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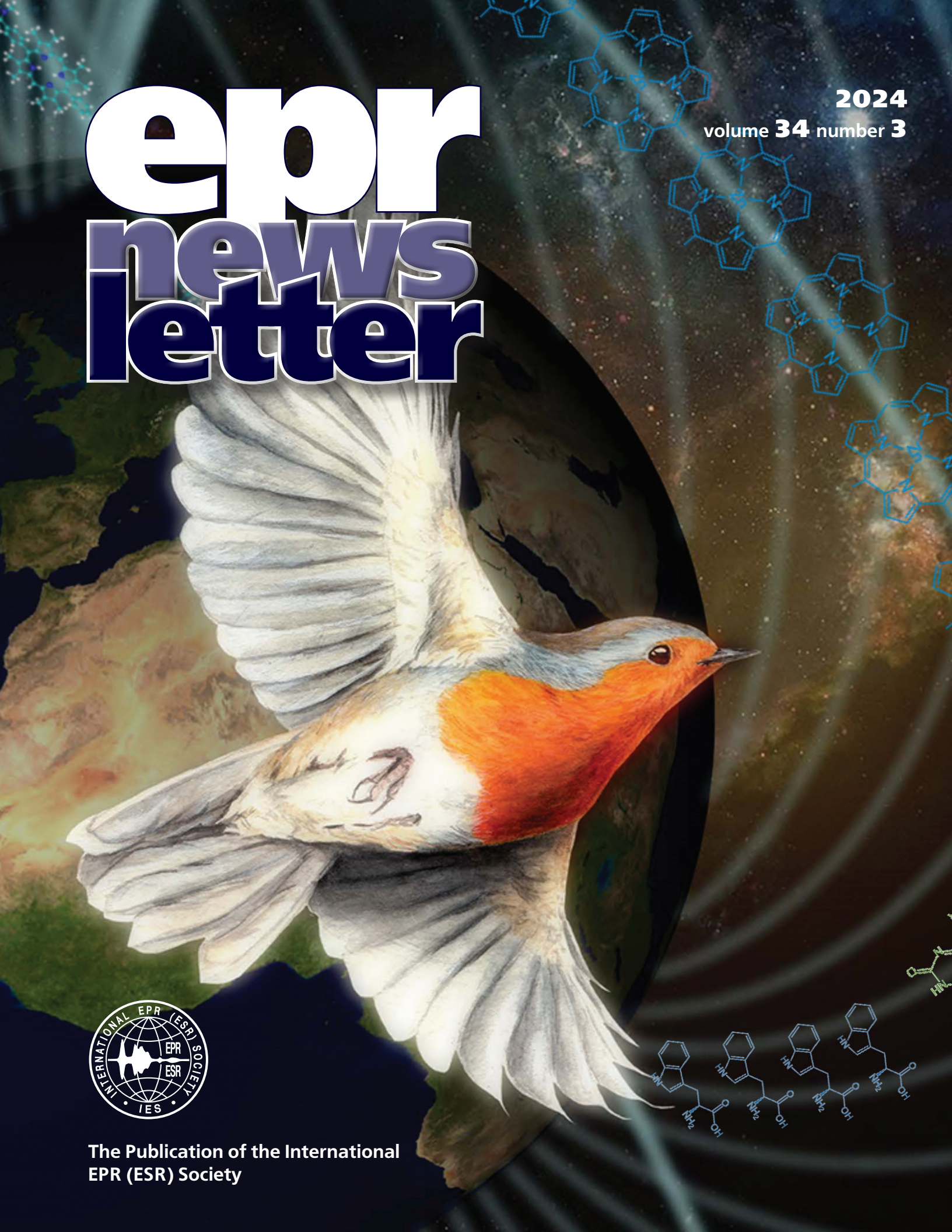

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Please feel free to contact us with items (news, notices, technical notes, and comments) or ideas for the *EPR newsletter*.

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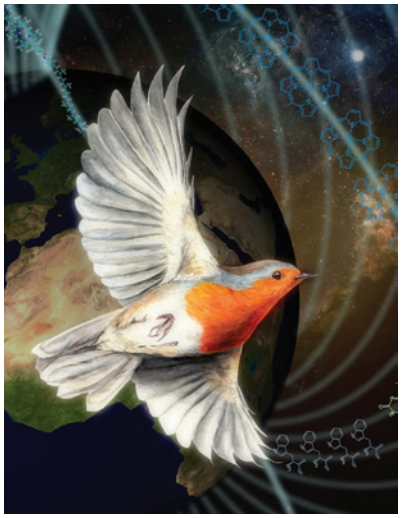

The cover picture illustrates some elements of the research of Christiane Timmel, recipient of the IES medal for Chemistry 2024.

The European robin in flight is a beautiful illustration by biologist Dr Corinna Langebrake. The robin is a night migratory song bird known to use the Earth's magnetic field to aid its annual migration. It was shown that blue light photoexcitation in the robin's Cry4a cryptochrome leads to formation of magnetosensitive flavin-tryptophan spin correlated radical pairs following rapid electron transfer down a tetrad of tryptophan residues (https://doi.org/10.1038/s41586-021-03618-9). Photo-induced spin polarization and directional field responses have also been demonstrated in artificial photosynthetic reaction centres such as the carotenoid-porphyrin-fullerene chemical compass (https://doi.org/10.1038/s41467-019-11655-2). Photoexcitation (or chemical reduction/oxidation) of other supramolecular structures such as molecular wires based on porphyrin structures allow quantification of spin delocalization in their triplet (or doublet) states (https://doi.org/10.1016/j.jmr.2017.01.005).

Cover illustration (montage): Corinna Langebrake, Ilia Solov'yov, Christiane Timmel.

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Editorial

Dear colleagues,

Did you have fun with the quiz I proposed in my editorial in the previous double issue of the *EPR newsletter* 34/1-2 (p. 2)? You may remember, you could guess whose research is illustrated on the cover of the current issue, prior to reading its cover legend. Well, did any of you succeed? I am looking forward to hearing from you. By the way, are you as charmed by this cover picture as I am? Surely, nobody could remain indifferent!

Yes, of course, as stated in the cover picture legend, it illustrates some elements of the research of Christiane Timmel, recipient of the IES medal for Chemistry 2024 (her interview, p. 7), but also it is a piece of art indeed... It illustrates Christiane's research in a very exquisite and romantic manner. Corinna Langebrake, Ilia Solov'yov, and Christiane Timmel did a great job with this montage. However, I would even say that in a wider sense, the beautiful bird in its free flight may also be considered to be a symbol of EPR in the prime of its 80 years of achievements and discoveries. There are no obstacles to the flight of thought of former and current researchers who devoted their lives to research in diverse fields of science using advanced EPR methods!

This boundless flight of thought is demonstrated in a comprehensive overview of the prospects of EPR and its glorious future given in the Letter of the President Marina Bennati and in interviews of former IES Presidents: Harold Swartz, Keith McLauchlan, James Norris, John Pilbrow, Wolfgang Lubitz, Jack Freed, Hitoshi Ohta, Lawrence Berliner, Klaus Möbius, Thomas Prisner, and Songi Han, supplemented by interviews of Gunnar Jeschke, President of the European Federation of EPR Groups, Jiangfeng Du, President of the Asia-Pacific EPR Society, and Frédéric Jaspard and Sylwia Kacprzak, representatives of Bruker BioSpin, IES Patron for 35 years (34/1-2, pp. 3, 4, 7–13). To keep a balance, in the current issue we offer the floor to the younger generation of EPR researchers, namely, to former IES Young Investigator Awardees starting from 2015: Ilia Kaminker, Claudia Tait, Sergey Veber, Fazhan Shi, Shunsuke Furuya,Thomas Schmidt, and Asif Equbal.

Wisdom and Experience Meet Enthusiasm and Passion!

To acknowledge the youthfulness of EPR and point toward even more exciting future developments, Gareth Eaton, Sandra Eaton, and Kev Salikhov announced a special issue of *Applied Magnetic Resonance* (Springer), Major Sponsor of the IES (p. 19). The special issue "Celebration of 80 Years of EPR Part I" is already published as volume 55, issue 9. Part II is under preparation. Bearing in mind the deadline for submissions of November 30, 2024, you may still have a chance to add your drop of honey to the common hive and share with the magnetic resonance community the results of your latest research by submitting your manuscript to this journal.

Not to forget, I hasten to reassure those of you who may have doubted our respect for our traditions when you did not find a traditional report on 57th Annual International Meeting of the RSC ESR Group in the list of content of this issue. Not to worry, Chris Wedge, RSC ESR Group Secretary, sent me this report and we will publish it in the forthcoming issue. However, we could not resist the temptation to give a spoiler and mention some of the bright moments of this conference, one of most important events in the life of the magnetic resonance community: awarding the Bruker Prize to Songi Han (see cover of 34/1-2), an interview with Jim Norris (first Lifetime Achievement Award in Spin Chemistry, pp. 9, 10), and awarding the JEOL Prize 2024 to Jörg Fischer (pp. 11, 12), to name a few.

Bye for now, we are working on the *EPR newsletter* 34/4, and you are welcome to join us with your EPR-related material!

Laila Mosina

Interviews with Former IES Young Investigator Awardees starting from 2015

EPR newsletter: Following interviews of former IES Presidents to mark the 80th anniversary of the EPR discovery by Evgeny Zavoisky and the 35th anniversary of the IES (*EPR newsletter* 34/1-2), could you please share with us your opinion about the future of EPR and the development of its applications and methods?

