Assistant) at the newly founded University of Regensburg, I was charged with building up an EPR laboratory. In those days, the first computers were attached to the EPR machines. What about ENDOR? I had never been in or near to a laboratory with expertise in ENDOR. So I had to study the literature, which gave me the impression that there were two different ENDOR worlds: for solid state samples, low temperatures and low rf-powers were applied in home-built machines; for solution studies, high power setups existed in a few laboratories. I favored a home-built apparatus for solid-state samples. There were two very enlightening articles on ENDOR on color centers by Horst Seidel from Stuttgart University (e.g. Z. Physik **165**, 218 (1961)). He had realized, with tubes, a 'self-excited Hartley oscillator' as rf-source and I decided to transform it into a transistorized version. After about three years, supported by a gifted technician, our first publication with this unit which was also my first ENDOR study, appeared. It dealt with radiation-induced free radicals in a single crystal of barbituric acid (J. Magn. Reson. **21**, 221 (1976)). Only 0.25 W power gave proton-ENDOR signals with a remarkable S/N ratio. I was struck by the large range with which ENDOR could probe the environment of the unpaired electron in terms of weakly coupled proton interactions. This basic theme was later applied by us to questions of metal ion coordination in proteins starting with NO-ligated myoglobin. Over the years, the apparatus changed considerably. However, for more than a decade or so, the rf-coil/cavity setup of the first apparatus was kept. My initial hope of studying free radicals in the irradiated DNA polymer by ENDOR was, however, never fulfilled. I have made many attempts at several microwave frequencies, cw or pulsed, but a peculiar relaxation behaviour always prevented the observation of anything else but the free proton nuclear frequency line.

My First Encounter with ENDOR and with George Feher

Mikhail Falin
Kazan Physical-Technical Institute,
Russian Academy of Sciences,
Kazan, Russian Federation


George Feher (left) and Mikhail Falin (right).

In 1965, after graduating from the Kazan State University, I became a post-graduate at the Department of Radiospectroscopy headed by M. M. Zaripov, student of S. A. Altshuler. However, that autumn I was called up to the military service for one year. When I came back, my friend and I had to choose between two themes: to carry out investigations with classic EPR or with a completely new method, ENDOR. Frankly speaking, it was all the same for us. Moreover, at that time we had no idea what ENDOR was. To ensure, as it seemed to us, a fair and unbiased solution of this problem, we decided to raffle off this choice as follows. The titles of the themes were written on sheets of paper and packed in two opaque tubes and placed into a hat of a colleague. Then the multi-stage procedure to determine the queue of the access to the hat in order to exclude in the future all 'fortuities' and reproaches of 'cheating' was elaborated. This action took place amongst the circle of friends and colleagues in the laboratory. They watched this merry enterprise, which, in principle, determined the future for each of us. Finally, I got the first queue and with much ado trying to choose between two tubes I drew the ticket with ENDOR. Afterwards we had a nice banquet to celebrate this event.

I worked in the group that created the first ENDOR spectrometer using the 100 kHz modulation of magnetic field in the former Soviet Union. This type of a spectrometer was insensitive to human emotions. S. A. Altshuler, M. M. Zaripov and Yu. E. Polsky were among the first in the former Soviet Union to realize the great potential of ENDOR, this highly sensitive method, in studying hyperfine and transferred hyperfine interaction (THFI) of admixtures of ions in crystals. Pioneering results, THFI of non-Kramers ions, and THFI of rare-earth state Γ_8, to name a few, were obtained. I think I got a lucky ticket.

In September 1996 I had the pleasure to meet with George Feher, father-founder of ENDOR (see the photo). He came to Kazan for his Zavoisky Award. I was particularly impressed by his unaffected manners and humanity. After the ceremony I had to see him off to Moscow. Usually in September we have the nicest days of Indian Summer, warm and sunny. George Feher was told about this and therefore he did not overload himself with warm clothes. However, the weather arranged a surprise. It was extremely cold and rainy during the visit of George Feher to Russia. We took a flight to Moscow. It was cold in the plane (the heating did not function) and the cold dinner was served which we declined. So we arrived in Moscow with our teeth tap-dancing and immediately went to the hotel. My proposal to have a dinner at the restaurant and get warm was rejected by George Feher who said he would be much more comfortable and warm in the bathroom. We went to our rooms. I was very ▶

upset that I could not spend an evening with such an interesting man as George Feher who had to take a flight to Israel very early in the morning. Suddenly I heard a pertinacious knock at the door. I thought that George Feher changed his mind and we would go to have dinner. I opened the door and saw G. Feher indeed, who looked very worried. It turned out that there was a bathroom in his room and also hot water but a very little detail was missing, a plug, "probka" in Russian. I went to the reception and asked them to give us an extra plug but all available ones were too small. When we realized that we have to rely only on ourselves, we used our little gray cells and wound a piece of cloth around the little plug to match the size of the hole in the bathtub. As a result of this successful operation, George Feher remembered the Russian word "probka", which he repeated time and again, putting his thumb up.

Milestones in the Bruker Commercial ENDOR History

Peter Höfer
and
Dieter Schmalbein
Bruker BioSpin,
Rheinstetten, Germany

The first Bruker ENDOR/TRIPLE system was introduced as an accessory of the ER 200tt spectrometer. In retrospect, this accessory was an eminent milestone in the commercial success story of the Bruker EPR Division. ENDOR at the time was known as a complex technical issue which only a few people like Maki, Freed and Seidel had built for themselves and mastered its handling. Most of these setups were narrow band systems with tuned rf-circuits in order to achieve the high B_2 fields necessary for ENDOR in liquids. Besides the disadvantage of the complicated operation there was also the limitation of the rf-sweep range. For most of the systems it was necessary to change capacitors or coils in order to get the appropriate rf-range and frequencies below 3 MHz were mostly not achievable. Several attempts to build a commercial ENDOR system based on these techniques failed at Bruker as well as at our competitors.

The only solution to make ENDOR available for those who are not technical freaks was a broadband system without delicate tuning circuits. The Möbius group in Berlin with Klaus Peter Dinse and Reinhard Biehl showed the right way to do this. Based on their ideas we started a development which was one of the most demanding we had done at that time. It took us several years to design the electronics of the spectrometer in such a way that the high rf-fields did not cause any artifacts or baseline drifts, bumps or any other disaster. The final ENDOR resonator for variable temperature operation carried the ENDOR coil on the temperature dewar and was a result of innumerable attempts to achieve a stable system. In 1978 we were finally able to present the first commercial broad band ENDOR/TRIPLE system, the EN200 S/E/T, an accessory for the ER200tt. With well prepared samples from the Möbius group we could demonstrate the various multiple resonance methods with a quality never seen before on a commercial system. This was the breakthrough for the ENDOR technique in the EPR community. Even today we are still using a resonator based on the design of that time for CW-ENDOR/TRIPLE.

In the early 90´s a number of new ENDOR methods and digital technologies had emerged and the time was ripe for a new commercial ENDOR generation. Based on the technology of Direct Digital Synthesis (DDS) we developed the DICE ENDOR system. The DDS technology allows fast, precise and clean frequency switching. It overcame limitations in the modulation amplitude of FM-ENDOR, which was until then a severe handicap for the detection of broad lines. While the FM amplitude went only up to a few 100 kHz in the current ENDOR system, based on Wavetec and PTS synthesizers, it became almost unlimited in the DICE unit. For pure practical reasons we limited it to 5 MHz. Other ENDOR related techniques like amplitude modulation, ENDOR induced EPR (EIE), special and general TRIPLE were readily implemented.

The acronym DICE was derived from DIgitally Computed Excitation but also refers to the technique of stochastic ENDOR [1]. This method was implemented for the first time in a commercial CW-ENDOR system. Stochastic ENDOR is aiming for spin system with extremely long relaxation times. Under this condition very low modulation frequencies are required which conflict often with microphonic frequencies. A way out of this problem is to replace the sequential linear rf sweep by a diced sequence of random frequencies applied at a much higher rate than the normal FM. In this way the spins are subject to a low effective modulation frequency while technically the modulation frequency is high enough to avoid microphonic problems. As a side effect and of additional benefit the baseline becomes immune to external disturbances.

With the introduction of the DICE unit we also made our first step towards CW-ENDOR at another frequency than just X-Band. The first DICE unit had a maximum frequency of 150 MHz and was fully ▶

adequate to be use in Q-Band as well. For this step the only missing element was a Q-Band CW-ENDOR resonator. Based on our variable temperature CW-EPR resonator we developed the required CW-ENDOR probe EN 5106QT-E.

At the same time another technique was waiting for commercialization. Although the pulse-ENDOR sequences of Mims [2] and Davies [3] had already been known for quite some time, they were not used by many people because of the lack of suitable instrumentation. Since its introduction in 1987 the ESP 380 FT/CW spectrometer was picking up pace and was the perfect prerequisite for the implementation of pulse-ENDOR. The techniques of Electron Spin Echo Envelope Modulation (ESEEM) were, of course, an inherent capability on the ESP 380 but it was also common knowledge that pulse-ENDOR is a complementary technique to ESEEM. To implement pulse-ENDOR, pulsed radio frequencies and a pulse-ENDOR resonator were necessary. It was clear that a pulse-ENDOR accessory should be able to do more than just a single rf pulse. More refined techniques like 2D Mims ENDOR [4] the detection of nuclear FIDs and echoes, pulse TRIPLE and multiple quantum ENDOR were already published [5–8] and new ones were added continuously [9]. These new techniques showed that pulse-ENDOR is on common grounds with time domain NMR. In principle the DDS technology provided all the means for the implementation of these methods. With the development of a sophisticated high speed interface (the EIF board) we were able not only to pulse the rf but switch frequencies within a few tens of nanoseconds in a phase continuous way thus allowing all the above mentioned methods and many more. Still today, more than 10 years after its introduction, all the capabilities of the DICE pulse-ENDOR unit have not been exhausted by many.

An advanced rf unit is, however, only half of the story – it has to be complemented by a versatile pulse-ENDOR resonator. The wish list for the capabilities of this probe was long and we based the development on the Flexline dielectric resonator which was already part of the ESP 380. After not too many iterations, the rf coil with the desired characteristic was integrated without loss in pulse-EPR performance and the EN 4118X-MD4 was on the market as part of the ESP 360D-P pulse-ENDOR accessory. During the last decade this probe has served many scientists as a true all-rounder in pulse-EPR/ENDOR spectroscopy. Even experiments it was not designed for were preformed with this probe, e.g. longitudinal detection [10] and CW-EPR using an amplitude modulated longitudinal field [11].

In the late 90s we developed the W-band system for CW and pulse-EPR. From the very beginning it was clear that a pulse-ENDOR accessory was an absolute must for this instrument. The reasons are two fold. First, the increase in nuclear Larmor frequency dispersion results in a considerable gain in resolution for low frequency nuclear spins, an advantage which one wouldnt want to miss, and second, the alternative ESEEM technique is practically not available as it often doesnt work at W-Band. Of course, the large spread in nuclear Larmor frequency is a technical challenge in the development of a broad band efficient rf coil integrated in a tiny resonator environment of only a few millimeters in size. With the EN 680-1021H we have mastered this task and introduced another successful pulse-ENDOR probe.

The next step in our multi frequency pulse-EPR instrument line we made in 2002 with the SuperQFT microwave bridge. Parallel to the bridge development we started working on a dedicated pulse-EPR probe for Q-band. From the EPR point of view this probe should have a low *Q* for short dead-time and large bandwidth, but provide high efficiency to generate short pulses and give high sensitivity. As pulse-ENDOR was expected to be an application highlight in Q-band, this new probe was designed to incorporate an rf coil as well. The development efforts have resulted in a new high performance pulse-EPR/ENDOR probe in Q-band called EN 5107D2.

Interestingly, all our multi frequency endeavours were always accompanied by the DICE unit developed in the early 90s. Minor modifications were necessary only with respect to the maximum frequency which moved higher as demands grew with the higher microwave frequencies. Originally introduced on the ESP series the DICE unit later on became part of the ELEXSYS platform and is today a highly reputed and popular tool for structural analysis.

References

1. Brüggemann W., Niklas J.R.: J. Magn. Reson. A **108**, 25 (1994)
2. Mims W.B.: Proc. Roy. Soc. London **283**, 452 (1965)
3. Davies E.R.: Phys. Lett. A **47**, 1 (1974)
4. de Beers R., Barkhuijsen H., de Wild E.L., Merks R.P.J.: Bull. Magn. Reson. **2**, 420 (1981)
5. Mehring M., Höfer P., Grupp A., Phys. Rev. A **33**, 3523 (1986)
6. Höfer P., Grupp A., Mehring M.: Phys. Rev. A **33**, 3519 (1986)
7. Mehring M., Höfer P., Grupp A.: Ber. Bunsenges. Phys. Chem. **91**, 1132 (1987)
8. Mehring M., Höfer P., Käss H., Grupp A.: Europhys. Lett. **6**(5), 463 (1988)
9. Gemperle C., Schweiger A.: Chem. Rev. **91**, 1481 (1991)
10. Granwehr J., Forrer J., Schweiger A.: J. Magn. Reson. **151**, 78 (2001)
11. Fedin M., Gromov I., Schweiger A.: J. Magn. Reson. **171**, 80 (2004)

Motoji Ikeya (1941–2006)

Motoji Ikeya, Professor Emeritus, Osaka University passed away suddenly due to cardiac insufficiency on the early afternoon of March 14, 2006. A pioneer of ESR dating and dosimetry as well as a marvelous leader in the interdisciplinary research area of earth environment left this world. It was only his age of 65 at death. He fell down on the pavement at Nakanoshima, the central part of Osaka City on his way to a scientific meeting in Osaka University. It was an unusually chilly day with slight powder snow. He was rushed to a nearby emergency hospital but never came back.

