



Xth EFEPR Conference

Torino - 4-8 September 2016



UNIVERSITÀ
DEGLI STUDI
DI TORINO



*Gruppo Italiano
di Risonanza di
Spin elettronico*

WELCOME TO EF-EPR 2016

The local organizing committee, GIRSE (Italian ESR Group) and the University of Turin welcome you to the 10th Conference of the European Federation of EPR Groups (EF-EPR 2016).

This is the tenth edition of this Conference, which has become one of the premier international forums for the international scientific community developing and employing electron magnetic resonance techniques. Both the number and the quality of the scientific contributions received for the Conference and published in this booklet testify the vitality of EMR techniques that are continuously evolving towards more sophisticated experimental and theoretical approaches, and that are finding exciting applications in different frontier areas of science. It is indeed for this reason that EFEPFR brings together physicists, chemists, biologists and materials scientists in a stimulating interdisciplinary dialogue.

Thanks to the fruitful cooperation with IES, the International EPR Society, that is here gratefully acknowledged, we have the pleasure to welcome several non-European colleagues from the North America, South America and Asia.

We wish to thank the private and institutional sponsors who have supported our Conference and, first of all, our University, Università degli Studi di Torino, one of the oldest Italian Universities, founded in 1404. Our deep thanks go also to the IAB (International Advisory Board) members whose activity over the past 12 months has allowed to define the conference program, the members of the Local Organizing Committee who have devoted their intense and enthusiastic activities to foster the success of this conference. The colleagues of SAFOOD for their effective organizational support.

I conclude by renewing our welcome to all of you in the city of Torino and in Piemonte. Torino, evolved from a former industrial capital into a charming city, inserted among the 52 places to visit in 2016 by The New York Times. Torino is a city of remarkable tradition in teaching and research with its two large Universities and nearly hundred thousand students. It is also a charming city with lively exhibition spaces, museums and music festivals hosted in its regular structure of streets, reminiscent of the ancient Roman settlement. All these features are described in the specific Section of the Conference website.

Welcome and enjoy your staying in Torino

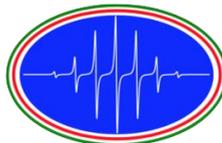
Elio Giamello and the Local Organizing Committee

Xth EFEP Conference Torino 2016

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Xth EFEP Conference Torino 2016

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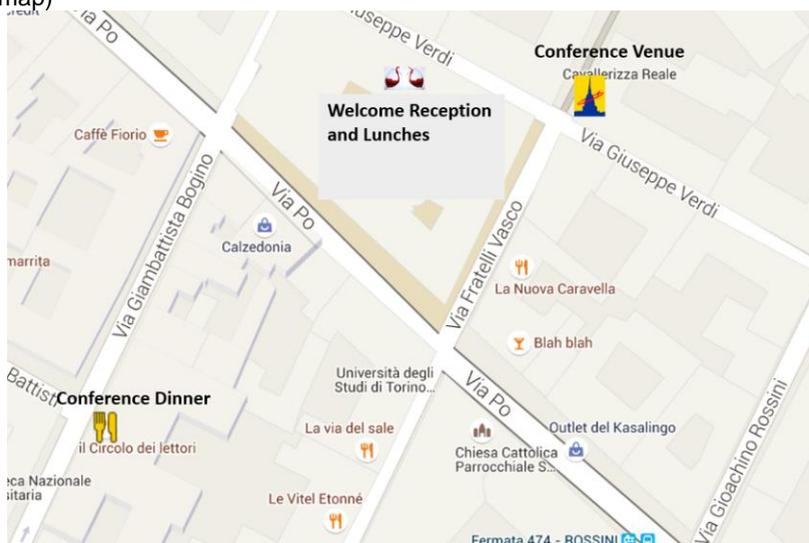
1.1. Registration and Welcome Reception

Registration and welcome reception will be held on Sunday 4th September from 19:00 h to 22:00 h in the courtyard of the Rectorate of the University, Via Giuseppe Verdi, 8 (see map).



1.2. Conference Venue

The conference will take place at the main hall of the University "La Cavallerizza", Via Giuseppe Verdi 9. The Hall is located in the City centre (see map)



1.3. Conference Office

The registration desk, will be opened from 18:00 to 21:00 on Sunday 4th in the courtyard of the Rectorate of the University (Via Giuseppe Verdi, 8.) From Monday 8th onwards the desk will be located at the entrance of the Hall "La Cavallerizza" opening from 8:00 am and during the coffee breaks, lunch and poster sessions.

1.4. Public Transportation

Torino has a widespread network of buses, trams and a subway line, which allow reaching every corner of the city. Bus tickets can be bought at news agents and tobacconists. A single ticket costs 1.50 € and lasts 90 min after validation on the bus. Further information can be found at <http://www.gtt.to.it/cms/en/>.

1.5. Internet-WiFi

The **eduroam**, free wireless (WiFi) service is available at the conference site. WiFi connection will also be available for people without access to eduroam. In this case, for security reasons, individual access codes (usernames and password), will be provided at the registration.

1.6. Speakers

Speakers are asked to bring their presentation to the conference room at least 15 min before the session starts. Members of the local organizing committee will be available to assist in uploading the presentations.

1.7. Posters

Posters will be exposed during the whole duration of the conference in the Rectorate of the University, where lunches will take place. The poster places will be numbered in the same way as the poster abstract in the abstract book. Two poster prizes will be awarded by the International Electron Paramagnetic Resonance Society (IES). Poster awards will be hand out on Thursday 8th during the IES dedicated session.

1.8. Meals and Coffee Breaks

Coffee breaks will be served in a room beside the conference Hall. Lunch meals will be served in the courtyard of the Rectorate in Via Verdi 8.

1.9. Social events

A **Welcome Reception** will be held on Sunday 4th September from 19:00 h to 22:00 h.

There will be a **drink reception** and buffet on Monday at 18:00 sponsored by Bruker, after the Bruker presentation.

Wednesday afternoon will be dedicated to social activities. For registered members three activities are proposed:

- 1) A guided tour at the **Reggia di Venaria** a masterpiece of Baroque just outside Torino
- 2) A guided tour to the historical cellars of **Fontanafredda** in the Langhe region.
- 3) A guided walking tour discovering the **centre of Torino**.

For the first two events special buses will be available at 14:30.

1.10. Conference Dinner

The conference dinner will take place on Wednesday evening in the restaurant **Il Circolo dei Lettori**, Via Bogino, 9 (see map) at 20:30. The Restaurant is located in the Palazzo Graneri della Rocca, a XVIII century palace, a few minutes walking from the Conference venue.

1.11. Telephone numbers

Local Organizing Committee:

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Taxi services

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+390115737

1.12. IES activities

A special session will be devoted to the IES activities on Thursday 8th at 11:00. During the session the IES awards will be presented to Dr. S. Veber, Prof. E. Groenen, Prof. S. Subramanian and Prof. C. Scholes.

1.13. The Ulderico Segre Prize

Ulderico Segre (1946-2008) was an Italian scientist who contributed to the advancement of theoretical and computational modelling in the field of magnetic resonance spectroscopies. To honour his memory, and on behalf of the Segre family, the Italian Group of Electron Spin Resonance **GIRSE** is proud to announce the third edition of the Ulderico Segre Prize. The Prize is awarded for an outstanding doctoral thesis in the field of magnetic resonance. This year's Segre Prize is awarded jointly to Dr. C. Tait and to Dr. G. Cutsail. The winners will deliver a lecture on Tuesday 6th September at 16:40.

Tourist Information

Detailed tourist information can be found on the Conference website. In the following you find a list of selected Cafè, Restaurants, Trattorie and Pizzerie. In the case of some restaurants reservation is suggested (phone numbers reported in some cases).

CAFÈS AND APERITIFS (HISTORIC, LIBERTY....)

- **Caffè Fiorio** - Via Po 8
- **Baratti & Milano** - Piazza Castello 27
- **Al Bicerin** - Piazza della Consolata 5
- **Caffè Elena** - Piazza Vittorio Veneto 5
- **Caffè Reale** - Piazzetta Reale 1
- **Caffè San Carlo** - Piazza San Carlo 156
- **Caffè Torino** – Piazza San Carlo 204
- **Caffè Mulassano** – Piazza Castello 15
- **Bar Zucca** - Via Antonio Gramsci 10

RESTAURANTS AND PIZZERIE

TOP LEVEL

- **Del Cambio** (Piazza Carignano 2, +39 011 546690)
- **Vintage 1997** (Piazza Solferino 16H, +39 011 5136722)
- **Al Garamond** (Via Pomba 14, +39 011 8122781)
- **VO** (Via Andrea Provana 3/D, +39 0118390288)
- **Casa Vicina** - Eataly Lingotto (Via Nizza 224, info@casavicina.com)

PIEMONTESE CUISINE

- **Tre Galline** (Via Gian Francesco Bellezia 37, +39 011 4366553)
- **Stefano Fanti-Circolo dei Lettori** (Via Bogino 9, +39 011 432 6827)
- **Ristorante Consorzio** (Via Monte di Pietà 23, +39 011 2767661)
- **Taverna dell'Oca** (Via dei Mille 24, +39 011 837547)
- **Ristorante Sotto la Mole** (Via Montebello 9, +39 0118179398)
- **L'Agrifoglio** (Via Andrea Provana 7/E, +39 011 8136837)
- **Casa del Barolo** (Via dei Mille 10 bis, +39 011 532 038)
- **Alla Locandina** (Via Montebello 24, +39 011 8122981)

ITALIAN CUISINE

- **Le Vitel Etonné** (Via San Francesco da Paola 4)
- **Ristorante Rural** (Via San Dalmazzo 16)

- **Enoteca Bordò** (Via Carlo Ignazio Giulio 4)
- **Contesto Alimentare** (Via Accademia Albertina 21/E)
- **Osteria della Mezzaluna** (Via Bertola 57)
- **Trattoria da Mauro** (Via Maria Vittoria 21)
- **Porto di Savona** (Piazza Vittorio Veneto 2)
- **OppostO** (Piazza Vittorio Veneto 1)

FISH & SEA FOOD

- **Trattoria dello Spirito Santo** (Largo IV Marzo 11)
- **Trattoria Anna** (Via Gian Francesco Bellezia 20)
- **Mare Nostrum** (Via Matteo Pescatore 16)
- **Ristorante Bastimento** (Via della Rocca 10/C)
- **Oinos** (Via della Rocca 39/G)

PIZZERIE

- **Amici miei** (Corso Vittorio Emanuele II 94)
- **Sfashion Café** (Via Cesare Battisti, 13)
- **Il Tabisca**, Piazza Vittorio Veneto, 16
- **Otto e tre quarti** (piazza Solferino 8/c)
- **Mammamia** (Corso San Maurizio, 32)
- **Sicomoro** (via Stampatori 6)
- **Pizzeria La Stua** (via Giuseppe Mazzini 46)
- **Pizza Ad Hoc** (Via Giovanni Plana, 7)
- **La Monachella** (Via Santa Croce, 2)
- **La Spaccanapoli** (Via Giuseppe Mazzini, 19)
- **Tre da Tre** (Via Giuseppe Verdi, 33)

ICE CREAM – GELATERIE

- **Alberto Marchetti**, Via Po 35 bis
- **Alberto Marchetti**, Corso Vittorio Emanuele II 24 bis
- **GROM**, Via Accademia delle Scienze 4
- **Fiorio**, Via Po 8
- **Fiorio**, Piazza Gran Madre di Dio 2
- **Nivà**, Gelato Piazza Vittorio Veneto 7
- **Gasprin**, Corso San Maurizio 49/A
- **+ di un Gelato**, Galleria Subalpina, 32



**Xth International Conference of European Federation
of EPR Societies
4-8 September 2016, Torino, Italy**

Conference Program

Sunday 4th September			
h19.00-22.00	Registration and Welcome Party		Courtyard of the Rectorate of the University
Monday 5th September			
h8.45-9.00	Gian Maria Ajani , Rector of the University Elio Giamello , Chair of EF-EPR		Welcome and Conference Opening
Session 1		Chair: W. Lubitz	
h9.00-9.45	PL01	Stefan Stoll	<i>"Is This Peak Real?": Uncertainty Quantification in DEER/PELDOR Spectroscopy</i>
h9.45-10.15	KN01	Stefan Weber	<i>Exploring Electron-Spin Polarization to Unravel Electron- Transfer in Photoactive Proteins</i>
h10.15-10.35	OP01	Graham Smith	<i>Zero Deadtime Pulsed EPR</i>
h10.35-11.05	Coffee Break		
Session 2		Chair: M. Lucarini	
h11.05-11.35	KN02	Olivier Ouari	<i>Free Radicals as Polarizing Agents for DNP/MAS ssNMR at High Fields</i>
h11.35-11.55	OP02	Klaus Moebius	<i>Möbius-Hückel Topology Switching in Expanded Porphyrin Molecules: EPR, ENDOR, and DFT Studies of Doublet and Triplet Open-Shell Systems</i>
h11.55-12.15	OP03	Anna Eibel	<i>Novel Reaction Pathways of P- based Photoinitiators studied via EPR and TR-EPR</i>
h12.15-12.35	OP04	Antonio Barbon	<i>Resolving the electronic structure of ambivalent close shell-open shell molecules</i>
h12.35-14.30	Lunch		Posters

Session 3			Chair: B. Guigliarelli
h14.30-15.00	KN03	Sabine Van Doorslaer	<i>Peering in the Pocket: EPR of Heme Proteins Before and After Immobilization in Porous Materials.</i>
h15.00-15.20	OP05	Sara Della Monica	<i>Effects of clinical laser treatments on the EPR spectrum of dental tissues</i>
h15.20-15.40	OP06	Elisabetta Mileo	<i>A new sterically shielded nitroxide-based spin label for in cell SDSL-EPR studies</i>
h15.40-16.00	OP07	Martina Huber	<i>Parkinson's Protein α-Synuclein: Membrane Binding Modes and Conformations by cw-EPR and DEER</i>
h16.00-16.30	Coffee Break		
h16.30-17.00	KN04	Lorenzo Sorace	<i>Vanadium(IV) complexes as potential multifunctional molecular qubits</i>
h17.00-18.00	Bruker presentation		
h18.00-19.30	Bruker Reception		
Tuesday 6th September			
Session 4			Chair: Z. Sojka
h9.00-9.45	PL02	Damien Murphy	<i>Applications of EPR for the Study of Earth Abundant Transition Metal Catalysts</i>
h9.45-10.15	KN05	Hervé Vezin	
h10.15-10.35	OP08	Elisa Albanese	<i>Defects and Defect Induced Room Temperature Ferromagnetism in Metal Oxides: a Combined EPR and DFT Study</i>
h10.35-11.05	Coffee Break		
Session 5			Chair: K. P. Dinse
h11.05-11.35	KN06	Marc Newton	<i>Exploring and Exploiting Colour Centres in Diamond</i>
h11.35-11.55	OP09	Stefano Paleari	<i>Conduction Electron Spin Resonance in Bulk Germanium and Germanium Quantum Wells</i>

h11.55-12.15	OP10	Piotr Pietrzyk	<i>Interaction of non-innocent ligand with transition-metal ions – insight into electronic and magnetic structure of Ni(II)-NO adduct in ZSM-5 zeolite</i>
h12.15-12.35	OP11	Alexander Bedilo	<i>Characterization of Surface Electron-Acceptor Sites during Catalytic and Solid-State Reactions by EPR</i>
h12.35-14.15	Lunch		Posters
Session 6		Chair: C. Scholes	
h14.15-15.00	PL03	Anton Savitsky	<i>ELDOR-Detected NMR: a Powerful EPR Technique for Hyperfine and Polarization Transfer Studies.</i>
h15.00-15.30	KN07	Inés García Rubio	<i>Iron Catalysts: What Hyperfine Spectroscopy Can Tell us to Understand their Structure</i>
h15.30-15.50	OP12	Hitoshi Ohta	<i>Development of Multi-Extreme THz ESR System</i>
h15.50-16.10	OP13	Malte Drescher	<i>Laser-Induced Magnetic Dipole Spectroscopy</i>
h16.10-16.40	Coffee Break		
Session 7 Ulderico Segre Prize (GIRSE)		Chair: D. Carbonera	
h16.40-16.55	SP01	Claudia E. Tait	<i>Triplet state delocalization in conjugated porphyrin systems investigated by EPR</i>
h16.55-17.10	SP02	George Cutsail	<i>ENDOR Characterization of an Iron for Nitrogen Reduction</i>
h17.10-17.30	OP14	Olav Schiemann	<i>EPR-Based Metal Ion Trilateration</i>
h17.30-17.50	OP15	Marilena Di Valentin	<i>Triplet-state spectroscopic ruler for high-sensitive PELDOR spectroscopy</i>
Poster Session		h17.50-19.30	

Wednesday 7th September			
Session 8		Chair: M. Chiesa	
h9.00-9.45	PL04	Vincenzo Barone	<i>From Structures and Magnetic Tensors to Full EPR Spectra of Large Free Radicals in Different Environments</i>
h9.45-10.15	KN08	Sergei A. Dzuba	<i>Determination of Pair Distance Distribution in Pulsed EPR of Spin Labels Using Monte Carlo Approach: Applications to Peptide Antibiotics and DNAs</i>
h10.15-10.35	OP16	Oleg Poluektov	<i>Electronic Structure of Charge Separated States in Organic Photovoltaic Cells: A Combined EPR and DFT Study</i>
h10.35-11.05	Coffee Break		
Session 9		Chair: E. Groenen	
h11.05-11.50	PL05	Carole Duboc	<i>Multi-Frequency EPR Spectroscopy Combined with Quantum Chemistry for the Investigation of the Magnetic Anisotropy of Manganese (II, III and IV) Complexes</i>
h11.50-12.20	KN09	George Mitrikas	<i>Modulation Depth Enhancement of ESEEM Experiments using Pulse Trains</i>
h12.20-12.40	OP17	Aharon Blank	<i>Direct measurement of the flip-flop rate of electron spins in solid-state</i>
h12.40-13.00	OP18	Bela E. Bode	<i>Quantifying Binding and its Cooperativity from PELDOR Modulation Depths</i>
h13.00-14.30	Lunch		Posters
Social events (or free afternoon)			
h14.30-18.30	Guided tour at the <u>Reggia di Venaria</u> Guided tour to the historical cellars of <u>Fontanafredda</u> Guided walking tour discovering the <u>centre of Torino</u>		
h20.30-24.00	<i>Conference dinner at "Il Circolo dei lettori"</i>		

Thursday 8th September			
Session 10		Chair: E. Goovearts	
h9.00-9.45	PL06	Thomas Prisner	<i>Improved Pulse Sequences for Dipolar Spectroscopy with Broadband Excitation Pulses</i>
h9.45-10.15	KN10	Marina Bennati	<i>Electron-Nuclear Polarization Transfer for Sensitivity Enhancement in EPR and NMR</i>
h10.15-10.35	OP19	Gunnar Jenske	<i>Optimization of Band-Selective Inversion Pulses</i>
h10.35-11.05	Coffee Break		
Session 11 IES activities		Chair: H. Ohta	
h10.05-11.30	IES1	Sankaran Subramanian	<i>Time-domain in vivo imaging</i>
h11.30-11.50	IES2	Sergey Veber	<i>Thermally and photoinduced magnetostructural transitions in Copper-Nitroxide Based Molecular Magnets</i>
h11.50-12.15	IES3	Edgard Groenen	<i>EPR at 275 GHz: from nitroxides to transition-metal sites in proteins</i>
h12.15-12.40	IES4	Charles P. Scholes	<i>ESR from the Scholes Lab: ESR Fellow Lecture</i>
h12.40-13.30	General Assembly of IES and Awards presentation		
h13.30 - 14.30	Lunch		Posters
Session 12		Chair: A. Schnegg	
h14.30-15.15	PL07	Daniella Goldfarb	<i>Distance Measurements Using Gd(III) Labeling: Opportunities and Pitfalls.</i>
h15.15-15.35	OP20	Dmitry Azamat	<i>Spin-Phonon Relaxation Processes of Transition Metal Ions In ZnO</i>
h15.35-15.55	OP21	Peter Rapta	<i>EPR Spectroscopy and in situ EPR/UV-vis-NIR Spectroelectrochemistry of Metal Complexes with Noninnocent Ligands</i>
h15.55-16.10	Conclusive remarks		

Oral Contributions

ABSTRACTS

- **PL: Plenary Lecture**
- **KN: Key-Note Lecture**
- **OP: Oral Presentation**
- **SP: Segre Prize**
- **IES: IES Awards**

Plenary Lectures

“Is this peak real?”: Uncertainty quantification in DEER/PELDOR spectroscopy

Stefan Stoll

Department of Chemistry, University of Washington, Seattle WA, USA

DEER/PELDOR spectroscopy is a solid-state pulse EPR technique that is used to measure distances between spins, most commonly between protein-bound spin-labels separated by $r = 1.5 - 8$ nm. From the experimental time-domain signal, a distance distribution $P(r)$ is extracted using Tikhonov regularization, a model-free least-squares approach. $P(r)$ contains a wealth of structural and energetic information on the conformational landscape of the protein. The disadvantage of Tikhonov regularization is that it does not directly provide error bars for the resulting $P(r)$, rendering correct analysis difficult and prone to over-interpretation by non-experts. We introduce a probabilistic Bayesian statistical approach that quantifies uncertainty in $P(r)$ arising from noise in the time-domain signal. This method uses Markov-Chain Monte Carlo (MCMC) to calculate credible intervals (error bars) for $P(r)$ at each r . These error bars provide practitioners with a quantitative basis to address questions such as whether or not small features or apparent shoulders in $P(r)$ are significant.

Applications of EPR for the Study of Earth Abundant Transition Metal Catalysts

Damien M. Murphy

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Homogeneous catalysts based on platinum group metals (PGM) are ubiquitous in synthetic chemical transformations. These PGM-based catalysts are highly attractive for a number of reasons including tolerance of functional groups and reaction media, ease of handling and high activity in a range of processes. However, the continued use of PGMs in pharmaceutical, fine chemical, agrochemical and related sectors is ultimately limited by several factors, including high (and volatile) costs, toxicity and sustainability. The replacement of these PGM-based systems with catalysts based on earth-abundant metals (EAM), which are readily available, cheap, non-toxic and environmentally friendly, is therefore highly desirable^[1].

Recent research in EAM-based catalysts (Fe, Co, Ni), and indeed on other first row transition metals (Ti, V, Cr, Mn, Cu), has found that the mechanisms involved are often quite unique. Divergence in behavior EAMs from PGMs is common, not least because they tend to form paramagnetic intermediates, but also they undergo far more single-electron-transfer (SET) processes than their simple PGM-counterparts. These 3d metals can undergo facile one electron oxidation state changes and associated spin state changes, with easy ligand redistribution, unlike the more predictable PGMs with two-electron changes between diamagnetic oxidation states. Furthermore, creative ligand architectures that can stabilize radical intermediates, are serving to further extend the possible range of catalytic applications by the EAM-based catalysts.

Owing to the involvement of paramagnetic centres in these catalytic systems, EPR is the ideal characterization tool to explore the mechanisms involved. In this presentation, the role of EPR to explore the chemistry of the low valent EAM-based systems bearing Fe(I),^[2] Co(II)^[3] and Ni(I),^[4] will be presented along with other 3d metal complexes, illustrating how electronic and steric control at the metal centre by the coordinating ligand, can be revealed using a range of advanced EPR techniques

References.

1. P Chirik, R. Morris, *Accs. Chem. Res.*, **2015**, *48*, 2495-2495.
2. CJ Adams, et al., *J. Am. Chem. Soc.*, **2012**, *133*, 10333-10336.
3. E Vinck, et al., *Inorg. Chem.*, **2012**, *51*, 8014-8024.
4. MJ Page, et al., *Chem Eur J.*, **2012**, *19*, 2158-2167; R.C. Poulten, et al., *J. Am. Chem. Soc.*, **2013**, *135*, 13640.

ELDOR-detected NMR: a powerful EPR technique for hyperfine and polarization transfer studies

Anton Savitsky

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Electron-electron Double Resonance (ELDOR)-detected NMR (EDNMR) is growing in popularity as a means to characterize the hyperfine structure of complex chemical systems. First developed in the Schweiger laboratory,¹ it uses selective microwave pulses which simultaneously pump EPR and NMR transitions of the spin manifold, so called spin-forbidden transitions, where both the electron and nuclear spins change their projection direction ($\Delta m_S = \pm 1$, $\Delta m_I = \pm 1, \pm 2$). As compared to conventional ENDOR techniques it has a much higher sensitivity and does not exhibit nucleus-dependent or pulse-dependent spectral artifacts and does not require additional radio-frequency hardware. Historically, the wide spread adoption of EDNMR has been hampered by what is termed the central blind spot. Spin-forbidden transitions that are sufficiently close in absolute frequency to the allowed EPR transition are masked due to the simultaneous pumping of this allowed transition, i.e. transitions within 5-10 MHz. This problem can, however, be solved by performing experiments at high magnetic fields and, thus, higher nuclear Larmor frequencies.

In this presentation the EDNMR technique is introduced. Its general applicability for hyperfine studies is discussed. Several examples are given which include the experimental results on nitroxide radicals^{2,3} and transition-metal containing systems^{4,5}. Advantages and disadvantages of the method as compared to conventional ENDOR and ESEEM techniques are pointed out. Additionally, selected examples of EDNMR application to electron-nuclear polarization transfer studies are presented using molecular systems containing Mn(II) and Gd(III) tags.

References.

1. P. Schosseler, T. Wacker, A. Schweiger, *Chem. Phys. Lett.* **1994**, 224, 319-324.
2. Nalepa A., Möbius K., Lubitz W., Savitsky A., *J. Magn. Reson.* **2014**, 242: 203-213
3. Cox N., Nalepa A., Pandelia M.-E., Lubitz W., Savitsky A., **2015**, In: Peter ZQ, and Kurt W (eds) *Methods in Enzymology*, Vol. Volume 563, pp. 211-249, Academic Press
4. Rapatskiy L., Ames W.M., Perez-Navarro M., Savitsky A., Griese J.J., Weyhermueller T., Shafaat H.S., Hogbom M., Neese F., Pantazis D.A., Cox N., *J. Phys. Chem. B* **2015**, 119, 13904-13921
5. Cox N., Lubitz W., Savitsky A., *Mol. Phys.* **2013**, 111: 2788-2808

FROM STRUCTURES AND MAGNETIC TENSORS TO FULL EPR SPECTRA OF LARGE FREE RADICALS IN DIFFERENT ENVIRONMENTS

Vincenzo Barone

Scuola Normale Superiore, piazza dei Cavalieri 7, Pisa, Italy; website: dreams.sns.it

EPR spectroscopy is still one of the most useful experimental techniques to analyse the structure, dynamics, and magnetic properties of open-shell species. However, disentanglement of the different factors tuning the overall spectra requires effective yet reliable theoretical calculations. Recent progresses in this field are very encouraging, and it is becoming often possible to compute reliable magnetic parameters as well as to simulate the whole spectra from first principles without adjustable parameters.