Ilia Kaminker,
IES Young Investigator Award 2015:

I want to share my thoughts on the future of high-field Electron Paramagnetic Resonance (EPR), which is a focus on my research group. Although high-field EPR has the potential to provide unique insights into various paramagnetic systems, it has not become as widespread as one might expect. This is primarily due to the complexity of the instrumentation required for high-field EPR.

Historically, high-field EPR experiments have always been conducted at the cutting edge of technology, and this remains true today, with high-field EPR largely being reserved for research groups and institutions capable of developing their own instrumentation.

Recent advancements in in high-temperature superconductors will allow soon for >50 T EPR-grade superconducting magnets potentially making ultra-high-field EPR experiments accessible beyond specialized facilities like the National High Magnetic Field Laboratory. Perhaps more importantly, these advancements will lead to the development of a new generation of affordable, liquid nitrogen temperatures, 7–20 T magnets, significantly lowering the barrier to acquiring a high-field EPR spectrometer.

A 50 T EPR experiment would require a ~1.4 THz frequency source. Steady progress in solid-state sources by Virginia Diodes Inc. has resulted in devices operating up to 1.5 THz, albeit with only a few μW of power output. Nonetheless, a standalone 50 T CW EPR experiment should become feasible in the near future. Still, accelerator-based experiments will likely remain the only viable option for fields beyond 50 T or in scenarios requiring higher power.

The future for high-field pulsed EPR, however, is more challenging. Pulsed EPR experiments require a high-power pulsed source with precise, sub-ns amplitude and phase control. At traditional EPR frequencies (X and Q-band), this has been achieved using traveling wave tube (TWT) amplifiers and, more recently, solid-state devices. While constant progress is made, none of these technologies is easily scalable to higher frequencies. Until recently, extended interaction klystrons (EIKs) offered a reliable solution for pulsed EPR up to ~9.5 T / 260 GHz. However, the end-of-production announcement by Communication Power Industries (CPI) for all EIK devices in July 2024 has dealt an unexpected blow to developing future high-field pulsed EPR instruments.

In conclusion, while the future of high-field and ultra-high-field CW EPR appears rather bright, the lack of high-power sources will continue to hinder the advancement of high-field pulsed EPR. This challenge highlights the critical need for close collaboration between researchers in THz device technology and experts in pulsed EPR instrumentation.

Claudia Tait,
IES Young Investigator Award 2016
(John Weil Award):

Two of the most fascinating aspects of EPR spectroscopy are what I believe will ensure it continues to be relevant and attractive in the future: its versatility in being able to address a wide variety of problems across scientific disciplines, and the diversity of aspects it encompasses, from instrumentation and method development to data analysis and simulation, which makes being an EPR spectroscopist so interesting. Future developments of EPR can luckily rely on a solid foundation developed since its inception 80 years ago and draw inspiration from how advancements in microwave and electrical engineering and information technology have been translated into improved EPR instrumentation and theoretical modelling capabilities, enabling new applications and a deeper fundamental understanding of spin physics. These advancements have continuously broadened the

range of applications of EPR spectroscopy and increased the amount of information that can be extracted on structure, properties and dynamics of a wide range of systems probed through the electron spin, allowing us to now work towards studying proteins in their native cell environment, unravelling catalytic reaction mechanisms by measuring paramagnetic states in situ and investigating spins in optoelectronic devices and batteries during operation, to give just a couple of examples. EPR spectroscopy is however still far from reaching its full potential in my view and there is plenty of scope to continue to push the boundaries of what can be achieved with this type of spectroscopy in all of its variants through further improvements in instrumentation, methods and theory, fully embracing opportunities provided by advances in electronics and computer science. Additionally, the development of clear procedures and guidelines for measurements and reliable data analysis and interpretation has the potential to facilitate the use of EPR spectroscopy beyond groups with extensive dedicated expertise and broaden its reach within the scientific community. With the ability to study ever more complex systems and gain ever deeper insights, EPR spectroscopy will continue to be an exciting field of research and an important spectroscopic tool across biology, chemistry, material science and physics.

Sergey Veber,
IES Young Investigator Award 2016:

I foresee significant advancements in the field of EPR spectroscopy, particularly in biomedical applications, the continued active use of EPR methods in studying catalytic processes, mechanisms of photoinduced charge separation in various media, and the investigation of molecular magnetic materials. The development of pulsed EPR spectroscopy methods, especially for biological and pharmaceutical applications, continues. Currently, EPR spectroscopy competes favorably with widely used methods such as FRET, often possessing several advantages. However, the widespread application of EPR is hindered by the high cost of equipment. In this regard, we may expect positive changes in the near future.

Collaborative efforts within the EPR community in the coming years could facilitate the transition of pulsed EPR spectroscopy from a narrowly specialized exotic method to a widely adopted mainstream tool for studying biological processes relevant to pharmaceuticals and medicine. This transition undoubtedly expands the community, bringing in more "users" – experts from biology and medicine. Although this may result in the loss of the community's compactness and its accompanying sense of closeness and familial atmosphere, I believe that breakthrough in biomedical applications for the benefit of humanity are what the EPR community should strive for diligently and focusedly.

My scientific interests are primarily focused on molecular magnetic materials. Given the practical importance of magnetism in today's high-tech world and the miniaturization of building blocks in almost every technology, there is no doubt that molecular magnetism, currently an active area of science, continues to be a hot topic with promising breakthrough applications in the future. Apart from its practical importance, it is fascinating and exciting to study the magnetic properties of matter at the molecular level. Although the prospects for the development of EPR spectroscopy in this area may not be as promising as in bio-EPR, the variability of research objects and the possible range of EPR methods applied make me enthusiastic. I have been fortunate to use both relatively standard X-, Q-, and W-band equipment and "exotic" high-frequency homebuilt spectrometers with frequencies up to 700 GHz, as well as EPR facilities equipped with synchrotrons and free-electron lasers. It is difficult to imagine such diversity for most other physico-chemical methods. And it is crucial to emphasize the broad possibilities for the further development of the EPR method, providing promising opportunities for young researchers starting their research in the field.

Fazhan Shi,
IES Young Investigator Award 2017:

Electron paramagnetic resonance (EPR) is a highly interdisciplinary research field with significant application value across various domains. Since the observation of the first EPR spectrum by Zavoisky in 1944, the development of principles, methods, and technologies has enabled its application in physics, chemistry, materials science, and other areas. Although EPR has not yet achieved the widespread clinical application as nuclear magnetic resonance imaging, recent research has focused on exploring radical changes in biological metabolism and monitoring physiological activities through reactive oxygen species. Advances in pulsed EPR technology have made it possible to detect molecular conformation changes through spin labeling.

Usually, EPR spectrometers require samples to be placed in a resonant cavity for measurement. Due to detection limitations, conventional EPR relies on ensemble averaging of signals from billions of molecules. Recently, microscopic magnetic resonance technologies based on diamond quantum sensing have enabled the detection of single-molecule EPR spectra. This technology combines the advantages of conventional EPR with single-molecule sensitivity, thereby opening up new frontiers for EPR research. Given the extensive work needed in both the development of technology and the exploration of application areas, we provided a detailed summary of the research progress, unresolved technical barriers, and application directions for this emerging field earlier this year in Reviews of Modern Physics on the topic 'Single-molecule scale magnetic resonance spectroscopy using quantum diamond sensors'. Here I will provide a brief overview of the core content closely related to EPR.

Over a past decade, the research achievements have demonstrated single-molecule EPR spectroscopy for spin-labeled proteins, peptides, nucleic acids, and an endofullerene molecule, vanadium-oxygen ions in solution. These achievements establish a foundational experimental basis for the development of single-molecule EPR technology. However, several technical issues remain to be addressed, including improving spectral resolution, measuring distances between different spin labeling sites on single molecules, in situ single-molecule detection in cells, and developing light-stable free radical labels. As single-molecule magnetic resonance technology matures, it will enhance the ability of EPR, yielding significant applications across physics, chemistry, materials science, and life sciences, together with conventional ensemble magnetic resonance. For instance, applications in biological research could include single-molecule conformational and dynamic measurements related to molecular interactions and functional changes, while single-molecule EPR measurements could offer ultra-sensitive molecular biomarkers for clinical diagnostics. I look forward to the participation of more outstanding young scholars in this research field, to advance EPR technology and its applications collectively.

Shunsuke Furuya,
IES Young Investigator Award 2018
(John Weil Award):

As a theoretical physicist familiar with quantum entanglement of strongly correlated quantum many-body systems but with none of the technical details of experiments, I maintain involvement in ESR, which has always been my favorite experimental technique. It seems to me that ESR spectra are just like an interesting intricate jigsaw puzzle where a beautiful picture emerges when solved.

I constantly search and investigate novel quantum phenomena arising when an infinite number of electron spins in the material collaborate or compete. The ESR spectrum can be a key to understanding the physical picture of such correlated quantum phenomena. However, ESR conceals the picture in a tricky way. The information about the intriguing phenomenon is encrypted in the ESR spectrum. We need to decrypt the signal and eventually figure out a clear picture of the underlying physical phenomenon.