He was born in Osaka and graduated from the Department of Electronic Engineering, Osaka University in 1963 and awarded a Doctor's degree for ESR research on alkali-halide crystals in 1970. He spent his early research days of Nagoya University (1967–1970) and as a research associate at the University of North Carolina (1970–1973). He returned to Japan in 1973 and was appointed to be Professor in Yamaguchi University. He stayed at the University of Stuttgart, Germany in 1976 as a researcher of the Alexander von Humboldt Foundation for research on crystal defects and magnetic resonance. He returned from Yamaguchi to Osaka University in 1987, appointed to be Professor of the newly established Department of Earth and Space Science.

His prime work, ESR dating, was first reported in Nature **255**, 48–50 (1975) as "Dating a Stalactite by Electron Paramagnetic Resonance". Because the method has an advantage over conventional ^{14}C dating in its time range, it has been mainly used as a preferred dating method covering the latter half of Quaternary period about a million of years. ESR dating has lead to a lot of important discoveries in archeology, geomorphology, paleo-anthropology and other wide areas of earth environmental research. ESR Dosimetry was also performed on articles of victims of the atomic bombs in Hiroshima and Nagasaki. The research extended to accident dosimetry and resulted in his visit to the Chernobyl reactor and other radiation accident sites. Another remarkable work of Motoji in ESR was development of various imaging devices, typically the scanning ESR

microscope, which consists of an ESR cavity with a pin-hole and a sample scanning mechanism. Now we can categorize this as a near field microscope in the microwave region, but it was really something in those days. Besides development of radiation dosimeters, his ESR work was extended to various items like icy materials which should be present on outer planets and comets, as well as fault gouge or fossils and bio and nano-materials. His laboratory was visited by ESR researchers from many countries of the world. He has over 300 publications so far.

He was a person full of ideas and warm human feelings. His cheerful and enthusiastic attitude toward class lectures was very popular among students. He loved Goethe and often mentioned a passage from Faust. Sometimes, he said by way of jest that he had sold his soul to Mephistopheles for his fine scientific works, so that he might lose his life soon!! Also his sense of humor is well depicted by cartoons in his book "New Applications of Electron Spin Resonance" (World Scientific, 1993, 2002).

His two other books in Japanese are "ESR Dating" (Ionics, 1987) and "ESR Microscope" (Springer-Tokyo, 1992). He loved fieldwork with geologists and never stopped thinking of new ideas for research even during his journey in the bus or at regular lunch time with students and researchers.

After the heavy loss of human lives and large destruction by the Kobe Earthquake in January 1995, his interest moved to the future more than to dating the past. In an atmosphere not favorable to earthquake prediction, he courageously promoted the research on earthquake precursor phenomena and seismo-electromagnetic phenomena. Actually, he did extensive interdisciplinary experiments on different types of earthquake precursor phenomena. His effort bore fruit as a book "Earthquakes and Animals" (World Scientific, 2004). It is considered as a pioneering book in this area of study and naturally became a best seller within a short period of publication. He also wrote two books in Japanese on this subject – "Why Do Animals Behave Unusually? –Birth of Electromagnetic Seismology–" (NHK Publisher, 1998, 2006) also translated into Chinese by C. Huang (Sichen Press, 2000) and "Precursors of Large Earthquakes" (Seisyun Press, 2000, 2005). Recently he published a pictorial book in Japanese for children on how to take precautions observing some earthquake precursors (Parade Book, 2005). He appeared on many TV-channel science shows in such as BBC and Discovery to explain his earthquake precursor studies.

After his retirement from the Faculty of Science, Osaka University, he continued his research career as Specially-Appointed Professor at the Institute of Scientific and Industrial Research, Osaka University. He used to mention what to do in his remaining lifetime and hoped to write another ESR text book and another researcher-oriented book on seismo-electromagnetic phenomena. In the meantime, he was appointed to give various lecture talks including an open session at 2006 APRU Earthquake Symposium at San Francisco due on April 22.

As always, he had been planning several inventions and one of them was a scientific device called "E-sign", a kind of static electric field sensor. The idea occurred to him from an old legend that iron nails under a magnet fell down before the Ansei earthquake in Japan (1855). The trial sample of "E-sign" arrived at his home after his departure on the day of March 14, 2006. He had planned to bring it to Osaka University on March 15 in order to obtain the physical data for the device.

His funeral service was carried out in a hush atmosphere of deep sorrow on March 17, 2006, when it gently rained. His coffin was sent off with so many flowers.

He is survived by his wife Yoshiko Ikeya, and his son (Jun), daughter (Yuri) and his two grandchildren. We really regret his loss and would like to express our sincere condolence to his family. We pray for the repose of his soul.

Chihiro Yamanaka
Osaka University, Osaka, Japan

Pro & Contra

High-Field Pulsed ENDOR — Pros and Cons

ENDOR '50 dedicated

Daniella Goldfarb*

Department of Chemical Physics,
Weizmann Institute of Science,
Rehovot, Israel

Introduction

The introduction of high-field/frequency (HF) EPR by Lebedev [1] set the stage for the development of continuous-wave (CW) HF electron-nuclear double resonance (ENDOR), first reported by Möbius and co-workers at W-band (95 GHz, 3 T) [2, 3]. Next, the first pulsed HF EPR spectrometer, again at W-band, was reported by the Leiden group [4], paving the way for the appearance of pulsed ENDOR on the scene [5]. Most of the HF pulsed ENDOR studies reported so far have been carried out on homebuilt spectrometers with a microwave (MW) bridge based on Russian technology operating at 95 or 140 GHz [4, 6, 7]. The Frankfurt group has recently reported pulsed ENDOR at 180 GHz [8] followed by the exciting development of a 275 GHz pulsed ENDOR spectrometer in Leiden [9]. The number of HF pulsed ENDOR applications is expected to increase significantly as a consequence of the introduction of a power upgrade to the Bruker W-band spectrometer [10].

Since its first report in 1992 [3] many different studies involving HF ENDOR have been published in the fields of Physics, Chemistry, Materials and Biology. The problems addressed range from trapped radical intermediates in biological systems [11–15] transition metal complexes in proteins [16, 17] and porous materials [18, 19] to fullerenes [20] and semiconductors [21]. In all these studies the use of HF ENDOR provided either new information, and/or facilitated spectral interpretations. A number of excellent reviews have been recently published on HF EPR [12, 22–24], which include HF ENDOR as well, and volume 43 of Magnetic Resonance in Chemistry has been devoted to HF EPR. The present article is not intended to be an extensive review of HF ENDOR but rather a personal perspective on the new opportunities and advantages offered by pulsed HF based on the experience we have accumulated in our lab during the last 8 years. All advances described in terms of sensitivity and resolution are of course not unique to pulse ENDOR but apply also to CW ENDOR. Finally, since nothing is ever perfect, we shall present the disadvantages along with a future outlook.

Common Pulsed ENDOR Sequences and Other Experimental Aspects

Although the Mims [25] and Davies [26] ENDOR sequences, shown in Fig. 1a and b, were introduced several decades ago, they are still the 'working horses' of pulse ENDOR experiments. In both experiments the ENDOR spectrum is obtained by recording the echo intensity as a function of the frequency of the radio-frequency (RF) pulse. A change in the echo amplitude occurs when the RF is on-resonance with an NMR (ENDOR) transition, generating a so-called ENDOR signal. The Davies ENDOR experiment is based on the selective excitation of only one of the EPR multiplet transitions (see Fig. 1e), and therefore, the first MW π pulse has to be selective with respect to the hyperfine splitting. Consequently, this sequence is most suited for systems with medium to large hyperfine couplings ($A > 2$ MHz). Mims ENDOR, on the other hand, does not require selective pulses but suffers from 'blind spots' because the ENDOR signal is scaled by $1/2(\sin^2\pi A\tau)$, where A is the hyperfine splitting. Accordingly, it is usually applied when the hyperfine splitting is small, $A < 2$ MHz, where typical τ values of 0.15–0.25 µs place the blind spots well outside the ENDOR spectral range. If lower values of τ are required and cannot be used due to spectrometer 'dead time' it is possible to apply the remote detection Mims (Re-Mims) ENDOR sequence [27]. In general, ^{1}H spectra are usually recorded by the Davies ENDOR sequence, whereas Mims ENDOR is preferred for ^{2}H measurements.

The intensity of the ENDOR signal is referred to as the ENDOR effect, which is defined as:

$$F_{\mathrm{ENDOR}} = \frac{1}{2}\frac{I(RFoff) - I(RFon)}{I(RFoff)}, \quad (1)$$

where $I(RFon)$ and $I(RFoff)$ correspond to the echo intensity with RF on and with RF off, respectively. Usually the ENDOR effect is the same for the α and β manifolds. The maximum ENDOR effect is obtained with RF pulses of 180°.

When the hyperfine coupling is large, then the RF nutation frequency, ω_2, depends also on the hyperfine coupling. For the simple case of an isotropic interaction it is given by:

$$\omega_2 = \gamma E B_2, \quad E = 1 + \frac{M_S a_{\mathrm{iso}}}{\nu_I}, \quad (2)$$

where E is the so-called hyperfine enhancement factor. Equation (2) shows that when the hyperfine coupling is large compared to the nuclear Larmor frequency, ν_I, a lower RF power is required for generating a π pulse. For low γ nuclei, that exhibit large hyperfine couplings, like ^{14}N and ^{55}Mn, the hyperfine enhancement factor is a very useful parameter.

ENDOR is a difference spectroscopy and therefore it often suffers from low sensitivity compared to EPR and this is a major obstacle in ENDOR applications. The ENDOR effect can be increased through the application of improved pulse sequences. One such example is the pulsed version [28, 29] of the CW special TRIPLE experiment [30, 31], shown in Fig. 1c. This technique requires two RF pulses, one exciting ν_α and the other the corresponding ν_β. Hence, the relation be-

* Author's address: Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel, 76100. E-mail: daniella.goldfarb@weizmann.ac.il

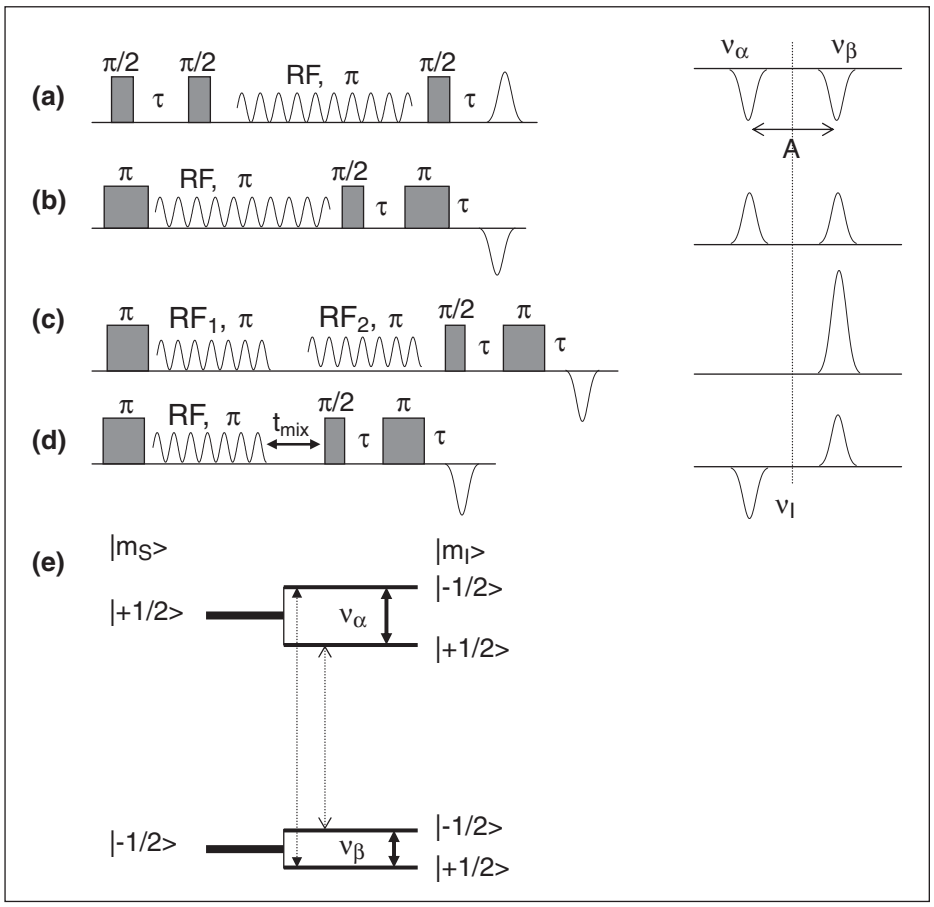


Fig. 1. Pulsed ENDOR sequences and the resulting ENDOR spectrum for $S = 1/2$, $I = 1/2$. (**a**) Mims ENDOR, (**b**) Davies ENDOR, (**c**) TRIPLE, (**d**) VMT ENDOR. (**e**) Energy level diagram for $S = 1/2$, $I = 1/2$.

tween the two ENDOR frequencies should be known a priori. This condition is often satisfied at HF where the ENDOR frequencies are symmetrical with respect to the Larmor frequency (see Eq. (4)). Using Special TRIPLE a maximum of twofold increase in the ENDOR effect can achieved [28]. In another version of this experiment, called General TRIPLE [32, 33], one RF frequency is set to a particular ENDOR transition while the other is scanned [29, 34]. The resulting spectrum shows which ENDOR signals belong to the same M_S manifold as that excited by the first RF pulse, thus yielding the relative sign of the hyperfine couplings. When a number of paramagnetic centers contribute to the ENDOR spectrum the General TRIPLE sequence correlates signals belonging to the same center and the same M_S manifold. Scanning the frequency of both RF pulses produces a two-dimensional spectrum with cross peaks between ENDOR lines belonging to the same M_S manifold. In orientationally disordered samples the shape of the cross peaks can provide the relative orientation between the principal directions of the hyperfine interactions involved [35].