In this contribution, I present an overview of the latest theoretical approaches with special reference to Density Functional Theory (DFT), which represents the most convenient method (if not the only one) for large systems of current technological and biological interest. After an overview of the theoretical background, accurate computations for semi-rigid radicals and bi-radicals in the gas phase are considered^{1,2} and used to benchmark different functionals and basis sets to be employed for larger systems³.

Next, I consider the role and proper treatment of vibrational averaging³ and environmental effects^{3,4} toward the description of large flexible systems in condensed phases⁵. In this connection, an integrated QM/MM/PCM approach is particularly effective and has been recently extended with more reliable MM parameters⁶ possibly taking polarization into the proper account.⁷ Finally, the use of computed magnetic parameters in the simulation of complete spectra is shortly sketched.⁸ Nitroxide radicals will be used throughout to provide specific examples of the different topics. Most of the latest developments have been performed in the framework of the ERC Advanced Grant DREAMS: 320951.

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Multi-frequency EPR Spectroscopy combined with Quantum Chemistry for the Investigation of the Magnetic Anisotropy of Manganese (II, III and IV) Complexes.

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In view of understanding the chemical reactivity and/or the physical properties of transition metal ion complexes a large number of experimental techniques and theoretical tools are used to characterize their electronic and magnetic properties. Magnetic anisotropy, or zero field splitting (zfs, D and E being the axial and rhombic parameters of the zfs, respectively), is among the most powerful probes of the structural and electrostatic environment for transition metal ions with a spin greater than 1/2.

In this context, our main objective was the prediction of the zfs, either by establishing correlations between the zfs and the structural features of the complexes, or by calculating the zfs using appropriate quantum chemical methods. These approaches should allow (i) the confident prediction of the structure of complexes for which no structural data is available (as in the case of many biological systems), (ii) the development of structural probes (in enzymes for instance) and (iii) the design of new materials.

Our works, focused on mononuclear Manganese complexes at the + II, +III and + IV oxidation states, highlight how the combination of experimental and theoretical approaches can be fruitful in this area. Both are required to understand the physical origin of the electronic parameters to rationalize the observed experimental correlations.

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Improved pulse sequences for dipolar spectroscopy with broadband excitation pulses

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Pulsed dipolar EPR spectroscopy uses the magnetic dipole-dipole interaction between two unpaired electron spins to measure distances in the 1-8 nm range on macromolecules. Single and double frequency pulse EPR techniques exist to accomplish this goal with applications in structural biology and material sciences^{1,2}. One limitations of the method arises from the fact that not the whole spin ensemble or at least a well-defined part of the spin ensemble can be excited by classical rectangular pulses, different from NMR spectroscopy. Another limitation arises from short transversal relaxation times of spin labels, especially in lipid membranes, limiting the observation time window and therefore accessible distance range³. This complicates the separation of intra- and inter-molecular contributions to the dipolar time domain signal, making quantitative determination of distances, especially if broad distance distributions exist, very challenging. We will show our approaches how to tackle both of these problems with broadband phase and amplitude modulated pulses for single and double frequency dipolar spectroscopy on biradical model compounds and spin labeled membrane protein complexes⁴⁻⁶.

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Distance measurements using Gd(III) labeling: opportunities and pitfalls

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Distance measurements between two spin labels attached at well-defined sites in proteins and nucleic acids by double electron-electron resonance (DEER) spectroscopy have become an established structural tool in Structural Biology. Such measurements are carried out on frozen solutions and provide information on conformational distribution and conformational changes induced by ligand binding. The standard spin labels used for this purpose are based on nitroxide radicals. In recent years we, and others, have demonstrated the utility of high frequency DEER distance measurements in proteins using a new family of spin labels based on Gd³⁺ chelates.¹ These are particularly useful due to the high sensitivity at they have at high fields. The DEER performance depends on the width of the EPR spectrum, which is determined by the Gd³⁺ zero field splitting (ZFS), and the flexibility of the tether used to attach the Gd³⁺ chelate to the protein. We will present W-band Gd-Gd DEER distance measurements on different protein systems using a variety of Gd³⁺ tags and will discuss potential pitfalls in the standard data analysis for the case of short distances and small ZFS due to breakdown of the weak coupling approximation. Ways to overcome these pitfalls will be presented. Finally we show that owing to the high sensitivity of Gd³⁺-Gd³⁺ distances measurements and the stability of Gd³⁺ chelates, in-cell distance measurements are within our reach. Examples of in-cell Gd-Gd distance measurements on Gd³⁺ labeled ubiquitin and calmodulin delivered into HeLa cells using osmotic shock and electroporation will be described.

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Key-Note Lectures

Exploiting electron-spin polarization to unravel electron-transfer in photoactive proteins

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Light-generated and short-lived spin-correlated radical pairs have been suggested to play pivotal roles in the cryptochrome/photolyase protein family. They are involved in a number of light-induced responses, such as DNA repair or signalling-state generation in photoreception. We examine such transient states in the proven magnetoreceptor *Drosophila melanogaster* (fruit-fly) cryptochrome and, for comparison, in the related DNA-repair enzyme *Escherichia coli* DNA photolyase using out-of-phase electron-spin echo envelope modulation, a pulsed electron paramagnetic resonance (EPR) method that allows for the direct determination of exchange and dipolar contributions to the electron-spin-spin interaction, and transient EPR,¹ by which it is possible to study radical-pair formation under physiological conditions. With the dipolar and exchange interaction parameters at hand, radical-pair partners along a conserved electron-transfer path comprising of tryptophans can be identified and the extent of singlet-triplet splitting determined with respect to the coupling of the unpaired spins to the magnetic field of the Earth.²

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Free radicals as polarizing agents for DNP/MAS ssNMR at high fields

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Dynamic Nuclear Polarization (DNP) is currently one of the most efficient methods to increase the sensitivity of solid-state MAS NMR spectroscopy. In a DNP experiment, the large polarization of unpaired electrons (usually from a stable free radicals) is transferred to surrounding nuclei by microwave irradiation, providing maximum theoretical sensitivity enhancements of a factor 658 for ¹H and 2620 for ¹³C. In the past 5 years, the optimization of the structural and magnetic properties of the Polarizing Agents (PAs) has significantly contributed to the increase of the signal enhancement at 9 T and to the success of the technique. Enhancements (ϵ) of 50-200 are today routinely obtained at 9.4 T and 100 K, allowing the investigation of an ever broader range of molecular systems including biomolecules, hybrid materials, polymers, or microcrystals. However, the enhancement factors are still far from the predicted maximum values. Indeed, the development of optimum polarizing agents is not trivial due to the multidimensional optimization problem and to the non-full understanding of the polarizing processes at high-fields. We will report our recent efforts on the design, preparation and characterization of new polarizing agents for high-field DNP, notably by discussing parameters such as the electron-electron dipolar interaction, the glassy matrix and the electron relaxation.¹⁻³

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Peering in the Pocket: EPR of Heme Proteins Before and After Immobilization in Porous Materials.

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Globins are found in all kingdoms of nature and their functions are multiple, including O₂-transport and storage, redox functions, protection against reactive oxygen and nitrogen species (ROS/RNS), and signalling functions. Furthermore, many of the globins are very stable even under non-natural conditions. Neuroglobin, for instance, retains its structure in a wide range of pH values and is resistant to temperatures up to 90°C. The high stability and the functional versatility make these proteins potential building blocks for the construction of biosensors. However, for these means, the proteins need to be included in inorganic matrices.

In this talk, it will be shown that continuous-wave and pulsed EPR form an excellent characterization tool to gain insight into the inner-working of different globins and to trace their structural changes when incorporated in mesoporous materials, such as titania and silica. Furthermore, although the mesoporous semi-conducting titania are in principle ideal materials for the construction of amperometric biosensors, they also act as photocatalysts and can break down the incorporated biomolecule. EPR offers again the appropriate instrument to test the influence of light on the creation of reactive species and the potential subsequent denaturation of the protein.

Vanadium(IV) complexes as potential multifunctional molecular qubits

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Compared to spins in doped semiconductors molecular spin systems are better suited to satisfy some of the requirements for the implementation of a real qubit, like addressing and control of qubits entanglement; on the other hand, the short lifetime of the quantum superposition of states, T_m , has up to now posed some limitations in their use as qubits. Recently mononuclear V^{IV} complexes with dithiolenes, when dispersed in nuclear spin-free solvents like CS₂, have been reported to show quantum coherence times, T_m , long enough to perform quantum operations at low temperature. Their use in real devices operating at room temperature is however still hampered by the rapid decrease on increasing the temperature, of the spin-lattice relaxation time, T_1 , which acts as a limiting factor for T_m . [1]

In this talk I will present the results we recently obtained using a multi-technique approach based on the combination of ac susceptometry and pulsed EPR techniques to investigate T_1 and T_m of S=1/2 molecular systems, which led us to identify vanadyl based complexes as promising spin center for QIP applications. For such systems, T_1 remains long over a broad range of temperatures and magnetic fields. [2] Further, Rabi oscillations at room temperature have been observed in the molecular semiconductor TiOPc (Pc = phthalocyanine) containing large concentration (up to 10%) of VOPc. The combination of these features with its high thermal stability and high processability makes this material extremely appealing, as it can be used as paramagnetic semiconductors in spintronics devices. [3]

Furthermore, recent results will be presented which revealed that the effectiveness of the vanadyl moiety in enhancing quantum coherence up to room temperature is related to a less effective mechanism of spin-lattice relaxation compared to the non-oxo counterpart. Record coherence times at room temperature (1.04 μ s) and Rabi oscillations were indeed observed for a vanadyl complex of nuclear spin free ligand, even at relatively high VO²⁺ concentration (5 \pm 1%) % whereas this was not possible for the corresponding trischelate complexes. [4]

This work is supported by ERC through AdG grant MolNanoMaS 267746 (to R. Sessoli) and by MIUR (Futuro in Ricerca 2012 - RBFR12RPD1)

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Exploring and Exploiting Colour Centres in Diamond

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Defects in diamond have great potential for use in photonic and quantum technologies.¹ For example, the negatively charged nitrogen vacancy centre (NV⁻) in diamond consists of a lattice vacancy, where one of the nearest neighbour carbon atoms has been replaced with a nitrogen atom, which has trapped an electron. The ground state has S=1 and the centre gives rise to optical emission in the red-near infrared. It has been shown, even at room temperature, that the spin state of a single NV⁻ defect can be initialised (100% spin polarised in M_S=0 state) with green light, manipulated with microwaves and optically read out (ODMR). These properties have already been extensively exploited with demonstrations including high precision magnetic field imaging/sensing, quantum simulation and quantum information processing. Full exploitation of the optical and spin properties of colour centres in diamond necessitates that we control their position, orientation and environment to optimise all of the desirable properties simultaneously.

In this talk I will review our understanding of the production, in diamond, of intrinsic defect complexes by irradiation and annealing, and the capture of vacancies and self-interstitials by impurities. New Electron Paramagnetic Resonance (EPR) and optical spectroscopic data will be presented on the production of preferentially orientated defect complexes by electron irradiation and/or annealing whilst the sample is subjected to a large (up to 4 GPa) uniaxial stress. Near 100 % preferential orientation can be achieved for a number of different defects. Preferential orientation will be used to unravel the complexities of self-interstitial migration in diamond.

Furthermore, recent results will be presented where uniaxial stress has been used *in-situ* to investigate both the reorientation and the spin relaxation properties of the single substitutional nitrogen centre (N_s⁰) in diamond. The design and performance of the EPR stress probe, which is compatible with a standard EPR cryostat, will be described. It will be shown that uniaxial stress can be used to influence spin diffusion and change spin-spin relaxation.

This work is supported by EPSRC grants EP/M508305/1, EP/M013243/1, EP/L015315/1, EP/J500045/1, EP/J007951/1, the De Beers Group of Companies, the Gemological Institute of America, the UK Quantum Technology Hub: NQIT - Networked Quantum Information Technologies and the EPSRC Centre for Doctoral Training in Diamond Science and Technology

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Iron Catalysts: What Hyperfine Spectroscopy Can Tell us to Understand their Structure

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Iron(III) has very interesting catalytic properties due to its *d*-electrons that can be modulated by its molecular environment. For this reason, one can find in nature or synthesize in the laboratory lots of different iron-based catalysts, monoatomic or clusters, either in sites of low symmetry or coordinated to highly symmetric organic chelators. In all cases, the properties of the *d*-orbitals are decisive in determining the catalytic properties of iron. In this contribution we will illustrate the determination of the spin state and *g*-values through EPR methods using examples of iron catalysts with very different characteristics. In addition, the study of the hyperfine interactions with magnetic nuclei in close vicinity of the iron yields also useful structural information and allows mapping the electron spin density distribution. The strategy for experimental determination of the hyperfine couplings of nitrogen and/or hydrogen nuclei will be shown.

As examples, we will consider an artificial heterocubane with a [Fe₄N₄] core that can reversibly store up to four electrons at very negative potentials. In this case¹, the interpretation of hyperfine data reveals that the unpaired electron is predominantly located at one Fe center with some delocalization to the coordinated olefin moiety ($\rho \approx 18\%$) and to the nitrogen atom in the same chelating ligand ($\rho \approx 0.8\%$).

The second system is a group of proteins, where a single iron ion is coordinated by an organic ring of porphyrin. This cofactor, called heme group, is ubiquitous in life systems where it performs very different functions (catalytic, transport...). For this sort of proteins, hyperfine couplings reveal electronic details related to the structure that can possibly be discussed in terms of the biological function.

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Determination of Pair Distance Distribution in Pulsed EPR of Spin Labels Using Monte Carlo Approach: Applications to Peptide Antibiotics and DNAs

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Pulsed electron-electron double resonance technique (PELDOR, or DEER) is applied to study conformations and aggregation of peptides, proteins, nucleic acids, and other macromolecules. For two spin labels attached to the same macromolecule, experimental data allow for determination of their distance distribution function, $P(r)$. $P(r)$ is derived as a solution of a first-kind Fredholm integral equation, which is an ill-posed problem. We suggest a new regularization approach which is based on reducing the number of distance points in which the distribution function is sampled. For solving the integral equation, a Monte Carlo algorithm is proposed. This approach could serve as a useful complement to the traditional approaches basing on Tikhonov regularization, especially in the case of low signal-to-noise ratio. The applications are described of determination of distance distribution for doubly spin-labeled peptide antibiotics and DNAs. An example is shown in Fig. 1.

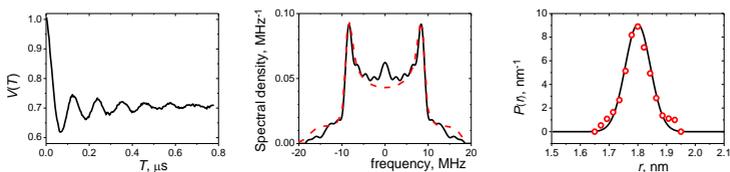


Fig. 1. Results of determination of distance distribution for doubly spin-labeled peptide antibiotic ampuლოსporin A in frozen methanol solution. Left: original PELDOR time trace.¹ Middle: its Fourier transform (solid line) and best-fitted result of Monte Carlo trials (dashed line). Right: best-fitted distance distribution function (circles) along with the result² of calculations for the same experimental system in which Tikhonov regularization was employed.

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Modulation Depth Enhancement of ESEEM Experiments using Pulse Trains

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The electron spin echo envelope modulation (ESEEM) effect is the key element of many powerful pulsed EPR techniques that are used to determine weak hyperfine and nuclear quadrupole interactions in solids. While some of these methods provide optimum resolution for given paramagnetic systems, they may suffer from poor sensitivity due to small modulation depths, low abundances of magnetic nuclei and/or additional multinuclear suppression effects. For this reason, the development of ESEEM experiments with improved sensitivity is still a challenge for pulsed EPR methodology.

Recently we have developed a new way to increase the modulation amplitude of ESEEM experiments that are based on electron spin coherence¹. The method uses a train of N refocusing π -pulses where each one of them redistributes the electron spin coherence among allowed and forbidden EPR transitions. This in turn leads to a significant enhancement of the ESEEM effect, depending on the strength of the hyperfine interaction and the number of applied pulses, N.

Here we present the different aspects of this methodology which includes both 1D and 2D pulse sequences. After a short introduction to theory for nuclei with $I=1/2$, the advantages and limitations of the methods will be discussed with experimental examples. Furthermore, we will extend our study to quadrupolar nuclei ($I>1/2$) for which analytical solutions cannot be obtained. We will focus on the interesting case of ¹⁴N, a nucleus that is often involved in paramagnetic centres of biological relevance, and based on numerical simulations we will examine possible ways to optimize the modulation enhancement. Finally, the possibility to implement the multiple echo detection schemes², recently introduced as a way to increase signal-to-noise ratio in pulsed EPR experiments, in the new ESEEM methods will also be discussed.

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KN10

Xth EFEP Conference Torino 2016

**Electron-Nuclear Polarization Transfer for Sensitivity
Enhancement in EPR and NMR**

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Oral Presentations

Zero Deadtime Pulsed EPR

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Zero Deadtime EPR refers to the measurement of a pulsed EPR signal *during* a high power (high turning angle) microwave pulse. Such measurements are potentially useful when trying to measure extremely short relaxation times (of the order of 10ns or less), including both T_2 and $T_{1\rho}$. Such short relaxation times are often seen in exchange coupled systems or in experiments with high radical concentrations, as might be used in DNP experiments, or in dynamics studies in the liquid state or with many transition metal systems.

Such “during pulse” measurements are not possible in conventional cavities because of high power levels transmitted to the detector during the pulse, where signals from the excitation pulse are usually many orders of magnitude larger than even very strong signals from the sample. However, such measurements do become possible in high performance induction mode cavities, which provide high levels of isolation between transmitter and detector, whilst simultaneously giving high signal sensitivity from the sample.

It is the observed transient response of the system during a high turning angle pulse (before saturation) that can allow direct information on both $T_{1\rho}$ and T_2 of the system. The shorter the relaxation times – the higher the B_1 fields required for unambiguous results.

In such measurements what is important is the signal to clutter ratio, rather than the signal to noise ratio, where the clutter comes from the excitation pulse, and both signal and clutter are usually well above the noise level. Such measurements are thus only possible with relatively highly concentrated samples – and a key question is: what signal level is required to make this technique work?

In this paper I will describe a 94 GHz induction mode system¹ that provides extremely high levels of isolation between transmitter and detector and allows zero deadtime measurement of a number of different systems, including nitroxide samples in low loss solvents at 1mM concentration levels. I will show it is possible to measure relaxation times less than 10ns, using this technique, using 1kW input power levels, and this has relevance for liquid state DNP.

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Möbius-Hückel Topology Switching in Expanded Porphyrin Molecules: EPR, ENDOR, and DFT Studies of Doublet and Triplet Open-Shell Systems

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The one-sided Möbius band topology with its characteristic 180° twist has inspired philosophers, artists and scientists since a long time. On the molecular level, the Möbius band symmetry exists only seldom in Nature, but recently spectacular discoveries of remarkably stable small ring-shaped proteins of Möbius topology from plants, the Cyclotides, have been reported. They have a potential for use as stable protein-engineering templates for drug design. Only in the last 13 years a few organic chemistry groups succeeded to synthesize novel compounds with Möbius symmetry by means of theory-based molecular design and ingenious chemical synthesis strategies. Theory predicted that sufficiently large [n]annulenes with a closed-shell electron configuration of $4n$ π -electrons should allow for sufficient overlap stabilization to be synthesizable by twisting them into the Möbius topology of their hydrocarbon skeleton. In 2007, the group of L. Latos-Grażyński¹ in Wrocław successfully synthesized an expanded free base porphyrin, [28]hexaphyrin, which can dynamically switch between Hückel and Möbius π -conjugation via polarity and/or temperature changes of the matrix solvent.

The present EPR, ENDOR and DFT work² on the radical cation state of free base [28]hexaphyrin is the first study of a ground-state open-shell system that exhibits a temperature-controlled Hückel-Möbius topology switch, similar to what was observed earlier for the closed-shell precursor¹. Our work has now been extended to the open-shell photo-excited triplet states of [28]hexaphyrin³. State-of-the art DFT theory studies come to the conclusion that, besides hyperfine couplings, the zero-field splitting interaction between the two unpaired electron spins is a viable sensor for electronic-structure changes upon Möbius-to-Hückel topology switching.

Among the most promising applications of such novel Möbius-Hückel topological switch molecules are their high non-linear optical properties (NLOP).

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Novel Reaction Pathways of P-based Photoinitiators studied via EPR and TR-EPR

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We have discovered alternative reactions of bisacylphosphane oxide (BAPO) photoinitiators upon irradiation. The reaction pathways have been established mainly by

EPR and time-resolved EPR (TR-EPR). In the presence of water or alcohols, an additional astonishingly long-lived radical is formed beside the well-established benzoyl and phosphanoyl radicals. This was previously shown and mechanistic suggestions were discussed.^{1,2} The TR-EPR spectra are dominated by the triplet mechanism (TM). The additional radical exhibits a doublet pattern with a hyperfine coupling constant of ca. 3 mT. Our observations point to the new radical being formed via a secondary process, involving the reaction of the phosphanoyl radical with water. Based on our experimental results and DFT calculations, we suggest a reaction mechanism comprising the nucleophilic attack of water or alcohol at the carbonyl group adjacent to the P-radical center, yielding a C-centered radical. In conventional cw-EPR experiments this radical exhibits a well-resolved hydrogen hyperfine splitting pattern, which can be very well simulated based on our structural considerations. TR-EPR experiments with nucleophilic salts further support the proposed electrophilic behavior of BAPO-based phosphanoyl radicals.

Our experimental findings might be relevant with respect to the application and development of novel water-soluble BAPO-based photoinitiators.

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Resolving the electronic structure of ambivalent close shell-open shell molecules

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Conjugated quinoidal molecules are used in molecular electronics and optoelectronic devices for a wide range of applications because of their intriguing, non-trivial electronic properties. These are related to the ambivalent property of being both diamagnetic closed shell, but at the same time a paramagnetic open shell molecule; the two forms are formally two resonance forms. As a result, the molecules can in principle be described in terms of biradicaloid contribution to the ground state.

A series of thiophene-based heterophenoquinones, displaying biradicaloid character, have been studied by using a combination of Electron Paramagnetic Resonance (EPR), Nuclear Magnetic Resonance (NMR), Raman, Infrared (IR) and X-ray diffraction measurements. This combined approach provided a detailed picture of the so far bleared electronic structure of the molecules.

We have now a clear picture of the system, that can be described in terms of two nearby states: a closed-shell diamagnetic state and a nearby biradical state, which is thermally populated¹, but, at the same time, with contamination of states.

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Effects of clinical laser treatments on the EPR spectrum of dental tissues

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Lasers are known to create a thermal damage to the target tissues by a photo-thermal effect and a side effect of this reaction is an increase in the temperature of the surrounding non-target tissues; the heating of these non-target tissues may create a permanent or reversible damage. EPR spectroscopy may be used for the investigation of the thermal damages produced on dental tissues by different types of lasers commonly employed in clinical routine. In particular, it can provide a complementary method of assessment of temperature increase in teeth, validating cameras and thermocouples records and FEM calculations. A characterization of the laser-induced signals on both unirradiated and irradiated dental tissues have also important implications for dosimetry of ionizing radiation with tooth enamel, as the local increase of temperature may generate some confounders in the EPR spectrum of dental tissues, both by generating additional signals that may overlap the radiation induced signal and by possibly changing the radiation sensitivity of the treated tissues.

The two clinical protocols actually in use in dental clinics for dentine desensitization and for root canal disinfection were analysed. For both protocols, differences between EPR spectra of fragments of untreated parts of molar teeth and fragments from the parts treated using the clinical protocols were studied. Moreover, a more in-depth investigation about the origin of the laser-induced signals on the unirradiated dental tissue was carried out, with the support of the literature. The spectra of laser-treated samples were analyzed considering how the laser-induced signals change with radiofrequency power values and how spectra from different teeth belonging to different donors differ from each other. Samples treated by the root canal disinfection protocol show an EPR spectrum in which at least two different signals are clearly visible. The presence of these two signals are the indication that the thermal effect of the laser on the dental tissue is an inhomogeneous heating of the volume, with a gradient of temperature varying from a few hundreds to more than 600 °C.

Acknowledgments:

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A new sterically shielded nitroxide-based spin label for in cell SDSL-EPR studies

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The cell interior is well recognized as an incredibly concentrated and complex medium: proteins work in an environment wherein they specifically interact with other proteins, nucleic acids, ligands, and are subjected to an extreme "macromolecular crowding" which makes the cellular environment difficult to reproduce *in vitro*.¹

Studying protein structural dynamics and protein-protein interactions at the molecular level in their native environment is very attractive and challenging.

A powerful approach to study and follow conformational changes in soluble or membrane proteins is the technique of Site-Directed Spin Labelling (SDSL) combined with Electron Paramagnetic Resonance (EPR) spectroscopy.² Thanks to its inherently higher absolute sensitivity, compared to NMR, and to its sensitivity restricted to paramagnetic species (no background interference), SDSL-EPR spectroscopy has the potential to evolve into an efficient method for in cell structural studies.

A major hurdle yet limiting this approach is the short persistence of currently available nitroxide spin labels in the cellular context; indeed, antioxidants such as ascorbate and glutathione, and enzymes can reduce nitroxides into diamagnetic hydroxylamines in few minutes, thus reducing dramatically the experimental window.³ Herein, we will present the development of a new maleimido-proxyl-based spin label resistant to bio-reduction and report CW and Pulsed (DEER) EPR experiments on its performance in probing structural dynamics of *E. coli* NarJ, a chaperone protein involved in the biogenesis of the membrane-bound respiratory nitrate reductase complex.⁴

Moreover, EPR experiments and results on the resistance of this new nitroxide spin label towards reduction by ascorbate, cellular extracts and inside cells (oocytes and bacteria) at room temperature will be discussed.