Solving those intricate puzzles sometimes requires complex theoretical tools like quantum field theories. They are originally a language of elementary particle physics and nowadays a popular tool to figure out the physical picture of collaborative phenomena of infinitely many electrons in quantum materials. Quite naturally, quantum field theoretical approaches enjoy success in understanding ESR in quantum magnets.

The necessity of such complex theoretical tools arises from the complexity of correlated quantum phenomena in those materials. In the last decades, experimental and theoretical physicists have collaborated to obtain the physical picture. The puzzle is becoming even more complex for the close relation of quantum phenomena to recent technological advances such as quantum information and spintronics. Those developments will yield novel ESR

puzzles, which will be even more difficult but worth solving. It is easy to imagine that we need to invent another suitable theoretical tool to solve those puzzles. This time, the tool would involve a next-level collaboration with AI.

Thomas Schmidt,
IES Young Investigator Award 2021 (John Weil Award):

Pulse Electron Paramagnetic Resonance (EPR) is a powerful tool that complements other structural biology methods. It is particularly valuable for studying biomolecular systems that are challenging to analyze with traditional methods, such as large, multimodal, heterogeneous protein complexes. These systems often exceed the size limits for NMR, are too dynamic for X-ray crystallography, and too diverse for Cryo-EM. However, the further development of advanced pulse programs in EPR could enable detailed insights into protein-substrate interactions, including population distributions, distances, and local chemical environments. This would enhance our understanding of drug binding, molecular interactions, and their kinetics.

While many methods suffer from time averaging, pulse EPR offers the unique advantage of freezing samples, allowing it to bypass averaging and instead observe individual substates. This capability enables us to analyze heterogeneous samples that are otherwise challenging to study. Specifically, we successfully utilized the T1-edited DEER sequence to measure distances within monomer and dimer species of both the B1-adrenergic receptor and the nucleation unit of Huntington's protein. This demonstrates that relaxation-based edited pulse experiments are a powerful tool for addressing a broad range of biomolecular questions.

Perdeuteration of proteins has enabled the measurement of distances up to 160 Å, while also allowing for the site-specific introduction of protons, detectable through the Tm-edited DEER experiment. This technique has made it possible to study interactions between deuterated calmodulin and its protonated substrate. However, further advancements are needed to correlate the paramagnetic centers of the deuterated protein with distances to site-specific protons in the substrate. Achieving this would provide additional molecular constraints without the need for introducing more paramagnetic labels – only requiring the incorporation of protonated precursors during protein expression. Moreover, this method could be extended to other isotopes, such as fluorine labeling, paving the way for an isotope-filtering sequence prior to the Tm-edited DEER experiment, potentially rivaling NMR's 3D experiments.

In conclusion, pulse EPR holds great promise for the future of structural biology, as ongoing advancements continue to expand its ability to study biological systems that are otherwise inaccessible to traditional methods.

Asif Equbal,
IES Young Investigator Award 2022:

We are in the most exciting era for Electron Paramagnetic Resonance (EPR) research. With their unparalleled sensitivity, electron spins lie at the core of magnetic resonance techniques, offering unmatched precision in detecting and manipulating quantum states. Pulsed EPR has proven particularly successful in biological sciences, where it unravels the intricate dynamics of proteins using spin labels or endogenous metal centers. In material sciences, EPR is invaluable for studying catalysis, transition metal complexes, and semiconductors, providing crucial insights into their electronic structure, defect states, and reaction mechanisms. EPR influence extends beyond traditional materials and biological characterization into Quantum Information Science (QIS). Electron spins are playing a vital role in quantum sensing and spin-based quantum computing. The study of spin-orbit coupling, crucial for next-generation optic based quantum technologies, increasingly relies on EPR. In this pursuit, the integration of EPR with computational methods such as Density Functional Theory (DFT) and machine learning is enhancing the accuracy of spin dynamics predictions and driving the discovery of novel materials with unique quantum properties.

The synergy between EPR and Nuclear Magnetic Resonance (NMR) has unlocked new avenues, particularly through Dynamic Nuclear Polarization (DNP). This hyperpolarization technique has bridged the gap between the EPR and NMR communities, attracting a new generation of researchers working at the intersection of these fields. DNP not only enhances polarization but also offers electron-nuclear (hyperfine) correlation spectroscopy, broadening its impact beyond traditional applications.

The development of dual NMR-EPR detection instruments at high magnetic fields, even under magic angle spinning, has paved the way for exploring new classes of materials. This includes defect centers like NV-P1 in diamond and silicon carbide, which are critical for advancing quantum materials. Advances in cryogen-free magnet technologies and high-field EPR are enabling cost-effective, high-resolution studies at ultra low temperatures, pushing the boundaries of EPR research. One of the most exciting developments is the resurgence of light-activated EPR and DNP. Light-Activated DNP is particularly promising, as it can enable nuclear spin hyperpolarization by orders of magnitude, even at room temperature. Moreover, by harnessing the interaction of light with matter, it is possible to probe and manipulate spin states using optical detection. Integrated Optics-EPR-NMR can provide new insights into photocatalytic processes and the dynamics of light-sensitive materials, in general.

As EPR explores new frontiers, particularly with pulsed EPR, it is poised to play an increasingly vital role in various interdisciplinary research. The cross-fertilization between EPR and fields like quantum computing, spintronics, and energy storage makes EPR an indispensable tool for the next generation of research and technology development. The future of EPR is bright and it is the right time to embrace it.

Interview with Professor Christiane Timmel on the Occasion of Her IES Medal in Chemistry 2024

EPR newsletter: *Dear Professor Timmel, on behalf of the readers of the EPR newsletter we congratulate you on your IES Medal in Chemistry 2024. We are most appreciative that you agreed to answer the questions of this interview. Why did you start towards your career in science?*

I am so grateful to both my parents, a mathematician and a physical chemist, who nurtured my interest in science and maths from an early age. They were passionate about both their subjects and life. Later on, during my chemistry degree in Dresden I was taught by amazing academics, including Professors Salzer and Großmann who were truly inspiring teachers and scientists. The conscious decision to take up a career in science and academia was a mix of sheer love of the subject, the generous encouragement to do so by my family, especially my parents as well as my wonderful chemist husband and of course the support of my kind supervisors and colleagues especially Professors Keith McLauchlan and Peter Hore.

Who introduced you into magnetic resonance?

I was introduced to NMR first by Professor Großmann during my time at Dresden (where Gunnar Jeschke and I first met!). Gisbert Großmann was a passionate teacher, a brilliant scientist and above all a very kind and generous man. Of course, it was Peter who really inspired in me a love for all things electron spin and Keith who, very patiently indeed, supported my desire and first steps in building a spin chemistry and spectroscopy lab.

What are your main interests of work in magnetic resonance?

Anything involving spin is exciting, isn't it? A desire to understand spin effects in molecular wires, be they linear or cyclic, metal based or free base, in doublet or triplet states, has really driven much of our interest in the last years, work I have done with our wonderful collaborator Harry Anderson. And of course, systems evolving in time are really at the heart of much of what we do in the group. Photogenerated spin polarization, as studied by time resolved EPR, is therefore most attractive, especially if combined with optical spectroscopy. EPR is most powerful when it is not applied in isolation. It works best in a team, like scientists.

What is your opinion about the future of EPR and the development of its applications and methods?

Light induced EPR and spin polarisation effects have taken centre stage in much of today's work in the field of magnetic resonance be it in search for new phenomena in the world of quantum information science and quantum sensing or indeed in boosting the sensitivity and applicability of magnetic resonance in structure determination and reaction dynamics. I believe the playground of time resolved EPR is extremely versatile, full of surprises and still offers much as yet uncharted territory which we should explore both experimentally and theoretically. I am very excited about the future directions in which TREPR will take us.

What is your message to the young generation of magnetic resonance researchers?

It is the same message I would give to all young researchers: work on questions you find most exciting, be driven by curiosity not fast gains, look out for your peers, give them and those that have come before you credit where it is due. In the long run, your true worth depends on both, the science you do and how you treat those around you. Science is not a business. We should do it because we want to learn about our world, it is a team effort. Collaborate with people you trust and who respect you and, in return, treat them with the same respect, kindness and generosity. I believe everybody will win, science included.

Interview with Professor Hiroshi Hirata on the Occasion of His IES Medal in Instrumentation and Methods Development 2024

EPR newsletter: *Dear Professor Hirats, on behalf of the readers of the EPR newsletter we congratulate you on your IES Medal in Instrumentation and Methods Development 2024. We are most appreciative that you agreed to answer the questions of this interview. Why did you start towards your career in science?*

When I was an undergraduate student, I encountered news of the discovery of high-temperature superconductivity in 1986. Drs. Bednorz and Müller (IBM Research at Zurich) got the Nobel Prize in Physics next year for their significant breakthrough in discovering superconductivity in ceramic materials. After their discovery, newspapers and television programs reported a worldwide chase for a treasure hunt of high-T_c materials. That event had an impact on a young undergraduate student who was learning electrical engineering in a small college. In that time, I realized that scientific progress dramatically impacts our society. This event significantly motivated me to pursue graduate training and a Ph.D. Moreover, this event was a turning point in my career and in working in academic institutions.

Who introduced you to magnetic resonance?