The sign of the hyperfine coupling is often an important parameter. For example, in the case of the isotropic hyperfine constant, a_{iso}, the sign provides additional insight into the electronic structure. Moreover, from practical aspects, it can be used to obtain unique sets of simulation parameters leading to a more accurate spectral analysis. Finally, it provides a good reference when density functional theory (DFT) calculations are carried out for interpreting the hyperfine interaction in terms of structure. It was shown that DFT predicts very well the sign of the interaction [36, 37]. The experimental determination of the absolute sign of the hyperfine coupling requires large thermal polarization. This is usually not achieved at X-band frequencies but is rather easily obtained at high fields and low temperatures. For high spin system, $S > 1/2$, the sign can be determined by the proper selection of the EPR transition (see below) [38]. This approach, however, does not apply to $S = 1/2$ systems. There, a variant of the Davies (or Mims) ENDOR sequence, the variable mixing time (VMT) ENDOR, shown in Fig. 1d, can be used [39, 40]. In this experiment an additional time interval, t_{mix}, which allows for relaxation to take place, is introduced after the RF pulse and before the echo detection sequence, and the ENDOR effect is measured as a function of t_{mix}. For a short t_{mix} and a long enough repetition time, which allows the system to return to equilibrium between consecutive sequences (the conditions of standard ENDOR experiments), the ν_α and ν_β signals have the same intensity. As t_{mix} increases and becomes on the order of the electron spin lattice relaxation time, T_{1e}, the intensity of ν_α decreases and can even become negative, while those of the ν_β manifold remains positive. This asymmetry is observed, however, only under sufficient thermal polarization and when the electron-nuclear cross relaxation, T_x, and the nuclear relaxation , T_n, times are long relative to T_{1e}. Unequal doublet intensities can be observed also at short t_{mix}, when T_x and T_n are longer than the repetition time, t_R, ($t_{mix} \ll T_{1e} \ll t_R$ and T_n, $T_x > t_R$), namely saturation of the nuclear transitions [40]. In principle this experiment should apply to any spin system and negative ENDOR effects were observed for high spin ^{57}Fe(III) [41] as well.

The majority of pulse ENDOR experiments are carried out at low temperatures; for nitroxide and other organic radicals liquid nitrogen cooling is sufficient, whereas paramagnetic transition metal ions call for measurements in the range of 1.2–15 K. At high frequencies, such as 95 and 140 GHz, the cavity tuning and the phase of the signal are highly sensitive to subtle changes in the temperature/He flow. Consequently, in addition to the desired resonance effect, the RF pulse usually also causes undesirable local heating resulting in small cavity detuning and leading to an additional decrease in the echo intensity. Therefore, when the RF power varies with frequency (as is usually the case) it results in a baseline with broad humps, which interferes with the observation of the ENDOR signal. This is particularly problematic for broad peaks and/or very weak ENDOR effects. This problem is overcome by acquiring the ENDOR spectrum by varying the RF frequency randomly rather than sequentially, thus allowing averaging baseline distortions arising from heating effects. Currently, all ENDOR experiments measured in our lab are carried out using random acquisition.

Our spectrometer is a home-built spectrometer operating at 95 GHz. The MW bridge was built by the Donetsk Physico-Technical Institute, Donetsk in the Ukraine, the magnet is 6 T superconducting magnet

in a solenoid configuration with cryogenic sweep coils providing a sweep range of ±0.3 T [6]. The spectrometer is controlled by the SpecMan software developed together with the ETH lab [42]. The flexibility required for running multidimensional experiments and for implementing different acquisition modes is highly demanding in terms of the software that manages the spectrometer. Therefore, software development is usually a significant bottleneck in the set up of home-built highly versatile pulsed spectrometer. The recent development of such a software, SpecMan, which is now available to the community, should open this bottleneck and make the construction of home-built spectrometers easier.

Virtues of High-Field ENDOR

Because the ENDOR method is derived from the EPR experiment, it benefits from all the advantages of HF EPR, and, unfortunately also from its disadvantages. For examples, if the EPR spectra of two radicals can be resolved at a high field, then this will automatically allow one to resolve their ENDOR spectra. Likewise, if the EPR spectrum of a sample with a large *g*-anisotropy becomes so widely spread at HF resulting in a poor signal-to-noise (S/N) ratio, this would automatically translate into extreme difficulties to record the ENDOR spectrum. Hence, in this section which presents the cons of HF ENDOR, we first list the virtues of high-field EPR that affect the ENDOR experiment.

EPR Sensitivity

When sensitivity is considered, one has to distinguish absolute and relative sensitivities because the amount of sample that can be introduced into the cavity of HF EPR spectrometers is usually significantly smaller than in standard X-band spectrometers. Consequently, the amount of sample available has to be taken into account (for a detailed discussion on this issue the reader is referred to ref. 24). However, when the amount of sample is limited, such as in single crystals of proteins, then HF EPR is highly advantageous [43, 44]. This has been first demonstrated by the Leiden group who studied tiny crystals of the copper protein azurin.

A considerable improvement in sensitivity is obtained for half integer high spin systems ($S = (2n + 1)/2$, $n > 1$) such as Mn(II) and Fe(III) ($S = 5/2$) and Gd(III) ($S = 7/2$). Here, when the magnetic field, B_0, is much larger than the zero-field splitting (ZFS) parameter D, the second-order orientation dependence of the central $|-1/2\rangle \rightarrow |1/2\rangle$ EPR transition become negligible. This results in narrow signals also in orientationally disordered samples, thus leading to increased sensitivity. Since we have started to use high field EPR we have become highly susceptible to Mn(II) impurities.

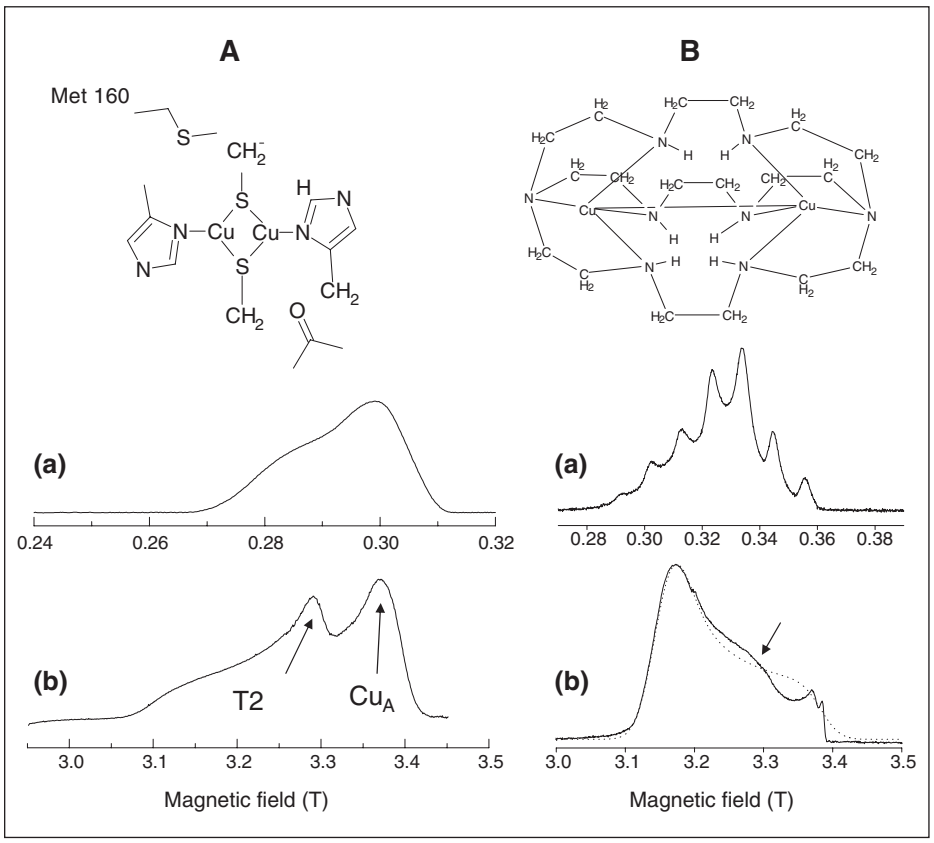


Fig. 2. A) X-band (**a**) and (**b**) FS-ED EPR spectra of M160T9 recorded at 10 K. **B**) (**a**) X-Band FS-ED EPR spectrum of a frozen solution of Cu_2RGT and (**b**) the corresponding W-band spectrum. The arrow points to the mononuclear Cu(II) complex. The structure of the paramagnetic centers is shown on the top of the figure.

EPR Resolution

HF EPR offers improved resolution for paramagnetic centers with different *g*-values. Similarly, small *g*-anisotropies can be resolved at HF. However, in systems that suffer from large *g*-strain, as in many Cu(II) complexes, although the *g*-anisotropy resolution improved, the Cu hyperfine splitting is often lost. Two such examples are shown in Fig. 2. The X-band spectrum of the recombinant water soluble fragment, M160T9, of subunit II of *Thermus thermophilus* cytochrome *c* oxidase ba_3, which contains the Cu_A electron-mediating site [45], is compared to the W-band spectrum on the left-hand side of Fig. 2. The structure of the Cu_A site is shown at the top of the figure. It is a mixed-valent binuclear center with one unpaired electron, $S = 1/2$, delocalized over the two copper atoms [46]. In the X-band spectrum the signal of a mononuclear type 2 (T2) Cu(II) impurity, is not resolve in the $g_\perp$-region. At W-band the $g_\perp$ features of the Cu_A and T2 are well resolved, thus allowing to obtain Cu_A ENDOR signals free of T2 contributions. The spectra on the left-hand side of Fig. 2 are of a mixed valent binuclear copper complex, $S = 1/2$, with an azacryptand ligand, RGT, shown on the top of the figure. The measurements at two frequencies are complementary because the W-band spectrum resolves the *g*-anisotropy while the X-band one provides the Cu hyperfine couplings.

High-spin systems that have also a relatively large hyperfine interaction, such as ^{55}Mn(II) often exhibits forbidden transitions ($\Delta m_S = 1, \Delta m_I = \pm 1$) that arise from the cross-terms of the ZFS and the ^{55}Mn hyperfine interaction. The appearance of these transitions reduce the resolution also for single crystals. Single crystals of the Mn(II) protein concanavalin A are large enough and EPR measurements can be carried out at X-band as well. Figure 3 shows that spectra are poorly resolved due to the presence of *D* strain and forbidden transitions. In contrast, the W-band spectra of concanavalin A single crystals are highly resolved. Such a resolution is ▶

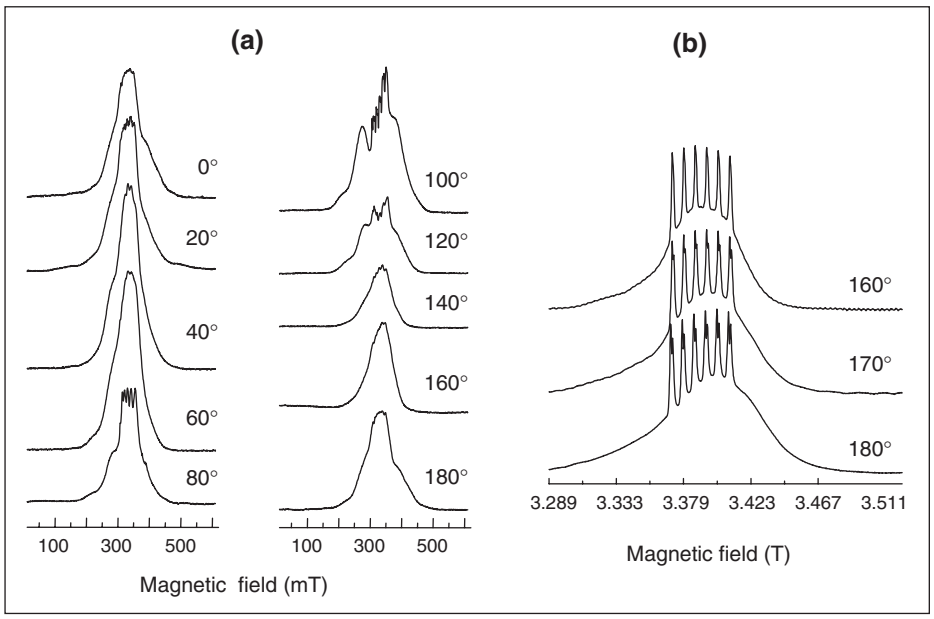


Fig. 3. FS-ED EPR spectra of a single crystal of concanavalin A recorded at (**a**) X-band (4.2 K) with the magnetic field in an arbitrary plane, (**b**) W-band with the magnetic field in the *ac* plane. The rotation angles are relative to an arbitrary 0° position.

required for single crystal ENDOR measurements where the EPR lines are tracked as a function of orientation.