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Parkinson's Protein α -Synuclein: Membrane Binding Modes and Conformations by cw-EPR and DEER

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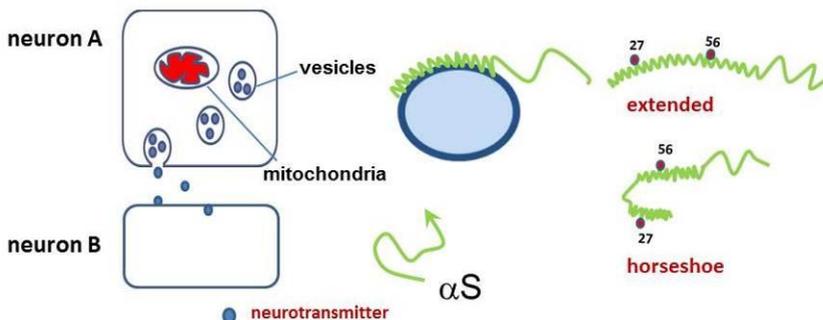
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Human α -Synuclein (α S) is a natural protein in the brain, where it associates with neuronal junctions (synapses), however with so far unexplained function. The protein became notorious because it seems involved in Parkinson's disease. As an intrinsically disordered protein, α -Synuclein is extremely flexible and therefore novel methods to study are needed.

Since the binding of α S to membranes, and more specifically to natural membranes, is thought to be crucial in relation to its pathological and physiological function we develop methods to determine its properties from membrane binding to fibrillization. Spin-label, continuous-wave EPR on proteins with single spin labels provides local membrane-binding information and double electron-electron resonance (DEER) the conformation.¹ The relation of membrane conformation to other states of α S, such as the amyloid fibril state² are discussed.



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Defects and Defect Induced Room Temperature Ferromagnetism in Metal Oxides: a Combined EPR and DFT Study

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Metal oxides manifest their most interesting chemical, electronic and magnetic properties after introduction of foreign components (dopants) or defects (e.g. oxygen vacancies) in the lattice. In the last years, enormous effort has been devoted to the understanding of their physical and chemical properties. The interplay between experiment and computation has been shown to be extremely useful in this field. In particular, for materials that present paramagnetic centers, the interplay between EPR spectroscopy and DFT calculations is of crucial importance.

In this work, we analyze the nature of isolated N-dopants in different oxides (i.e. SnO₂, ZrO₂ and BaO) and their magnetic interaction and examine the possible ferromagnetism due to oxygen deficiency in TiO_{2-x} by means of a combination of DFT and EPR data.

We adopted a hybrid DFT functional (B3LYP), i.e. a self-interaction corrected functional, which is particularly appropriate to better describe the band gap and the spin properties of solid systems.

The inclusion of a nitrogen dopant into the oxide lattice is a credible approach to tune the absorption properties, as demonstrated for several oxides.¹ The effects of N-doping were similar among the three oxides that we considered. The nature of the impurity state is always localized at the dopant site, which may limit their application in photocatalytic processes. These indeed require highly delocalized photoexcited carriers within the material.

The presence and the interaction of more paramagnetic centers, generated by N dopants (i.e. diluted magnetic semiconductor, N-ZrO₂ and N-BaO) or by oxygen vacancies (TiO_{2-x}), has recently attracted a lot of interest because of their potential applications both in spintronics and opto-electronics.² However, the nature and the origin of this room temperature ferromagnetism are often controversial. To this end, a systematic study of several possible doped structures has been performed and the corresponding magnetic configurations were investigated. In this way, the interaction between two isolated paramagnetic centers has been theoretically evaluated in terms of effective pair exchange interaction. Finally, the expected Curie temperature for the transition from anti-ferro to ferromagnetic phases has been estimated by means of Heisenberg mean field model.

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Conduction Electron Spin Resonance in Bulk Germanium and Germanium Quantum Wells

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Germanium has been under the spotlight of researchers for several decades and it has been studied both from the theoretical and experimental point of view. Its characteristic conduction band, with four minima at the edges of the Brillouin zone, is a playground for material scientists.

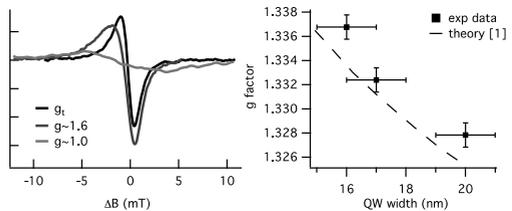


Fig. 1 (left) lineshapes at different g in bulk Ge; (right) g factor of conduction electrons in Ge QWs as a function of the QW width at $T = 2$ K.

Here we present the electrically detected magnetic resonance of conduction electrons in bulk Ge crystal and in Ge quantum wells (QWs). The carriers were generated in the bulk by illumination, while they were introduced in the QWs by modulation doping.

In the bulk, we observed ESR lines with axial symmetry and principal g values $g_p = 1.920$ and $g_s = 0.839$, as expected for electrons in conduction band-like states. In the QWs there is a dependency on the thickness of the well, in agreement with the model proposed by Baron et al. [1]. Relaxation times have been estimated by the saturation curves and linewidth, providing exceptionally long values with respect to the bulk.

The ability of tailoring the g factor in a semiconductor is appealing because it opens new pathways, allowing spintronic functionalities on a silicon-compatible technology.

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Interaction of non-innocent ligand with transition-metal ions – insight into electronic and magnetic structure of Ni(II)-NO adduct in ZSM-5 zeolite

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The paramagnetic mononuclear nickel adducts with small molecules Ni^{II}-XY are the key species implicated in various catalytic systems. For an in-depth understanding of the fundamental chemistry of the Ni-XY units, a detailed description of the electronic and magnetic structure can be achieved by means of advanced EPR and quantum chemical methods. In case where XY molecule is a non-innocent ligand, electronic structure of the adduct results from complicated spin and charge flow channels (e.g. O₂),¹ or nearly perfect spin pairing as in the present case of NO.

Herein, we report the results of CW-EPR and HYSORE investigations (Fig. 1a,b) corroborated by quantum chemical investigations (DFT, CASSCF) of the Ni(II)-NO adducts inside zeolite ZSM-5. Identification of the adsorption adduct was assured by means of IR, EPR, and HYSORE methods allowing for extraction of **g** and ¹⁴N hyperfine tensor parameters. CASSCF calculations showed that the configuration |(d_{xy})²(d_{xz})²(d_{yz})²(d_z)²↑(d_{x²-y²)²↑(π_x*)⁰(π_y*)[↓]| represents dominant contribution (87%) to the electronic wave function. It indicated that the magnetic properties originated from antiferromagnetic coupling between two open-shell subsystems: Ni(II) and NO (Fig. 1c), resulting in vanishing spin density at nitrogen atom and leaving one unpaired electron at the nickel centre, which remained in agreement with the HYSORE results.}

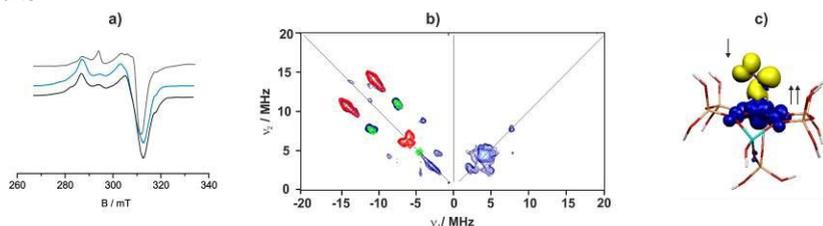


Figure 1. Exemplary a) CW-EPR and matched HYSORE spectra of Ni(II)-NO/ZSM-5 adduct along with c) its broken-symmetry spin density contour.

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Catalytic and Solid-State Reactions by EPR

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Electron-acceptor sites capable of ionizing compounds with ionization potentials ~ 7 eV after their adsorption exist in high concentrations on the surface of alumina and some other metal oxides.¹ The resulting radical cations and radical products of their transformations can be quantitatively studied by EPR acting as spin labels characterizing such electron-acceptor sites. In the current communication an original technique developed for characterization of electron-acceptor sites in the course of catalytic or solid-state reactions and the obtained results will be reported.

Weak electron acceptor sites were observed on the surface of nanocrystalline MgO destructive sorbent during solid-state reaction with CF₂Cl₂ characterized by an unusual long induction period.² The reaction rate was observed to correlate with the concentration of electron-acceptor sites tested radical cations formed by ionization of anthracene or perylene as spin probes. Similar correlations were observed for CF₂Cl₂ decomposition over Al₂O₃, which was found to react with CF₂Cl₂ at substantially lower temperature due to higher concentration of electron-acceptor sites.

The catalytic activity of nanocrystalline MgO or Al₂O₃ in 1-chlorobutane dehydrochlorination was found to increase significantly during the reaction, which is accompanied by modification of the surface and bulk with chloride ions. A good correlation was observed between the catalytic activity and the concentration of weak electron-acceptor sites.

The experimental correlations between the concentrations of the electron-acceptor sites and the catalytic activity in reactions catalyzed by acids suggest that these reactions are likely to occur on such sites rather than on more abundant traditional acid sites. Such sites also seem to be responsible for some bulk solid-state reactions. EPR appears to be an excellent technique for characterization of such very active surface sites.

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Development of Multi-Extreme THz ESR System

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Development of multi-extreme THz ESR in Kobe will be presented. It covers the frequency region from 0.03 to 7 THz. Here the multi-extreme conditions correspond to the high magnetic field up to 55 T using the pulsed magnet¹, the high pressure up to 1.5 GPa using the transmission type piston cylinder pressure cell², and the detection of micrometer size sample using the micro-cantilever ESR³.

Recently we have developed the transmission type hybrid-type pressure cell, which consists of NiCrAl alloy inner cell and Cu-Be alloy outer cell, and have achieved the pressure up to 2.7 GPa⁴. Observation of pressure induced phase transition in Shastry-Sutherland Model Substance SrCu₂(BO₃)₂ will be discussed as an example of high pressure THz ESR.

Moreover, we have extended the micro-cantilever ESR measurements up to 1.1 THz recently, which is the world record for such mechanical detection of ESR, using the torque method⁵. We are also seeking the possibility to apply the micro-cantilever ESR for the ESR measurement of metal protein using the Faraday method.

In connection development on the magnetization detected ESR using SQUID (Superconducting Quantum Interference Device) magnetometer (SQUID ESR) may be also presented⁶.

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Laser-Induced Magnetic Dipole Spectroscopy

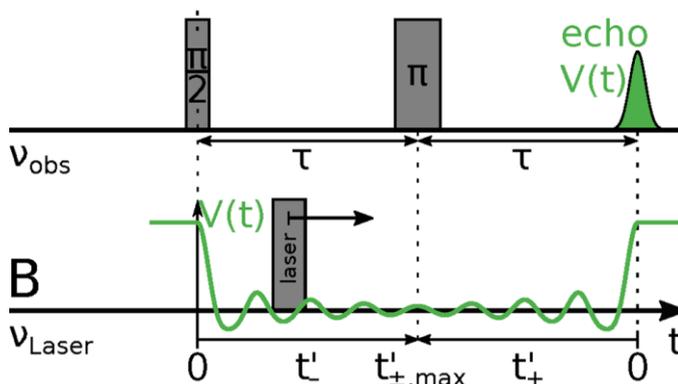
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Pulse electron paramagnetic resonance measurements of nanometer scale distance distributions have proven highly effective in structural studies. They exploit the magnetic dipole–dipole coupling between spin labels site-specifically attached to macromolecules. The most commonly applied technique is double electron–electron resonance (DEER, sometimes also called pulsed electron double resonance (PELDOR)).

Here we present the new technique of laser-induced magnetic dipole (LaserIMD) spectroscopy¹ based on optical switching of the dipole–dipole coupling.



In a proof of concept experiment on a model peptide, we find, already at a low quantum yield of triplet excitation, the same sensitivity for measuring the distance between a porphyrin and a nitroxide label as in a DEER measurement between two nitroxide labels.

On the heme protein cytochrome C, we demonstrate that LaserIMD allows for distance measurements between a heme prosthetic group and a nitroxide label, although the heme triplet state is not directly observable by an electron spin echo.

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EPR-Based Metal Ion Trilateration

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Metal ions are important for the folding, structure and catalysis of biomolecules. We will present an EPR-based metal ion positioning system for paramagnetic ions in such biomolecules¹. In this approach site directed spin labeling with nitroxides or trityl radicals is used and the label coordinates are determined by means of *in silico* methods. Then the label-to-ion distances are measured by Pulsed Electron-Electron Double Resonance (PELDOR or DEER) or Relaxation Induced Dipolar Modulation Enhancement (RIDME)^{2,3,4}. Finally the ion site is localized within the fold of the biomolecule by means of trilateration. This approach was successfully tested on Cu(II) in azurin yielding a deviation of 2 Å with respect to the crystallographic site. The source of this error is mainly related to the error of the label coordinates. The imperfection of the *in silico* labeling methods will be shown by localizing the label positions by X-ray crystallography and PELDOR measurements⁵.

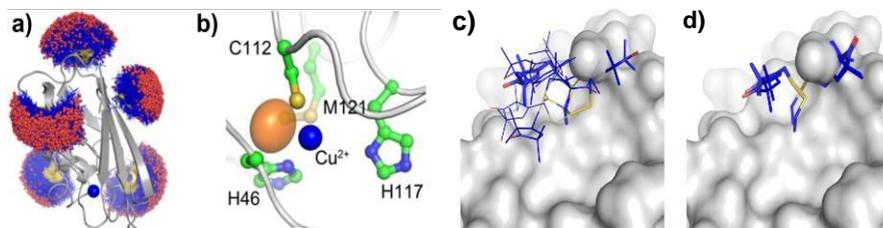


Figure 1. a) X-ray structure of azurin with the *in silico* generated MtSSI label ensembles (red/blue). The Cu(II) is shown as blue sphere. b) The EPR-based trilateration result (orange sphere) superimposed on the X-ray structure. c) The label positions as found by localizing them experimentally with PELDOR and d) their positions as found by X-ray crystallography.

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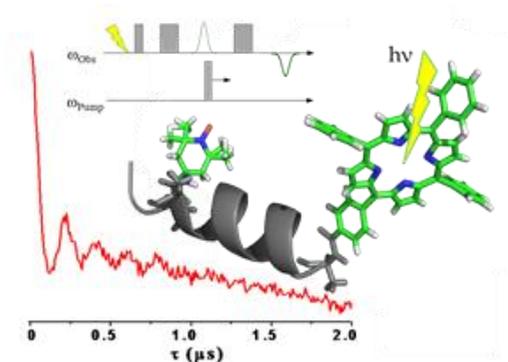
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Triplet-state spectroscopic ruler for high-sensitive PELDOR spectroscopy

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We present a novel pulsed electron paramagnetic resonance spectroscopic ruler to test the performance of a recently developed spin labelling method for measuring nanometer scale based on the photoexcited triplet state.¹ Four-pulse electron double resonance (PELDOR) experiments are carried out on a series of helical peptides, labeled at the N-terminal end with the porphyrin moiety, which can be excited to the triplet state, and with the nitroxide at various sequence positions, spanning distances in the range 18-80 Å. The PELDOR traces provide accurate distance measurements for all the ruler series, showing deep envelope modulations at frequencies varying in a progressive way according to the increasing distance between the spin labels. The upper distance limit is evaluated and found to be around 80 Å. The PELDOR-derived distances are in excellent agreement with theoretical predictions. We demonstrate that high sensitivity is acquired using the triplet state as spin label by comparison with Cu(II) porphyrin analogs.

The methodology has been extended from the peptide model system to paradigmatic proteins, where the porphyrin derivative probe is endogenously bound, in order to prove that this labelling approach has a high potential for measuring nanometer distances in more complex biological systems.



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Electronic Structure of Charge Separated States in Organic Photovoltaic Cells: A Combined EPR and DFT Study

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Our current research is aimed to resolve fundamental mechanisms of photochemical energy conversion and devise integrated systems that can capture, convert, and store solar energy. Solar-based technologies such as Organic Photovoltaic (OPV) allow to convert and to store solar energy in the form of electrochemical potential. This technology could provide sufficient energy to satisfy the global economic demands in the near future. Understanding the charge separation and electronic structure at a molecular level is crucial for improving the efficiency of OPV materials. To address these questions we investigate charge separation and stabilization mechanisms at semiconductor polymer-fullerene interfaces by employing an advanced suite of experimental and theoretical techniques, namely: multidimensional EPR spectroscopy in combination with Density Functional Theory (DFT) calculations. Under illumination of the OPV active blends, two paramagnetic species are formed due to photo-induced electron transfer between the conjugated polymer and the fullerene derivative. They are the positive, P^+ , and negative, P^- , polarons on the polymer and fullerene, respectively, and correspond to radical cations and radical anions. DFT calculations have been used to calculate the electronic structures of the fullerene anions and polymer cations (Figure 1). These calculations allow us to extract magnetic resonance parameters and to map spin density distributions of the charge separated species. The same parameters were experimentally obtained from advanced EPR spectroscopies. The good agreement of the calculated magnetic resonance parameters with those determined experimentally is a validity proof of the DFT calculations. Thus, we were able to obtain delocalization length of the positive charge along the polymer chain for a number of efficient OPV polymers. To the contrary, it was shown that negative charge is located on the cage of the fullerene and not delocalized between several molecules. For the first time we acquire not only the value of the g-tensors for soluble derivatives of C_{60} and C_{70} derivatives of fullerene but also the directions of the magnetic axis in the molecular frame. The relation of these data to the efficiency of the charge separation process in OPV is discussed.

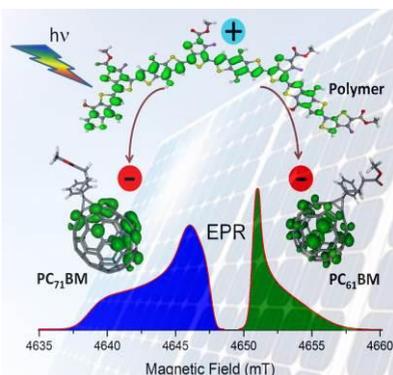


Figure 1. Delocalization of the spin densities along the polymer chain and on the soluble derivatives of fullerenes as determined by high-frequency EPR and DFT calculations

Direct measurement of the flip-flop rate of electron spins in solid-state

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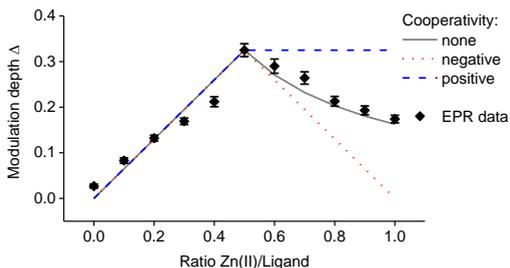
Electron spins in solids have central role in many current and future spin-based devices, ranging from sensitive sensors to quantum computers. Many of these apparatuses rely on the formation of some well-defined spin structure (e.g. a 2D array) with controlled and well-characterized spin-spin interactions. Arguably, the most important interaction-related quantum process that may interfere with the coherent operation of these devices is the so-called "flip-flop" event, where two spins interchange their quantum state. Thus, accurately quantifying the rate of this process under different conditions is of importance. However, direct measurement of this rate turns out to be very problematic. One indirect way is based on measurements of the spins' coherence time as a function of various parameters (temperature, spins concentration, pulses flip angles) and try to extract from this data some estimation of the flip-flop rate in bulk samples. We present and pursue an alternative method for experimentally measuring for the first time the rate of this flip-flop process through the acquisition of the spin diffusion coefficient of the electron spins in solid state. Namely, we measure only the quantum-mechanically-derived spread of the electron spins' wavefunction in time (since there is of course no real-space diffusion in solids). This is carried out for a sample of P doped ²⁸Si, measured by conventional ESR induction-detection with pulsed gradient field echo (PGSE) method, as well for a sample of NV centres in diamond measured by optically-detected magnetic resonance, which is also carried out in conjunction with the PGSE method. These measurements are extremely challenging since they involve spin diffusion coefficients as low as 10⁻¹⁴ m²/s and are of significant relevance to many spin-based quantum applications.

Quantifying Binding and its Cooperativity from PELDOR Modulation Depths

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Pulse dipolar EPR, especially the PELDOR (pulsed electron-electron double resonance or synonymously DEER for double electron electron resonance) have established a valuable addition to the armoury of structural sciences and are becoming increasingly applied in the context of structural biology.¹ While ever more complex systems are being approached increasing the scope of systems to be investigated and pushing the range of distances accessible from the frequency information in the time domain data, the modulation depth of a PELDOR experiment bears information on the number of spins per complex² but is most often neglected. Here, we use model studies mimicking templated dimerization using spin-labelled terpyridine ligands to demonstrate that multimerisation equilibria and binding constants and cooperativities may be accessible from PELDOR data.³ PELDOR experiments as well as additional broadband PELDOR experiments⁴ and use of relaxation filters⁵ demonstrate that terpyridine binding to Cu(II) is anti-cooperative while binding to Zn(II) is non-cooperative and binding to Fe(II) and Co(II) is cooperative. The additional information from the modulation depths opens interesting opportunities for biological applications.⁶



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Optimization of Band-Selective Inversion Pulses

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In double electron electron resonance (DEER) distance measurements, overlap of the excitation bands of observer and pump pulses can lead to artefact contributions. In the five-pulse DEER experiment, which provides access to longer distances through a prolonged dipolar evolution time,¹ further artefacts appear if spin packets are partially excited by the two pump pulses. The ideal excitation profile that would completely suppress all artefacts is rectangular and cannot be attained in practice. The best approximation demonstrated to date in the context of DEER measurements is provided by hyperbolic secant pulses.²

Optimization of the excitation profile of DEER pump pulses is constrained by available microwave power, by the maximum pulse length at which the dipolar evolution function can still be obtained with high fidelity, and by the bandwidth required for obtaining sufficiently large modulation depth. We demonstrate that an asymmetric hyperbolic secant pulse strikes a better compromise between these requirements than the previously considered symmetric hyperbolic secant pulse.

Furthermore, we consider numerical optimization of the amplitude and frequency modulation function of the pulse. We show that, even for pulses that are only 64 ns long, electron spin transverse relaxation with phase memory time of 2 μ s is not negligible and must be included for optimization. We discuss whether the frequency response of the resonator should be considered already during optimization or whether correction of a generic waveform³ for the resonator response function is feasible.

Finally, we discuss the simplifications of the hardware model and of the spin system that are necessary for waveform optimization and that compromise performance of the pulses when applied on a real spectrometer to a real sample.

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Spin-phonon relaxation processes of transition metal ions in ZnO

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Diluted magnetic semiconductors based on ZnO with transition metal ions (TM=Ni, Co, Mn, Fe) are widely used nowadays for testing concepts for spintronics applications. The $3d^6$ transition metal ions such as Fe^{3+} and Mn^{2+} with electron spin $S=5/2$ potentially provide a spin multiplet for use in the implementation of quantum algorithms. Recently, systems with the same ground state electron configuration as Mn^{2+} in single-crystal MgO ¹ and in colloidal ZnO quantum dots² have been suggested for quantum computing applications.

Here, we report the spin dynamics of transition metal ions in ZnO. Inversion recovery with electron spin echo detection has been used in order to measure the spin-lattice relaxation time T_1 for transition metal ions in hydrothermal grown ZnO single crystals. The main feature of T_1 data for Co^{2+} and Ni^{3+} ions is an extremely fast relaxation rate. ZnO:Co crystals under study exhibit unique properties such as formation of nearest-neighbor antiferromagnetically-coupled dimer centers. The cross relaxation transitions between Co^{2+} and exchange-coupled pairs provide an essential contribution to the relaxation rates at low temperatures. In an addition, the EPR spectrum of the ZnO:Co²⁺ system was studied from 80 to 295K. The exponential line broadening with temperature in the high-temperature region was fitted to an Orbach process, with an excited state at 225 cm^{-1} .

To estimate the relaxation rates of Fe^{3+} ions in ZnO, we consider direct (one-phonon) and a two phonon Raman processes. The fitting of inversion recovery data revealed a Debye temperature significantly lower than the value known for the host matrix.

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EPR Spectroscopy and in situ EPR/UV-vis-NIR Spectroelectrochemistry of Metal Complexes with Noninnocent Ligands

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Metal complexes with a noninnocent ligand exist either as a metal–ligand radical $M^{n+}(L^{\cdot})$ or a higher valent metal complex $M^{(n+1)+}(L^{\cdot})$.¹ However, for noninnocent ligands the distribution of the electron density between the central atom and the ligand is more complex making it difficult to determine the physical/formal oxidation state of the central atom. Extended charge delocalization is typical for these complexes in different oxidation states and subtle changes of electronic structure could significantly alter the redox site within the complex. Recently we reported several nickel complexes exhibiting EPR spectra that are neither typical Ni(III) nor organic radical in character.^{2,3} The investigated metallocomplexes clearly represented a system with a substantially noninnocent character of the ligand. Characteristic Ni(III) EPR signals show obviously large *g* values and large anisotropy due to coupling with the metal nuclear spin, while the organic radical centered species show a *g* value close to 2.00. Variety of EPR signals were observed for one-electron oxidized Ni(II) complexes going from predominantly phenoxyl radical character with very little contribution from the d-orbitals of redox active Ni(II)^{4,5} to the formation of $[Ni(II/III)L]^+$ species with strong noninnocent character exhibiting a rhombic EPR signal with a large *g*-tensor anisotropy.^{2,3} Two different species with different *g* values at low temperatures having characteristic features of both nickel(III)-phenolate and nickel(II)-phenoxyl radical states were observed for some cases.⁵ In this contribution the redox behaviour of variety of Ni, Cu and Co metallocomplexes with noninnocent ligands which have been studied by cyclic voltammetry, EPR, in situ EPR–UV/vis/NIR spectroelectrochemistry and theoretical calculations is discussed.

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Segre Prize

Triplet state delocalization in conjugated porphyrin systems investigated by EPR

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Porphyrin-based molecular materials are of considerable interest in the fields of molecular engineering, artificial photosynthesis and spintronics. Electronic communication between the porphyrin units in these assemblies is essential for application in these fields and has been investigated in a series of linear and cyclic π -conjugated porphyrin arrays by probing the triplet state delocalization using time-resolved EPR.

Information on the extent of triplet state delocalization as a function of the number of porphyrin units and the geometry of the porphyrin system was obtained from the zero-field splitting (ZFS) parameters, spin polarizations and hyperfine couplings measured using time-resolved EPR and ENDOR. Interpretation of the experimental results was aided by DFT calculations.

Time-resolved EPR and magnetophotoselection experiments have shown a reorientation of the zero-field splitting tensor between a single porphyrin unit and longer linear arrays, resulting in alignment of the main optical transition moment and the Z axis of the ZFS tensor.¹ The reorientation of the ZFS tensor was confirmed by orientation-selective ¹H ENDOR measurements.