As a Ph.D. student at Tokyo Institute of Technology, I studied ultrasonic actuators' analysis and design methods. In this field, I planned to become a junior faculty member in the Department of Electrical Engineering and Computer Science at Yamagata University, Japan. In those days, working as a postdoctoral fellow after a Ph.D. training was uncommon in Japan. A few months before I got my Ph.D., an official procedure for hiring a junior faculty had yet to start. However, I had no concerns and focused on my Ph.D. dissertation and defense. One afternoon in December 1992, I got a phone call from my former adviser at Yamagata University. He told me there was a hiring cancellation because of the department's situation. Then, I suddenly had concerns about my future employment. Also, he told me that Prof. Mitsuhiro Ono, in the same department, is looking for a candidate for a junior faculty. Before I met Prof. Ono, he was involved in a research project to build a low-field CW-EPR imager at 700 MHz for small animals (mice or rats). Originally, he had studied absorbing materials for microwaves. Therefore, he had a microwave engineering background. Although I did not know EPR, I visited his lab. Then, I had a laboratory tour to see his experiments and instruments. Also, he interviewed me. Since I worked in the field of ultrasonic electronics and was familiar with electromagnetic waves and wave equations, EPR instrument development was like my engineering home ground. In addition, I had another reason for feeling that EPR instruments were familiar to me. I had a license for an amateur radio station and played with VHF antennas for radio communications (it was before mobile phones became popular). Also, I was enjoying an electronics hobby, such as building audio amplifiers to listen to music. Finally, Prof. Ono offered me a junior faculty position in his department. I was fortunate to get a junior faculty position despite having no EPR experience. This accident of losing my expected position led me to the field of magnetic resonance. Later, I noticed that he developed a bridged loop-gap resonator (BLGR) for small animal experiments. For the BLGR, a paper by S. Pfenninger et al. published in Rev. Sci. Instrum. (1988) is well known. But this RSI paper cited a report of the BLGR by Ono et al. published in Chem. Lett. (1986) as an early work. Unfortunately, Ono's BLRG paper in 1986 has been less recognized because of the low global circulation of Chem. Lett. (The Chemical Society of Japan) before the Internet and electronic publication era.

What are your main interests in work in magnetic resonance?

In my early career, I was interested in the resonator development for low-field CW-EPR in 300 MHz to 1.2 GHz. My interest then included tunable resonators and frequency and matching (coupling) control techniques for compensating animal movement during EPR measurement. In 2003, I started work on low-field CW-EPR imaging at 650 MHz. Then, I was interested in fast EPR image acquisition. Until the mid-2000s, people thought CW-EPR imaging was a slow acquisition modality. It was right in those days. However, EPR imaging with fast magnetic field scanning (100 ms or less) has been beneficial in performing 4D spectral-spatial EPR imaging. Such data acquisition enables functional imaging using specific spin probes to measure the tumor microenvironment. In EPR imaging, there are technical challenges to enhancing the capability of EPR imaging for small animals and image reconstruction techniques. Since my background is in electrical engineering, instrument development and imaging techniques are my current research interests in magnetic resonance. In addition to the technical development, biomedical applications are very important for low-field EPR imaging of small animals. Meaningful and essential questions in biomedical applications lead to a new challenge in EPR imaging techniques. Therefore, my research interests now include measuring and visualizing parameters in the tumor microenvironment, such as the partial pressure of oxygen and extracellular pH.

What is your opinion about the future of EPR and the development of its applications and methods?

The developments and applications of EPR will continue to grow. However, EPR folks need to tackle challenging problems in their research fields. I mention three points about the future of EPR and its applications here.

(i) Numerical modeling and simulation: 40 years ago, the memory of a personal computer was less than 1 megabyte, and the CPU clock was 10 MHz. However, these days, the memory is tens of gigabytes, and multi-core processors operating at several GHz are standard in a personal computer or even in an Apple Watch. Like that, computing power has enormously increased in the last decades. One can process complex numerical modeling and time-consuming computing for EPR-related phenomena with high computing resources in the future.

(ii) New spin probes: In functional EPR measurement for biological problems, we always need powerful spin probes, specifically sensing target information. Suitable spin probes can expand new horizons in EPR applications. For example, triarylmethyl radicals such as OX063 or OX071 tremendously contributed to progress in low-field pulsed EPR imaging. Some new spin probes are being developed to expand the field of EPR biomedical applications.

These spin probes can precisely sense important information in the applications.

(iii) Materials science and technology: Materials science and technology are essential for EPR, in addition to biomedical applications. Quantum computing is a hot subject with much room for growth. Electron spins have a vital role in quantum computing and materials science. Therefore, EPR applications such as sensing electron spin in quantum devices and new functional materials continuously expand.

What is your idea of teamwork in science?

Teamwork is essential in conducting our research. Any group needs teamwork in their daily work. Even though my students have individual research projects, I always ask them to work as a team. This attitude enhances the strength of the group. Collaboration with other groups is another type of teamwork. For example, my expertise is in electrical engineering and instrument development. This strength in research can complement the strengths of biomedical or chemistry people. Historically, nuclear magnetic resonance imaging (MRI) and X-ray computed tomography (CT) have similar backgrounds. Dr. Paul Lauterbur (Chemistry Professor) and Sir Peter Mansfield (Physics Professor) were awarded the 2003 Nobel Prize in Physiology and Medicine for their discoveries concerning "magnetic resonance imaging". So, a chemist and a physicist invented MRI technology, which became a powerful tool for answering biomedical questions, such as patient diagnoses in clinics. Teamwork over different disciplines may generate a new field of interdisciplinary research.

What is your message to the young generation of magnetic resonance researchers?

Young magnetic resonance researchers should challenge the new problems that turn down common sense. Young researchers have much more energy and motivation than senior members. Ambitious studies by young researchers may break through the already established field. Another point I want to mention is to connect your expertise to other research groups or knowledge. That connection fosters multi-disciplinary projects that cannot be conducted by yourself alone. If you intentionally communicate with other researchers (not only EPR folks), it may give you new ideas or opportunities for new collaborations. Your research career is long, like a marathon in your life. So, young magnetic resonance researchers should keep energy and a positive attitude toward their research, even if it comes rain or shine in your project.

Interview with Professor James R. Norris on the Occasion of His Lifetime Achievement Award in Spin Chemistry

EPR newsletter: *Dear Professor Norris, on behalf of the readers of the EPR newsletter we congratulate you on your Lifetime Achievement Award in Spin Chemistry by the Royal Society of Chemistry ESR Group. We are most appreciative that you agreed to answer the questions of this interview. Why did you start towards your career in science?*

As a youth, I was interested in how things work, such things as toys, watches, bicycles, etc. Often, I took them apart and then attempted to put them back together thus learning how to make my own devices of interest. Since I was not allowed to purchase a BB gun, using the scientific method (at the time I just called it experimentation), I made a blow gun from electrical conduit, wire coat hangers, cotton balls, and glue. After several constructions and modifications, the blow gun was extremely powerful and far more dangerous than any commercial BB gun. The darts easily penetrated metal garbage cans. My wife says my mother had no idea what I was doing.

Who introduced you into magnetic resonance?

In 1959 I entered the University of North Carolina (UNC) to major in physics. Because calculus was not offered in my high school, a major in physics was not allowed. Consequently, I chose physical chemistry as my major.

In my third and fourth years at UNC my intention to attend graduate school was solidified by the excitement of participating in the research laboratory of Professor Richard C. Jarnagin where I zone refined anthracene. Jarnagin investigated excitons in anthracene single crystals grown from the melt and needed the highly purified anthracene provided by zone refining. The challenge to investigate nature at a fundamental level fascinated me. Jarnagin recommended both Clyde Hutchison at the University of Chicago or Sam Weissman at Washington University, St. Louis, both known for pioneering work in EPR. I chose Weissman who is a well-known pioneer of chemical applications of EPR. Weissman used EPR spectral line broadening and/or narrowing in aromatic free radical chemistry to measure electron exchange rates in liquid solutions. Using the same math and physical model that explored EPR spectral line broadening, my studies measured rotational rates of biradicals tumbling in liquid solution.

What are your main interests of work in magnetic resonance?

After graduate school I became interested in studying photosynthesis using EPR. The first light driven, chemical reaction in green plants and algae resulted in a free radical signal readily observable by EPR. A cation of chlorophyll a was proposed as the origin of the EPR signal in vivo. However, the EPR signal in the photosynthetic organism was narrower than the EPR signal observed in oxidized chlorophyll extracted from the organism by roughly the square root of two. Some investigators explained this difference in the EPR properties of extracted chlorophyll versus the signal in intact organisms as merely an environmental change. I believed the change in the EPR linewidth was too large since such large changes were not observed elsewhere. Instead, I proposed that two interacting molecules of chlorophyll, dubbed the "special pair", were involved in the first step of photosynthesis. Spin exchange between two interacting chlorophyll molecules resulted in a decrease in the linewidth by the observed square root of two. The resulting general model was that the line width decreases by the square root of the number of interacting molecules. For about ten years this model was not fully accepted until the x-ray structure of the photosynthetic reaction center revealed

The larger dog is a 2 year old Labrador Retriever named Crystal. The smaller dog is a 4 month old Australian Shepherd named Daisy.

two closely interacting molecules as the primary donor of photosynthesis.