Observation of 'EPR-Silent' Samples

Usually integer high-spin transition metal ions, such as Mn(III) or Ni(II), are EPR-silent at conventional frequencies due to the large ZFS interaction which raises the energy level splittings such that it cannot be accessed by the available MW frequency. At high fields such systems can be detected and thereby open the possibility to study a whole range of substances [47]. The understanding of the EPR spectra of such samples often require multifrequency measurements, including frequencies higher than the more conventional 95 and 140 GHz.

The improved sensitivity and resolution discussed above are obviously transferred to the ENDOR experiment. In this context, the question that arises is what is considered as a high field. There is no absolute answer to this question and it obviously depends on the relative size of the various magnetic interaction involved. When the *g*-anisotropy is of prime interest then the requirement is that the anisotropy should exceed the inhomogeneous line broadening [22]. Accordingly, for some systems, even X-band is sufficient while for others, such as chlorophyl radical ions, frequencies as high as 360 GHz may be needed [22]. For high-spin systems, the measure is the relative sizes of D and B_0. In this case, integer and half integer spin systems should be distinguished. While for the latter increasing the field results in improved resolution, for the former it makes the detection of traditional 'EPR-silent' samples possible. In practice, the community usually refers to $B_0 > 2.5$ T and $\nu_0 > 70$ GHz (using superconducting magnet and millimeter wave technologies) as 'high'. But, it is obvious that today's 'high' field is tomorrow's 'conventional' field.

In addition to the above advantages, which are inherent also to the ENDOR experiment, there are a number of advantages that are unique to ENDOR and are discussed next.

Nuclear Zeeman Resolution

The higher the field the better the resolution of different elements and isotopes is. This is most significant for strongly coupled low γ nuclei, such as ^{14}N and ^{17}O, the signals of which overlap at X-band with those of weakly coupled proton. The protons, needless to say, are highly abundant in most samples. Figure 4 shows the Davies ENDOR spectrum of a frozen solution of a Cu(II) complex with histidine ($CuHis_2$), recorded at the $g_\perp$. While the X-band spectrum is poorly resolved and exhibits overlapping ^{1}H and ^{14}N signals, the W-band spectrum shows only ^{1}H signals ($\nu_I = 145$ MHz) with clear singularities that resolve different types of protons.

^{23}Na and ^{27}Al have close γ values and therefore at typical X-band fields, 0.35 T, their Larmor frequencies, 3.94 and 3.88 MHz, respectively, are not resolved. This is problematic in oxides, such as zeolites, where both are often present. At W-band they can be resolved as shown in Fig. 5, which displays the spectrum of a trapped S_3^- radical in the cage of the aluminosilicate sodalite. It shows a peak at the ν_{Al} and two doublets attributed to ^{23}Na, which is present in sodalite as cations balancing the charge of the framework Al. This shows that the S_3^- radical interacts closely with the Na cations.

Simplification of Spectral Analysis

At HF the ENDOR frequencies can often be described using first order approximations, thereby simplifying the spectral analysis. For example, the general expression for the two ▶

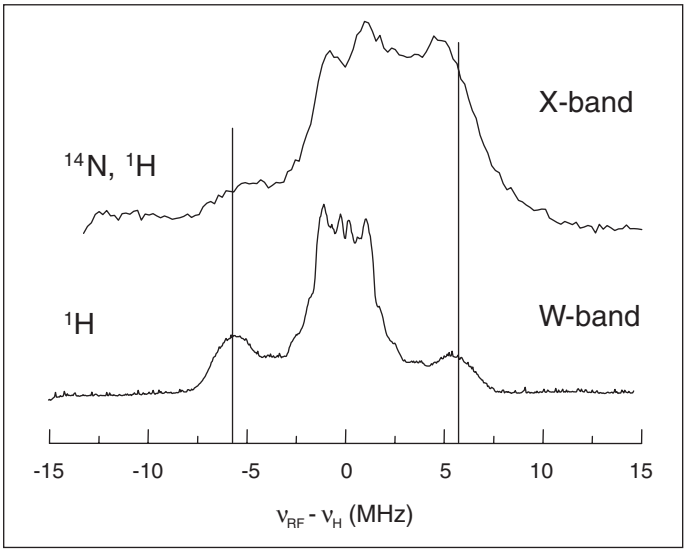


Fig. 4. X- and W-band Davies ENDOR spectra of a frozen solution of $CuHis_2$. The frequency axis is given with respect to the ^{1}H Larmor frequency. The vertical lines mark the ^{1}H doublet of the α-protons.

ENDOR frequencies, ν_α, ν_β, for a $S = 1/2$, $I = 1/2$ system are given in general by [48]:

$$\nu_\alpha = \left[\left(\frac{1}{2}A - \nu_I\right)^2 + \frac{1}{4}B^2\right]^{1/2},$$

$$\nu_\beta = \left[\left(-\frac{1}{2}A - \nu_I\right)^2 + \frac{1}{4}B^2\right]^{1/2}, \qquad (3)$$

where for an axially symmetric hyperfine interaction $A = T_\perp(3\cos^2\theta - 1) + a_{iso}$, $B = 3T_\perp \sin\theta\cos\theta$, and θ is the angle between the direction of the unique component of the hyperfine interaction, and the magnetic field. When $\nu_I \gg B$, the B term in Eq. (3) can be neglected and the expression for the ENDOR frequencies becomes significantly simpler.

$$\nu_{\alpha,\beta} = \left|-\nu_I + M_S A\right|. \qquad (4)$$

This yields an ENDOR spectrum consisting of a doublet, symmetrically situated about ν_I (see Fig. 1). For protons at 95 GHz the first-order approximation is almost always valid.

The symmetry about ν_I has important consequences because it allows one to apply the pulsed Special TRIPLE experiment also to solids. In this experiment (see Fig. 1c) RF_1 and RF_2 should be on resonance with ν_α and ν_β, respectively (or vice versa), hence the relation between the two frequencies should be known a priori. This condition is met when the frequencies are described by Eq. (4), but not by Eq. (3) because B is unknown. An example of a spectrum recorded using the Special TRIPLE experiment is given in Fig. 6.

The ENDOR spectra of quadrupolar nuclei with $I > 1/2$ are also significantly simpler if the nuclear quadrupole interaction (nqi) can be treated to first order. In this case the ENDOR frequencies corresponding to the $m_I \rightarrow m_I - 1$ transitions are given by:

$$\nu^\alpha_{m_I} = \nu_\alpha + (2m_I - 1)\nu_q,$$
$$\nu^\beta_{m_I} = \nu_\beta + (2m_I - 1)\nu_q, \qquad (5)$$

where

$$\nu_q = \frac{Q_{zz}}{2}\left[(3\cos^2\beta - 1) + \eta\sin^2\beta\cos 2\alpha\right], \qquad (6)$$

$$Q_{zz} = \frac{3e^2Qq}{4I(2I-1)h} \text{ and } \eta = \frac{Q_{xx} - Q_{yy}}{Q_{zz}}.$$

The angles β and α give the orientation of the magnetic field with respect to the principal axis system of the quadrupole tensor. For nuclei with half integer nuclear spin, such as $I = 3/2$ and 5/2, the ENDOR transition corresponding to m_I $1/2 \rightarrow -1/2$ is independent of the nqi to first order, while to second order it exhibits an anisotropy which is proportional to Q^2_{zz}/ν_I. Consequently, the higher the magnetic field, the simpler is the ENDOR spectrum and a better resolution is expected in orientationally disordered. The first-order approximation is always valid at W-band for ^{2}H, and often also for ^{14}N, ^{17}O and ^{27}Al.

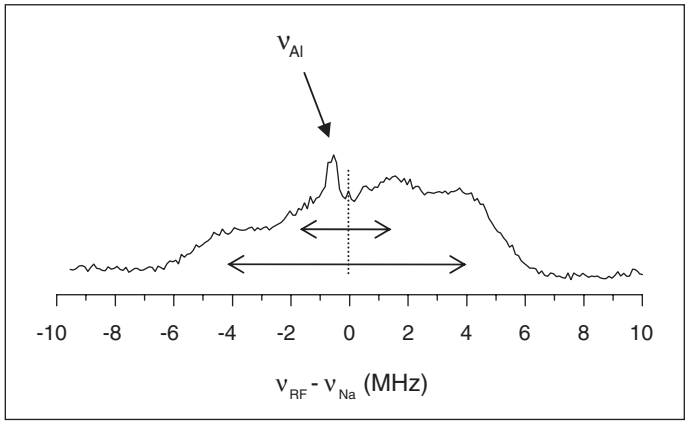


Fig. 5. W-band Davies ENDOR spectra of blue-sodalite. The ^{23}Na hyperfine doublets are marked as arrows while the dotted line corresponds to ν_{Na}.

An example of an ^{27}Al ENDOR spectrum with well resolved quadrupolar splittings is shown in Fig. 7a [49]. This is a spectrum of a dehydrated sample of Cu(II) exchanged into the zeolite faujasite. The spectrum is highly resolved because it was recorded close to the $g_{||}$ position. It comprises of a superposition of two equivalent quintets, with a splitting of 1.5–1.8 MHz, as indicated in Fig. 7b. This single-crystal-like spectrum clearly shows that the quintet splitting is due to the quadrupolar splitting of the ^{27}Al nucleus ($I = 5/2$) and the small difference in the splitting are due to second order effects. The distance between the centers of the two quintets yield a hyperfine coupling of 4.2 MHz. The ^{17}O quadrupole coupling of water ligands in the aquo-complex of Gd^{3+} in a frozen solution was also nicely resolved in the W-band spectra [50].

For high-spin systems, such as ^{55}Mn(II), $S = 5/2$, there is a total of $2I(2S + 1)$ al- ▶

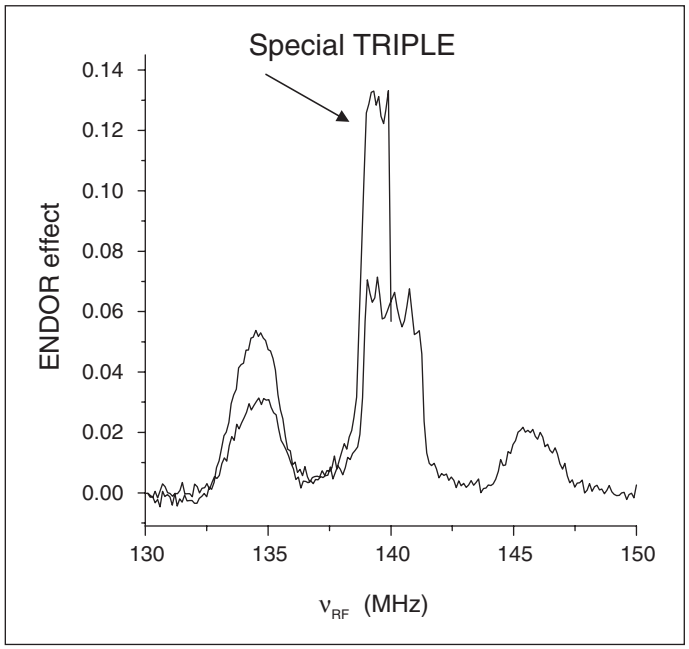


Fig. 6. W-band ^{1}H Davies ENDOR spectrum compared with the Special TRIPLE spectrum of a frozen solution of $CuHis_2$ in D_2O.

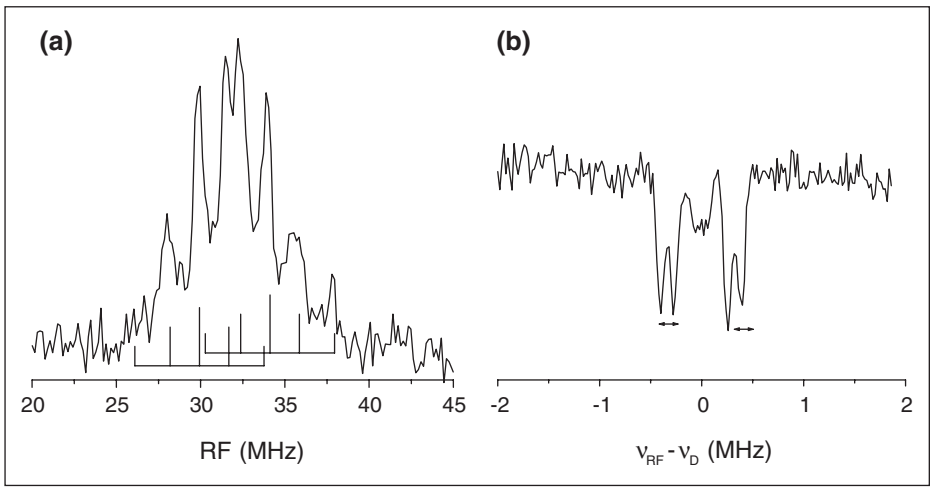


Fig. 7. (**a**) W-band ^{27}Al Davies ENDOR spectrum of dehydrated Cu(II) exchanged fuajasite recorded close to the $g_{||}$ position, (**b**) The ^{2}H- Mims W-band ENDOR spectra of a frozen solution of Cu_2RGT in D_2O recorded at the $g_{||}$ position. The arrows mark the quadrupole splitting.

lowed ENDOR transitions given to first order by:

$$\nu_{m_S,m_I} = \left|-\nu_I + M_S A\right| + (2m_I - 1)\nu_q . \quad (7)$$

It has been shown that if the ZFS is substantial (with respect to the electron Zeeman) it can affect the ENDOR frequencies [51, 52]. The effect is on the order of AD^2/ν_0^2 and therefore, at high enough fields this dependence is eliminated. This was shown for ^{57}Fe ENDOR of ^{57}Fe(III) substituted sodalite, recorded at X and W-band [41, 51]. When the hyperfine coupling is large, as for ^{55}Mn or ^{51}V, it should to be considered up to second or even third order. To second order in the hyperfine interaction, and to first order in the quadrupole interaction, while neglecting the ZFS, the ENDOR frequencies are [53, 54]:

$$\nu_{M_S}(Mn) = M_S A - \nu_I + \nu_q(2m_I - 1) + \frac{a_{iso}^2}{\nu_0}\left[-S(S+1) + (M_S)^2 - M_S(2m_I - 1)\right]. \quad (8)$$

The ^{55}Mn hyperfine components of the central EPR transitions are usually well resolved at HF and therefore each can be selected in an ENDOR experiment as shown in Fig. 8 for a single crystal of concanavalin A. Selection of the $|-1/2, \pm 5/2\rangle \leftrightarrow |1/2, \pm 5/2\rangle$ transitions produces only one line for each of the $M_S = \pm 1/2$ manifolds, while for the others, two resolved lines are present [53], the splitting of which is $2\nu_q$ (see Eq. (7)). Interestingly, the linewidth increases with the m_I value. This is attributed to the quadrupolar splitting which scales with the m_I value and therefore slight misalignment and differences between the two Mn^{2+} types will be enhanced for higher m_I values. In contrast to the $M_S = 1/2$ ENDOR lines the $M_S = -1/2$ lines do not exhibit quadrupolar splittings and the shifts of the frequencies of different m_I components are significantly smaller. This resolution difference arises from the second order (see Eq. (8)) contributions of the hyperfine interaction. For one manifold it has the same sign as the quadrupolar term whereas for the other it has the opposite sign. This shows that the first order approximation for the ^{55}Mn hyperfine interaction is not valid even at W-band and higher fields are required.