The observed trends in proton and nitrogen hyperfine couplings with the size of the porphyrin systems indicate uneven spin density distributions over the linear porphyrin arrays.² In these linear systems, the extent of delocalization of the excited triplet state was also found to depend on the conformation of the porphyrin chain. Excitation-wavelength dependent transient EPR and ENDOR experiments were used for preferential excitation and investigation of different conformations.³ Complete delocalization of the excited triplet state was observed in the cyclic six-membered porphyrin nanoring.²

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ENDOR Characterization of an Iron for Nitrogen Reduction

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The reduction of nitrogen to ammonia by bacteria or the energy intensive Haber-Bosch process is necessary for human life. Nature performs this reaction utilizing the iron-rich metallocofactor found in nitrogenase enzymes. It has been shown that N₂ reduction by nitrogenase occurs on an Fe face of the [7Fe9SMoC] cluster.¹ It is well demonstrated that small inorganic complexes of Mo and W readily bind N₂ and facilitate protonation at one or more N atoms to furnish M(N_xH_y) species that can be characterized prior to the final production of NH₃. However, the direct protonation of a Fe-N₂ species to any Fe(N_xH_y) product that can be structurally or spectroscopically characterized has been elusive. While the structure of the catalytic [(TPB)Fe(N₂)] [Na(12-crown-4)₂] (TPB, tris(phosphine)borane) complex² is analogous its non-catalytic silyl equivalent,³ the structure of any catalytic intermediates are unknown. This presents an unique opportunity to identify catalytic intermediates and elucidate structure through advanced EPR techniques.⁴ Proposed structures of N₂ and N_xH_y bonding to Fe(I) will be presented in addition to unique 'spring bonding' information as resolved by ENDOR spectroscopy.

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IES Session

Time-domain in vivo EPR imaging

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The development of instrumentation for Imaging of unpaired electron distribution in small animals and phantoms using time-domain (pulsed Fourier Transform) EPR approach will be briefly described. Unlike MRI which addresses the distribution of the abundant water molecules in living systems, EPR imaging requires the administration of bio-compatible free radicals into the imaging subject. Relaxation times T_1 and T_2 of most unpaired electron systems are in the micro or sub-micro second regime and the frequency band width to be excited when space-encoding gradients are applied will be in the tens of MHz range. Stable organic free radicals such as nitroxides are OK for CW EPR imaging since covering a large 'bandwidth' via magnetic field sweep is straightforward. Further, lossy biological samples have very small skin-depth at MW frequencies restricting *in vivo* EPR imaging to the Radiofrequency region just as in MRI. These characteristics warrant the use of very narrow line width spin probes, generation of nanosecond range of high power pulses and very fast acquisition of the FIDs. Recently developed triarylmethyl radicals with narrow line widths are ideal for EPR imaging. These are also sensitive to oxygen broadening. EPR imaging is particularly useful in monitoring hypoxic zones in tumours which are highly resistant to radiation and chemotherapeutic treatments. At the National Cancer Institute we have developed high resolution 3D time-domain and CW EPR imaging strategies at 300 to 750 MHz range.^{1,2} In this presentation our FT-EPR imaging and *in vivo* tumour oximetric strategies are highlighted. Using constant time pure phase encoding and utilizing spin-echo and inversion recovery modes, quantitative *in vivo* oximetry in animal models of tumour are being routinely carried out (Fig.1). We also co-register tumour oximetric images with the corresponding functional MR images to investigate the influence of hypoxia and antiangiogenic drugs on tumour growth. Recently, co-registration EPR images with hyperpolarized MR spectroscopic imaging is being carried out to investigate tumour biochemistry. Results will be presented and discussed.

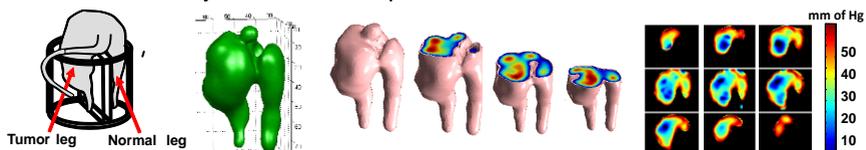


Fig.1 Left to right: Schematic of mouse with SCC tumor-bearing and normal legs in the resonator, surface rendered 300 MHz FT EPR 3D image, slices through the image, and T_2^* -weighted transverse oximetric slices through the image showing heterogeneous tumour hypoxia.

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Thermally- and Photoinduced Magnetostructural Transitions in Copper-Nitroxide Based Molecular Magnets Studied by Multifrequency EPR

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Copper-nitroxide-based molecular magnets of the $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ family (where hfac is hexafluoroacetylacetonate, and L^{R} is a pyrazolyl-substituted nitroxide ligand) are interesting and appealing systems exhibiting various magnetic anomalies triggered by temperature or light, which can generally be viewed as spin-crossover-like phenomena. Significant structural rearrangements accompany magnetic anomalies in $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ and lead to considerable crystal volume changes. Taking into account the reversibility of these changes, complexes of $\text{Cu}(\text{hfac})_2\text{L}^{\text{R}}$ family are often called “breathing crystals”.¹

The presence of paramagnetic copper(II) ions and stable nitroxide radicals in the polymer chains of breathing crystals makes EPR widely applicable to these systems. In addition to the determination of typical parameters (g-tensor and hyperfine splitting constants), EPR allows the monitoring of magnetostructural switching between different states² and evaluation of exchange interactions in the exchange-coupled clusters of copper(II) with nitroxides³ and those between the exchange-coupled clusters. Multifrequency EPR (9-244 GHz) was found very useful and informative for disentangling different interactions in breathing crystals.⁴

This talk highlights the capabilities of multifrequency EPR in investigations of breathing crystals and related exchange-coupled systems and obtaining crucial information on magnetic interactions inaccessible by other techniques.

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EPR at 275 GHz: from nitroxides to transition-metal sites in proteins

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During the last decades EPR spectrometers have been developed that operate at increasingly higher microwave frequencies and higher magnetic fields and, consequently, offer an increased Zeeman resolution. Besides, a multi-frequency approach to the study of paramagnetic systems over large magnetic-field ranges has become feasible, which helps to distinguish the contribution to an EPR spectrum of an internal magnetic interaction from that of the interaction with the external magnetic field. In my presentation I will summarize some of the contributions of the Leiden group to these developments, and emphasize our achievements at 275 GHz.

The continuous-wave EPR spectrum of a nitroxide at 275 GHz will serve to demonstrate the Zeeman resolution at 10 T and the sensitivity that we have reached using a single-mode cylindrical cavity. For nitroxide spin-labeled protein sites in membrane proteins, such experiments provided the resolution necessary to disentangle the effects of hydrogen bonding and polarity of the micro-environment.¹ The merits of a multi-frequency approach will be illustrated for high-spin Fe(III) centers, in Fe(III)-EDTA² and in the iron-transport protein transferrin.³ The consistent interpretation of EPR spectra at frequencies between 9 and 275 GHz required in both cases an advanced description of the distribution of the zero-field splitting.

When single-mode cavities are used at high microwave frequencies, only small amounts of sample are necessary. The sub-millimeter capillary in our set-up at 275 GHz has an active volume of about 20 nl. For the study of transient paramagnetic intermediates of (bio)chemical reactions, the small volume and narrow capillary have advantages and disadvantages. In this context, both rapid-freeze quench EPR and a novel approach to the study of transients called "temperature-cycle EPR" will be discussed.

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ESR from the Scholes Lab: ESR Fellow Lecture

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This lecture will be a short overview of progress in ESR from the Scholes lab over the last forty years. It will focus on: 1. ENDOR of Heme and Metalloproteins. 2. Rapid-Flow and Stopped-Flow ESR.

ENDOR (electron nuclear double resonance) was applied initially to the heme environs in ferric metmyoglobin to elucidate hyperfine and nuclear quadrupolar information. Spin densities, biologically important changes in electronic structure, ligand identities, and iron-proton distances were obtained. Next, ENDOR was focused on the heme and coppers of cytochrome oxidase, a ubiquitous enzyme which consumes 95 % of the oxygen that aerobic organisms breathe. Subsequently, ENDOR of copper and manganese enzymes was followed. Structural and functional highlights revealed by ENDOR will be presented, biochemical and molecular biology advances needed to support this work will be outlined, and apparatus requirements will be discussed.

Stopped-flow and Rapid-flow ESR required technical development of micro-resonant dielectric structures intimately coupled to miniature mixers with precise control of fluid flow. Using numerous site-directed nitroxide spin labeling sites engineered in-house, protein folding throughout the cytochrome *c* molecule was followed. Folding at times longer than a millisecond was followed by stopped-flow ESR. Rapid, sub-millisecond prefolding/compacting was monitored by rapid-flow ESR at a single field. To obtain overall spectra of rapidly folding protein, rapid-flow and rapid field sweep were combined. Recently obtained information on prefolding of protein at times less than 100 μ sec will be shown.

POSTER ABSTRACTS

Towards Temperature-Cycle EPR: Chemical kinetics.

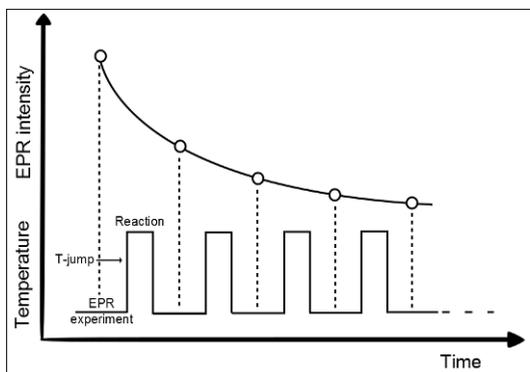
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We report on the development of Temperature-Cycle EPR, a novel EPR technique at 275 GHz to study intermediates and kinetics of (bio)chemical reactions involving paramagnetic species. Such investigations are paramount to reveal the mechanism underlying the reactivity of any (bio)chemical system, from enzymatic catalysis to polymer degradation. In particular, high-frequency EPR offers high resolution and, if coupled to single-mode cavities, high-sensitivity.

Our new method exploits the minuscule resonant volume (20 nL) of the single-mode cavity of our 275 GHz EPR spectrometer to heat a frozen sample directly in the EPR cavity, in a homogeneous, reproducible, and controllable manner¹. This *in-situ* heating (or “temperature jump”) brings the sample to a temperature at which the reaction takes place for an arbitrary period of time. Temperature-Cycle EPR is based on a sequence of such temperature jumps applied to a sample, and allows to investigate kinetics and to detect short-lived intermediates (see Scheme). Important characteristics of Temperature-Cycle EPR are the small amount of material required, and the fact that only one sample is needed to carry out a kinetic study. Both features constitute an advantage over other methods, such as Rapid Freeze Quench EPR.



We will present our first results on two model reactions: one being the reduction of a nitroxide radical in water-glycerol solution, and the other the reduction of Mn(IV) to Mn(II) in aqueous solution. We thereby prove that Temperature-Cycle EPR is a promising new approach to investigate paramagnetic transients and kinetics of chemical systems, worth being developed further.

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Towards Temperature-Cycle EPR: Calibration of the temperature jump

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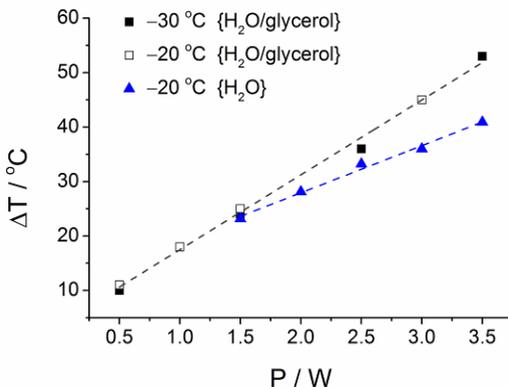
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We report on the development of Temperature-Cycle EPR, a novel technique to study kinetics of (bio)chemical reactions involving paramagnetic species.

This technique is based on cycling the system between a state in which the reaction does not take place and a state in which the reaction does take place. In aqueous samples, the temperature jumps are induced by an infrared laser and bring the system from the frozen to the liquid state. The performance of Temperature-Cycle EPR depends on the precise characterization of the temperature jumps.

We utilize EPR-based temperature measurements for calibration of the laser-induced temperature jumps. Second-moment analysis along two dimensions of continuous-wave EPR spectra of nitroxides enables EPR thermometry in a broad temperature range. Simulations show that the temperature can be derived in both the slow-motion and the fast-motion regime, which is experimentally verified at 275 GHz for H₂O/glycerol (50/50% by volume) and pure water. We demonstrate that this tool allows the calibration of temperature jumps induced by infrared laser irradiation of a submicroliter sample in the single-mode cavity of a 275 GHz spectrometer. Temperature jumps up to 50 °C have been realized (Figure), which allows for great flexibility in heating a sample for kinetic studies by Temperature-Cycle EPR.



Microenvironment of ionic liquids studied by time-resolved EPR of photoexcited triplet complexes

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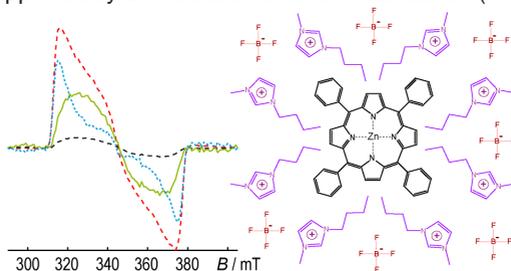
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Ionic liquids (ILs) exhibit a number of unusual and advanced properties making them perspective media for many chemical processes of fundamental and applied significance, especially in field of green chemistry. Herewith, we investigate the influence of microviscosity and nanostructuring of ILs on spin dynamics of the dissolved photoexcited molecules. We use three ILs [Bmim]PF₆, [Bmim]BF₄ and [C₁₀mim]BF₄ as solvents and photoexcited Zn tetraphenylporphyrin (ZnTPP) as a probe. We employed time-resolved electron paramagnetic resonance (TR EPR) technique to investigate spectra and kinetics of spin-polarized triplet ZnTPP in the temperature range 100–270 K. TR EPR data clearly indicate the presence of two microenvironments of ZnTPP in frozen ILs at 100–200 K, being manifested in different spectral shapes and different spin relaxation rates. For one of these microenvironments TR EPR data is quite similar to those obtained in common frozen organic solvents (toluene, glycerol, N-methyl-2-pyrrolidone). The second microenvironment reveals the remarkably slow relaxation of spin polarization, being much longer than in the case of common solvents. The formation of heterogeneities upon freezing of ILs was confirmed by additional experiments using continuous wave EPR and stable nitroxide as a probe. Thus, TR EPR of photoexcited triplets can be effectively used for probing heterogeneities and nanostructuring in frozen ILs. In addition, the increase of polarization lifetime in frozen ILs is an interesting finding that might allow investigation of short-lived intermediates inaccessible otherwise.

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The application of bismuth germanate in X-band EPR spectroscopy

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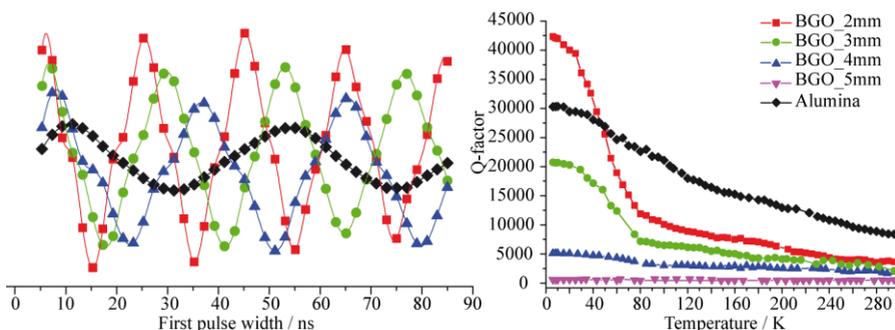
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The microwave (MW) resonator is perhaps the only part of EPR spectrometer which can be modified/developed to fit the experimental conditions in the best way and thus increase the sensitivity of EPR setup. In this work we replace the standard alumina insert in the Bruker X-band ER 4118X-MD-5W1 resonator by the bismuth germanate ($\text{Bi}_4(\text{GeO}_4)_3$, BGO) of the same resonant range (X-band) and analyze the CW and pulse EPR performance of such resonators depending on the dimensions of BGO insets. The Q-value of empty resonators, B_1 saturation curve and CW spectra of DPPH sample were measured in a temperature range of 6 – 295 K and analyzed. CW sensitivity improvement in the factor of 4 with 2 mm inner diameter BGO insert in comparison with alumina one was achieved at room temperature. The performance of BGO dielectric resonator in pulse EPR experiments was also characterized and maximum sensitivity improvement in the factor of 3.5 with 2 mm inner diameter DI at room temperature was achieved. The CW EPR baseline measured at 300, 77 and 6 K confirms the absence of BGO-attributed signals proving the high purity of the material used.

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Origin of the puzzling narrow line in the EPR spectrum of triplet C₇₀

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X-band light-induced continuous wave EPR (LEPR) spectroscopy and pulse electron spin echo (ESE) techniques were employed to study triplet fullerene C₇₀, ³C₇₀, in glassy decalin and o-terphenyl.

Spin-lattice relaxation times T_1 of ³C₇₀ were directly obtained by ESE inversion recovery dependences in the temperature range 30 - 100 K¹. The temperature dependence of T_1 was fitted by the Arrhenius law with an activation energy of 172 cm⁻¹. This indicates that the dominant relaxation process of ³C₇₀ is described by an Orbach-Aminov mechanism involving the higher triplet state t_2 which lies 172 cm⁻¹ above the lowest triplet state t_1 . The presence of the higher triplet state in C₇₀ is in good agreement with previous results from phosphorescence spectroscopy.

The EPR lineshapes of ³C₇₀ observed in the temperature range between 50 and 130 K (for decalin) as well as between 77 and 200 K (for OTP) were successfully simulated². The results show that the central narrow LEPR line does not originate from an S=1/2 radical, but arises from jumps of the EPR lines within the LEPR spectrum of ³C₇₀ between symmetrical LEPR positions provided by a paramagnetic relaxation process of ³C₇₀. This process can be described by a relaxation-induced coherence transfer between two resonance transitions having close transition frequencies.

The obtained temperature behavior of the narrow LEPR line intensity of ³C₇₀ is in agreement with the pronounced Orbach-Aminov temperature dependence of spin-lattice relaxation of ³C₇₀.

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Mn(II) Spin-Labels for High-Field pulse EPR Nanometric Distance Measurements

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Recently, high spin Mn(II) ($S=5/2$) complexes have found uses as spin-labels for nanometric distance measurements^{1,2} by pulse EPR techniques, such as pulse electron double resonance (PELDOR aka DEER), which are versatile biophysical tools for probing the structures and functions of complex biological systems. Compared to the more commonly used nitroxide ($S=1/2$) spin labels, metal-based systems are more stable under reducing conditions (e.g. inside a cell). Furthermore, Mn(II) is endogenous in biological environments and besides being found naturally in biomacromolecules, it can often replace Mg(II) in others, such as kinases, nucleic acid constructs and nucleotide binding domains due to their similarity in size and charge. Another consideration is that although the use of higher magnetic fields and higher frequencies inherently improves the sensitivity of the measurements, at high field the EPR spectrum of radicals broaden due to their g -anisotropy, which poses technical challenges and complicates the analysis due to orientation selection effects. In contrast, high spin Mn(II) centres have small g -anisotropies and at high fields their EPR spectra is dominated by their central $| -1/2 \rangle | 1/2 \rangle$ transition, which narrows proportionally to D^2/ν_0 , where D is a zero-field splitting parameter and ν_0 is the spectrometer frequency. 95 GHz PELDOR distance measurements between [Mn(DOTA)] centres attached to polyproline II helices as well as between genetically encodable Mn(II) spin-labels capable of self-assembly from naturally available components will be discussed.^{3,4}

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Coherent pump pulses in Double Electron Electron Resonance spectroscopy

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The recent introduction of shaped pulses to Double Electron Electron Resonance (DEER) or Pulsed Electron Double Resonance (PELDOR) spectroscopy has led to significant enhancements in sensitivity through increased excitation bandwidths and improved control over spin dynamics.¹⁻⁵ The application of DEER has so far relied on the presence of an incoherent pump channel to average out most undesired coherent effects of the pump pulse(s) on the observer spins. However, in fully coherent EPR spectrometers that are increasingly used to generate shaped pulses,^{6,7} the presence of coherent pump pulses means that these effects need to be explicitly considered.

We have examined the effects of coherent rectangular and sech/tanh pump pulses in DEER experiments with up to three pump pulses.⁸ Even in the absence of significant overlap of the observer and pump pulse excitation bandwidths, coherence transfer pathways involving both types of pulses generate spin echoes of considerable intensity. These echoes introduce artefacts, which, if not identified and removed, can easily lead to misinterpretation.

The echo shapes and relative intensities observed in experiments with coherent monochromatic or hyperbolic secant pulses at different microwave frequencies can be quantitatively modelled using a simple spin quantum dynamics approach that includes instrumental transfer functions. Based on an analysis of the echo crossing artefacts, we propose efficient phase cycling schemes for their suppression in four-, five-, and seven-pulse DEER. This enables the use of advanced DEER experiments, characterized by high sensitivity and increased accuracy for long-distance measurements, on novel fully coherent EPR spectrometers.

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EPR Study of Structural Phase Transitions in Metal-Formate Frameworks

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Recently, a novel type of highly porous materials called metal-organic frameworks (MOFs) emerged and attracted attention of the scientific community¹. These crystalline compounds are unique due to the high degree of porosity which can be utilized for gas adsorption related applications. Additionally, many MOFs containing paramagnetic transition-metal ions exhibit peculiar magnetic properties. The organic part in several of such compounds consists of polar molecules which below a certain phase transition temperature order into a ferroelectric-type phase, making these materials single-phase hybrid multiferroics².

We use X-band and Q-band continuous-wave (CW) and X-band pulse EPR as well as pulse ENDOR spectroscopic techniques to investigate and characterize structural phase transitions in Mn²⁺ and Cu²⁺ doped MOFs with general chemical formula [A][Zn(HCOO)₃]_n (where $n = 1, 2$ and Aⁿ⁺ is molecular cation such as NH₄⁺, (CH₃)₂NH₂⁺ or NH₃(CH₂)₄NH₃²⁺). The temperature dependent CW EPR spectra reveal that the paramagnetic ion-probes are indeed sensitive to the local structural changes occurring at the phase transitions. Spectral simulations are used to obtain the **g**, hyperfine **A** and fine structure **D** tensors and temperature dependencies of their components allowing to characterize the observed phase transitions. Pulse EPR and ENDOR measurements are performed to study the structure of the frameworks in the low temperature phases. The EPR measurements are supported by the density functional theory calculations.

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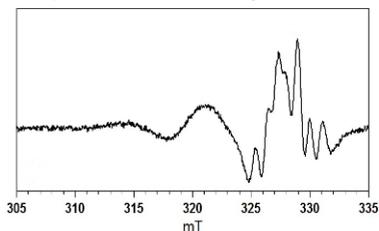
Epr and voltammetric studies of copper(ii) complexes with glutamate and arginate in aqueous solution

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There are increasing evidences which support an important role for metals in neurobiology. In this work, we did a characterization by EPR and Square Wave Voltammetry (SWV) techniques of Cu(II) bis and ternary complexes with Arginate (Arg) and Glutamate (Glu) which are abundant in the brain. It is well known that aminoacidate ligands coordinate Cu(II) giving rise to CuN₂O₂ coordination environment in which the two nitrogen atoms could be either in a *trans* or in a *cis* conformation; moreover, if Cu(II) is simultaneously coordinated to the both L or D enantiomers, the *cis* conformer has the side chains on the opposite sides of the equatorial coordination plane, while the *trans* conformer on the same side. If one ligand has the L configuration and the other has the D, a reverse stereochemistry is obtained. The peculiarity of Arg and Glu is that in physiological conditions they show the side chains with opposite charges and electrostatic interactions might stabilize preferentially one of the two conformers. The aqueous solution EPR spectra of bis and ternary complexes at room temperature, differently from what



would be expected, show a pattern with six or seven superhyperfine (shf) lines, as shown in figure, ascribable to the existence of an equilibrium between the *cis* and *trans* conformers with slight differences in the magnetic parameters. The presence of both species in solution is confirmed by SWV peaks which are asymmetrical and could be fitted by summing two gaussian curves with slight different centers and widths. Increasing gradually temperature up to 305K the shf lines modify their intensities due to the change of the *cis/trans* ratio. The frozen solution EPR spectra at 150K show the existence of only one species indicating that the low temperature stabilizes only one conformer. Some theoretical studies suggest that the *cis* conformer is the thermodynamic more stable species in aqueous solution, so it is possible to conclude that moving from low to high temperatures the equilibrium favours the *trans* conformer. The experimental magnetic parameters suggest for each complex a tetragonally elongated octahedral coordination geometry. From the shf lines intensities we note that at 275 K the *cis* conformer is much more abundant for [Cu(L-Glu)₂] complex because of the possible interaction between negative side chain carboxylate anions and water molecules axially bound; analogously, at 305 K the *trans* conformer is less abundant for [Cu(L-Arg)(D-Glu)] complex owing to a probable electrostatic interaction between the two opposite charged guanidinium and carboxylate groups.

Water Dynamics in the Hydration Shell of Model Biological Membrane by Electron Spin Echo Envelope Modulation

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Biological water plays a crucial role in the functionality of biomolecules. The coupling between dynamics of the hydration shells and the biomolecules is nowadays heavily debated. Among other issues, water dynamics at low temperatures is also discussed, especially in relation with the phenomenon of dynamical transition from harmonic to anharmonic motions observed in biological systems near 200 – 230 K in neutron scattering and in other techniques. In this respect, development of the methods giving direct information about water dynamics in the nearest hydration shell is desirable.

Recently, the Electron Spin Echo Envelope Modulation (ESEEM) approach was developed for detection of motion of deuterated molecules near the spin label.¹ Here, this approach is applied to the hydration shells of model biological membranes, containing lipids spin-labeled in their polar heads. It is shown that water molecules near the label (~ 0.5 nm away) are mobile even at temperatures below 200 K. The lipid composition of the membrane strongly influences these low-temperature water molecular motions. In the unsaturated POPC membrane the crossover temperature from restricted to unrestricted molecular motions is at least 15 K below that found in the fully saturated DPPC membrane. This result correlates with the dynamical transition inside the POPC and DPPC membranes observed with pulse EPR and Raman spectroscopies.²

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Pulse-ESR based nutation spectra of $g=2.004$ signal; frequently observed signal in BaTiO_3

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Barium titanate (BaTiO_3) has attracted great interests for ferroelectric, piezoelectric and positive temperature coefficient of resistivity (PTCR) properties. These properties are affected by various metals doping and defects such as oxygen vacancy. CW-ESR spectroscopy is one of the powerful tools to detect paramagnetic metal ions and defects, so that a number of authors have discussed relationship between paramagnetic origins and electronic properties. Particularly, ESR signal around $g=2.004$ which is frequently observed in BaTiO_3 has been believed as quite important origin closely related to PTCR phenomena. However, the assignment of the signal is different depending on authors such as V_{Ba} (Ba vacancy), $V_{\text{Ba}}\text{-F}^+$ (Vacancy of Ba and O), V_{Ti} and Fe^{3+} . The correct assignment is a controversial issue, and hence, clarifying is important in order to consider precise PTCR mechanism. For that purpose, we applied pulse-ESR based nutation spectroscopy for the first time. Nutation spectroscopy gives us straightforward information on the spin quantum number which cannot be driven in terms of CW-ESR spectroscopy.