While defending the "special pair" model, a triplet state with an unusual EPR spin polarized pattern was discovered by Leigh and Dutton in photosynthetic systems with the normal electron transfer chain blocked. I immediately realized the observed spin polarization pattern was not from the typical intersystem crossing of aromatic molecules but instead was from the chemistry of reverse electron transfer that preserved spin angular momentum. Understanding and using the unusual "spin" pattern of this triplet was the basis for new spectroscopic methods to study photosynthesis and other chemical systems.

What is your idea of a teamwork in science?

Using spin chemistry to study the photosynthetic process in green plants and algae involved extensive teamwork and collaboration from many different, talented individuals over many years. In general teamwork is the key to successful research. I am thankful for such teamwork, otherwise my studies on spin chemistry would have been impossible. Also, I experienced that collaborating with competing research teams can sometimes be fruitful and enjoyable. My personal experience during the ten years the "special pair" model was questioned at every scientific meeting serves as an example of defending one's research despite adversity.

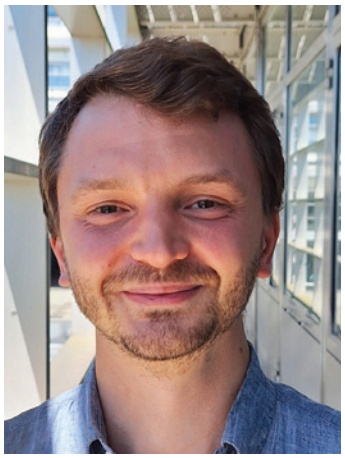
What is your message to the young generation of magnetic resonance researchers?

Identifying and understanding the fundamental principles of a problem cannot be overestimated. EPR is a fundamental technique and as such cannot be discarded. Consequently, the future of EPR and techniques under the EPR umbrella are secure. Also, new advancements in instrumentation coinciding with the availability of commercial EPR ensures unusual opportunities in areas not yet explored extensively by EPR.

What is next after the Lifetime Achievement Award in Spin Chemistry?

Some ten years ago, I retired to live in a rural area in the mountains of North Carolina far from the big city of Chicago and its hectic pace and traffic. I now enjoy fly fishing, photography, woodworking, vegetable gardening, two dogs and beautiful sunsets. I certainly was not thinking about spin chemistry even though it was a very important part of my life for 45 years. Consequently, this lifetime achievement award in spin chemistry was totally unexpected and an honor for which I am very grateful.

JEOL Prize 2024



Jörg Fischer:

First, I would like to thank the RSC ESR conference organizers and JEOL for allowing me to present my work at the 57th Annual International Meeting of the ESR Spectroscopy Group of the Royal Society of Chemistry at the University of Warwick. I felt honored to contribute to the JEOL prize talk competition in 2024 alongside Janko Hergenhahn, Yue Ma, Yasmin Ben-Ishay, Stuart Mathieson Graham, Arianna Actis, Maximilian Mayländer and Sergei Kuzin.

The conference series has been a personal highlight and a source of motivation throughout my PhD. I always enjoy the mutual scientific exchange and the high quality of scientific presentations, as well as meeting the EPR/ESR community. During my PhD, I focused on method development and the application of EPR spectroscopy for monitoring catalysts under reaction conditions while detecting product formation or educt consumption, often referred to as operando spectroscopy. My work primarily involved Cu-exchanged zeolites for methane-to-methanol conversion, and later, I became interested in N_2O conversion over Fe-exchanged zeolites [1, 2]. These projects require rather unusual conditions for EPR measurements, such as high temperatures up to 773 K and pressures ranging from high vacuum to 10 bar. One consequence of the high temperature is that the signal-to-noise ratio is typically very poor, limiting the time resolution of the measurements due to the need for signal averaging. This often prohibits elucidating the relevant kinetics of the typically very broad EPR spectra of the metal sites under investigation. However, this limitation can be circumvented, at least for fully reversible reactions, by applying modulation excitation spectroscopy with phase-sensitive detection (MES-PSD). This concept, originally introduced in IR-spectroscopy about 20 years ago, is based on the idea of periodically perturbing the system by an external trigger, such as concentration, light, electric potential, temperature, or pressure [3]. The periodic switching between different gas compositions allows for accumulating a large number of reaction cycles. The averaging of these cycles improves the signal-to-noise ratio without losing time resolution, as the signal-to-noise of an individual cycle is not important. Since the frequency and phase of the perturbation are known, data treatment analogous to a digital lock-in amplifier can be applied to further increase the sensitivity for the species undergoing reversible changes during the reaction cycle.

The work I presented in the JEOL competition session focused on implementing MES-PSD in EPR spectroscopy and its first application to Fe-containing zeolites for N_2O decomposition. For this reaction, we alternated an N_2O-containing gas feed for the oxidation of the Fe sites with a CO-containing gas for the subsequent reduction of the Fe centers. The measurements allowed us to elucidate the active center for N_2O decomposition over Fe-containing zeolites. In agreement with previous reports, the active site is a square-planar Fe(II) site in beta-cationic positions where N_2O activation and the related redox cycle take place [4]. The recorded apparent activation energies for both reduction and oxidation are in good agreement with activity tests, allowing us to correlate our spectroscopic findings with bulk activity. Furthermore, we showed that time resolutions of about 10 ms, even for broad Fe(III) spectra typically found for Fe-exchanged zeolites, could be achieved by recording the spectrum first along one field position and then, subsequently in synchronization with the trigger, advancing the field. This allows for measurements on the same time scales and signal-to-noise ratios typically achieved with other spectroscopic tools such as X-ray absorption, IR, and UV-Vis spectroscopy.

I want to thank the organizing committee of the 2024 RSC EPR conference for awarding me this prize and JEOL for their generous sponsorship. Furthermore, I want to express my gratitude to Gunnar Jeschke for his supervision and mentorship over the last four years. I greatly appreciated the freedom I had in pursuing my research and the trust he placed in me. None of the work I presented would have been the same without the many fantastic collaboration partners I had the joy of working with. Therefore, I want to thank Hugo Karas, René Tschaggelar, and Oliver Oberhänsli from our group, as well as Andreas Brenig, Vitaly Sushkevich, Jeroen van Bokhoven, Filippo Buttignol, David C. Cano-Blanco, and Davide Ferri.

1. J.W.A. Fischer et al., Angew. Chem. Int. Ed., 62 (2023), Article e202303574
2. J. W. A. Fischer et al., Catal. Today 2024, 429, 114503
3. A. Urakawa et al., Chem. Eng. Sci., 63 (2008), pp. 4902-4909
4. M. Bols et al., Nat. Catal. 4 (2021) 332

Gunnar Jeschke:

Jörg Fischer joined my group in October 2020 coming from University of Konstanz. There and in Stefan Stoll's group in Seattle he had already gathered experience with EPR spectroscopy. Focusing on continuous-wave (CW) EPR, his project is rather unusual in

my group. It is also a "tandem project", involving close collaboration with a doctoral student from another research group, who works on the same application with other techniques. Whereas tandem projects are rather common in my group in molecular biology, this is the first such project in catalysis. Jörg developed new methodology for separating active paramagnetic species from "bystander" species in heterogeneous catalysis. To prove catalyst activity, he applied operando spectroscopy. In this approach, EPR spectra are measured while the catalyst is at work. Simultaneously, the reaction is monitored by on-line observation of the consumption of reactants or the formation of products.

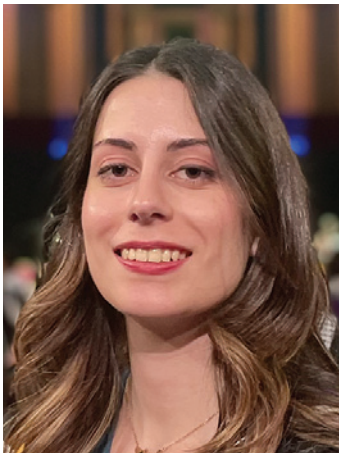
Whereas operando EPR spectroscopy already existed, Jörg pioneered modulated excitation EPR spectroscopy. This involves periodically switching the reaction gas composition and analyzing the spectra by digital phase-sensitive detection. Thus, Jörg suppressed not only signals from bystander species, but also noise. I remember him sitting at the table in my office and explaining the outcome of the only one-week long first measurement campaign with his setup. The results exceeded my expectations by far.

To arrive at this point had not been easy. Although Jörg could profit from the experience of several collaboration partners at Paul Scherrer Institute with other operando spectroscopies, the need for a microwave resonator in EPR spectroscopy complicated things. Among else, Jörg optimized the gas flow in our home-built high-temperature resonator and designed a fitting digitally controlled reaction gas line. Probably due to the Covid pandemic, the digital mass flow controllers had a lead-time of 17 weeks. This is not at all negligible on the time scale of a doctoral thesis.

Not only did Jörg strongly push his main project, his curiosity drove him to apply his skills in related side projects. At some point, I became worried that he might open too many lines of research in parallel. However, Jörg coped well with all what he had put on his own desk. A side-project highlight is a robust CW EPR Q-band (35 GHz) resonator that accepts the same 3 mm outer diameter tubes that we use in X-band. In applications to heterogeneous catalysis, where you wish to measure exactly the same sample at different frequencies, this is important.

Besides, Jörg is a good ambassador of EPR spectroscopy in the field of catalysis. He knows that data from complementary techniques is required in this field. Without my prompting, he immersed himself into synchrotron measurements. In fact, he lobbied me so that he could apply for beam time at the European Synchrotron Radiation Facility in Grenoble – and he got it approved. I am very happy that Jörg Fischer found recognition from the EPR community through the JEOL Prize 2024.