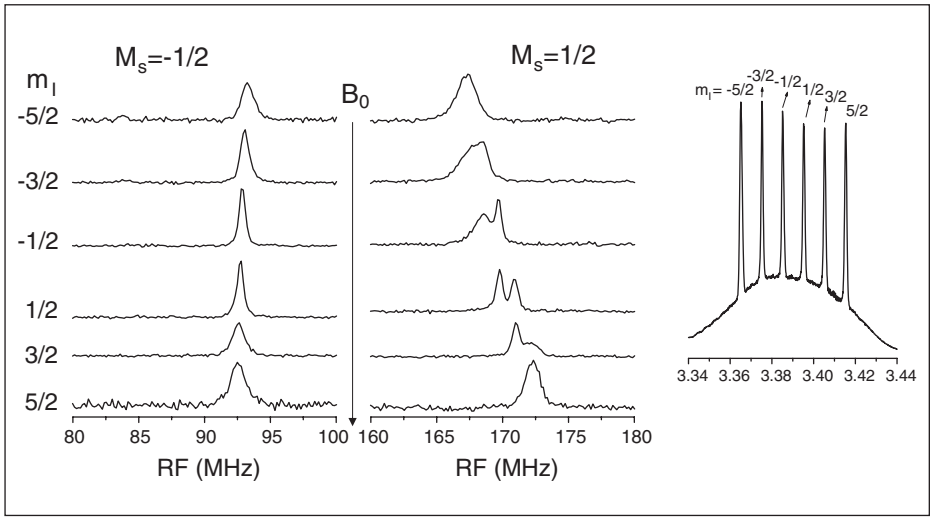


Fig. 8. W-band ^{55}Mn Davies ENDOR measured at the lowest-field ^{55}Mn hyperfine component in the spectral regions of the $M_S = \pm 1/2$ manifolds for a crystal orientation $B||a$. The inset shows part of the corresponding FS-ED EPR spectrum and the field positions where measurements took place.

Weakly Coupled Low γ Nuclei

Signals of weakly coupled nuclei appear around the corresponding ν_I, consequently for low γ nuclei , such as ^{2}H, this results at X-band in very low ENDOR frequencies, which are usually hard to detect. Therefore, X-band ^{2}H ENDOR is not often reported. At W-band, these signals move to about 20 MHz and are easily detected. It should be noted that ^{2}H is most useful as a probe for exchangeable protons and can be used to derive structural information if the quadrupolar splittings can be resolved because the direction of the principal axis is along the X-D bond. The ^{2}H Mims ENDOR spectra of a frozen solution of Cu_2RGT (Fig. 2b) in D_2O recorded at $g_{||}$ is presented in Fig. 7b. The spectrum is well resolved, exhibiting a quarupolar splitting, $2\nu_q$ of 140 kHz. At this particular field position the spectrum is single-crystal-like and therefore ν_q can be used to estimate the orientation, β, of the N-D bond with respect to $g_{||}$ using Eq. (6). Neglecting η which is relatively small and taking $e^2Qq/h = 210$ kHz for the ND deuterons [55, 56], $\beta = 79°$ is obtained from Eq. (6). The angle between the NH bond and the Cu-Cu direction is 89° in the crystal structure. This is in a good agreement considering the uncertainty in e^2Qq/h and the assumption that $\eta = 0$. This provides experimental evidence for $g_{||}$ being along the Cu-Cu direction as expected for the trigonal bi-pyramidal coordination geometry of the copper ions [57].

Orientation Selection

A common methodology in ENDOR investigations of orientationally disordered systems is the acquisition of orientation selective spectra that provide additional structural infor-

mation in terms of orientations [58]. This applies to systems where the EPR spectrum is dominated by a large anisotropic interaction such as *g*-anisotropy. ENDOR spectra are then recorded at different field positions within the EPR powder pattern. Due to the limited bandwidth of the applied microwave pulses with respect to the width of the EPR powder pattern, only a set of paramagnetic centers with specific orientations relative to the magnetic field contribute to the ENDOR spectrum at each field setting. Therefore, such series are used to determine the relative orientation of the hyperfine and the *g*-tensor. These give structural information because the orientation of *g* is usually related to local symmetry axes. Figure 2 shows that such experiments can be carried out on Cu_2RGT at W-band but not at X-band where the inhomogeneous linewidth is primarily determined by the Cu hyperfine interaction and the presence of $7M_I$ manifolds does not allow for sufficient orientation selectivity. Figure 9 shows an example of W-band ^{1}H ENDOR orientation-selective spectra of a frozen solution of Cu_2RGT. The spectral changes are clear and were used to determine the hyperfine tensors of two different protons in the molecule [57].

The Sign of the Hyperfine Coupling

Usually the sign of the hyperfine splitting cannot be determined from the ENDOR spectrum because the ν_α and ν_β signals are indistinguishable. This holds also for the signals corresponding to $\nu_{-1/2}$ and $\nu_{1/2}$ in a high-spin system. Once a controlled asymmetry can be introduced into the spectrum they can be identified and the sign of *A* can be determined. For high-spin system, $S > 1/2$, this can be accomplished by a proper selection of the EPR transitions (Fig. 10a). The presence of a small ZFS suffices to introduce the needed separation between the various transitions to allow selective excitation. For example, the FS-ED EPR spectrum of a frozen solution of $Mn(H_2O)_6^{2+}$ is shown in the inset of Fig. 10b. It consists of a well-resolved sextet superimposed on a broad asymmetric background with a total width of about 1000 G. The six narrow peaks correspond to the ^{55}Mn ($I = 5/2$) hyperfine components of the $|-1/2, m_I\rangle \rightarrow |1/2, m_I\rangle$ EPR transitions centered at $g = 2$. The background is due to a superposition of the powder patterns of all other EPR transitions with integrated intensities in the following order: $|-5/2, m_I\rangle \rightarrow |-3/2, m_I\rangle > |-3/2, m_I\rangle \rightarrow |-1/2, m_I\rangle > |1/2, m_I\rangle \rightarrow |3/2, m_I\rangle > |3/2, m_I\rangle \rightarrow |5/2, m_I\rangle$ due to the thermal polarization. The ^{1}H ENDOR spectrum, recorded at the field position denoted by a (bottom trace, Fig. 10b) consists of a superposition of two 'Pake' doublets. The inner one, with a splitting of about 1 MHz corresponds to distant solvent protons whereas the second, with $A_\perp$ and $A_\parallel$ singularities at ±1.25 and ±3.67 MHz, are due to the water ligands. The rather symmetric appearance of this spectrum indicates that it originates primarily from a $|-1/2, m_I\rangle \rightarrow |1/2, m_I\rangle$ EPR transition. However, considering the FS-ED spectrum and the field at which the spectra were measured, contributions from the $|-5/2, m_I\rangle \rightarrow |-3/2, m_I\rangle$ and $|-3/2, m_I\rangle \rightarrow |-1/2, m_I\rangle$ EPR transitions are expected as well. A close look at the low-frequency end of the spectrum indeed reveals signals from the $M_S = -3/2$ manifold superimposed on the $A_\parallel$ feature of the $M_S = \pm 1/2$. The ENDOR spectrum recorded at positions b, outside the range of the $|-1/2, m_I\rangle \rightarrow |1/2, m_I\rangle$ EPR transitions (top trace, Fig. 10b), where the major contributions to the spectrum come from the $|-3/2, m_I\rangle \rightarrow |-1/2, m_I\rangle$ transition is significantly different. It clearly shows the $A_\parallel$ and $A_\perp$ features of the $M_S = -1/2$ manifold, along with the $A_\perp$ singularity of the $M_S = -3/2$ manifold. The powder pattern of the $M_S = 1/2$ manifold has completely disappeared. This spectrum yield that $A_\parallel > 0$ and $A_\perp < 0$ as expected for an hyperfine interaction dominated by a dipolar interaction [38].

A similar approach was used to determine the sign of the ^{17}O hyperfine coupling of $Mn(H_2{}^{17}O)_6^{2+}$ [36]. The spectrum recorded at the field position, indicated by a in the FS-ED spectrum (inset of Fig. 11), the ENDOR

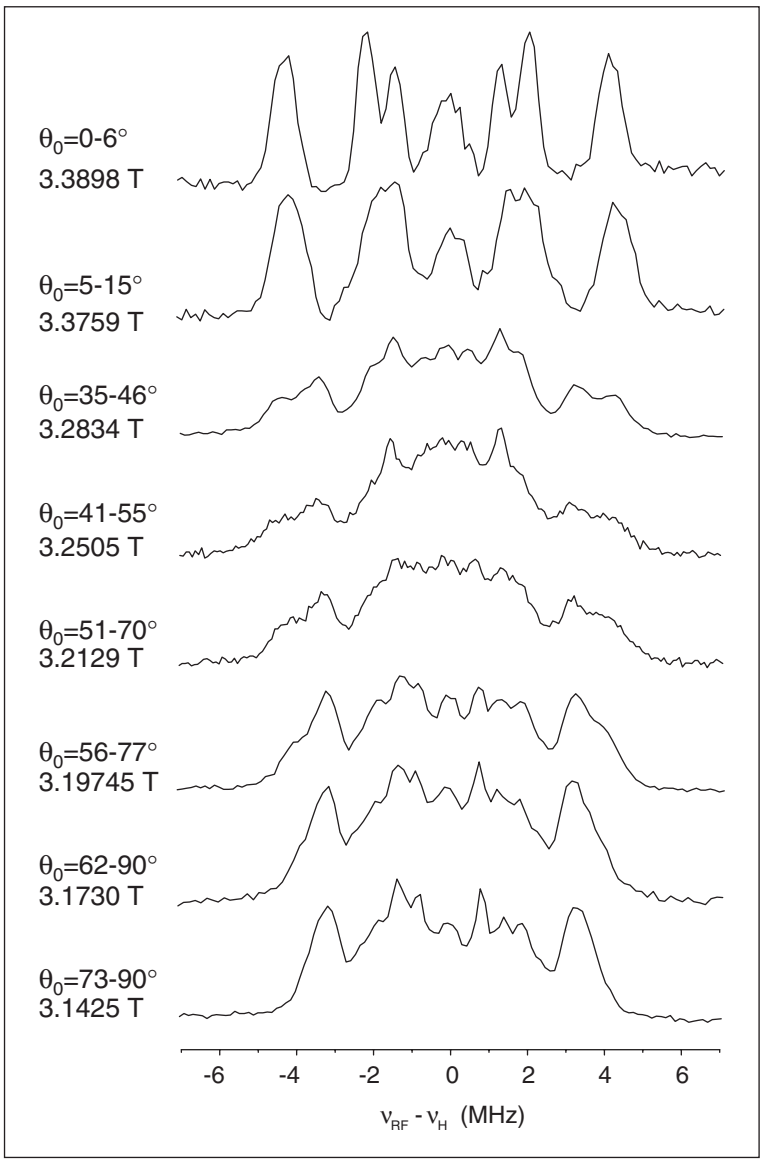


Fig. 9. Field-dependent W-band ^{1}H Davies ENDOR spectra of a frozen solution of Cu_2RGT. The orientation selected (with respect to $g_\parallel$) and the observer fields are noted in the figure.