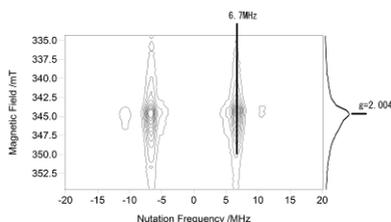


Fig. 1. 2D-Nutation spectra of BaTiO_3 powder.

Fig.1 shows two-dimensional nutation spectra of BaTiO_3 powder observed at 10 K. An echo-detected field swept spectrum is given on the right hand side in Fig1. From the spectra, nutation frequency of $g=2.004$ is determined to be 6.7MHz. ω_1 (frequency corresponding to $S=1/2$) is 2.2MHz under our experimental condition. Observed ω_n (6.7MHz) is close to $3\omega_1$, showing that the origin of $g=2.004$ is not due to vacancy such as V_{Ba} , $V_{\text{Ba}}\text{-F}^+$, V_{Ti} reported by several authors. An assignment to a paramagnetic metal cation is suitable, i.e. Fe^{3+} (high spin sextet state). In the presentation, we will also report a result of elemental analysis (ICP-MS or GD-MS).

Towards Reliable Extraction of Multiple PELDOR Distances

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Pulse electron paramagnetic resonance (EPR) spectroscopy has become an important complementary method for structural biology. Especially the PELDOR (or DEER) method is being applied to biological systems of ever increasing complexity.¹ Both, analysis and interpretation of PELDOR data using DeerAnalysis have been well established,² with the focus of extracting the mean distance of the system under study. Furthermore, promising approaches for overcoming the multi-spin problem have been described.³

However, only few studies so far have addressed the resolution of multiple distances.⁴ A systematic study with rigorous benchmarking of the experimental and processing requirements for reliable extraction of two or more peaks from a distance distribution is lacking as is the corresponding proof-of-principle in a model or biological system. This situation can lead to over-interpretation of structure in the distance distribution and thus, structural information.

In this study, we combine numerical simulations with experiments on a synthetic model system to systematically assess the feasibility of extracting multiple PELDOR distances. To this end, a trimodal distance distribution was generated from nitroxide-labelled, terpyridine-based ligands of different lengths templated on a divalent metal ion.⁵ The influence of dipolar evolution time (resolution) and noise level (sensitivity) on peak separation was investigated and results were subjected to thorough statistical analysis (validation tool in DeerAnalysis). Our data illustrate the importance of an adequate resolution of the data to allow accurate interpretation and will pave the way towards a reliable extraction of multiple PELDOR distances.

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EPR spectroscopy of isomorphous Metal Organic Frameworks single crystals and powders with rtl-topology

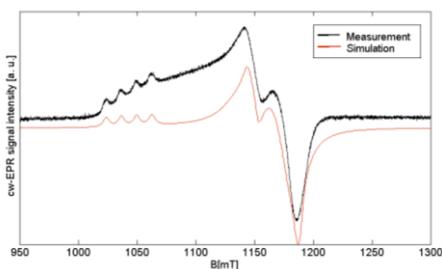
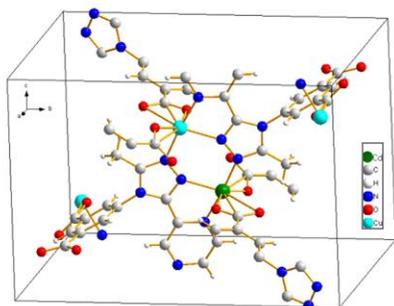
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Metal organic frameworks (MOF) compounds are exciting porous materials that are based on metal ions and organic ligands.¹ MOFs are materials with large application potential such as gas storage, separation, and sensing. Furthermore, in case of mixed-metal MOFs multifunctional catalysts could be envisaged.² EPR is a versatile tool to characterize the electronic structure and coordination environment of paramagnetic ions in such mixed-metal MOFs as well as possible magnetic interactions among the ions

Here we will present our latest single crystal and powder cw EPR study of a Cu²⁺/Cd²⁺ containing mixed-metal MOF.² Our investigations provide the cupric ion g and hyperfine coupling tensors including tensor orientations for MOFs with low Cu²⁺ concentrations. In addition magnetic interactions among the cupric ions are explored for MOFs with higher Cu²⁺ contents.



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EPR study of high coverage TEMPO labeled Au Surfaces

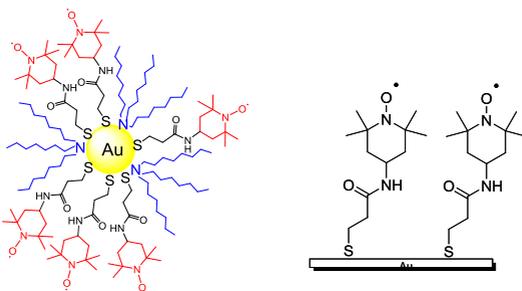
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A series of Au nanoparticles functionalised with high coverage of TEMPO-modified disulfide have been prepared and studied by EPR, UV-Vis, TEM microscopy, Energy Dispersive X-ray analysis (EDX) and Thermogravimetric Analysis (TGA). In order to increase the coverage of spin labels on the particle surface, heat-induced size evolution and ligand exchange reactions were used. A one-pot reaction at room temperature led to gold nanoparticles with a controlled large size (ca. 7 nm) and high coverage of radicals.¹ These nanoparticles showed a $|\Delta m_s| = 2$ transition at half-field which gives direct evidence of the presence of a high-spin state and allows an EPR study of the nature of the magnetic coupling between the spins. The results showed dominant antiferromagnetic interactions between radicals but at lower temperatures a ferromagnetic contribution was observed.

The same diradical has been studied in solution, crystal and anchored to Au(111) flat surface showing anisotropic magnetic properties.^{2,3}



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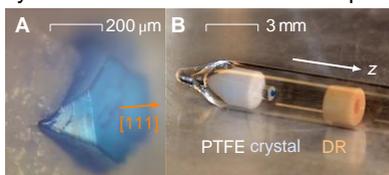
Continuous Wave Single Crystal Electron Paramagnetic Resonance of Cupric Ions in the Zn(II) Doped Porous Coordination Polymer Cu_{2.965}Zn_{0.035}(btc)₂

Stefan Friedländer¹, Anastasia Kultaeva¹, Andreas Pöpl¹

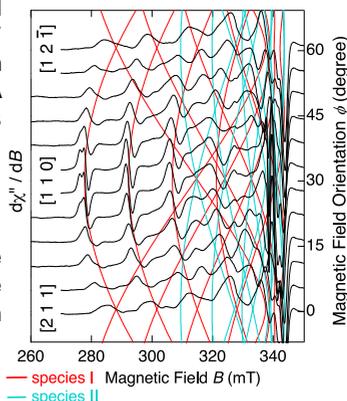
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We will present our latest research on metal-organic framework (MOF) compounds which offer a large application potential in various areas such as adsorption, separation, catalysis, and sensing. While many of these materials contain paramagnetic ions as major framework constituents, EPR investigations of MOF systems are often restricted to powder materials because single crystals are only available in sub-millimetre sizes. However, the elucidation of the structure of the adsorption complexes requires knowledge about the orientation of the magnetic tensors which can only be deduced from single crystal experiments.¹ We show that the use of dielectric resonators with high permittivity

enhances significantly the sensitivity of the EPR experiment and in that way offers the opportunity for single crystal studies of these porous, low density materials with very small volume samples at low temperatures and non-ambient atmospheres in conventional EPR spectrometers.² Here we will present our studies of Cu(II) containing small MOF single crystals. The local paramagnetic Cu(II) ion probes were used to identify the magnetic **g** and **A** tensor orientation with respect to the crystal axes and to monitor changes at gas adsorption experiments for the first time in EPR for MOFs. We explored that the paddle-wheel units of the porous, low density material are deformed upon gas adsorption which is represented by a line broadening effect in the angular resolved single crystal EPR spectra. This allows to predict an improved model for the mixed paddle-wheel structure.



enhances significantly the sensitivity of the EPR experiment and in that way offers the opportunity for single crystal studies of these porous, low density materials with very small volume samples at low temperatures and non-ambient atmospheres in conventional EPR spectrometers.² Here we will present our studies of Cu(II) containing small MOF single crystals. The local paramagnetic Cu(II) ion probes were used to identify the magnetic **g** and **A** tensor orientation with respect to the crystal axes and to monitor changes at gas adsorption experiments for the first time in EPR for MOFs. We explored that the paddle-wheel units of the porous, low density material are deformed upon gas adsorption which is represented by a line broadening effect in the angular resolved single crystal EPR spectra. This allows to predict an improved model for the mixed paddle-wheel structure.



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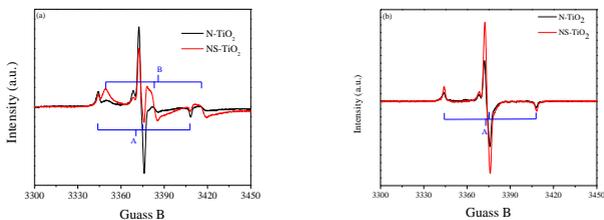
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Understanding the charge transfer mechanism in NS-codoped TiO₂ nanocatalyst using EPR spectroscopy

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In the present work, N and NS-codoped TiO₂ nanocatalysts were prepared by hydrothermal method. The characterization results confirmed that sulfur and nitrogen was doped into the TiO₂ lattice and created new intermediate state owing to narrowed the band gap. EPR studies revealed that lower intensity of the paramagnetic N[•] center detected in NS codoped compare to N-TiO₂ nanocatalyst in the dark, suggesting that sulfur aided to decrease the lattice oxygen vacancies and kept nitrogen as in diamagnetic form. Furthermore, under illumination the observed growth and decay rates of paramagnetic N[•] center supported that the charge transfer process occurred in NS codoped TiO₂ and benefited for an enhanced the RhB degradation as well as TEMPO-H formation.



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Phenol compounds as a New Materials for EPR dosimetry in radiation therapy

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INTRODUCTION

Among the various dosimetric techniques used for characterizing the radiation beams used in radiation therapy, the Electron Paramagnetic Resonance (EPR) arouses increasing interest for applications in various therapy procedures.

When a compound is irradiated with ionizing radiations free radicals are produced and their concentration is proportional to the absorbed dose. This allows for dosimetric measurements through EPR technique which is able to quantitatively determine the radical concentration.

Our research group has started an investigation of the EPR response of some phenols compounds for possible dosimetric applications.

In this work we report the EPR investigation of IRGANOX 1076 pellets and thin films exposed to various type of radiation beams.

Phenols are compounds possessing a benzene ring attached to a OH group. After irradiation the final product is a stable phenoxy radical. The stability of such radical can be improved by adding other alkyl chains which can be attached to the benzene ring. In particular, the phenol *octadecyl(3,5-ditertbutyl-4-hydroxyphenyl) propionate* (IRGANOX 1076) gave interesting results.

Materials and methods

Phenolic pellets and film were prepared in order to characterize beams with high dose gradient and which require accurate knowledge of the precise dose delivered. Photon and electron irradiations at various energies were performed with the Siemens Primus Low linear accelerator present at ARNAS Ospedale Civico Palermo. Thermal neutron irradiations were performed at the thermal neutron column at the Triga Mark II reactor of LENA (Laboratorio Energia Nucleare) Pavia (Italy). ESR dosimeters were readout by means of a Bruker ECS106 spectrometer equipped with a TE102 rectangular cavity at room temperature.

Results

The dosimetric features of these EPR dosimeters were investigated and the results regarding the dependence on microwave power and modulation amplitude are reported. The dependence on beam type and energy, the detection limits for various beam typologies, signal stability after irradiation were analyzed. The dose response was found to be linear for all beams used in the dose range analyzed. The possibility of obtaining depth dose profile was investigated

Conclusion

In conclusion, the phenols shows radiometric features that designate it as a new material for EPR dosimetry.

EPR DOSIMETRY WITH ALANINE FOR TOTAL BODY IRRADIATION USING AN ANTHROPOMORPHIC PHANTOM

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Introduction: The Total Body Irradiation (TBI) is a radiation therapy technique widely used in clinical hemato-oncological treatment of patients that underwent bone marrow transplantation or peripheral stem cell transplantation.

Typically, the administration of TBI treatment provides irradiations in 3 consecutive days with a double daily fractionation, although other dose fractionation modes have been widely adopted in the clinic procedures. Although this technique allows to irradiate the whole body from head to toes, it has some limitations such as the lack of homogeneity of the dose distribution (which can show variations of 20% in the different areas), irradiation of critical organs such as lungs, liver, intestine and eyeballs that receive a dose comparable to the nominal one and require appropriate shielding and a proper evaluation of the dose absorbed by them. The positive outcome of this type of radiation therapy is closely related to a precise and accurate measurement of dose distribution delivered to the patient in the various body districts. In this work the dose administered in a anthropomorphic (RANDO) phantom during TBI treatments was evaluated by means EPR dosimetry with alanine. The estimate of the dose was carried out at various points inside the phantom that has been irradiated with a clinical TBI beam configuration by applying a proper shielding provided for the lungs. Doses measured through EPR were compared with those measured with a semiconductor diode.

Materials and Methods : The ESR measurements were made by means of cylindrical pellets of alanine for commercial use. The irradiations were performed using a 6 MV photons beam from a clinical linear accelerator. The experimental set-up used is that of TB irradiations.

The following irradiations were then carried out: Calibration curve in the clinical range from 0.5 to 10 Gy within a solid water phantom. Irradiation in anthropomorphic (RANDO) phantom giving a total dose of 4Gy at the abdomen.

Results The results obtained through alanine dosimeters were compared with measurements performed by diodes and the dose differences between these dose values do not exceed ~6.5%. Alanine doses were found to be slightly lower than those measured with diodes and further investigations are planned for analyzing these discrepancies.

Conclusions Alanine dosimetric system shows a quite good sensitivity and stability and it seems promising for dosimetry of these radiation beams.

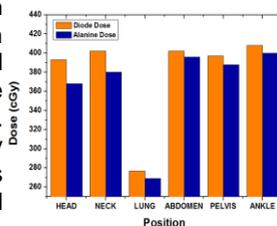


Fig. 1 Comparison between the measured dose with diodes and alanine dosimeters in various anatomic regions inside the anthropomorphic phantom used.

EPR of V⁴⁺ and Cu²⁺ ions in single crystals of pyrovanadates: β -Mg₂V₂O₇, α -Zn₂V₂O₇

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The EPR spectra for the V⁴⁺ and Cu²⁺ ions were recorded in single crystals of β -Mg₂V₂O₇ and α -Zn₂V₂O₇ at X-band (9.6 GHz) at 120 and 295 K. Vanadium-mixed oxides (V-Mg-O, V-Zn-O) are important in catalytic processes, such as oxidative dehydrogenation of hydrocarbons and selective catalytic reduction of NO by ammonia, synthesis of supported V₂O₇ catalyst, insulin-mimetic agents and rechargeable Li batteries. The electrical conductivity of Mg and Zn pyrovanadates strongly depends on the impurity ions and thermal treatment, which governs the formation of V⁴⁺ defects. [V.A. Ioffe, V.S. Grunin, Z.N. Zonn, S.E. Ivanov, I.S. Yanchevskaya, Izv. Akad Nauk SSSR, Neorg. Mater., 1977, 13, 1484.] Therefore, investigation of defect centers in these compounds is a very important topic. The point symmetry of both Mg and V ions is C_i in triclinic β -Mg₂V₂O₇ crystals, and there exist two magnetically inequivalent sites for Mg and V ions. The EPR spectra of the V⁴⁺ and Cu²⁺ ions are observed in only one of the two magnetically inequivalent positions in β -Mg₂V₂O₇. One V ion is 4-fold tetrahedrally coordinated, while the VO₄ tetrahedron of the second V ion is distorted due to bonding with the fifth oxygen ion. There is only one magnetically inequivalent site for V⁴⁺ ions in monoclinic α -Zn₂V₂O₇, with the point symmetry being C_i, in trigonally bipyramidal fashion. The Cu²⁺ ion is 6-fold octahedrally coordinated in β -Mg₂V₂O₇, while it is 5-fold tetrahedrally coordinated in α -Zn₂V₂O₇ in a trigonally bipyramidal fashion. A rigorous least-squares fitting of EPR line positions in three mutually perpendicular planes to spin-Hamiltonian (SH) parameters, enabled determination of the orientations of the principal axes of the Zeeman and HF interaction matrices. The SH parameters of V⁴⁺ ions in β -Mg₂V₂O₇ and α -Zn₂V₂O₇ at 295 K are:

	g _z	g _x	g _y	A _z (GHz)	A _x (GHz)	A _y (GHz)
Mg ₂ V ₂ O ₇	1.930	1.977	1.996	0.480	0.185	0.147
Zn ₂ V ₂ O ₇	1.928	1.971	2.014	0.504	0.189	0.170

In β -Mg₂V₂O₇ and α -Zn₂V₂O₇ the SH parameters of V⁴⁺ ions are similar. The Mg and Zn ions are differently coordinated in these host crystals, therefore the Cu²⁺ ion, substituted for these ions, has quite different from each other SP parameters: g_z = 2.000 < g_x = 2.283, g_y = 2.355, A_z = 0.25 GHz > A_x, A_y ≈ 0.05 GHz (unresolved EPR lines) in β -Mg₂V₂O₇ and g_z = 2.388 > g_x = 2.123, g_y = 2.050, A_z = 0.24 GHz > A_x, A_y ≈ 0.05 GHz (unresolved EPR lines) in α -Zn₂V₂O₇. Formation of defect centers V⁴⁺ is related to local distortion of stoichiometry and impurity ions.

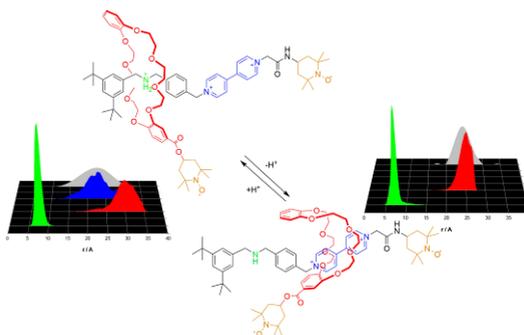
Structural changes of a doubly spin-labelled chemically driven molecular shuttle probed by PELDOR

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Gaining detailed information on the structural rearrangements associated with stimulus-induced molecular movements is of utmost importance for understanding the operation of molecular machines. Here pulsed electron-electron double resonance (PELDOR) was employed to monitor the geometrical changes arising upon chemical switching of a [2]rotaxane that behaves as an acid-base controlled molecular shuttle (Scheme 1). To this aim the rotaxane was endowed with stable nitroxide radical units in both the ring and axle components.¹ The combination of PELDOR data and molecular dynamic calculations indicates that in the investigated rotaxane the ring displacement along the axle, caused by the addition of a base, does not alter significantly the distance between the nitroxide labels but it is accompanied by a profound change in the geometry adopted by the macrocycle.²



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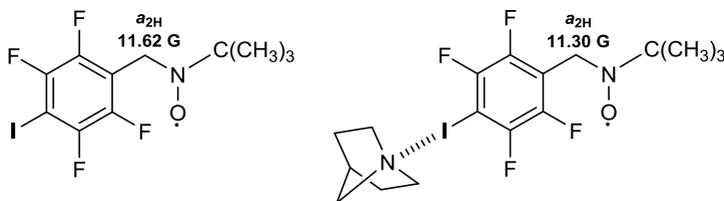
Novel Nitroxide Radical Spin Probes for Exploring Halogen Bonding Interactions in Solution by ESR

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Halogen bonds (XBs) are attractive noncovalent interactions between covalently bound, electron-deficient halogen atoms and Lewis bases.¹ XB has been employed for a wide range of applications, including liquid crystalline and magnetic materials, chiral discrimination, ion pair recognition, supramolecular polymer formation, porous material design, and chemical separation.¹ Despite the progress achieved through the studies mentioned above, our understanding of XB remains limited in important aspects. In particular, quantitative descriptions of halogen bonding in solution lag far behind those available for other noncovalent forces such as hydrogen bonding or interactions of π systems.

As a part of our continuing studies on the use of ESR spectroscopy to characterize supramolecular architectures,² here we propose new fluorinated iodoarenes nitroxide spin probes to investigate halogen bonding interactions in solution. These probes include the benzyl *tert*-butyl nitroxide moiety that was found to be a very suitable probe to investigate supramolecular interactions.³

Evidence for the formation of halogen bonding complex between the radical probe and a variety of Lewis bases was obtained from the measure of the benzylic hydrogen hyperfine splitting constant. ESR titrations were used to determine association constants for the interactions of a variety of Lewis bases with the proposed fluorinated iodoarenes spin probes.



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Finding the reactive electron in paramagnetic systems: EPR spectroscopy and quantum chemistry applied to the 1,3,5-triphenyl verdazyl radical

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One of the biggest challenges in studying catalytic reactions is characterizing intermediate states and identifying reaction pathways. Oftentimes, intermediate states with unpaired electrons are formed which provide an opportunity to study the compound via electron paramagnetic resonance (EPR). Combining EPR with density functional theory (DFT) represents a powerful synergistic approach to accomplish these goals. Once the catalytic intermediates and reaction pathway are known, rate-limiting steps critical to parameters like overpotential and turnover number may be identified and eliminated. We study 1,3,5-triphenyl verdazyl using continuous-wave (CW)-EPR, Electron Nuclear Double Resonance (ENDOR) and DFT (cf. Figure 1) as an instructive example of how theory and experiment can complement each other to find the reactive electron. The concomitant analysis allows visualization of the strengths and weaknesses of the employed techniques.

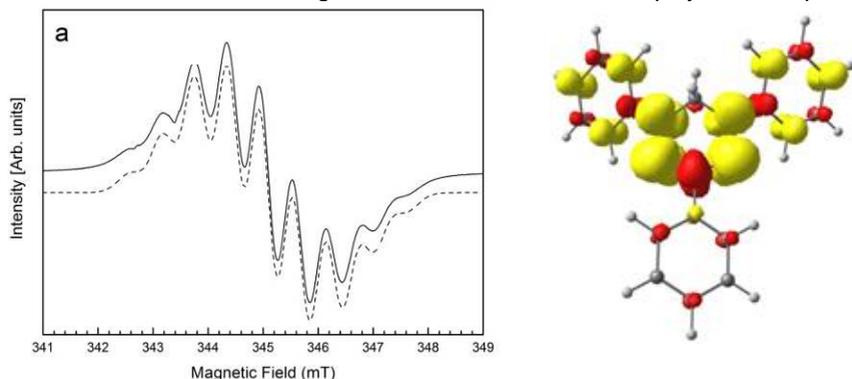


Figure 1. (left) cw-EPR spectrum of 1,3,5-triphenyl-verdazyl (T = 296 K); (right) calculated spin-density distribution with positive and negative densities indicated in yellow and red, respectively.

A combined EPR-molecular dynamics investigation of penetration of antioxidant lipid-based nitroxides in lipid bilayer.

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Nitroxide radicals are known to protect against oxidative processes in different media and under different stress conditions¹. In order to enhance the bioavailability of these antioxidant compounds, we settled out an efficient method to improve the affinity of nitroxides to lipid particles and membrane and other oxidation-susceptible sites *in vivo*. To this purpose, a series of liponitroxides having a pyrroline nitroxide moiety linked either to a glycerol or to a steroid unit has been synthesized, and their inclusion inside phospholipid bilayers has been investigated by Electron Paramagnetic Resonance (EPR) spectroscopy². The antioxidant behavior of these nitroxides has been studied in azo-initiator induced lipid peroxidation by means of the Thiobarbituric Acid Reactive Species (TBARS) assay; a correlation with their penetration depth within the bilayer has been found.

Beside, we carried out an *in silico* molecular dynamics study aimed to investigate their penetration within the bilayer. To this purpose, we extended the AMBER force-field to provide an accurate description of large and flexible nitroxide free-radicals including new atom types fitted based on geometries, vibrational frequencies and potential energy surfaces computed at the DFT level³. These systems underwent an atomistic MD simulation using GROMACS 5.0 in NPT ensemble at 310 K. As a result, the liponitroxide depth inside the bilayer has been determined; the aim is to find out a correlation between its antioxidant activity and its positioning inside the liposome in order to better design novel active compounds.

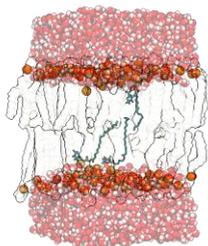


Figure 1.
liponitroxide mixed
composition bilayer

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Separation of Chromium Species Relevant to Ethylene Tetramerization Using EPR

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Ethylene tetramerization is used industrially for the synthesis of 1-octene, which is used as a co-monomer for polyethylene.¹ Increasing demand has propelled research into selective tetramerization. However, the precise nature and action of

the active catalyst is still subject to much debate.² Electron paramagnetic resonance (EPR) spectroscopy is a powerful technique for studying relevant complexes and catalysis *in-situ*. Here, we seek to separate overlapping species and assign their oxidation states to monitor the fate of chromium species upon precatalyst activation.

We have tested a model system consisting of discrete Cr(I) and Cr(III) complexes and separated the two chromium species using an inversion recovery filter as shown in Fig. 1.³ The use of this method on an activated Cr precatalyst for monitoring the various species formed will be illustrated.

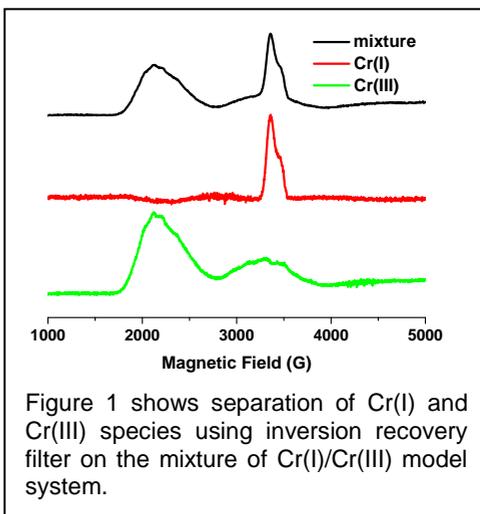


Figure 1 shows separation of Cr(I) and Cr(III) species using inversion recovery filter on the mixture of Cr(I)/Cr(III) model system.

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Clinical Application of the EPR Spectroscopy: Heme-Nitrosylated Hemoglobin and Oxidative Stress in Women Consuming Oral Contraceptives.