IES Poster Prize at the 2024 RSC Meeting Warwick



Angeliki Chatziathanasiou:

First of all, I would like to thank the International EPR (ESR) Society for awarding me the IES poster prize at the 57th Annual International Meeting in Warwick. The conference was a wonderful opportunity to learn more about advanced EPR studies and discuss my fellow scientists' outstanding work. I would also like to thank my supervisor, Dr. Maxie Roessler, and the members of the Roessler group, who are my daily inspiration and the actual proof of the wide variety of EPR applications in biophysics, chemistry, materials, and biology!

Climate change and the vast increase in Earth's population have become primary issues, forcing humanity to face the global food crisis. To fulfil the demand for higher food quantity and quality under the pressure of varying environmental conditions, research efforts are focused on the development of agrochemicals such as herbicides, to improve the viability and efficiency of agriculture. However, the overuse of such herbicides has led to the build-up of resistances as well as introducing a negative impact on human health. In my project, we are working towards sustainable agriculture, by investigating a novel herbicide target, photosynthetic complex I (PS-CI), and its quinone-binding site. This unique enzyme (also known as NADH dehydrogenase type-1, NDH-1) creates additional proton motive force to power ATPase and boosts the ratio of ATP:NADPH, when the cellular energy demands are high. Additionally, I am drawing on my group's experience and expertise with respiratory complex I (R-CI), PS-CI's homolog in the respiratory chain, which shares significant similarities in both structure and function and is much better understood.

The presence of unpaired electrons in the photosynthetic mechanism makes electron paramagnetic resonance (EPR) the method of choice for structural and functional studies on photosynthetic systems. Despite the complexity and size of our enzyme of interest, EPR spectroscopy can focus on the paramagnetic centres and specifically investigate the interactions of quinones and potential herbicides within the active site.

In my poster, I was able to demonstrate several preliminary, but crucial results of my project: The first step was the purification of photosynthetic complex I in large scale, using a 12 litre photobioreactor. Then, I worked towards creating an activity assay to observe and quantify the activity of PS-CI directly – perhaps surprisingly, there is currently no way of knowing how active the enzyme is! For this purpose, PS-CI was successfully reconstituted for the first time in a lipid-bilayer system (namely protein containing liposomes) in order to investigate the activity in a native-like environment. The system can be further developed to provide an insight on the quinone turnover and proton pumping activity of PS-CI. Then, CW and pulsed EPR measurements were used to verify the identity of PS-CI, by detecting the three Fe-S clusters of the complex and comparing their g values with the literature. CW-EPR spectra were also recorded in the presence and absence of two known inhibitors of R-CI, piericidin A and diflumetorim, to explore their inhibition potency on PS-CI. The diminished intensity of the Fe-S cluster EPR spectra suggests that both compounds inhibited the complex, with diflumetorim causing greater inhibition. I could quantify the extent of inhibition using a Bruker EMX spectrometer, equipped with a high sensitivity resonator and a Cryogenic closed-circuit Helium cryostat (Centre for Pulse EPR, PEPR, at Imperial College London). Once I have a working activity assay, I plan to supplement these spectroscopic results with biochemical data. In the future, I plan to employ pulsed EPR techniques in ▶

the presence of various quinones (the natural substrate, R-CI inhibitors, and spin-labelled compounds), aiming to unravel their binding mechanism and bonding interactions withing the active site pocket.

In conclusion, in my PhD I am hoping to understand the fundamental catalytic mechanism of photosynthetic complex I, which couples electron flow through the Fe-S cluster to proton translocation across the thylakoid membranes. This understanding will arise from unraveling how quinones (both natural substrates and inhibitors) bind and get reduced in the Q-site, as well as quantifying and getting a detailed picture of the impact of different inhibitors on PS-CI activity. In the longer term, we aim to use our knowledge to improve the agrochemical industry and to design a new generation of more sustainable herbicides.

Lastly, I would like to thank Imperial College London and the Institute of Chemical Biology – Centre for Doctoral Training for providing me the opportunity to pursue my PhD, as well as the EPSRC and Syngenta for the funding.

Maxie Roessler:

Angeliki joined my research group on a very competitive scholarship from the Centre of Doctoral Training in Chemical Biology in October 2022 after completing her Master and Bachelor in Chemistry at the University of Crete. Before coming to Imperial, she already had a strong interest and background in photosynthesis, having worked on hydrogen production by photosynthetic bacteria. Yet, EPR spectroscopy was completely new to Angeliki, as were the challenges of growing and isolating a very complex membrane protein! During her MRes year (her PhD program is a 1+ 3 year program), she more than rose to these challenges, winning the prize for the overall best plant-based MRes project.

From the outset, I was very impressed by Angeliki's independence. She took ownership of her project from day 1. Briefly, the project goal is to understand the quinone binding site and potential inhibitors of photosynthetic complex I, an enzyme that can increase ATP production in plants. This is interesting from a fundamental perspective (since we don't know how this enzyme works yet) and of potential interest for agriculture, as discovery of new inhibitors of this enzyme could lead to new and more sustainable agrochemicals. The project requires diverse skills, from challenging biochemistry to biophysical techniques and, of course, EPR spectroscopy. As the project is co-funded by Syngenta, Angeliki needs to liaise with our industrial collaborators and she does this every effectively. For example, she convinced me that we need to look into docking programs seriously in order to predict how inhibitors will bind in the enzyme that she is investigating and tailor our EPR-based approach. This approach – not least thanks to Angeliki finding the 'right' people to talk to at Syngenta – is now looking very promising.

Angeliki is still relatively early on in her PhD project and there is much EPR spectroscopy still to come. However, having overcome the significant challenges enabling her to purify photosynthetic complex I effectively in house, she is now in an excellent position to do so. The IES poster prize is a highly deserved recognition of Angeliki's hard work, independence, and creativity – but also her enthusiasm and positive energy! I look forward to mentoring her over the remaining years of her PhD.

IES Poster Prize at the 2024 RSC Meeting Warwick

Lucca Sielaff:

This year's RSC EPR conference in Warwick will remain a special memory for me. Not only because it was my first RSC conference, but also because I had the honour of receiving the IES poster award for my work on time domain ENDOR experiments. I want to express my gratitude to the IES for awarding me this price. It was a great pleasure to share my research findings with the EPR community during the conference and I am delighted to have the opportunity to do so in this newsletter.

My work is centred around the development of new experimental methodologies in EPR spectroscopy, in particular focusing on advancing Electron Nuclear Double Resonance (ENDOR) techniques. Recently, ^{19}F-ENDOR spectroscopy has emerged as a powerful tool in structural biology, allowing distance determination in the range of 6–15 angstroms [1]. Established pulsed ENDOR experiments use a selective radio frequency (RF) pulse whose frequency is varied stepwise to detect the ENDOR spectrum. This experimental approach is susceptible to power broadening, depending on the duration and power of the used RF pulse. While longer RF pulses cause less power broadening, they compromise sensitivity by reducing the number of participating nuclei in signal formation. Time domain (TD) ENDOR experiments circumvent this problem by using strong, non-selective RF pulses to detect the free evolution of nuclear coherence [2]. Subsequent Fourier transformation of the recorded time trace yields the ENDOR spectrum. Despite the advantage of increased resolution and sensitivity, TD ENDOR experiments have been rarely used in the past, due to the narrow excitation profile of commonly used RF pulses. In my poster, I showed how TD ENDOR can be used for ^{19}F ENDOR distance measurements. I recorded TD ENDOR traces of nitroxide model systems containing a fluorine nucleus at a distance of about 1 nm from the radical. Fourier transformation of the recorded time traces yielded nearly noise-free ENDOR spectra, showcasing the superior sensitivity of the experiment. Since TD ENDOR experiments are unaffected by power broadening, the intrinsic ENDOR line width can be analysed in more detail. Understanding the intrinsic ENDOR line width is crucial for extracting distance distributions from ENDOR data. Additionally, the ENDOR line width sets a resolution limit for long-distance measurements. A comparison of the TD ENDOR traces of fully deuterated and partially deuterated model compounds revealed that intranuclear dipolar coupling between protons and the fluorine nucleus is a major contribution to the intrinsic ENDOR line width. To evaluate the data, I used a home-written density-matrix-based simulation routine developed by Annemarie Kehl, that allows us to explicitly include interactions like chemical shift anisotropy and intranuclear dipolar coupling into the simulations. Additionally, we performed SEDOR ENDOR experiments, a triple resonance method that allowed us to directly measure the intranuclear dipolar coupling. To

our knowledge, SEDOR ENDOR has only been performed for single crystals so far [3].

In conclusion, I introduced TD ENDOR for ^{19}F-ENDOR distance measurements and showed the advantages of the method. However, we are only starting to explore the possibilities behind TD ENDOR and related experiments. In the future, we hope to extend the resolution limit of ^{19}F ENDOR distance measurements using TD ENDOR and gain further insights into nuclear spin dynamics.

Last but not least, I want to thank my supervisor Marina Bennati for her continuous support and Annemarie Kehl and Andreas Meyer for their contributions to this work.

1. A. Meyer et al. Angewandte Chemie International Edition 59.1, 2020, 373-379.
2. C. Gemperle, A. Schweiger. Chemical reviews 91.7, 1991, 1481-1505.
3. H. Thomann, M. Bernardo. Journal of the American Chemical Society 118.24, 1996, 5806-5807.