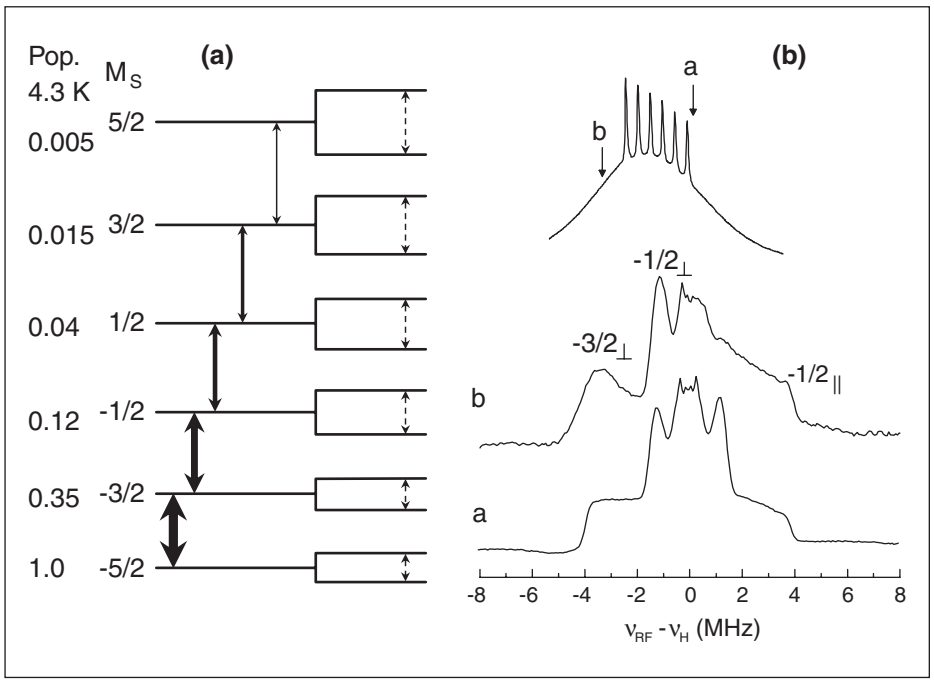


Fig. 10. (**a**) Energy level diagram for $S = 5/2$, $I = 1/2$. The solid arrows mark the EPR transitions and the dotted arrows the ENDOR transitions. The relative populations of the levels are given for 4.3 K and the arrow's thickness represents the relative intensity, (**b**) W-band ^{1}H Davies ENDOR spectra of $Mn(H_2O)_6^{2+}$ measured at two different field positions, *a* and *b*, as indicated in the inset which shows the FS-ED EPR spectrum.

spectrum shows a doublet situated symmetrically with respect to the Larmor frequency of ^{17}O. The lines have a splitting of 8 MHz. At this field, 3.41 T, the $|-1/2, 5/2\rangle \rightarrow |1/2, 5/2\rangle$ EPR transition is selected predominantly and the corresponding ENDOR signals show at $\nu_I(^{17}O) \pm A/2$, according to Eq. (7) (quadrupolar splittings are unresolved). The ENDOR spectrum recorded at the field position labeled b, 3.35 T, arises mainly from the $|-3/2, m_I\rangle \rightarrow |-1/2, m_I\rangle$ EPR transitions, resulting in an asymmetric ENDOR spectrum with respect to $\nu_I(^{17}O)$, with the $M_S = -1/2$ manifold line at $|-\nu_I(^{17}O)\} - A/2|$ and the $M_S = -3/2$ line at $|-\nu_I(^{17}O)\} - 3A/2|$. The latter is three times as broad, as expected. From this spectrum the sign of the hyperfine coupling was determined to be negative (recalling that $\nu_I(^{17}O)$ is negative). At X-band the $\nu_I(^{17}O)$ signals overlap with the ^{1}H signals, reducing significantly the spectral resolution [59].

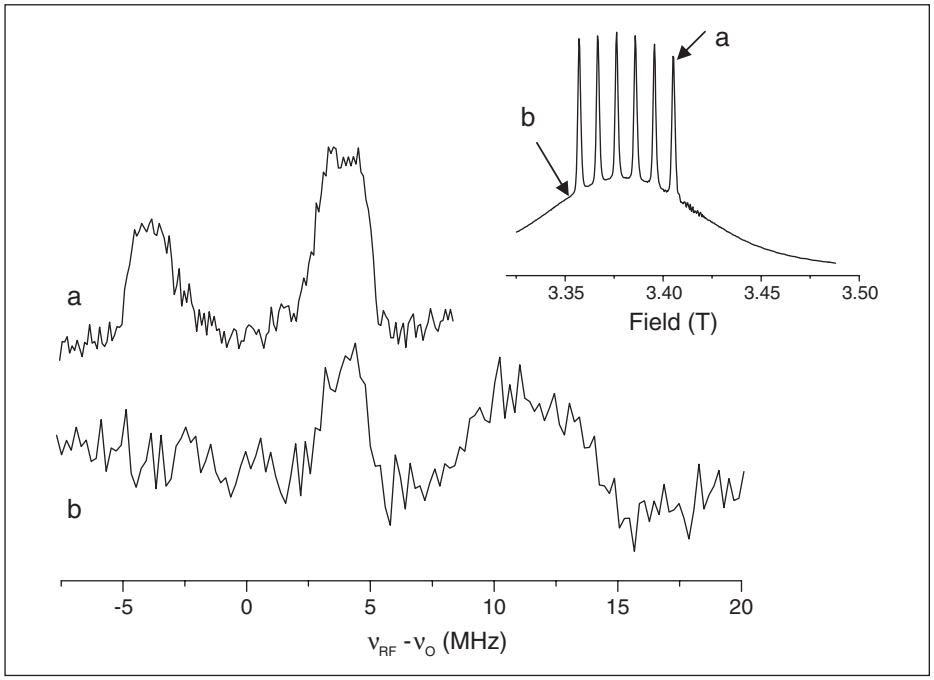


Fig. 11. W-band ^{17}O Davies ENDOR spectra of the Mn aqua-complex at two different field positions, which are indicated on the field sweep echo detected spectrum (inset).

While for high-spin systems the determination of the sign of the hyperfine couplings relies on the selective excitation of specific EPR transitions, for $S = 1/2$ it takes advantage of the large thermal polarization and the spin-dynamics [39, 40] and the VMT experiment described above can be applied. VMT Davies ENDOR spectra of frozen solution of a Cu(II)-^{13}C-glycine complex recorded at $g_\perp$ are shown in Fig. 12. The top spectrum shows an asymmetric doublet, of which the line at −1.3 MHz is weaker. As t_{mix} increases, the relative intensity of this line increases, while that of the high-frequency component decreases, thus yielding a negative coupling [37, 40]. The asymmetry at the short t_{mix} value is a consequence of partial saturation of the NMR transitions, and the low-intensity line corresponds to the β manifold [40], consistent with the negative sign.

Limitations of High-Field ENDOR

Like the advantages, the limitations of high-field EPR translates into the ENDOR as well. For example, sample with a very large *g*-anisotropy, like low-spin Fe(III) in hemes, will be widely spread and exhibit low S/N, this will immediately affect the ENDOR experiment for which the S/N constrains are larger. The sample volume is also a limitation. Since most of the 95 and 140 GHz spectrometers employ cylindrical cavities, capillaries with o.d. <0.8 mm are used. This is not a problem if the samples are stable solid or solutions. However, sample preparation poses a problem if air sensitive samples are to be prepared or if intermediated should be trapped. Freeze quench experiments using W-band capillaries were reported only recently [60].

While increasing the magnetic field has many advantages, as noted above, it is also associated with the reduction in the hyperfine enhancement factor, which is particularly important in the case of ^{14}N ENDOR. Our experience has shown that we have difficulties observing ^{14}N ENDOR of strongly coupled nuclei, which are usually easily observed at X-band (although they suffer from low resolution due to overlap with ^{1}H ▶

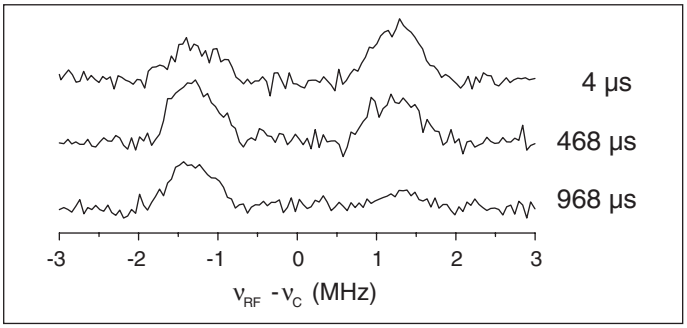


Fig. 12. W-band VMT Davies ENDOR spectra of a frozen solution of a Cu(II) ^{13}C-Glycine complex. All spectra were recorded at $g_\perp$. The t_{mix} values are marked on each trace.

signals). One of the reasons could be the significant reduction in the hyperfine enhancement factor, thereby reducing the effective B_2, thus requiring longer RF pulse, during which most of the electron spin polarization obtained by the MW inversion π pulse has been lost. This, along with the broadening due to the relatively large quadrupolar interaction may be the reason for the difficulty. For ^{14}N an excellent substitution is the two-dimensional X-band HYSCORE (hyperfine sublevel correlation) experiment, where weakly and strongly coupled nuclei appear in different quadrants and are therefore well separated. Also Q-band HYSCORE have been shown recently to be very effective for determine hyperfine and quadrupolar interactions of ^{14}N [61–63] and ^{17}O [64].

Finally, some of the pros described above can be already manifested at Q-band frequencies. In this case the use of electromagnet is more convenient and the maintenance is cheaper than superconducting magnets. In addition, the sample size is larger. Therefore, the number of pulsed Q-band ENDOR applications have recently increased significantly [65–67]. While this can be sufficient in the case of paramagnetic transition metal, for radicals the field of 1.2 T is usually not sufficient for achieving the resolution required.

Future Outlook

While the recent development and applications of high-field ENDOR show that it is a promising tool for the detailed characterization of paramagnetic centers in terms of geometry and electronic properties, research efforts in a number of directions are still required for the full realization of its potential. So far, ENDOR measurements are routine at 95 and 140 GHz, but not at higher fields/frequencies. For some applications to radicals and integer high-spin system this is not high enough. Hence the development of ENDOR at higher frequencies, where the EPR part has already been developed, like 275 and 360 GHz, are very important. The design of two-dimensional correlation ENDOR techniques, which will facilitate data analysis, resolve overlapping signals, provide the number of identical nuclei in a given center and determine the proximity of various magnetic nuclei, is needed. These must be associated with improved long-term stability of the spectrometers at low temperatures. In addition, improvements in sample handling techniques to allow freeze-quench experiments and facilitate the handling of air-sensitive samples are required. In terms of data analysis, the extraction of the hyperfine and nuclear quadrupole interactions from a series of orientation-selective ENDOR spectra or single crystal rotation patterns requires spectral simulations. Depending on the complexity of the system, such simulations may be rather time-consuming, calling for the development of highly automated, quick and user friendly simulation procedures. The last stage in the data analysis, which comprises the interpretation of the hyperfine coupling in terms of geometry and electronic structure, requires the establishment of DFT methods that are best suited for predicting such parameters.

Currently, the pulse ENDOR experiment are carried out in the frequency domain due to bandwidth limitation of the RF pulse. If short enough RF π pulses, in the range of tens of ns were available, then one could gain significant S/N from by performing a real time domain experiment. Such a technological development will turn pulse ENDOR as powerful as FT NMR because it will open the door to a variety of multidimensional experiments.

Acknowledgment

I greatly appreciate collaboration with Sharon Ruthstein in the preparation of this article.

References

1. Lebedev Ya.S. in: Modern Pulsed and Continuous-Wave Electron Spin Resonance (Kevan L., Bowman M.K., eds.) pp. 365–404. New York: Wiley 1990.
2. Burghaus O., Rohrer M., Gotzinger T., Plato M., Möbius K.: Meas. Sci. Technol. **3**, 765–774 (1992)
3. Möbius K.: Appl. Magn. Reson. **9**, 389–407 (1995)
4. Weber R.T., Disselhorst J.A.J.M., Prevo L.J., Schmidt J., Wenckebach W.T.H.: J. Magn. Reson. **81**, 129–144 (1989)
5. Disselhorst J.A.J.M., van der Meer H., Poluektov O.G., Schmidt J.: J. Magn. Reson. A **115**, 183–188 (1995)
6. Gromov I., Krymov V., Manikandan P., Arieli D., Goldfarb D.: J. Magn. Reson. **139**, 8–17 (1999)
7. Bennati M., Farrar C.T., Bryant J.A., Inati S.J., Weis V., Gerfen G.J., Riggs-Gelasco P., Stubbe J., Griffin R.G: J. Magn. Reson. **138**, 232–243 (1999)
8. Hertel M.M., Denysenkov V.P., Bennati M., Prisner T.F.: Magn. Reson. Chem. **43**, S248–S255 (2005)
9. Blok H., Disselhorst J.A.J.M., Orlinskii S.B., Schmidt J.: J. Magn. Reson. **166**, 92–99 (2004)
10. Schmalbein D., Maresch G.G., Kamlowski A., Höfer P.: Appl. Magn. Reson. **16**, 185–205 (1999)
11. Rohrer M., MacMillan F., Prisner T.F., Gardiner A.T., Möbius K., Lubitz W.: J. Phys. Chem. B **102**, 4648–4657 (1998)
12. Lendzian F.: Biochim. Biophys. Acta Bioenergetics **1707**, 67–90 (2005)
13. Poluektov O.G., Utschig L.M., Dubinskij A.A., Thurnauer M.C.: J. Am. Chem. Soc. **127**, 4049–4059 (2005)
14. Wilson J.C., Wu G., Tsai A-l, Gerfen G.J.: J. Am. Chem. Soc. **127**, 1618–1619 (2005)
15. Kay C.W.M., Bittl. R., Bacher, A., Richter G., Weber S.: J. Am. Chem. Soc. **127**, 10780–10781 (2005)
16. Carmieli R., Manikandan P., Epel B., Kalb (Gilboa) A.J., Goldfarb D.: J. Am. Chem. Soc. **123**, 8378–8386 (2001)
17. Goldfarb D., Narasimhulu K.V., Carmieli R.: Magn. Reson. Chem. **43**, S40–S50 (2005)
18. Arieli D., Delabie A., Vaughan D.E.W., Strohmaier K.G., Goldfarb D.: J. Phys. Chem. B **106**, 7509–7519 (2002)
19. Carl P.J., Vaughan D.E.W., Goldfarb D.: J. Phys. Chem. B **106**, 5428–5437 (2002)
20. van den Berg G.J.B., van den Heuvel D.J., Poluektov O.G., Holleman I., Meijer G., Groenen E.J.J.: J. Magn. Reson. **131**, 39–45 (1998)
21. Orlinskii S.B., Blok H., Groenen E.J.J., Schmidt J., Baranov P.G., de Mello Donega C., Meijerink A.: Magn. Reson. Chem. **43**, S140–S144 (2005)
22. Möbius K., Savitsky A., Schnegg M., Plato M., Fuchs M.: PCCP **7**, 19–42 (2005)
23. Jeschke G.: Current Opinion in Solid State and Materials Science **7**, 181–188 (2003)
24. Bennati M., Prisner T.F.: Rep. Prog. Phys. **68**, 411–448 (2005)
25. Mims W.B.: Proc. R. Soc. Lond. A **283**, 452–457 (1965)
26. Davies E.R.: Phys. Lett. A **47**, 1–2 (1974)
27. Doan P.E., Hoffman B.M.: Chem. Phys. Lett. **269**, 208–214 (1997)
28. Epel B., Arieli D., Baute D., Goldfarb D.: J. Magn. Reson. **164**, 78–83 (2003)
29. Mehring M., Höfer P., Grupp A.:J. Phys. Chem. **91**, 1132–1137 (1987)
30. Kurreck H., Kirtse B., Lubitz W.: Electron Nuclear Double Resonance Spectroscopy of Radicals in Solution, chapt. 3. Weinheim/New York: VCH 1988.