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Clinical statistical studies identified an increased risk of venous thromboembolism in females under consumption of oral contraceptive pills (OCPs) indicating disturbance of vascular homeostasis.¹ However, the impact of OCPs on endothelial function and redox status of the vasculature was not properly analyzed.

We measured the bioavailability of nitric oxide, a main mediator in vascular function, as an index of vascular homeostasis by quantitation of the heme-nitrosylated hemoglobin (5-coordinate- α -HbNO) level in venous erythrocytes using a subtraction EPR method;² in parallel, vascular oxidative status was assessed by measurement of plasma peroxides (using a spectrophotometric assay based on the 3,3',5,5'-tetramethylbenzidine oxidation) and of the thiol redox state (using the EPR spin probe, bis-(2,2,5,5-Tetramethyl-3-imidazoline-1-oxyl-4-yl)disulfide, an nitroxide biradical that cleaves into monoradical with distinctive EPR spectrum in presence of reduced thiols); in addition, the endothelial function was assessed by digital reactive hyperemia pulse tonometry (EndoPat). Young female subjects (reportedly healthy volunteers, N=104) were divided into subgroups defined as user or not of OCPs containing *ethinyl estradiol* and different types of progestogens.

We observed that the HbNO level was significantly lower in venous erythrocytes of female subjects consuming OCPs versus control female subjects (162.1 \pm 9.0 and 215 \pm 13 nmol/L, $P = 0.0003$) as was the concentration of reduced thiols (reduced by 12% from control). This correlated with increased level of plasma peroxides (1.92 \pm 0.16 mmol/L, N=24; versus 1.05 \pm 0.13 mmol/L, N=22, in control; $P = 0.001$). Interestingly, the level of paramagnetic form of oxidized ceruloplasmin-Cu(II) was also significantly higher in the group under OCP administration. The EndoPat index showed a trend towards impairment in subjects consuming OCPs, and was significantly lower in users of pills containing drospirenone. These subjects also had the lowest HbNO level (120.1 \pm 8.0 nmol/L).

Conclusion: This cross-sectional cohort study demonstrates that a decrease of HbNO measured by quantitative EPR in human venous erythrocytes is correlated with the development of the endothelial dysfunction under OCPs consumption, in parallel with increased vascular oxidative stress.

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TEMPO Functionalized Graphene Oxide

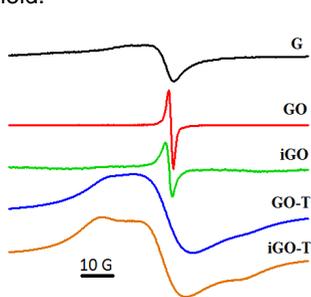
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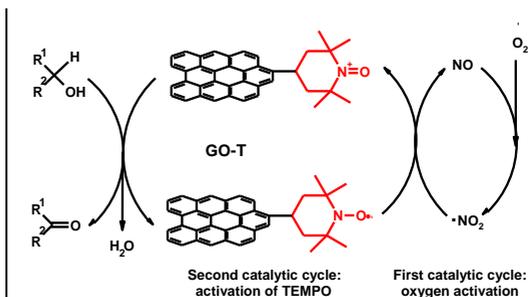
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TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl, a stable nitroxide free radical), was covalently grafted on graphene oxides (GOs) through an amide bond and the new composite solid materials were characterized by thermal analysis, infrared, Raman and electron spin resonance spectroscopy (ESR). It was found that TEMPO functionalized GO can be successfully used as recoverable solid catalysts for selective oxidation of alcohols, using NO_x as cocatalyst and air as final oxidant, under very mild conditions.

Functionalization of GO with TEMPO was performed in two steps: in the first step the activation of -COOH groups from GO was achieved by transforming them into the corresponding acid chloride -COCl; the second step is represented by the reaction of -COCl with 4-amino-TEMPO. The materials thus obtained were used in the selective oxidation of five alcohols (benzyl alcohol, 1-phenylethanol, diphenylmethanol, furfuryl alcohol and 1-octanol) into the corresponding aldehydes and ketones. The oxidation yield depends on the reactivity of the alcohols, i.e. benzyl alcohol can be oxidized selectively to benzaldehyde in an almost quantitative yield.



ESR spectra of graphite (G), GOs (GO, iGO), and TEMPO functionalized GOs (GO-T and iGO-T).



Proposed aerobic oxidation mechanism of alcohols using TEMPO functionalized GO as catalyst and NO_x as cocatalyst.

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Hydrogen Atom Bonding and Hydrogen Atom Transfer in Phenols: Investigation by CIDNP

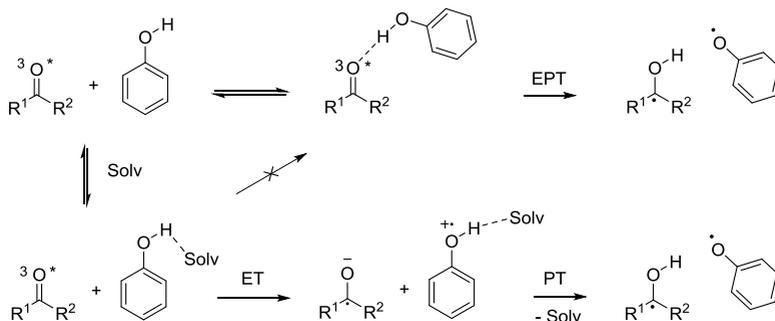
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Polarizing effects in magnetic resonance can be advantageously utilized for establishing molecular reactivity. In this contribution we will show how chemically-induced dynamic nuclear polarization (CIDNP) provides information on hydrogen-bond assisted hydrogen-atom transfer. We have photolyzed phenols substituted with piperidine bases in the presence of benzophenone. The correspondingly recorded CIDNP traces were evaluated in terms of H-transfer efficiency. These CIDNP experiments and theoretical calculations show that for those phenols capable of establishing intramolecular hydrogen bonds between the pendant base and the phenolic OH group, the mechanism of the reaction with triplet benzophenone changes upon change of the solvent: In the non-polar solvent benzene they undergo concerted electron proton transfer (EPT), which affords neutral ketyl and phenoxyl radicals. In the polar solvent acetonitrile, the reaction proceeds via an electron transfer (ET) from the phenol to the benzophenone triplet, resulting in the formation of a ketyl radical anion and a phenoxyl radical cation, followed by proton transfer (PT) affording neutral ketyl and phenoxyl radicals.



In-vitro and in-cell EPR distance measurements for studying structural dynamics of Calmodulin

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Pulsed double electron-electron resonance (DEER), also named PELDOR (pulse electron-electron double resonance), is a well-established method to extract distances between paramagnetic centers in the 2-8 nm range by measuring the dipole-dipole interaction between electron spins. The use of Gd³⁺ labeling at high fields such as W-band (95 GHz, ~3.5 T) offers several advantages for DEER measurements, including high sensitivity and good chemical stability of the label towards reducing agents. Gd³⁺-Gd³⁺ DEER has been recently validated on a series of molecular rulers¹. To develop the technique towards in-cell distance measurements, we applied it to the calcium-binding messenger protein Calmodulin (CaM, 16.7 kDa). CaM has two calcium-binding domains and is able of binding up to 4 Ca²⁺ ions. Upon Ca²⁺ binding, the protein undergoes a conformational change to a more extended conformation. This enables it to bind target proteins, as a result of which CaM assumes a collapsed conformation.

Site-directed spin labelling of CaM was performed using either the Gd³⁺-DOTA-maleimide tag, which is reactive towards cysteines, or the C3-Gd³⁺ tag², which is reactive towards the pAzF unnatural amino acid.² Pairs of site-directed mutations were introduced into the lobes at the N- and C- termini of CaM in order to attach the tags to the protein. In-vitro DEER measurements were performed on CaM in its Ca²⁺-free (apo), Ca²⁺-bound (holo) and -holo state with peptide. Gd³⁺-Gd³⁺ distance changes could be observed between the three different conformations of the protein, closed open and collapsed respectively. Our approach was extended to cell extracts, where interaction of proteins from the cytoplasm of HeLa human cancer cells led to the collapsed structure of CaM in the presence of Ca²⁺ and to the closed state in the absence of Ca²⁺. The behaviour was similar to the one observed in vitro. CaM was also successfully delivered inside HeLa cells using the electroporation technique. Internalization of the apo- and holo- forms of CaM generated a distance distribution similar to the one observed for apo-CaM both in vitro and in cell extracts, indicating that the Ca²⁺ concentration in the cytoplasm is kept to a very low level and the Ca²⁺ was removed from the delivered Ca.

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Sensitivity enhancement in ¹H and ²H ENDOR by cross polarization

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Electron-nuclear double resonance (ENDOR) spectroscopy combines microwave (MW) and radiofrequency (RF) irradiation to study interactions between nuclei coupled to a paramagnetic species. ENDOR plays a key role in electron paramagnetic resonance (EPR) and is widely applied on protein samples, but the sensitivity suffers from several factors, including nuclear saturation. One major drawback is the gap between electron spin relaxation time (T_{1e} , usually microseconds to milliseconds) and nuclear spin relaxation time (T_{1n} , usually many seconds). In particular, experiments performed in frozen solution at very low temperatures and/or low-gamma nuclei are affected by the nuclear saturation and might require measurement times of several days. Such limitations might be overcome by using the recently proposed electron-nuclear cross polarization ENDOR (CP-ENDOR).¹ In the last years, its performance and the improved sensitivity compared to standard Davies ENDOR has been demonstrated on ¹H-malonic acid, ¹H-BDPA as well as on a tyrosyl radical in E-coli ribonucleotide reductase.^{1,2} Here we present first CP-ENDOR results on the low-gamma nucleus ²H. The observed ENDOR effects are in best agreement with a theoretical analytical description of CP-ENDOR for a $I = 1$ nuclear spin system and also with predictions from numerical simulations.

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Solvent effect on the anodic oxidation of tannic acids: EPR/UV-vis spectroelectrochemical and DFT theoretical study

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Tannic acid (TA), a naturally occurring plant polyphenol, is composed of a central glucose molecule derivatized at its hydroxyl groups with one or more galloyl residues. Although extensive biochemical, biological, and biomedical studies of tannic acids have been already published¹, the electrochemical studies of this class of polyphenols are quite rare. The redox behavior of polyphenolic compounds is pH-dependent² and their deprotonated forms have an important role in their redox and antioxidant behavior³. In situ EPR and UV-Vis spectroelectrochemical experiments were performed to follow the oxidation reactions of TA in protic and aprotic media. The irreversibility during cyclic voltammetry was observed and the unstable semiquinone anion radical ($g = 2.0047$) formed upon TA oxidation was proved both in DMSO and water solutions. Delocalization of the unpaired electron within the whole galloyl unit for model radical structures was confirmed by the theoretical spin density calculations. According to experimental and theoretical results it was found that DMSO solvent prefers the deprotonation from OH groups which are not fixed via the spatial hydrogen bonds. For the water solution the opposite behavior was found. The theoretical computations confirmed that the spatial hydrogen bonds between the neighboring galloyl rings play an important role in the interpretation of experimentally detected redox and spectroscopic behaviors of tannic acids⁴. The investigation of the energetics for the electron/proton transfer enabled us to predict the redox behavior of natural compounds in the real systems.

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First-Principles Solid-State Calculations and Pulsed EPR Measurements: a Study of Ionic Substitutions in Hydroxyapatite

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Density functional theory (DFT) calculations are widely used to characterize the electronic structure and magnetic resonance parameters of paramagnetic molecules. Here we address the versatility of plane-wave DFT for studying impurities in solids in combination with pulsed EPR techniques. We focus on hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (nano)crystals as a host lattice, since it is very tolerant to many ionic substitutions. We show that the calculation of magnetic resonance parameters in conjunction with EPR/ENDOR experiment can successfully complement first-principles thermodynamic analyses of the impurity localization. Next, we attempt to connect the results of electron spin-lattice relaxation measurements with the calculated phonon properties of the host crystal. Finally, we illustrate the capabilities of the combined experimental-computational approach for studying the interplay of oppositely charged substitutions (Pb^{2+} , Mn^{2+} , CO_3^{2-} and NO_3^{2-} ions) in the structure of hydroxyapatite nanopowders.

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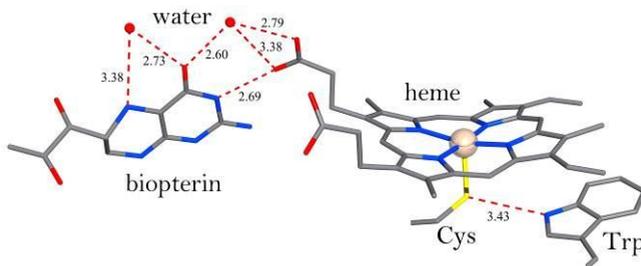
Study of bacterial NO-synthases

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In mammals, the NO-synthases (NOSs) are responsible for the production of nitric oxide (NO) involved in a number of biological activities ranging from signalling to cytotoxic processes. In the last 10 years, the improvement of gene sequencing techniques has led to the discovery of numerous proteins homologous to mammalian NOSs throughout the living kingdom in particular in bacteria.¹ Despite homology to mammalian NOS, bacterial NOSs bear some differences: essentially, they lack the reductase domain, bacteria do not generally have the machinery to synthesize the biopterin cofactor, and their NO production is smaller compared to NOSs.

We have used EPR spectroscopy to study the active site of bacterial NOSs and probe their possible mechanism and differences compared to the mammalian inducible NOS.²⁻⁴ We brought specific attention to the {FeNO}⁷ complex of the NOS of *Deinococcus radiodurans* which exhibit a particularly well resolved axial component that has been difficult to study otherwise in heme proteins.



Active site of NOS oxygenase domain showing the hemothiolate catalytic site with the pterin cofactor

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Characterizing haemoglobin of the European honeybee and the malaria mosquito using optical and EPR spectroscopy

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The respiratory system of insects consists of trachea, which connect the inner tissues with the atmosphere. Therefore it has been long assumed that no respiratory proteins, like haemoglobin (Hb), are present in the genome. However, in the last decades intracellular Hbs were discovered in several insects, such as the common fruit fly *D. melanogaster*¹. Analysis of the low-spin ferric forms of this haemoglobin, using electron paramagnetic resonance (EPR), revealed a bis-histidine coordination with a large dihedral angle between the histidine imidazole planes².

In order to improve our understanding of the respiratory proteins of insects, we focus here on Hb of the European honeybee *A. mellifera* (AmeHb) and of the malaria mosquito *A. gambiae* (AgaHb1). Optical absorption spectroscopy pointed out that AmeHb in its ferric form after protein purification exhibits a hexa-coordination with histidine residues binding at the proximal and distal side of the haem plane. Freshly purified AgaHb1, on the contrary, consists of an Fe(II)O₂ system evolving to a ferric hexa-coordinated haem form through slow temperature- and pH-dependent oxidation. Resonance Raman spectroscopy identified both AmeHb and AgaHb1 as closed conformations where the external ligand is strongly stabilised by surrounding amino acids.

Continuous wave and pulsed EPR techniques are used to probe the haem pocket structure of the ferric forms of the globins. Both Hbs feature a highly anisotropic **g**-tensor, which implies a large dihedral angle between the imidazole planes of the haem-ligating histidines. Furthermore AmeHb exhibits a very unusual structure with one of the four porphyrin nitrogens differing in hyperfine and quadrupole coupling. The histidine nitrogens suffer the same inequivalency. On the other hand, in AgaHb the porphyrin nitrogens are two-by-two magnetically equivalent, what is also observed for other globins. The hyperfine and quadrupole principal values of the histidine nitrogens coordinated to the haem iron are the same within the experimental error, although the corresponding tensors are not co-axial due to the dihedral angle between the imidazole planes of the amino acid residues.

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New Amidinoquinoxaline Nitrones as Antioxidants

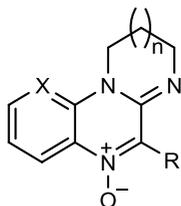
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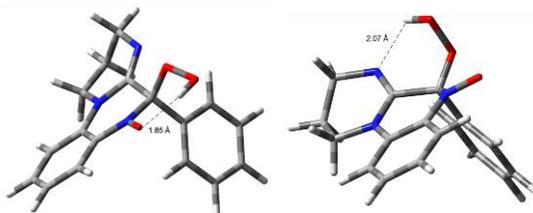
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Electron Paramagnetic Resonance (EPR)-Spin Trapping is one of the most reliable techniques for detecting and identifying short-lived free radicals.¹ Nitrones (*N*-oxides) represent the most commonly used spin traps² and they are continuously object of studies aimed at improving their efficiency and the stability of the corresponding spin adducts. A series of amidinoquinoxaline *N*-oxides was prepared and tested as spin traps by EPR spectroscopy^{3,5}. Although less reactive with respect to the previously synthesized benzoxazine analogues⁴ due to steric hindrance at nitrone α -carbon, all derivatives tested were able to efficiently scavenge the carbon- and oxygen-centered radicals used in this study. Additionally, very persistent HOO radical adducts have been found, likely due to their different possibilities to yield intramolecular H-bonds, as showed by proper DFT studies. Taking into account these features, the nitrones have been successfully studied as antimicrobials⁵ and, more recently as antioxidants



n: 0, 1, 2
R: aryl, alkyl
X: CH, N

in biological systems, showing also in this last case a promising behavior. In particular, the antioxidant activity of these compounds was assessed in the AAPH induced oxidation of phosphatidylcholine liposomes by measuring the TBARS production.



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The effect of a membrane mimicking detergent on Alzheimer's amyloid peptide aggregation studied by EPR

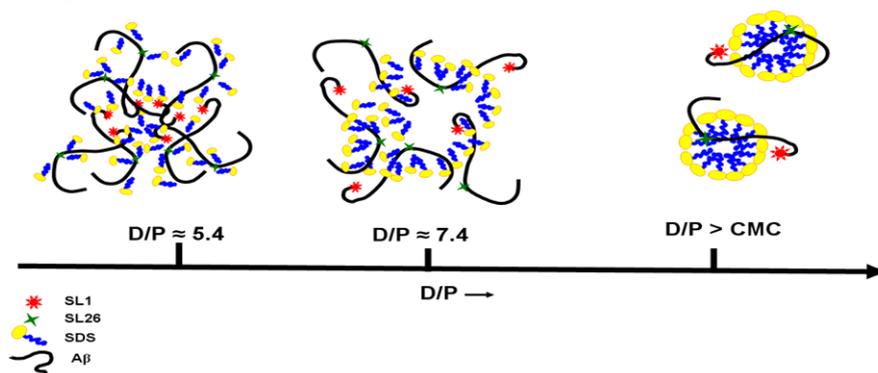
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The amyloid β ($A\beta$) is a peptide consisting of 40-42 amino acids that is found as the main component of the fibrils which constitute the amyloid plaques in the brains of Alzheimer's disease patients. We study the membrane interaction of $A\beta$ and its aggregates, because $A\beta$ -aggregates are suspected to interfere with cell membranes and thereby damage nerve cells.

We perform spin-label EPR on $A\beta_{1-40}$ in the presence of the sodium dodecyl sulfate (SDS) detergent as a membrane mimicking agent. The effect of SDS on $A\beta$ is studied using two positions of the spin label, the N-terminus and position 26. By comparing the two label positions the effect of local mobility of the spin label is eliminated, revealing $A\beta$ aggregation in the SDS concentration regime below the critical micelle concentration (CMC). We demonstrate that at low SDS concentrations, detergent/peptide (D/P) \approx 5.4, the N-terminus of $A\beta$ participates in the solubilization, most likely by being located at the particle/water interface. At higher SDS concentrations (D/P \approx 7.4) an SDS-solubilized state that is a precursor to the one $A\beta$ /micelle state above the CMC of SDS prevails (see Figure). We propose that $A\beta$ is membrane active and that aggregates include SDS. This study reveals the unique potential of EPR in studying $A\beta$ aggregation in the presence of detergent.¹



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Evaluating the photodynamic and antioxidant properties of carbon nanoparticles using EPR- spin trapping technique

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Photodynamic therapy (PDT) consists of inducing cell damage as a consequence of the generation of reactive oxygen species (ROS) by energy transfers from a photosensitizer (traditionally porphyrins) able to absorb light of a particular wavelength, transforming it into enough energy to excite the oxygen molecules.¹ By targeting the photosensitizer inside a tissue, the cell death may be induced. Due to the potential high efficiency and specificity, PDT holds great promise as a therapeutic strategy in cancer treatment and in the treatment of infections. The efficiency is related to the amount of ROS generated by the photosensitizer. The EPR – spin trapping technique is a direct and reliable method that can be used for the evaluation of the photodynamic properties of photosensitizers.² Here, a series of hydrothermal-derived carbon nanoparticles were prepared and tested for their photoactivity when activated by near-infrared light (NIR) by EPR spectroscopy associated to the spin trapping technique. We found that the carbon nanoparticles generate the highly cytotoxic specie singlet oxygen (¹O₂). Moreover, these nanoparticles shown high hydroxyl radicals scavenging activity in dark suggesting a possible antioxidant activity. As EPR – spin trapping is not only a technique to identify but also to quantify free radicals¹, it has been shown that the amount of ROS generated and scavenged is modulated by the method of synthesis of the particles. This study is the first step towards the possible development of morphologically and structurally tailored switchable theragnostic platforms for the treatment of cancer and other diseases.

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Sensing the quantum behaviour of magnetic nanoparticles by electron magnetic resonance

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We have investigated Magnetic Nanoparticles (MNPs) of spinel type iron oxide mineralized inside the internal cavity of two ferritin-type proteins, namely the ferritin protein from *Pyrococcus furiosus* (PFFt) and the Dps protein from *Listeria innocua* (LiDps)¹. These protein shells allowed an efficient synthesis of the particles with a narrow size distribution around 8 nm for PFFt and 3.5 nm for LiDps, with a total number of Fe ions inside these cages around 4500 and 450 respectively.

We have realized X-band Electron Magnetic Resonance (EMR) measurements at various temperatures in perpendicular and parallel configurations to probe transitions with different selection rules and, therefore, to explore the quantum nature of the two systems.

The experimental spectra were interpreted using an approach based on the giant spin model to describe the interaction of the MNP spin state with the external magnetic field. The huge dimension of the Hilbert space for these systems prompted us to use a simplified simulation approach, employing an effective smaller spin value and, accordingly, effective spin Hamiltonian and experimental parameters².

This method allowed the simulation of the EMR spectra for both kinds of particles. The simulations are quite in agreement with the experimental data, especially in the perpendicular configuration. The overall analysis indicates that the observed quantum behaviour has to be ascribed to the whole MNP and that the thermal population of excited spin states has a strong influence in the EMR behaviour of MNPs.

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Triplet states and paramagnetic defects as probes of molecular orientation in polymer films studied by EPR

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Introduction

Polymer photovoltaics has been the subject of intense research because of its potential as an alternative to silicon-based photovoltaics. The morphology of the photoactive material in 'bulk heterojunction' materials¹, composed of semiconductor polymers blended with fullerene derivatives, is a key factor for the photovoltaic efficiency. It is known that molecular order and crystallinity of polymer domains enhance charge transport properties and photovoltaic performances².

EPR spectroscopy can provide information on the partial orientation of molecules and molecular order in polymer/fullerene blends, because of the anisotropy of magnetic interactions in intrinsic or photoexcited paramagnetic states.

Materials and methods

We studied the preferential orientation of some conjugated polymers (P3HT and other low bandgap copolymers) in thin films obtained with different deposition techniques. We observed the polymers' photoexcited triplet states by using Time-Resolved EPR and pulsed laser photoexcitation. The angular dependence of the spectra was successfully reproduced using a uniaxial orientational distribution function.

Results

The examined polymers form highly ordered domains resulting in a strong angular dependence of triplet TREPR spectra. The deposition technique seems not to have a significant effect on the kind of order present in the film, but the results show a correlation between the solvent evaporation time and the degree of orientational order. The assignment of the magnetic interactions' principal axes to the molecular structure is achieved by studying the polymers' triplet states in a nematic liquid crystal matrix. From this information we identified the preferential orientation of the polymers on the deposition substrates and calculated the order parameter.

Conclusions

We measured orientational order and order parameters in several semiconducting polymer thin films, by using TREPR spectra of photoexcited triplet states. We demonstrated that EPR can provide not only information on paramagnetic species and photoinduced processes in the photoactive blends but gives also access to morphological details of the material.

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EPR as a Tool for the Characterization of Targeted Immobilization of Globins in Mesoporous Materials

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The recent development of mesoporous materials ($2\text{nm} < \text{Ø} < 50\text{nm}$)¹⁻³ has raised interest in the immobilization of proteins in these materials. As the mesoporous materials should be able to prevent the protein from degradation, these hybrid protein-silica materials are thought to be perfect candidates for biocatalyst and biosensor applications since we could use the chemical selectivity and catalytic properties of these proteins.

The **first step** towards the development of such a hybrid protein-titania material, is the characterization of the protein. Five different globins (heme-containing proteins) have been identified in humans to date: hemoglobin, myoglobin, neuroglobin, cytoglobin and androglobin. Cytoglobin of different fish (*Dissostichus mawsoni*, *Chaenocephalus aceratures* and *Danio rerio*) is investigated using a bunch of spectroscopic techniques: optical absorption spectroscopy, electron paramagnetic resonance (EPR) and resonance Raman spectroscopy (RRS). The results are compared with each other and with human cytoglobin.

In the **second step**, we investigate the mesoporous material that we would like to use for the incorporation. In this work, we will use mesoporous titania, which we will characterise using spin-probe and light-induced EPR experiments.

The **third (and final) step** consists of the optimization of the incorporation conditions and investigation of the hybrid protein-titania material using EPR. The incorporation conditions are tested for different globins.

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Electrochemically generated anion radical with alternating line-width effect of an explosive material FOX-7 – simulation and interpretation

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The molecule FOX-7, chemically 2,2-dinitroethene-1,1-diamine, is a relatively novel powerful insensitive explosive.¹ This energetic material represents a typical push-pull system which exists in solvent in several different forms.² The electrochemical reduction of FOX-7 in aprotic solvent leads to the reduction of nitro group by autoprotonation mechanism.³ The zwitterionic form of FOX-7 serves as a source of protons. Therefore the irreversible four-electron, four-proton reduction of FOX-7 proceeds. This autoprotonation mechanism is kinetically controlled and proceeds in two reduction steps accompanied by antecedent adsorption. The process of electrochemical reduction of FOX-7 involves oxygen-centred nitro anion radical intermediate ($g = 2.0051$) possessing alternating line-width effect (AL) as a result of intramolecular dynamic processes in the timescale of ESR splitting constants.