Marina Bennati:

I was excited to read the news of Lucca's IES poster award received at the RSC in Warwick. Lucca did his Master in physical chemistry and EPR spectroscopy at the University of Freiburg. I was delighted that he decided to join my lab in Göttingen during the summer 2023. Lucca started exploring time domain ENDOR for distance measurements with ^{19}F and immediately realized the subtle experimental issues related to pulse sequence and data analysis. These needed to be carefully addressed in order to record undistorted ENDOR spectra. Taking advantage of available model systems and a great interaction with other group members, he has been able to push the method and demonstrate its superior performance as compared to conventional frequency domain ENDOR. Lucca is an excellent motivated student with skills in experimental work as well as in magnetic resonance theory. He is also very engaged in teaching students and a friendly team player. For his performance, he has already received several distinctions, among others the German Steinhofer Prize 2023, the Best Thesis Award for talented students at the Freiburg Faculty of Chemistry and Pharmacy, as well as a competitive PhD Fellowship from the Göttinger Max Planck Research School for Physics of Biological and Complex System. Since his PhD is only in its first stage, I expect and look forward to many interesting developments! I would like to congratulate him on all his achievements and the well-deserved poster award.

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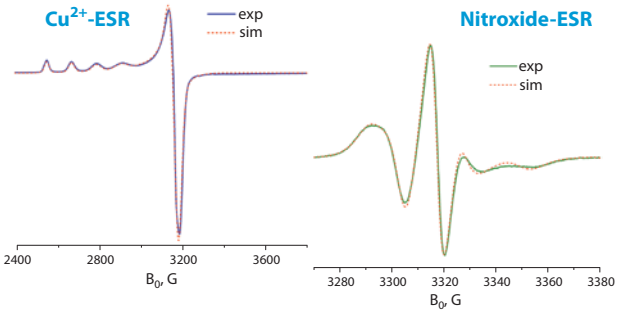
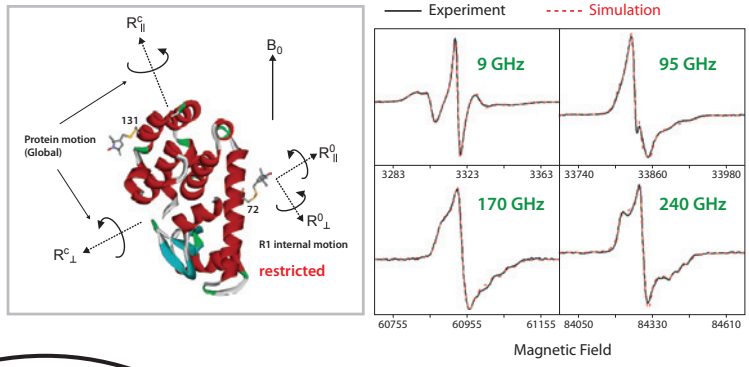
ESR Spectral Fitting



Multifrequency ESR



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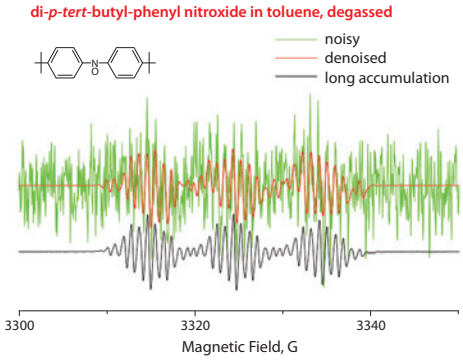
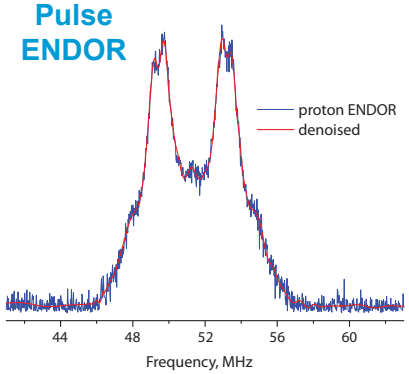


1) Perform
ESR Measurements
2) ESR Data Analysis
3) Advice on
ESR Experimental Design
4) Standard Samples
5) Contact Info Above

Pulse ENDOR



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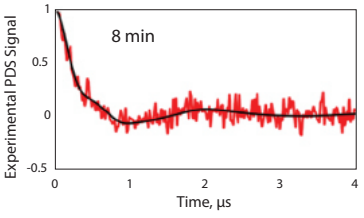

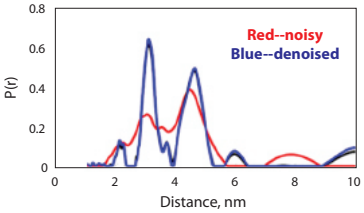

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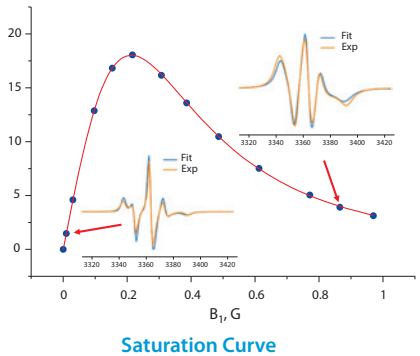
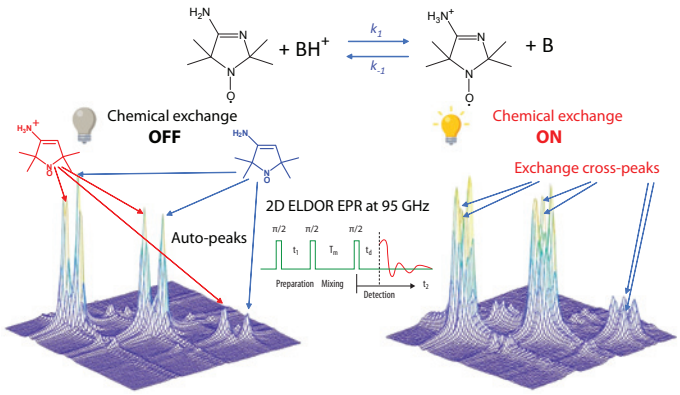


Saturation Curve

2D ELDOR



EPR Spectroscopy in Quantum Information Science

Alvaro Montoya, EPR Applications Scientist
Bruker BioSpin Corp., Billerica, MA

Quantum Information Science (QIS) is a vastly growing field of research in modern day science. What started as a far-reaching concept several decades ago, quantum research has now culminated into what many consider to be the "second quantum revolution". Researchers are now interested in exploiting the properties of quantum mechanics, such as superposition and entanglement, for practical use in real-world applications. Some of these include quantum computing, sensing, and communications. Successful fabrication and implementation of quantum devices will have monumental impacts on research, medicine, commerce, weather reporting and many other areas. The central component that makes this all possible is the quantum bit, or "qubit", and it is the basic unit of information in quantum computing (Figure 1). Unlike the classical bit, which can only occupy the states 0 or 1, the qubit can be in state 0, 1, or a superposition of both states at any given time.

This makes the qubit far superior to its classical counterpart because of its inherent ability to occupy a much larger state space. As a result, computational speeds can be dramatically increased, allowing for calculations that were virtually impossible with classical computers now very much possible using quantum computers. For a qubit to be considered viable for quantum applications, it must fulfill the well-established DiVincenzo criteria, which denotes necessary properties for qubits candidates [1]:

1. It must be initialized in a well-defined quantum state (e.g. a two-level system such as a nucleus or electron)
2. The superposition lifetime, or coherence time, of the qubit must be long lived
3. It must satisfy a set of universal quantum logic operations
4. It possesses a readout mechanism

Currently, there are several types of materials employed as qubits that fulfill this criterion and are used in quantum computers. Some of them include superconducting materials based on the Josephson effect (transmon qubits), trapped ions, and quantum dots. These all exhibit very long coherence times and are relatively scalable. However, they must be operated at extremely low temperatures or under high vacuum conditions for efficient performance [2]. Defect centers, such as nitrogen vacancies in diamond, have also gained consideration as qubits for quantum sensing due to their ability to be optically initialized and appreciable coherence times at a wide temperature range. However, it is difficult to produce defect centers in a controlled manner where they can be individually addressed. A new class of qubits have emerged for integration into quantum technologies in the form of molecular qubits. Rational design and chemical synthesis provide researchers with a vast playground to assemble qubits from top-to-bottom [1, 3]. Atoms can be arranged with precision and the electronic properties can be tuned accordingly. Electron spins in molecules as qubits are quite attractive since they are a natural two-level system (spin-up and spin-down) and are easily manipulated using microwave irradiation. For this reason, EPR spectroscopy has become a critical technique in identifying viable molecular electron spin qubits (MESQ). EPR spectroscopy allows for the unambiguous detection of unpaired electron spins, whether free radicals, transition metals, rare-earth ions, or photo-generated excited state systems, all of which are being investigated as potential qubits. In particular, pulse-EPR provides a wealth of information that is vital in determining MESQ systems that can be implemented into quantum technologies [4].