31. Dinse K.P., Biehl R., Möbius K.: J. Chem. Phys. **61**, 4335–4341 (1974)
32. Cook R., Whiffen D.H.: Proc. Phys. Soc. **84**, 845–848 (1964)
33. Biehl B., Plato M., Möbius K.: J. Chem. Phys. **63**, 3515–3522 (1975)
34. Epel B., Goldfarb D.: J. Magn. Reson. **146**, 196–203 (2000)
35. Goldfarb D., Epel B., Zimmermann H., Jeschke G.: J. Magn. Reson. **168**, 75–87 (2004)
36. Baute D., Goldfarb D.: J. Phys. Chem. A **109**, 7865–7871 (2005)
37. Baute D., Arieli D., Neese F., Zimmermann H., Weckhuysen B.M., Goldfarb D.: J. Am. Chem. Soc. **126**, 11733–11745 (2004)
38. Epel B., Manikandan P., Kroneck P.M.H., Goldfarb D.: Appl. Magn. Reson. **21**, 287–297 (2001)
39. Bennebroek M.T., Schmidt J.: J. Magn. Reson. **128**, 199–206 (1997)
40. Epel B., Poppl A., Manikandan P., Vega S., Goldfarb D.: J. Magn. Reson. **148**, 388–397 (2001)
41. Goldfarb D., Strohmaier K.G., Vaughan D.E.W., Thomann H., Poluektov O., Schmidt J.: J. Am. Chem. Soc. **118**, 4665–4671 (1996)
42. Epel B., Gromov I, Stoll S., Schweiger A., Goldfarb D.: Conc. Magn. Reson. B **26**, 36–45 (2005)
43. Coremans J.W.A., Poluetkov O.G., Groenen E.J.J., Canters G.W., Nar H., Messerschmidt A.: J. Am. Chem. Soc. **118**, 12141–12153 (1996)
44. Högbom M., Galander M., Andersson M., Kolberg M., Hofbauer W., Lassmann G., Nordlund P., Lendzian F.: Proc. Natl. Acad. Sci. U.S.A. **100**, 3209–3214 (2003)
45. Skitter C.E., Sanders D., Wittung P., Malmstrom E.G., Aasa R., Richards J.H., Gray H.B., Fee J.A.: Biochemistry **35**, 3387–3395 (1996)
46. Harding C., McKee V., Nelson J.: J. Am. Chem. Soc. **113**, 9684–9685 (1991)
47. Krzystek J., Park J.H., Meisel M.W., Hitchman M.A., Stratemeier H., Brunel L.C., Telser J.: Inorg. Chem. **41**, 4478–4487 (2002)
48. Schweiger A., Jeschke G.: Principles of Pulse Electron Paramagnetic Resonance. Oxford: Oxford University Press 2001.
49. Carl P.J., Vaughan D.R.W., Goldfarb D.: J. Am. Chem. Soc. **128**, 7160–7161 (2006)
50. Raitsimring A.M., Astashkin A.V., Baute D., Goldfarb D., Caravan P.: J. Phys. Chem. A **108**, 7318–7323 (2004)
51. Vardi R., Bernardo M., Thomann H., Strohmaier K.G., Vaughan D.E.W., Goldfarb D.: J. Magn. Reson. **126**, 229–241 (1997)
52. Astashkin A.V., Raitsimring A.M.: J. Chem. Phys. **117**, 6121–6132 (2002)
53. Sturgeon B.E., Ball J.A., Randall D.W., Britt R.D.: J. Phys. Chem. **98**, 12871–12883 (1994)
54. Grant C.V., Ball J.A., Hamstra B.J., Pecoraro V.L., Britt D.R.: J. Phys. Chem. B **102**, 8145–8150 (1998)
55. Michal C.A, Wehman J.C., Jelinski L.W.: J. Magn. Reson. B **111**, 31–39 (1996)
56. Usha M.G., Peticolas W.L., Wittebort R.J.: Biochemistry **30**, 3955–3962 (1991)
57. Kababya S., Nelson J., Calle C., Neese F., Goldfarb D.: J. Am. Chem. Soc. **128**, 2017–2029 (2006)
58. Hurst G.C., Henderson T.A., Kreilick R.W.: J. Am. Chem. Soc. **107**, 7294–7299 (1985)
59. Tan X., Bernardo M., Thomann H., Scholes C.P.: J. Chem. Phys. **102**, 2675–2690 (1995)
60. Jung C., Schunemann V., Lendzian F., Trautwein A.X., Contzen J., Galander M., Bottger L.H., Richter M., Barra A.L.: Biol. Chem. **386**, 1043–1053 (2005)
61. Gromov I., Shane J., Forrer J., Rakhmatoullin R., Rozentzwaig Y., Schweiger A.: J. Magn. Reson. **149**, 196–203 (2001)
62. Finazzo C., Harmer J., Jaun B., Duin E.G., Mahlert F., Thauer R.K., Van Doorslaer S., Schweiger A.: J. Biol. Inorg. Chem. **8**, 586–593 (2003)
63. Harmer J., Van Doorslaer S., Gromov I., Schweiger A.: Chem. Phys. Lett. **358**, 8–16 (2002)
64. Astashkin A.V., Feng C.J., Raitsimring,A.M., Enemark J.H.: J. Am. Chem. Soc. **127**, 502–503 (2005)
65. Hoentsch J., Rosentzweig Yu., Heinhold D., Köhler K., Gutjahr M., Pöppl A., Völkel G., Böttcher R.: Appl. Magn. Reson. **25**, 249–259 (2003)
66. Van Doorslaer S., Schweiger A., Kräutler B.: J. Phys. Chem. B **105**, 7554–7563 (2001)
67. Barquera B., Morgan J.E., Lukoyanov D., Scholes C.P., Gennis R.B., Nilges M.J.: J. Am. Chem. Soc. **125**, 265–275 (2003)

Notices of Meetings

Specialized Colloque AMPERE and AvH-Workshop: Advanced Materials as Studied by Spectroscopic and Diffraction Techniques

Vilnius, Lithuania
September 16–21, 2006
www.ff.vu.lt/ampere
(previously announced in *newsletter* 15/4)

6th European Federation of EPR Groups Meeting (EFEPR)

Madrid, Spain
September 5–8, 2006
efepr-2006.unicongress.com
(previously announced in *newsletter* 16/1)

Sendai-Berlin-Novosibirsk Joint Seminar on Advanced EPR 2006

Novosibirsk, Russia
28-31 August 2006,
www.kinetics.nsc.ru/sendai/sbn/index.htm
(previously announced in *newsletter* 16/1)

Asia-Pacific EPR/ESR Symposium **APES'06**

Novosibirsk, Russia
August 24–27, 2006
www.kinetics.nsc.ru/APES2006
(previously announced in *newsletter* 16/1)

22nd International Conference on Magnetic Resonance in Biological Systems

Göttingen, Germany
August 20–25, 2006
medusa.nmr.mpibpc.mpg.de/icmrbs
(previously announced in *newsletter* 16/1)

The 39th Annual International Meeting **Advanced Techniques & Applications of EPR**

University of Edinburgh, Edinburgh

April 2–5, 2006

This meeting included a joint session with COST P15 action: 'Advanced Paramagnetic Resonance Methods in Molecular Biophysics' led by Sabine Van Doorslaer. This was a lively conference with over 100 delegates and an unprecedented number of talks and posters.

The 2006 Bruker Prize Lecture by Professor Yuri Tsvetkov of the Institute of Chemical Kinetics and Combustion, Novosibirsk was introduced by Michael Bowman (Pacific Northwest National Laboratory, USA) who recounted meeting Yuri for

the first time and the early days of pulsed EPR. Professor Tsvetkov then presented his lecture on *Pulsed Dipolar ESR Spectroscopy and Its Applications*. We heard how early work on two pulse ESE spectroscopy led to the development of Pulse Double Electron Electron Resonance (PELDOR/DEER) for distance measurements by EPR. This was followed by a wine reception sponsored by Bruker.

The following Plenary lectures were presented: Lesley Yellowlees (University of Edinburgh) described *The EPR Spectroelectrochemical Study of Reduced Species*. Louis Claude Brunel (Florida State University) in his talk *Novel Approach to EMR: Fundamentals and Applications* told us about the efforts to develop CW and pulse instruments in the 200 GHz to 1 THz range at the National High Magnetic Field Laboratory. Daniella Goldfarb (Weizmann Institute of Science) described *The High field EPR/ENDOR Studies of Mn (II) Sites in Protein Single Crystals*. Georg Gescheidt (University of Graz) described his *Time-Resolved Studies of Radical Reactions Using CW EPR and CIDNP*. Chris Kay (University College London), newly moved from the Free University Berlin began the COST P15 session with his talk *From Alcohol Oxidation to Liver Regeneration: Applications of EPR to Biology*. Gunnar Jeschke (MPI for Polymer Research, Mainz) told us about the latest developments in *Pulsed ELDOR: Measuring More Than a Single Distance*. As well as the Plenary lectures we had a series of excellent short talks, a poster session and a student talk session.

The JEOL prize Medal for the best oral presentation by a young scientist, was presented to Janet Banham (Oxford University) for her talk *Testing the Limits of the DEER Method for Distance Measurements in Proteins*. Joint runners-up were Riccardo Garzelli (University of York) and Alexey Silakov (MPI Mülheim). All three student talks were of a very high calibre but sadly there was only one medal to be won. All three were presented with cheques by Peter Meadows (JEOL). Vasily Oganesyan (UEA, Norwich) the winner of the IBDG Young Investigator Award 2006 presented a talk on *Advanced Spectroscopic Methods in Bioinorganic Chemistry: A Theoretical Insight* before being presented with a certificate and cheque by the Inorganic Biochemistry Discussion Group.

This year there were 70 posters and as usual one was selected to win the poster prize with the traditional bottle of whisky going to Stefan Stoll (ETH, Zurich) for his poster on *Simulating Pulse EPR Spectra*.

Although this was a very busy meeting we managed to find time for a whisky tasting, sponsored by JEOL, on the Sunday evening. After a short talk by Paul Murray on whisky production, we all enjoyed a 'wee dram'.

Full abstracts of the Plenary lectures, short talks and posters are on the website www.esr-group.org.uk

Shirley Fairhurst

Collected by Candice Klug

This is a new feature highlighting young investigators in the field of EPR spectroscopy who have recently became faculty members.

Gail Fanucci

University of Florida

Gail Fanucci became an Assistant Professor of Chemistry at the University of Florida in the fall of 2004. Her training includes postdoctoral fellowships in site-directed spin labeling EPR spectroscopy of membrane proteins with David Cafiso at the University of Virginia and in solid state NMR of membrane proteins with Stan Opella at the University of Pennsylvania. Gail received her PhD in chemistry in 1999 from the University of Florida in the laboratory of Daniel Talham where she studied the structural and physical properties of metal phosphonate solids and langmuir-blodgett films. Her undergraduate degrees are in biochemistry and biophysics from the University of Scranton in Pennsylvania. Gail recently received an NIH grant to study the membrane binding properties of GM2AP, a GM2 accessory protein, using EPR spectroscopy and other biophysical techniques.

If you have recently become a new faculty member in EPR spectroscopy, or know someone who has, please contact an Associate Editor for inclusion in future *newsletters*. Thank you!
C. K.