For better understanding of the observed radical intermediate the temperature dependent measurements during continuous *in situ* electrochemical generation of radical anion were performed. The recorded spectra were simulated by using special program capable to distinguish the spin system parameters for different conformers (sites) in dynamic chemical exchange including the correlation time characterizing the rate of the observed dynamics.⁴ Observed dynamics describes well an asymmetric two-site exchange model for all the observed temperatures ($\approx 225 - \approx 335$ K). For temperatures below 270 K, the simpler two-site mirror exchange model can be applied as the result of the rapid exchange. With help of the optimized parameters, the structure of radical related to the observed dynamics was suggested and supported by quantum chemical calculations. It was clarified the nature of observed intramolecular dynamics. The observed AL effect is the result of the oscillations of both nitro groups within the molecule followed by transfer of an unpaired electron resulting into two conformers.

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EPR Spectroscopy on Hybrid Perovskite Materials

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Introduction. Organolead halide hybrid perovskites, with composition $APbX_3$ (A=organic cation such as methylammonium, X=Br or I), have emerged in the last few years as a most promising class of photoactive semiconductors for photovoltaic and optoelectronic applications due to their peculiar combination of properties. These materials are now being thoroughly investigated with different techniques, yet a lot of information on several aspects is still missing and is accessible by EPR spectroscopy, which has not been extensively applied so far¹ despite its long-standing application to related systems (e.g. perovskite oxides, organic semiconductors).

Materials and Methods. We applied CW and light-induced EPR to the most representative organolead halide perovskite ($CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$) and composite perovskite/organic semiconductor materials with the aim of identifying paramagnetic defects, photogenerated paramagnetic species and charge formation and recombination processes involving unpaired spin species. Hybrid perovskites microcrystalline powders and millimeter-sized single crystals were all conveniently synthesized from solution starting from precursors of the organic and inorganic components and following precipitation methods known in the literature. Extrinsic doping was achieved by incorporation of paramagnetic metals used to probe the local environment and the paramagnetic species dynamics.

Results. We observed a low level of intrinsic paramagnetic species both in single crystals and in microcrystalline powders. After photoexcitation of perovskite samples the formation of paramagnetic species is observed, although in very low yield. In composite perovskite/PCBM materials, a stronger photoinduced formation of charges, mainly observed as PCBM anion radicals, is detected, demonstrating a stabilization of separated charges in the mixed material. In some doped perovskite single crystals we observed a reversible quenching of paramagnetism induced by visible light absorption, a phenomenon attributed to trapping of charge carriers by the dopant species (notably VO^{2+}).

Conclusions. Several aspects of the intrinsic and photoinduced response of hybrid perovskites materials have been studied, confirming the useful applicability of EPR spectroscopy to this class of photoactive materials.

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EPR and DFT Study of the Ethylene Reaction with O⁻ Radicals on the Surface of Nanocrystalline MgO

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Radical forms of oxygen on the surface of oxides attract attention of researchers for more than five decades as possible intermediates in catalytic oxidation and photocatalytic processes. Different radical forms of oxygen (O⁻, O₂⁻ and O₃⁻) on the surface of nanocrystalline MgO are well-known.^{1,2} It was earlier demonstrated that EPR-silent species with the properties very similar to those of O⁻ radicals exist on the surface of magnesium oxide in addition to the O⁻ radicals observed by EPR.¹ In this study we characterized the reactivity of these two types of O⁻ radicals in reaction with ethylene.

It was demonstrated that reaction with ethylene yields different products for observable and unobservable O⁻ radicals. Conventional O⁻ radicals generated by the MgO illumination with UV light at room temperature in the presence of oxygen initiate hydrogen atom abstraction from ethylene to form secondary radicals H₂C=C⁻ with hyperfine splitting (A₁ = 59 G, A₂ = 6 G).

The O⁻ radicals not observed directly by EPR were synthesized by the MgO illumination in the presence of oxygen at 163 K followed by evacuation at 203 K. They were shown to react with ethylene to form an addition product with two groups of two equivalent protons with isotropic hyperfine constants A₁ = 38 G and A₂ = 23 G. Such radicals were obtained for the first time by reaction of O⁻ radicals with ethylene on the MgO surface. Their concentration was approximately equal to the concentration of [O⁻ O₂] complexes observed by EPR before the oxygen desorption.

The structures of both radicals were simulated by DFT, and a good match between the experimental and computational results was obtained. An excellent agreement of the experimental data with the results of the simulations carried out using the concept of uncharged O⁻ radicals suggested by us earlier³ supports this model. According to it the O⁻ radicals are formed on the MgO surface under illumination with the UV light due to homolytic splitting of chemisorbed water.

This study was supported in part by Russian Foundation for Basic Research (Projects 14-03-11110 and 15-03-08070).

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EPR line shape analysis of Gd(III) complexes

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Recently, the use of metal centres as spin labels for long-range site-to-site distance measurements in biomacromolecules and their complexes has attracted growing attention. In particular, spin labels based on Gd(III) complexes are of interest for in-cell EPR, distance measurements at high magnetic fields/high frequencies, as well as for spectroscopic selection schemes. While the broadly distributed zero field splitting (ZFS) parameters of Gd(III) complexes lead to the absence of orientation selection in pulsed dipolar spectroscopy, such distributions can also be inconvenient, since accurate determination of ZFS parameters is of importance with respect to several spectroscopic effects relevant to Gd(III)-based distance measurements. Furthermore, the magnitude and distribution of ZFS parameters may be an important criterion for selecting a spin label for a given application.

This contribution discusses different approaches for characterizing ZFS and its distributions by optimized fitting of line shapes of multi-frequency EPR data. The approaches are compared for a series of Gd(III) complexes in glassy samples. Due to the broad distributions of ZFS parameters, reliable fitting can only be performed under the assumption that ZFS is dominated by the terms of second order in spin operators, which are described by the well-known *D* and *E* parameters. We will discuss possible consequences of such an approximation. We compare two main approaches, one based on the assumption of Gaussian *D* and *E* parameter distributions,¹ and the other one based on Monte-Carlo modelling of the freely oriented ligands around the Gd(III) ion.² The applicability of the two models and the differences in the obtained *D* and *E* distributions will be discussed along with their precision and reliability. Such data are important for rational design of ligands for EPR experiments that use Gd(III) coordination complexes as spin probes.

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Intrinsic structure of α -Synuclein amyloid proteins in fibrils

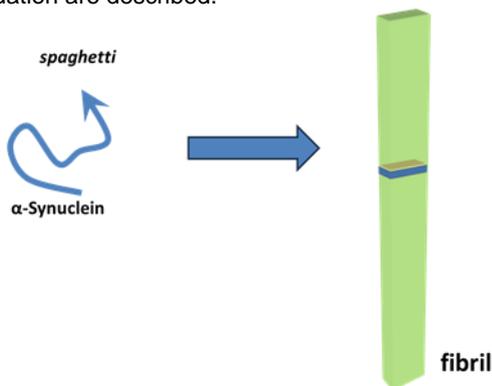
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Amyloid fibrils and plaques are the hallmark of neurodegenerative diseases. In Parkinson's disease, plaques (Lewy bodies) consist predominantly of the α -Synuclein (α S) protein. To understand aggregation, the molecular architecture of α S fibrils needs to be known. Here, we determine nm-distance constraints for the protein in the fibril by double electron–electron paramagnetic resonance (DEER) on doubly spin-labeled α S variants, diamagnetically diluted with wild-type α S to suppress intermolecular interactions. Intramolecular distances in three pairs (56/69, 56/90 and 69/90) are reported. An approach to derive a model for the fibril fold from sparse distance data assuming only parallel β -sheets is described. Using the distances obtained in this study as input, a model is obtained with three strands, comprising residues 56–90, in which the strands consist of 8–12 residues each. Limitations of the approach are discussed in detail, showing that the interpretation of the data does not yet yield an unambiguous structure model. Possible avenues to improve this situation are described.



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Localization of nitroxide radicals as guest molecules in mesoporous media

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The transport of particles into, through, and out of mesoporous materials with pore diameters between 2 and 50 nm has many applications in different chemical technological processes, e.g. for heterogeneous catalysis, chromatography or for drug delivery. In these processes the diffusion and localization of molecular species inside mesoporous systems play frequently a crucial role¹. One of the methods for investigation of dynamics and localization of guest molecules is EPR spectroscopy.

In this work the mesoporous organosilica material UKON2a with pore size of 6 nm and containing the carboxy functional groups was used. The localization of different guest molecules labelled with nitroxides inside UKON2a was investigated by different methods of EPR spectroscopy: ENDOR was used for distance measurements between the nitroxides and the walls of UKON2a, DEER was used for measurements of local concentrations of the nitroxides in UKON2a, and the information about local surroundings of the nitroxides was derived from ESEEM data.

With the combination of a broad variety of EPR methods we were able to precisely localize the guest molecules in the pores. We demonstrated that the distribution of the guest molecules in the pores is controlled by their properties as well as by the solvent and by the surface functionalization.

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Towards obtaining reliable distance distributions from 5-pulse DEER measurements

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Distance distribution measurement with Double Electron Electron Resonance (DEER) is an important tool for structural studies of proteins. The classically used 4-pulse DEER sequence, while normally being capable of delivering precise information on distance distributions between spins in a distance range up to 7-8 nm, suffers from a significant sensitivity drop if electron coherence decays quickly. This situation is often met with membrane proteins, limiting the longest accessible distances to 4.5 – 5 nm even with the most sensitive hardware. The situation can be significantly improved if pulses in the observer subsequence in DEER are repositioned in order to provide optimal dynamical decoupling conditions aiming at better preservation of the electron coherence. The number of pump pulses is correspondingly increased in order to maximize the dipolar evolution time. Borbat and co-workers demonstrated superior performance of the 5-pulse version over the 4-pulse DEER experiment,¹ while Spindler and co-workers extended the scheme to 7 pulses and used shaped pulses at the pump frequency.² It was immediately recognised that such experiments are sensitive to non-ideality of the pulses and thus require non-trivial approaches to data processing.^{1,2}

We show how artefacts in 5-pulse DEER measurements, potentially distorting the extracted distance distributions, can be reduced by applying optimal frequency and amplitude modulated pulses, as well as by utilising suitable excitation schemes. Specifically, asymmetric hyperbolic secant pulses (HS h) are used as pump pulses. Asymmetric HS h pulses exploit the high adiabaticity of the HS pulse of order 1^{3,4} to obtain a steep flank in frequency range where it is needed, i.e. on the side towards the observer. At the same time, such pulses take advantage of the extended time with higher amplitude of a HS pulse of higher order h in the frequency range where no steep flank is required.

We also discuss data processing for 5-pulse DEER, emphasizing the limits of artefact contributions still manageable to obtain reliable distance distributions.

Contributions by Andreas Dounas to optimizing the HS h pulses are gratefully acknowledged.

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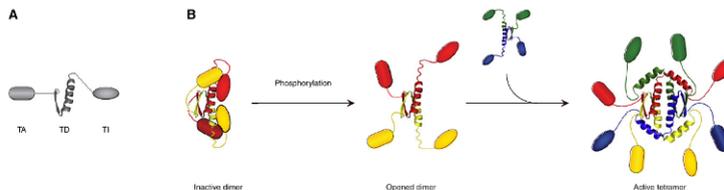
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EPR Spectroscopy on Quality Control Factor TAp63 α

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TAp63 α , a homolog of the p53 tumor suppressor, is the key quality control factor of maternal reproduction. TAp63 α is kept in an inactive, exclusively dimeric and kinetically trapped state but undergoes rapid phosphorylation-induced tetramerization and concomitant activation upon detection of DNA damage^{1,2}.



Model of the Inhibition of TAp63 α

(A) Schematic representation of TAp63 α showing the transactivation domain (TAD), tetramerization domain (TD) and transactivation inhibitory domain (TID). (B) Activation of TAp63 α requires disruption of the TAD-TD-TID interaction network resulting in an open conformation that enables tetramerization. Proposed mechanism from Reference 2.

For site-directed spin labelling, a cysteine free minimal construct of TAp63 α was generated (C_{free}-TAp63 α _{min}) in which the dimeric state is retained. This C_{free}-TAp63 α _{min} was spin labelled one residue at a time for all together 27 positions distributed over the full protein length. These two spin labelled proteins have been studied by PELDOR³ and for some due to the very close distance by CW EPR at multi-frequencies.

In the presentation, we will show our experimental results and first attempts of a construction of the dimeric configuration of the C_{free}-TAp63 α _{min}.

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ESR investigations of $\text{Y}_2\text{SiO}_5:^{143}\text{Nd}^{3+}$

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Here we investigate isotopically pure dielectric crystals Y_2SiO_5 activated by rare earth ions ($^{143}\text{Nd}^{3+}$ ions in concentrations 0.025% and 0.05%) which are currently considered as the most promising carriers of quantum information. The investigations by electron paramagnetic resonance method at cryogenic temperature is suitable for the determination of effective spin Hamiltonian parameters of the ground and the excited states of the impurity ions, which are crucial for the realization of Raman optical quantum memory and frequency conversion of photons between optical and GHz ranges.

The EPR spectra of $\text{Y}_2\text{SiO}_5:\text{Nd}^{3+}$ consist of two groups of lines. Each group contains eight lines that can be attributed to the hyperfine structure of $^{143}\text{Nd}^{3+}$ ion ($S=1/2$, $I=7/2$) (Fig.1). Experimental data were fitted using the following spin-Hamiltonian $\hat{H}=\mathbf{g}(S\cdot H)+S\cdot\mathbf{A}\cdot I$. Fit parameters were $\mathbf{g1}=\{4.02; 2.16; 0.82\}$, $\mathbf{A1} [K]=\{0.063; 0.027; 0.017\}$ and $\mathbf{g2}=\{4.20; 1.84; 0.72\}$, $\mathbf{A2} [K]=\{0.064; 0.025; 0.012\}$. in the local coordinate systems. The local coordinate systems of corresponding \mathbf{g} and \mathbf{A} tensors are rotated to each other.

This work is supported by the RSF (Grant no. 16-12-00041).

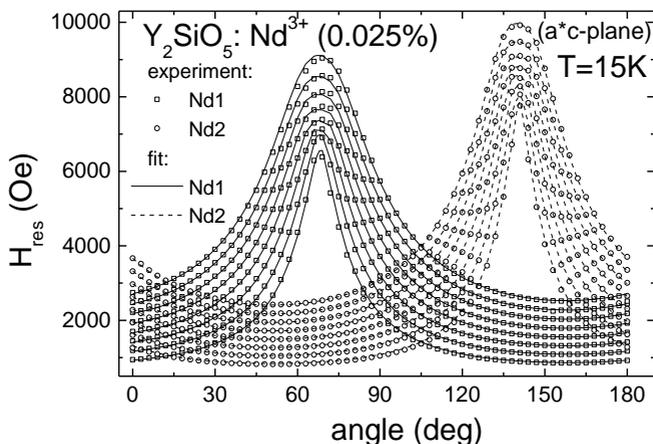


Fig. 1. Angular dependences of the ESR resonance fields of the Nd^{3+} ions in Y_2SiO_5 at $T=15\text{K}$ in a^*c -plane (axis a^* is perpendicular to the crystallographic bc -plane).

Non-Fenton processes of the formation of reactive oxygen species on amorphous ZrO₂ surface

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H₂O₂ decomposition is commonly catalysed by transition-metal-based systems, but also less conventional materials of non-redox nature, such as amorphous oxides, exhibit activity in generation of reactive oxygen species (ROS) from H₂O₂. The redox active materials show typical Fenton-like reactivity, while for the non-redox oxides formation of ROS is not trivial and involves interfacial electroprotic reactions.¹ In this contribution reactivity of amorphous ZrO₂ oxide toward formation of ROS was investigated by means of EPR spectroscopy, and auxiliary spectroscopic techniques (Raman and UV-Vis).

The presence of superoxo groups was confirmed by EPR spectroscopy. The EPR spectra recorded after treatment with H₂O₂ solution at various pH values represent a signal characteristic of surface-stabilized O₂^{•-} species. The obtained spin-Hamiltonian parameters values ($g_{xx} = 2.0029$, $g_{yy} = 2.0095$, $g_{zz} = 2.0329$) are typical of superoxides. Temperature behavior of the observed signal (10 K – 77 K) and additional HSCORE measurements showed that O₂^{•-}-species were stabilized via H-bonding with surface hydroxyls, on the contrary to a reference material of amorphous Nb₂O₅ (also active in ROS generation) for which the presence of hyperfine splitting due to ⁹³Nb ($I = 9/2$) nuclei indicated direct bonding with the metal core.¹

Generation of •OH radicals in the ZrO₂/H₂O₂ system was confirmed by means of EPR using DMPO spin trap and additionally by probe reaction with OPD substrate by means of UV-Vis spectroscopy.

The spectral intensities of the detected ROS changed strongly with pH of the reaction mixture. This observation indicated that the processes leading to ROS generation must involve a proton transfer. The experimental relationship between the concentration of •OH and O₂^{•-} radicals versus pH showed that both types of ROS were formed simultaneously following the electroprotic mechanism (HO₂⁻ + H₂O₂ = O₂^{•-} + •OH + H₂O). Thus, it was shown that amorphous ZrO₂ exhibited peroxidase-type reactivity, and consequently, the nature of ROS could effectively be controlled by varying pH of the reaction medium.

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Acknowledgement

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Optimising dynamic electron polarisation from the radical-triplet pair mechanism in aqueous solutions

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The rose bengal dye and TEMPO radical system has previously shown promise in generating large electron polarisation by the radical-triplet pair mechanism (RTPM) with a polarisation enhancement per quenching event of $P_n = -150 \pm 20$.¹

In this work, the polarisation of the rose bengal nitroxide system has been investigated with the aim of increasing the polarisation efficiency by adjusting the viscosity, pH, and oxygenation of the sample. Dry nitrogen was bubbled through samples before transfer to the EPR resonator in a nitrogen purged flow system. The magnetisation (relative to thermal) was determined as a function of time after a laser flash by an electron spin echo experiment. Examples of time resolved spectra are shown in Figure 1.

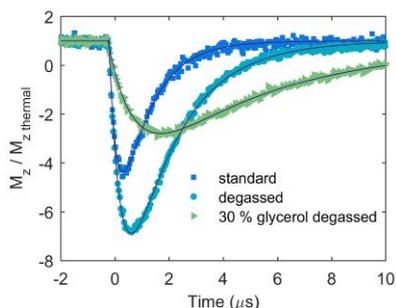


Figure 1. Examples of time resolved EPR spectra after laser flash for nitroxide radicals in different environments.

In contrast to predictions from theory,² the viscosity dependence of P_n was found to be surprisingly robust, with no noticeable change in the range investigated. As expected though, the net polarisation was longer lived with increased viscosity due to increases in nitroxide T_1 , and a reduction in the radical-triplet quenching rate, k_q . Thorough deoxygenation of the sample saw substantial changes in the net polarisation, due to increases in T_1 , and a reduction in quenching of the excited triplet by oxygen. P_n was not significantly altered by deoxygenation.

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EPR investigation of the role of germanium centers for the production of 110 °C TL peak in irradiated quartz

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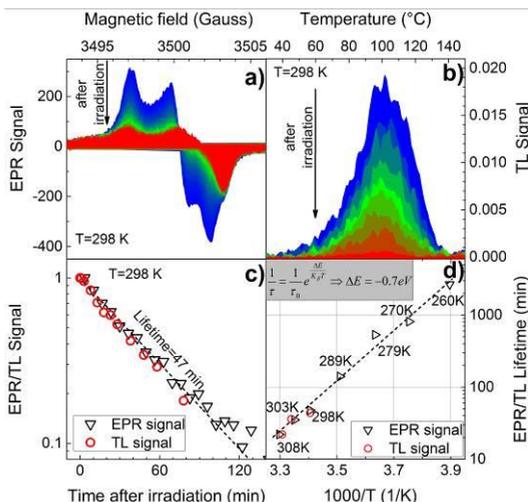
Electron paramagnetic resonance (EPR) spectroscopy was used to deepen and clarify the origin and the physical mechanisms of the well-known 110 °C thermoluminescent (TL) peak observed in irradiated synthetic and natural quartz.^{1,2} The great interest both from a fundamental perspective as well as for practical issues in this peak comes from the fact that quartz is the main material for dating archaeological and for retrospective dosimetry. Although, in last decades, many investigations has been carried out, a clear understanding of the mechanism and of the points defects responsible for the 110°C peak is still lacking^{1, 2}.

In this work we monitored the temporal decay of the EPR signal (Fig.1a), attributed to [GeO₄] center, and the 110°C peak (Fig.1b). Both unstable signals are characterized by a simple exponential decay with a comparable lifetime of 47 minutes at room temperature (Fig.1c). By the acquisition of the EPR and TL isothermal decays in a wide range temperature, we estimated the lifetime for each temperature (T) and by the behaviour of lifetime as function of 1/T (Fig.1d), we estimated the activation energy ($\Delta E = 0.7$ eV).

Our data strongly suggest a common physical mechanism for the observed EPR signal ([GeO₄] center), and the recombination center originating the 110 °C.

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EPR dosimetry on human fingernails: study of the variability of the endogenous signal

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Human fingernails and toenails have been studied for years by means of Electron Paramagnetic Resonance (EPR) spectroscopy to develop a new capability of estimating ionizing radiation doses received by individuals in case of radiological accidents.

A stable free radical has been identified as marker of the irradiation. Unfortunately, this marker presents the same characteristic than the endogenous signal observed in human nails. As this endogenous signal is more intense than the radio-induced component, the quantification of these radio-induced free radicals is extremely difficult to achieve. Moreover, if the endogenous signal is thermally stable up to 240°C, strong variations of its intensity were observed and possibly correlated on moisture content of nails. This effect is reproducible when repeating cycles of water soaking and drying. Such effect is not observed for the radio-induced components. An additional difficulty is the inter-individual variability of the endogenous signal intensity. In order to be able to propose a method of dosimetry based on EPR analysis on nails clippings, it was necessary in a first step to investigate the variability of the endogenous signal and to study the parameters influencing its intensity.

We will report on: the variability of the intensity of the endogenous signal over periods up to 2 years from different donors, the variability of signal shape for about 20 different donors and the variability of the moisture effect on the endogenous signal.

Monitoring alteration in Myosin by means of Electron Paramagnetic Resonance.

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Myosin is one of the three molecular motors that are present in eukaryotic cell genome and, together with actin, it is responsible for muscle contraction. During the completion of its function, myosin undergoes large amplitude motions that result in a change of its biochemical state, causing the powerstroke which is necessary for muscle contraction. Point mutations and post-translational modifications of this protein lead to contractile dysfunctions and the organism can incur in severe diseases and damages. The investigation of the mechanics of myosin at a molecular level, combined with the study of mechanical output such as force and shortening velocity, is required in altered systems for the rational design of drugs.

In this framework, Electron Paramagnetic Resonance (EPR) coupled with Site-Directed Spin Labelling (SDSL) is a powerful tool for the investigation of myosin molecular action in relation to structural alterations, as the technique has revealed to be sensitive to the different biochemical states of myosin during the cycle of binding and hydrolysis of ATP¹.

Skeletal muscle fibers from different organisms have been selectively labelled at Cys707, located in the myosin head, with IASL, an intrinsically rigid spin probe; in this way, the dynamics of the labelled-head under different stimuli has been investigated by means of Continuous Wave EPR. The recorded spectra give information about the structural state of myosin in different moments of the ATP cycle. The comparison between control samples and altered ones (aged, oxidized and mutated) has been used to make predictions on the structural changes that occur in myosin upon modifications and to provide a molecular explanation for the difference in force generation noticed in these samples.

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EPR investigations of enzyme-ligand complex in copper containing proteins

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Copper containing proteins are ideal subject for EPR studies devoted on gaining information about their catalytic site structure and activity. Some of them, such as Laccase (a blue copper oxidase) carry four copper atoms divided into T1, T2 and T3 copper centers, with T3 being binuclear and EPR silent; others like the oxidative enzyme Tyrosinase have only the T3 binuclear copper catalytic site^{1,2,3,4}.

The interest on extending knowledge about the molecular environment and the effect of the presence of exogenous ligands in these different kind of copper containing proteins led us to an EPR characterization of the spectroscopic behavior of the enzymes-ligand (E-L) complex both thorough multifrequency CW measurements (S, X, Q band) and pulse EPR measurements (Q-Band)⁵. Different protein samples like a bacterial Tyrosinase from *Streptomyces* strains from Algerian desert soil isolates, and a fungal Laccase from *Coriolopsis Gallica* will be analyzed and compared with commercial Ascorbate oxidase and Hemocyanin samples.

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EPR dosimetry on calcified tissue: Study of the variability of the radiation sensitivity

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EPR CW spectroscopy is currently used to estimate received doses of ionizing radiation by individuals accidentally overexposed. From the quantification of radio-induced free radicals in biological materials such as hydroxyapatite from human bones and teeth, received doses can be assessed, through a calibration process. In order to estimate associated uncertainties to calibration process and improve its accuracy, the dependencies of the radiation sensitivity of calcified human tissue have to be known, especially its variability at different energies.

We investigated the variability of radiation sensitivity for 3 photon energies for 40 human teeth (essentially molars) from different donors and 50 samples of different types of human bones (rib, phalanx, vertebra, ...) collected from hospitals. Irradiation were performed with Co-60 gamma-rays (E_{mean}=1.25 MeV), Cs-137 gamma rays (E_{mean}= 0.667MeV) and X-rays (E_{mean}=0.080 MeV) at doses ranging between 50 and 200 Gy.

The variability in the EPR sensitivity for Co-60 gamma-rays was estimated about 10%. Nevertheless, with low energy photon irradiation (E<100 keV) expanded variability of sensitivity were observed, reaching 80%. This could be explained by the fact that dose deposition process for photons with energy about 100 keV is dominated by the photoelectric effect. Indeed, this effect is highly dependent on materials atomic number, unlike the dose deposition process with higher photon energy which is dominated by Compton effect. Therefore, variability of dose sensitivity is more affected by calcified tissue composition, especially Ca, P and O contents.

For the same type of bone, the variability of the dose response is more important than for enamel. Significant variability is also observed between different bone types.

EPR-Based Localization of Metal Ions in Biomolecules

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Metal ions are present in many proteins and nucleic acids and are involved in numerous essential functions ranging from structure stabilization to enzyme catalysis. The knowledge of the location and coordination of metal ions in biomolecules is often important for understanding the role of metal ions in biomolecular functions. The localization of metal ions is, however, a quite challenging task that sometimes requires using a broad arsenal of experimental techniques. Here, a trilateration approach for the localization of paramagnetic metal ions is presented. The idea of the approach is that the position of a metal ion in a biomolecular structure can be determined via distance constraints measured between this ion and a number spin labels attached at selected positions of the biomolecular surface.