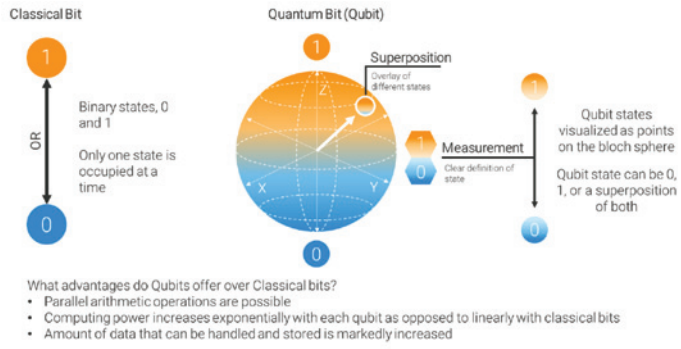


Figure 1: Comparison of the classical bit to the quantum bit, or "qubit".

I. Coherence and Sources of Decoherence: Relaxation Measurements

The coherence time is the chief figure of merit for a qubit to be considered feasible in a quantum device. It is imperative to preserve the superposition of the two-level system and reduce sources of noise that can disrupt it. Determination of T_2, the spin-spin/transverse relaxation time or coherence time, has become a focal point of EPR studies for MESQ's and Pulse-EPR provides direct access to this parameter. This is achieved by using a Hahn echo decay sequence, where the echo amplitude is monitored as the delay between the pulses is increased. It is also important to understand the spin-lattice relaxation (T_1) of the system, as this can provide information on other sources of decoherence, such as spin-phonon couplings. Determination of these parameters and what properties of the molecule or assembly contribute to decoherence is essential in all MESQ studies.

Zadrozny and co-workers showed excellent coherence times on a Vanadyl qubit system, $[V(C_8S_8)_3]^{2-}$ (Figure 2) [5, 6]. T_2's of almost a millisecond were achieved through the synthesized molecules in combination with different solvents and low temperatures. Large improve-

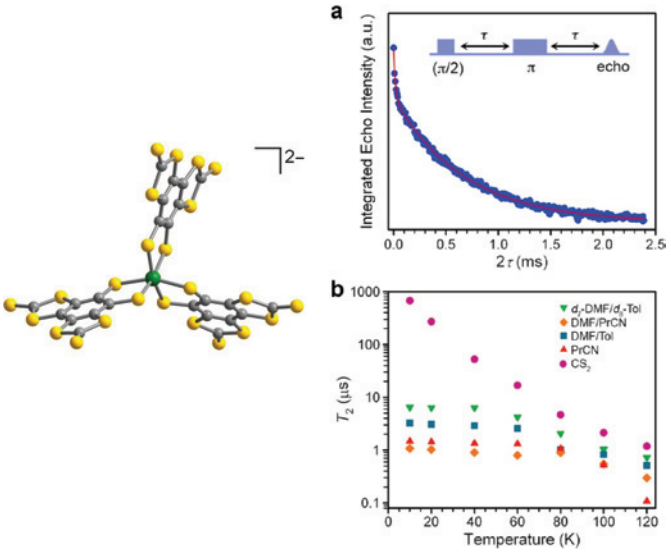


Figure 2: Structure of $[V(C_8S_8)_3]^{2-}$ (left) and corresponding T_2 data (right). Time domain data is shown fitted with a biexponential decay (a) while T_2 relaxation times of $[V(C_8S_8)_3]^{2-}$ are shown using different solvents and at varying temperatures (b) [5, 6].

ments of coherence times were achieved using CS_2, a nuclear spin-free solvent, displaying how the presence of magnetically active nuclei in the qubit environment contributes to decoherence.

II. Coherently Drive Spins: Rabi Oscillations

Another phenomenon of significance in a qubit candidate is the presence of Rabi oscillations. An electron spin showing oscillations in the time domain of Rabi type demonstrates coherent control over the system. In other words, the electron spin can be successfully placed in an arbitrary superposition of its quantum states. Observation of Rabi oscillations is achieved with pulse-EPR through the transient nutation experiment. Subsequent Fourier Transform (FT) of the time domain data provides the Rabi frequency (Ω_R), which determines the time required for a full spin flip between the quantum states. Oscillations are of Rabi type if there is a linear correlation between Rabi frequency with increasing microwave field strength, B_1. Knowing the Rabi frequency at a given microwave power along with the coherence time of the qubit allows for determination of the number of executable quantum logic operations before the superposition collapses. This figure of merit, Ω_M, is described by the equation $\Omega_M = 2T_m\Omega_R$.

A number of studies using molecular systems have successfully shown coherent quantum control through Rabi oscillations. Mayländer et al. developed a series of chromophore-radical systems for potential use as molecular qubits [7]. These systems are comprised of a chromophore linked to a stable radical where photoexcitation yields a stable, long-lived quartet state with long coherence times. This in combination with the ability to be optically initialized make them attractive candidates for quantum sensing. Transient pulse-EPR (Tr-pEPR) was used to study the PDI-trityl dyad system (Figure 3) at elevated temperatures up to 80 K, a much higher temperature compared to commercial qubit systems and other molecular qubits. Not only did the quartet state display very long coherence times (~3.0 µs), but the researchers were also able to drive multiple spin transitions coherently [7].

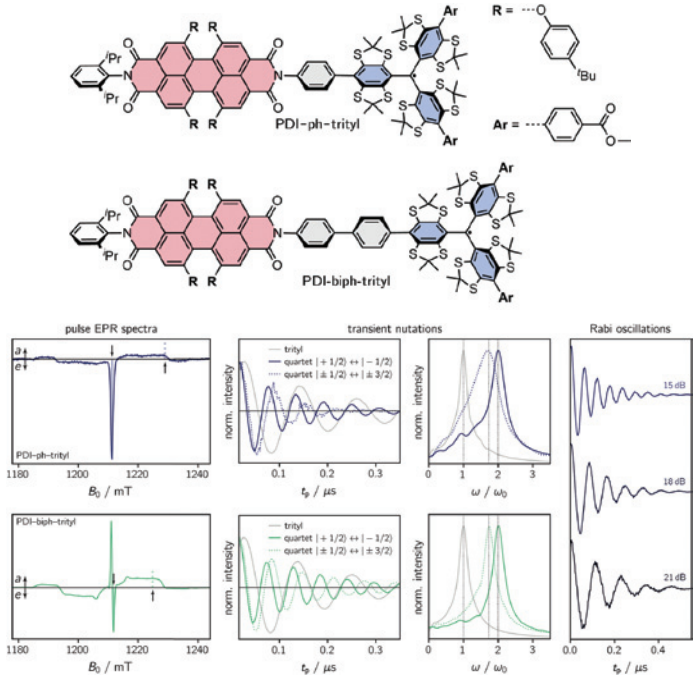


Figure 3: Structures of the PDI-radical systems studied with Tr-pEPR (top). Tr-pEPR spectra (bottom left) of the PDI-trityl systems using either phenyl (PDI-ph-trityl data shown in blue) or biphenyl (PDI-biph-trityl data shown in green) linkers with respective transient nutation data probing various spin transitions (bottom center) and observed Rabi oscillations (bottom right). All experiments were conducted at Q-band frequencies and at 80 K [7].

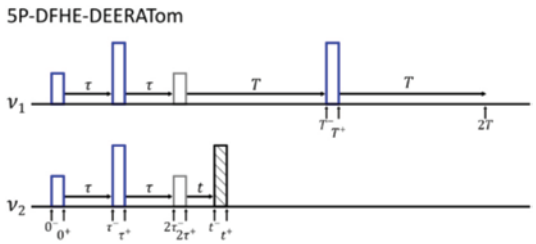


Figure 4: Designed pulse sequence used in this work, 5-Pulse Double Frequency Hahn Echo DEER-Assisted Tomography (5P-DFHE-DEERATom), for executing an entangling gate and quantum state tomography on a two-qubit system. Pulse turning angles are depicted by amplitude of the pulse with 90° pulses half the height of 180° pulses. Coherent pulses are in blue, incoherent pulses in black, and variable pulses in grey [8].

III. Quantum Gate Operations with EPR

Quantum logic gates are analogous to classical logic gates, where a gate operation will change the state, or vector, of the two-level system. In essence, these logic gates can be viewed as rotations on the Bloch sphere. EPR is also being explored for executing gate operations on qubit systems. There are several publications showing the use of EPR in executing two-qubit gates as well as entangling of two-qubit systems. Recently, Little at al. published an article addressing challenges and considerations for using EPR in executing quantum logic operations [8]. Using a bis-nitroxide model system in combination with Pulse-EPR and an arbitrary waveform generator (AWG), the researchers in this study were able to execute an entangling gate on the two-qubit system followed by designed pulse sequences for quantum state tomography, which allows for readout of the state of the qubit(s) (Figure 4). While there are still challenges to be addressed in performing these experiments, particularly in achieving high gate fidelities, it is an important step in improving Pulse-EPR methodologies for quantum logic operations.

IV. Conclusion

EPR spectroscopy is an invaluable tool in the pursuit of new MESQ's for Quantum Information Science. The ability to directly access the physical properties, electronic properties, and relaxation behavior of MESQ systems is a substantial advantage in comparison to other spectroscopic techniques. Additionally, EPR can be used for detection of Rabi oscillations to determine Rabi frequencies, which can be used to determine the number of quantum logic operations possible. In the future, improvement of hardware and pulse schemes will make quantum logic operations more feasible using an EPR spectrometer, allowing researchers in QIS to better evaluate the prospect of a molecular system as a qubit for quantum technologies.

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