Market Place

POSITIONS

Research Positions – In Vivo EPR and EPR Imaging

Research Training Positions are presently available in the EPR facility at the University of New Mexico Health Sciences Center, UNM Albuquerque, NM, USA. We are presently seeking highly motivated individuals to pursue research utilizing in vivo EPR Spectroscopy and Imaging. The facility is exceptionally well-equipped (Bruker E540 and E500 spectrometers) and is located in a unique multi-modal imaging building containing MRI, MEG and Optical collaborating labs. Ongoing NIH funded work is at the leading edge of several disease states including stroke (e.g. J Cereb Blood Flow Metab 24, 343-9), infectious disease (e.g. PNAS 101 13867-72 J Bacti 186 4046-9) and skin cancers (e.g. PNAS 103 4111-5, Mol Cell Biochem 279 105-12). We offer outstanding facilities and training, in a very enjoyable South-Western setting. Experience in either EPR, EPR Imaging or MRI is required, as is a PhD in a related field. Interested parties should send a current CV and statement of research interests to either Graham Timmins or Jim Ke Jian Liu at gtimmins@salud.unm.edu or kliu@salud.unm.edu.

Research Assistant Professor or Research Associate

Immediate openings (4) at Dartmouth Medical School in the Electron Paramagnetic Resonance (EPR) Center for the Study of Viable Systems for Research Assistant Professor (2) and Research Associate (2). For the Research Assistant Professor positions a PhD is required with expertise and experience in EPR instrumental development and/or microwave engineering. The selected individuals should be capable of independently carrying research developments that are consistent with the research directions of the EPR Center and eventually should be able to secure external funding for related research. For the Research Associate positions (requires MS or the equivalent in experience) the skills needed include expertise in at least one of the following: Tumor or Cell Biologist; EPR Instrumentalist; and microwave engineering skills. Submit complete curriculum vitae, statement of pertinent experience, and request three references be sent to: Harold M. Swartz, Dartmouth Medical School, 702 Vail, Hanover, NH 03755, fax: 603-650-1717, e-mail: harold.swartz@dartmouth.edu. *Dartmouth Medical School is an equal opportunity/affirmative employeer and encourages applications from women and members of minority groups.*

Postdoctoral Position in EPR Studies of Bio/Nano Systems

Applications are invited for a postdoctoral position in the Department of Physics at Boise State University to work in the area of electron paramagnetic resonance spectroscopy. The successful applicant will employ EPR in the studies of biomolecular and nanoscale systems in collaboration with researchers from biology, chemistry, materials science and engineering disciplines at Boise State University, and with scientists at national level EPR user facilities. Applicants must have a PhD in physics, chemistry, materials science, or a related field, and significant experience in the EPR samples preparation, data collection, analysis, and spectral simulations of solid and liquid samples. Experience with EPR studies of proteins and other biomolecular systems, spin labeled systems and/or bio/nano sensors will be a plus. Women and minorities are encouraged to apply.

To be considered, the following materials are required: (i) Vitae and list of publications, (ii) A summary of previous/current research in relation to the abovementioned areas (maximum of 2 pages), (iii) copies of two most important EPR-based publications, and (iv) a list of three references.

Applications may be submitted by e-mail: apunnoos@boisestate.edu, or mail to Dr. Alex Punnoose, Department of Physics, Boise State University, Boise, ID 83725-1570.

The appointment is for one to three years, depending on project funding and performance.

Postdoctoral Positions Available at Davis Heart and Lung Research Institute, The Ohio State University

A position is available for a scientist with experience in magnetic resonance instrumentation development and application. The candidate should have experience in EPR/MR hardware or software development and applications to chemical or biological systems. Salary commensurate with experience. Please reference PA06 in your application.

A position is available for a scientist with experience in cardiac NMR spectroscopy or imaging research to perform isolated heart and in vivo studies of alterations in myocardial energetics and metabolism in the postischemic heart. Salary commensurate with experience. Please reference PA07 in your application.

The Ohio State University is an equal opportunity/affirmative action employer. Qualified women, minorities, Vietnam era veterans and individuals with disabilities are encouraged to apply.

Send CV to:

Dr. Jay Zweier, 473 West 12th Avenue, Room 110, Columbus, Ohio 43210 or zweier-1@medctr.osu.edu.

EQUIPMENT

Do You Need Help in 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 rquine@du.edu

phone: 1-303-871-2419

For Sale:

ENI 3200L, ENI 3100L, ENI 320L, ENI 500L rf amplifiers.

Please address inquiries to:

eprequipment@chem.rochester.edu.

EPR Accessories and Supplies Available

We have some excess EPR accessories and supplies that might be of use to other labs. For example, we have a lot of chart paper, pens and ink for older recorders, and some spare parts and accessories such as VT Dewars for older spectrometers. If you need something for an older-style Varian or Bruker spectrometer, ask us – we might be able to help. Most items are available for shipping costs.

Gareth R. Eaton geaton@du.edu

For Sale: Varian Equipment

Resonance Instruments has available:

1. Replacement klystrons for Varian EPR bridges (at reduced prices) and other klystrons.

2. Varian V4500-41A low/high power microwave bridge with new klystron – excellent condition.

For more information on these units **please contact:** Clarence Arnow, President rii1@earthlink.net, 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.

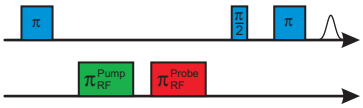
Please contact: James Anderson, Research Specialties, 1030 S. Main St., Cedar Grove, WI 53013, USA

phone/fax: 1-920-668-9905

e-mail: janderson36@wi.rr.com

Masterpieces in Multifrequency Pulse-ENDOR

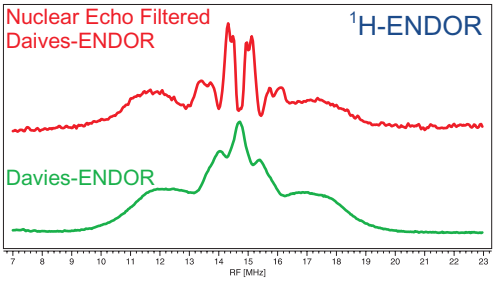
Demonstrated by Examples



X-Band

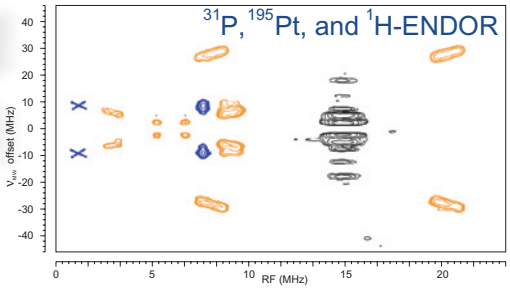
Techniques for Resolution Enhancement

T_{2n} Filtering



BDPA

Hyperfine Selective ENDOR

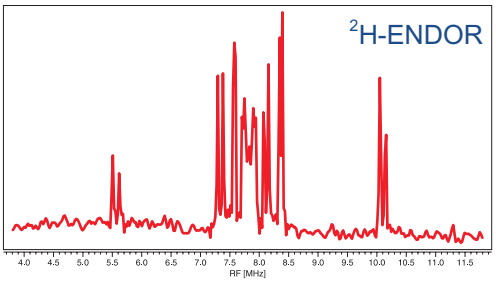


Bis(O,O'-diisopropyldithiophosphato-S,S')
Cu(II)/Pt(II) complex

Q-Band

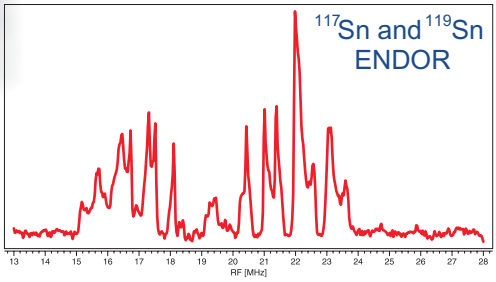
Higher EPR Frequency for Better Larmor Frequency Resolution

Low Frequency Nuclei



Squaric Acid Crystal

Isotopic Resolution

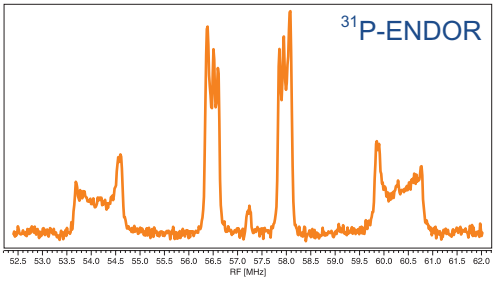


$VSnO_2$ in Collaboration with D. Murphy

W-Band

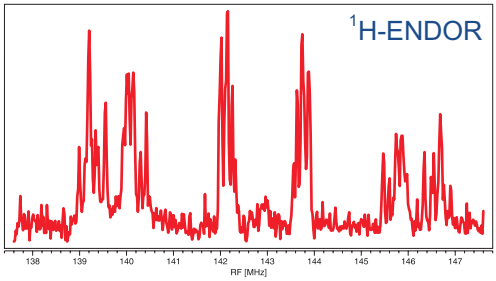
Limited Samples as Powders or Crystals

ENDOR Powder Patterns



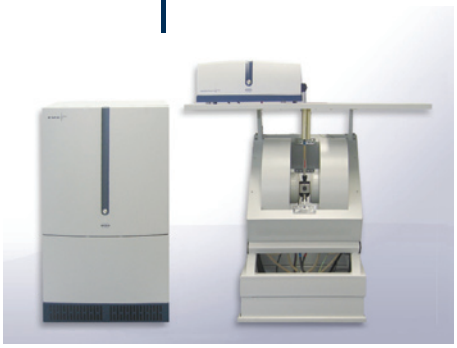
Bis(O,O'-diisopropyldithiophosphato-S,S')
Cu(II)/Pt(II) complex

Single Crystal Transitions



Diphenylnitroxide

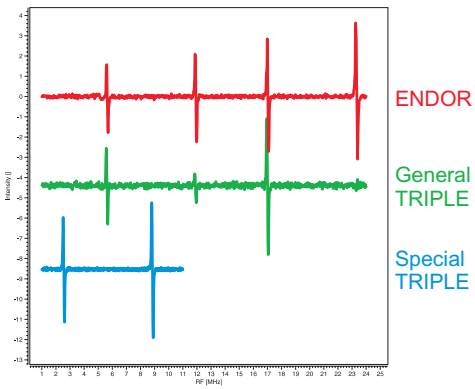
Explore the Possibilities of CW-ENDOR with the ELEXSYS & EMX plus



- Frequency and Amplitude Modulation
- RF frequency range 1-250 MHz
- ENDOR Induced EPR - EIE
- General and Special TRIPLE

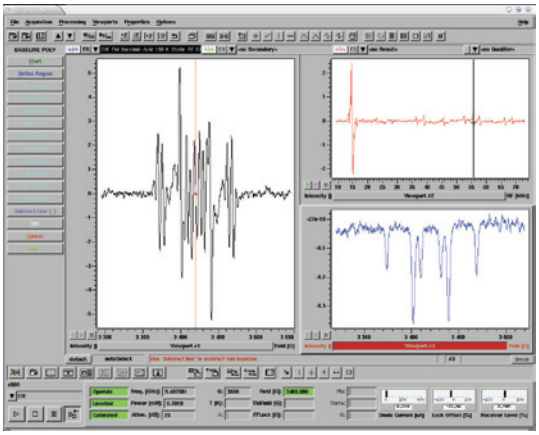
- Frequency Modulation
- RF frequency range 1-100

Untangle ENDOR transitions via TRIPLE

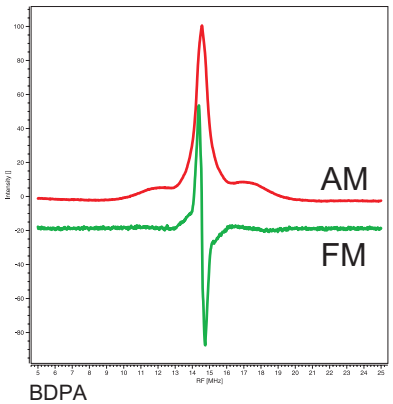


PNT

Software guides make complex experiments easy

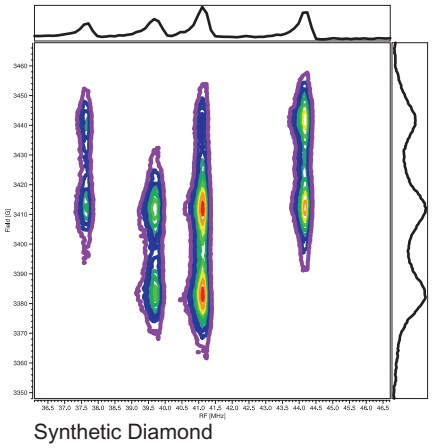


Enhance broad transitions with Amplitude Modulation



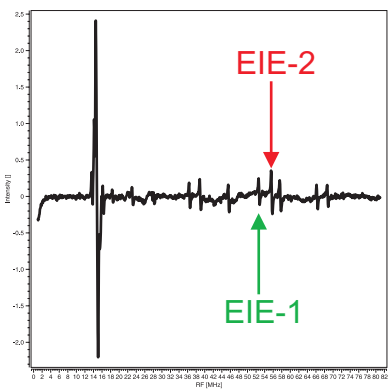
BDPA

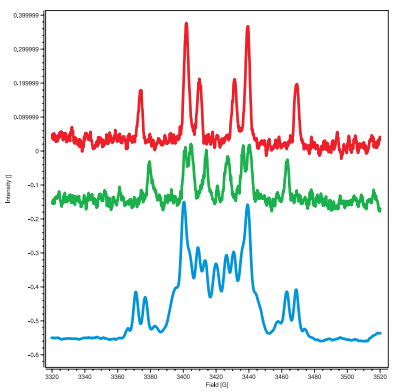
Assign ENDOR transitions to EPR transitions



Synthetic Diamond

Resolve individual EPR spectra based on ENDOR transitions





Succinic Acid Crystal