The approach was tested on the Cu(II) center of the structurally well-characterized protein azurin.¹ After site-directed spin labeling of azurin with a methanethiosulfonate spin label (MTSL) at six different sites, six Cu(II)/nitroxide distance constraints were measured by Pulsed Electron-Electron Double Resonance (PELDOR) and then used to locate the Cu(II) ion in the *apo* structure of azurin. The error of the trilateration of 0.26 nm was determined by comparison with crystallographic data of azurin. All possible sources of this error were evaluated, leading to the conclusion that the main error stems from the estimated locations of the MTSLs in the azurin structure. Using the crystallographic position of the Cu(II) ion, these locations were determined more precisely from orientational selective PELDOR data of azurin.² Interestingly, the determined locations were in very good agreement with the MTSL conformations determined for two azurin mutants by X-ray crystallography.

In addition, the possibility to extend the trilateration approach towards other metal ions, such as Fe(III) and Mn(II), has been considered. On example of Fe(III)-containing MTSL-labeled cytochrome P450cam it was shown that the Relaxation-Induced Dipolar Modulation Enhancement (RIDME) yield a better signal-to noise ratio and no orientation selectivity as compared to PELDOR.³ This reveals the potential of RIDME for further trilateration studies.

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Magnetic properties of the Au₂₅(SR)₁₈ clusters

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Introduction. In monolayer-protected gold clusters (MPCs) with core diameters of <1.6 nm, quantum confinement effects make the cluster display the same general features of "simple" molecules. Advanced synthetic procedures and knowledge of the structures of some molecular MPCs by X-ray crystallography have provided the necessary grounds for obtaining a deeper understanding of these systems. Au₂₅(SR)₁₈, which has a core of only 1 nm, is the most stable and characterized molecular MPC. Several of its properties have been studied in detail, such as its distinct electrochemical, NMR, and optical behaviors.¹⁻³ Whereas Au₂₅(SR)₁₈⁻ and Au₂₅(SR)₁₈⁺ are diamagnetic, the neutral form Au₂₅(SR)₁₈⁰ is paramagnetic, and can thus be studied by EPR techniques.

Materials and Methods. The Au₂₅(SR)₁₈⁰ clusters were protected by different thiolated ligands (SR), such as SC₂H₂Ph and linear or ramified alkyl-chain thiolates. The clusters were analyzed in frozen solution and in the solid state. For the latter, we used different materials ranging from amorphous films to single crystals. The EPR measurements were performed in the range from 5 to 290 K, using continuous wave (CW) and pulsed techniques (pulsed ENDOR, ESEEM).

Results. The solid-state magnetic properties were studied by cw-EPR techniques. Whereas interconnection of Au₂₅(SC₄H₉)₁₈⁰ clusters yields a polymer behaving as a one-dimensional antiferromagnetic system,⁴ the use of other ligands gives rise to different magnetic orderings. The magnetic properties were rationalized using a superatom-model approach that pointed to the importance of considering relativistic factors in understanding the properties of molecular Au clusters. The spin density distribution over the clusters was determined by pulsed ENDOR, and then compared to the NMR and DFT calculations results.

Conclusions. CW and pulsed EPR techniques, coupled to the use of atomically precise systems with controlled charge state, proved to be very powerful tools to unravel magnetic properties of molecular gold clusters.

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An EPR study on the role of illumination in the hazard assessment of nano-TiO₂

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Titania nanoparticles have been found to elicit toxic responses in vivo and in vitro systems.^{1,2} Several studies report that the toxic effects are largely modulated by physico-chemical properties of TiO₂ such as specific surface area and crystallinity.^{2,3} When illuminated, TiO₂ induce acute cytotoxic and genotoxic effects.⁴ Such effects are related to the ability of TiO₂ to generate reactive species like hydroxyl radicals HO[•], superoxide radicals O₂^{•-} and singlet oxygen ¹O₂. These species, generally referred as Reactive Oxygen Species (ROS), in low concentration have important physiological functions in cells, but in high amount are highly toxic to living organisms. Photo-activation may occur during toxicological testing following to exposure of the powders to indoor light prior the measurements. At the moment, there is not a consensus on the illumination conditions to be used during toxicological testing. Therefore, comparison of the data from different laboratories may be misleading. This study was performed within the FP7 EU project: "Shape-engineered TiO₂ nanoparticles for metrology of functional properties: setting design rules from materials synthesis to nanostructured devices" (SetNanoMetro) and aims to define standardized experimental conditions to be used in toxicological testing of TiO₂ nanopowders.

The reactivity of a set of TiO₂ samples having different physico-chemical properties has been firstly studied by means of electronic paramagnetic resonance (EPR) associated to the spin trapping technique by using a set of different probes and experimental conditions to identify the protocols that better simulate the reactivity toward cells. The selected protocols were used to test the powders in different illumination conditions.

The results show that very low amount of indoor light are able to activate TiO₂, albeit this activation occurs at different extent depending upon the type of materials. The data herein presented underline the importance of a controlled illumination during toxicological testing.⁵

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EPR study of polarons in blends for bulk heterojunction organic solar cells with nonfullerene acceptors

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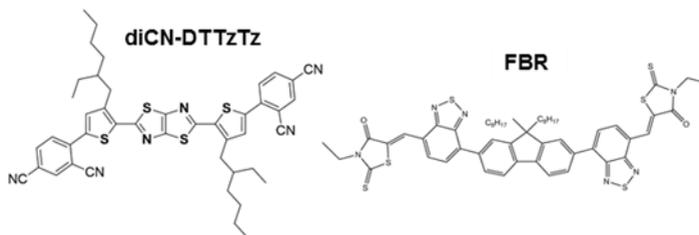
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Bulk heterojunction organic solar cells are demonstrating great potential for future photovoltaic applications with power conversion efficiencies now reaching over 10%. The ongoing research efforts in organic photovoltaics are now focusing on the development of new materials to address remaining issues of efficiency, stability and economical feasibility. An important opportunity is to replace the fullerene acceptors by alternative materials with better light absorption, higher chemical versatility and eventually lower cost.

In this context we investigated a recently synthesized 2,5-dithienylthiazolo[5,4-d]thiazole (DTTzTz) molecule as an alternative acceptor in combination with the standard donor polymer MDMO-PPV. Successful charge transfer was already established in similar systems by optical methods.¹ We have now further characterized the charge transfer in this system by light-induced EPR which is particularly suited for the study of the photogenerated charge carriers, called *polarons*.

Despite the demonstrated efficiency of charge transfer in donor:acceptor blends with diCN-DTTzTz, solar cells based on this material have shown poor device performance. Therefore we chose to perform parallel measurements on FBR, a novel nonfullerene small molecule acceptor synthesized by McCulloch *et al.*² Solar cell devices based on FBR with P3HT as donor polymer yielded promising power conversion efficiencies of 4.1%. Hence FBR:P3HT serves as a good reference system for our results.



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W-band EPR study of stable radicals in gamma irradiated L- and D-alanine

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L-alanine radicals have been explored extensively using EPR spectroscopy by numerous experimental groups for the long period of time since 1950s. It is well known that at least three different radicals induced by radiation are formed in single crystal of L-alanine at room temperature. As a result of extensive EPR, ENDOR (Electron Nuclear Double Resonance), EIE (ENDOR induced EPR) and HYSCORE (Hyperfine Sub-level Correlation) studies on irradiated L-alanine, a substantial amount of experimental data concerning electronic *g*-values and hyperfine coupling constants of magnetic nuclei in alanine-derived radicals are available. In order to reproduce obtained experimental data, various detail microscopic models were suggested to describe the first stable L-alanine radical. The other two radicals have not been explored in such details. Therefore, open questions are tempting today. Moreover, studies on L-alanine radicals, in contrast to D-alanine, were in spotlight, despite of EPR investigations of D-alanine which show different substructure and radical yield.

The most of the EPR spectroscopic investigations that have been performed were limited to low frequency (mainly X band i.e., ~ 9.5 GHz), and only a few studies have been performed in Q band (~ 35 GHz) and W band (~ 95 GHz). This technical limitation in spectral and time resolution restricts the wealth of information on the magnetic properties of these amino acid radicals from being accessed.

In this report, EPR measurements at high microwave frequency (W band) and corresponding high magnetic field were performed to enhance the resolution of the differences in the *g* values in order to get insight subtle differences in substructure of both enantiomers of alanine, L- and D-alanine. In addition, comparison of the temperature dependent relaxation data, focused on dynamics of the different parts of molecules of both enantiomers of alanine, will be reported.

WaDeESR: Wavelet Denoising for Continuous Wave-ESR

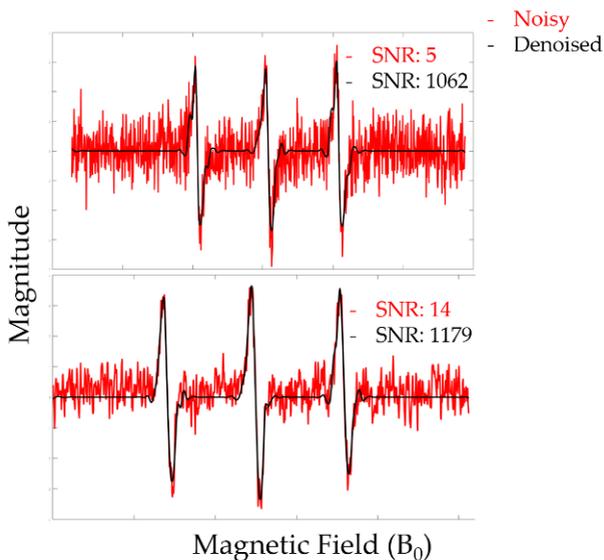
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Continuous-wave Electron Spin Resonance (cw-ESR) spectroscopy is the most commonly used ESR technique. It is extensively applied to study the dynamics and structure of biomolecules. To obtain the desired spectrum, signal averaging is used. This reduces noise by averaging multiple measurements on the same sample. This is typically time consuming especially for samples with low SNR, and can be limited by sample degradation. Also, it is mainly effective in canceling white (random) noise. We developed a novel wavelet denoising method for cw-ESR (WaDeESR) that substantially reduces the signal averaging required by about an order of magnitude (to obtain good SNR). Our extensive studies on model and experimental spectra have shown that our method performs significantly better than other denoising methods. An important feature of our method is its ability to identify and eliminate noise at and near the peaks of the spectrum, and to recover small satellite details.



Fluorescent vanadyl complexes as theranostic agents: synthesis, spectroscopical characterization and cell viability assays

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A number of vanadyl complexes have been reported to display anticancer activity¹. Vanadyl therapeutic agents have several advantages, e.g. a low systemic toxicity and a good combination of water solubility and lipophilicity, depending on the nature of the organic ligands. Unfortunately, very little is known as regards the molecular targets of vanadyl complexes in cells as well as their intracellular distribution. In addition, vanadyl complexes are well known to undergo complex speciation equilibria in aqueous solution: these processes may generate a range of chemical species with distinct pharmacological effects². All these pieces of information are relevant to the comprehension of the mechanism of action of vanadyl drugs. A theranostic approach, based on the simultaneous observation of both the effect of vanadyl complexes on cell viability and the disclosure of their intracellular fate, is possible by using vanadyl complexes functionalized with fluorescent ligands. In the present study,^{3,4} six vanadyl complexes with fluorescent acetylacetonate derivatives have been synthesized and fully characterized both in the solid state and in solution, in conditions close to those employed for *in vitro* drug subadministration. A combination of spectroscopical and electrochemical techniques has been applied (X-ray, EPR, Raman, electronic absorption and emission, cyclic voltammetry). Cell viability assays have also been performed on distinct cell lines. The results show that these complexes exhibit an average stability in solution; EPR data suggest the occurrence of partial ligand substitution in water/DMSO mixture. One complex exhibits a quantum yield suitable for confocal microscopy investigations. Some complexes have been shown to inhibit cell viability: this effect is clearly mediated by the ligands' properties.

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EPR characterization of new materials for water pollutants degradation (Mat4treaT project)

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Mat4treaT is a Marie Skłodowska-Curie RISE project funded by the European Commission. The project involves eight Universities and two non academic institutions from Italy, Spain, Denmark, Greece, Canada, Argentina and South Africa committed to work in the development of novel materials to be used in innovative integrated water tertiary treatments for organic pollutant removal¹.

Materials developed in the project include several oxides, polymeric and inorganic membranes, graphene-oxide and bio-based substances extracted from urban waste. Furthermore, several composite materials such as Si-Fe magnetic nanoparticles, functionalized silica monoliths, silica grafted photoactive substances or TiO₂-protein biocatalysts are synthesized and applied to different pollutant removal problems²⁻⁶.

Both the materials and the processes were characterized by different EPR techniques. In particular, photocatalytic and other redox processes were studied by spin trapping in the presence of DMPO and 4-oxo-TMP, for the identification of hydroxyl radical and singlet oxygen, respectively. Whereas the charge separation occurring during the irradiation of solid oxides and the consequently formation of holes and electrons were followed by solid state EPR measurements. Different semiconductor oxides (bare and doped) have been irradiated with UV and visible light under vacuum and in presence of oxygen atmosphere. In the former case it was possible to verify the formation of holes and in the latter one the formation and reaction of electrons.

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Relationship between structural intrinsic disorder and enzyme catalysis in UreG: a SDSL-EPR study

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Nickel delivery into the active site of urease, an essential enzyme for plants, fungi and bacteria, requires the presence of four accessory proteins, named UreD, UreF, UreG and UreE. UreG, responsible for hydrolysis of GTP, exists in solution as an ensemble of interconverting conformations with some degree of secondary and tertiary structure. For these reasons it has been classified as an intrinsically disordered enzyme.¹

The aim of this study is to investigate the relationship between the structural flexibility of UreG and its activity using *Site-Directed Spin Labeling* (SDSL) combined with *Electron Paramagnetic Resonance* (EPR) spectroscopy. SDSL-EPR has emerged as a powerful approach to study changes in protein structures and to follow folding/unfolding events that are not readily amenable with X-ray crystallography. This technique relies on the selective grafting of paramagnetic labels (e.g. nitroxide radicals) on cysteine followed by the monitoring of EPR spectra whose shape reflects the mobility of the spin label.² The structural behavior and the enzymatic activity of UreG were studied in the presence of additives that either decrease (i.e. GndHCl, temperature) or increase protein secondary or tertiary structure (i.e. SDS, TFE, TMAO). Circular Dichroism spectroscopy and Nuclear Magnetic Resonance were used as complementary approaches. Taken together, the results demonstrated that the activity of UreG strongly depends on its structural flexibility: folding-inducers abolish GTP hydrolysis while a moderately increase of disorder maintains or slightly increases protein catalytic activity.

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The colicin A pore-forming domain in *E. coli* lipid membranes studied by EPR spectroscopy

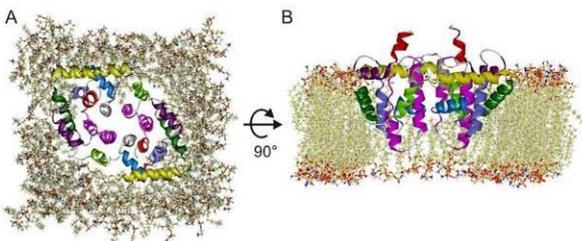
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Colicin A (ColA) is a plasmid-encoded water-soluble pore-forming toxin produced by *E. coli*.¹ The protein kills unprotected cells of related strains by inserting specific helical segments of the pore-forming subdomain into the cytoplasmic membrane to form voltage-dependent ion channels. The crystal structure of the soluble form of the pore-forming domain has been solved, but detailed structural data for the membrane-bound channel, in the closed as well as in the open state, is still missing. Currently two models are discussed for the closed channel state, the “Umbrella-Model” and the “Pen-knife-Model”.

Previous EPR results already provided first evidence for the closed channel state being in agreement with the suggested “Umbrella-Model”.^{2,3} In the present study, the *in vitro* investigation by site-directed spin labeling and EPR spectroscopy has been substantially extended, including mobility, polarity, accessibility and inter spin distance measurements.

Our results indicate that a larger fraction of the protein than previously suggested penetrates into the hydrophobic core of the membrane. The EPR distance measurements under *in vitro* conditions provide evidence that ColA in lipid bilayer membranes forms, contrary to earlier studies but in line with a more recent electron microscopy investigation⁴ an oligomeric structure. Pulse EPR distance measurements of ColA incorporated into living *E. coli* cells⁵ reveal clear indications for an oligomeric ColA structure also *in vivo*, proving that ColA is organized as an oligomer in the membrane integrated state also under physiological conditions. The results of the present EPR measurements were combined to suggest a model for the colicin A closed channel state conformation (Fig.1).



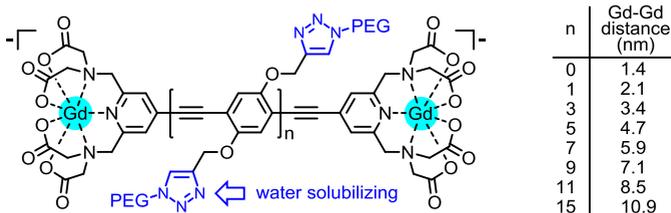
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Water soluble Gd(III) molecular rulers

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EPR techniques have become very important tools for the determination of structure and dynamics of (bio)macromolecules via distance determination between two spin labels. For evaluation and further development of the EPR techniques a set of geometrically well-defined diradicals with different spin-spin distances is highly valued. At best, these diradicals are soluble in the solvents that are used for application, e.g. in water/glycerol mixtures. Here we report on the design and synthesis of water soluble diradicals with Gd(III) as the paramagnetic moiety, so called Gd rulers.¹ Gd(III) complexes as spin labels recently came into focus because of their attractive spectroscopic properties, high chemical stability, and biocompatibility.



The ligand, e. g. 4-iodo-PyMTA,² and the spacer, the monodisperse oligo(*para*-phenyleneethynylene)s, were synthesized independently and then assembled to the Gd rulers.¹ Oligo(ethyleneglycol) (PEG) side chains were chosen to obtain water soluble Gd rulers. The synthetic strategy allows the side chain adjustment on a late step of the multistep synthesis. Furthermore, it promises a rapid access to Gd rulers with other ligands - an important aspect considering the influence of the ligand on the spectroscopic properties. The Gd rulers shown above are used to evaluate the Gd-based DEER, RIDME, and *cw*-EPR techniques as well as Gd-based DNP.³

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Defects in graphenic materials by EPR and DFT methods

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We have used EPR to characterize a series of defects, which are characterized by typical g-tensors, linewidths, intensity as function of the temperature¹.

Mostly, signals arise from the presence of conduction electrons, and of so-called 'edge states', that are unpaired electrons located at the edges of graphenic flakes; the relative molecular orbitals are not very much extended as for low-lying orbitals, and are located within few atomic rows from edges with zig-zag topology.

All the relative EPR signals are naturally and intrinsically generated by all graphitic materials^{1,2}.

We now extend our study to the defects that are formed inside the graphenic structure.

There is a full zoo of possible defects that can in principle originate EPR signals, like the presence of ad-atoms, holes, dislocation of atoms.

We have started to study and analyze each type of defect from an experimental as well as from a theoretical point of view.

Examples from each type of category will be given and shown.

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Electronic and Magnetic Interactions in Porphyrin Dimers

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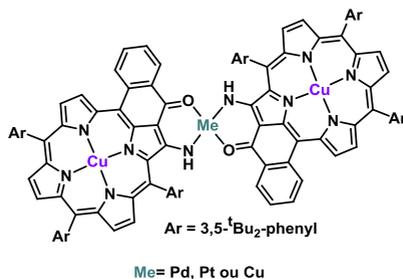
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The synthesis and study of highly conjugated π -systems is an active field of research because of their possible applications in molecular electronics.¹

Electronic interactions between porphyrins linked by covalent bonds were extensively studied. For instance, efficient electronic communication was demonstrated between triply fused porphyrins (A. Osuka et al.)² or triple bonds linked porphyrins (H.L. Anderson, M.J. Therien et al.).^{3,4} These properties were mainly highlighted by electronic spectroscopy and/or electrochemistry studies.

Porphyrins linked by coordination bonds have been much less investigated. Our group reported good electronic communication between nickel(II), palladium(II), and platinum(II) linked porphyrins. This was demonstrated by electronic spectroscopy, electrochemistry, or ultrafast energy transfer studies and also corroborated by DFT calculations.^{5,6}

Magnetic interactions between porphyrins are much less studied. Therefore, we are now studying the magnetic properties of copper(II), palladium(II), and platinum(II) linked copper(II)porphyrin dimers by performing EPR and SQUID measurements.



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Assessing the Possibilities of an Helium Cryogenic System for ESR Dating of Quartz

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Electron Spin Resonance (ESR) dating of quartz is based on the detection of various radiation-induced paramagnetic centers associated with defects present in the crystalline structure of quartz.^{1,2} Among them, Aluminium [AlO₄]⁰ and Titanium centers [TiO₄/M⁺]⁰ (M⁺ = Li⁺, H⁺ or Na⁺) have become so far the most widely used. However, unlike other materials like fossil tooth enamel, ESR signals of both the Al and Ti centers are not visible at room temperature and measurements should be performed at very low temperature instead.

A previous study of our group showed a strong influence of temperature on the ESR signal of the Al center: basically, the signal resolution and intensity are significantly increasing when the temperature decreases.³ In geochronology, ESR measurements of quartz are usually performed using liquid nitrogen systems, i.e. at temperatures between 77 and ~115 K, and measurements at < 77 K have almost never been carried out.

With the recent acquisition of an Elexsys E500 ESR spectrometer coupled with a 4112 HV Bruker Helium system, we got the opportunity to evaluate whether measurements close to Helium temperature may actually provide a significant improvement in ESR dating of quartz grains. To do so, we studied the behavior of Al and Ti centers in terms of sensibility and resolution of the signal at temperatures between 15 to 110 K and quantified the influence of temperature on the ESR signal of both centers. In particular, the impact on the ESR signal Ti-center has been specifically studied, since its great potential in ESR dating (i.e. fast bleaching kinetics and no residual ESR intensity, contrary to the Al center) is usually mainly limited by the difficulty to achieve reliable and reproducible measurements given the low signal-to-noise ratio usually encountered in quartz samples.

In addition, the influence of temperature on the doses derived from the ESR measurements has been evaluated, demonstrated that this Helium system could be used for dating quartz grains samples.

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New Photoactive Materials Based on Zirconium Dioxide Doped With Rare Earth Metal Ions

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The applications of visible light in photocatalytic reactions face an apparently irreconcilable contradiction. Using heterogeneous photocatalysts with lower band gap value, in fact, allows, on the one hand, the charge separation with lower energy photons (visible) but implies, on the other hand, to have less effective flat band potentials for Valence Band (VB) and Conduction Band (CB) therefore limiting (or even canceling) the photocatalytic activity.

To overcome this clear contradiction new generations of photocatalysts have been prepared and tested since the beginning of this century. The third generation of photocatalysts tries to go beyond titanium dioxide and was initially a prediction proposed by N. Serpone and A. Emeline. This was based on the idea of a wide band gap semiconductor (hence with excellent flat band potentials) containing extra electronic levels at intermediate energy in the band gap¹ capable of allowing the transition of electrons from the VB to the CB with a double excitation. The first evidence of this kind of mechanism was proposed by some of us for the Ce doped ZrO₂ system².

In the present study, we investigated the effect Rare Earth Oxide (REO; REO being CeO₂ and Er₂O₃) doping in zirconium dioxide matrix. The samples were prepared using the hydrothermal process and the REO loading 0.5, 1 and 5% molar. The X-Ray diffraction technique was used for the structural characterization while UV-visible diffuse reflectance (DRS) was used for the optical analysis, and the surface area was measured applying the Branauer Emmet Teller (BET) model on N₂ adsorption isotherms. The samples have then been analysed via electron paramagnetic resonance (EPR) to test their photoactivity and finally the new synthesized materials were tested in the reaction of degradation of methylene blue performed under irradiation by diodes (LEDs) emitting exclusively visible light. We found a correlation between the amount of photogenerated holes detected by EPR and the photocatalytic efficiency of the materials in the degradation of the dye.

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Paramagnetic Defects in bare and Ce doped ZnO: an EPR study

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Metal oxides semiconductors such as TiO₂ and ZnO, have been used for the photocatalytic degradation of a wide variety of environmental contaminants in the last decades. However, both TiO₂ and ZnO are activated only under UV irradiation because of their large band gap (3.2 and 3.4 eV respectively), which greatly limits their application in environmental decontamination, as solar spectrum only contains 5% of UV. Therefore, it is crucial to explore efficient methods to extend their photocatalytic response from UV to visible region.

Previous papers by some of us demonstrated that it is possible, through the dispersion of small amounts of cerium ions within the matrix of different oxides (namely zirconium dioxide or zinc oxide), to modify the photoactivity of the final material. Thereby, the modified oxide becomes photoactive in visible light and much more active in UV light¹⁻². Nevertheless the mechanism beyond the visible light activity of Ce doped ZnO is not yet clear.

In the present study, we synthesized via a hydrothermal method bare and Ce doped ZnO (with Ce molar content of 1 and 10%) and we characterized them both from a structural point of view by means of X-ray diffraction and transmission electron microscopy, and from a spectroscopic point of view, by means of Diffuse reflectance spectroscopy and Electron Paramagnetic Spectroscopy (EPR). EPR is indeed a technique which allows to indentify the paramagnetic centers formed during irradiation, and thus assessing the photoactivity of a material. In our case, we were able to identify several paramagnetic centers, related to the formation of stabilized holes in the material, and to verify that these centers are formed with UV light in the case of bare ZnO and with visible light in the case of Ce doped ZnO.

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Direct Insights into a Ti³⁺/Al³⁺ Tandem Catalyst through Advanced EPR Techniques

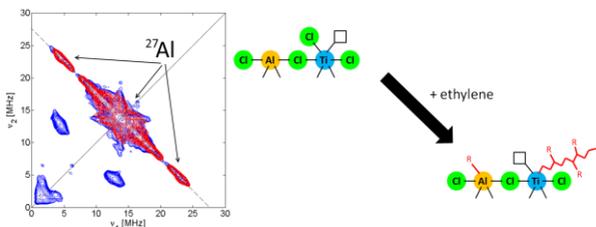
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The design of tandem catalysts for the synthesis of branched polyethylene (PE) has stimulated extensive research in recent years. In these systems one site oligomerizes ethylene to short α -olefins, which are successively incorporated in the growing polyethylene chains through an “in-situ branching” mechanism by a second, different, catalytic centre.

A bifunctional heterogeneous catalyst featuring isolated Ti³⁺ centres and strongly acidic Al³⁺ sites at the surface of chlorinated alumina was synthesized and characterized. By employing a wide range of physicochemical and spectroscopic techniques, the two sites, in close proximity, were demonstrated to act in a concerted fashion for boosting ethylene conversion to branched PE, without any activator.

In this work, EPR spectroscopy was employed to monitor and characterize the Ti³⁺ (3d¹) species, which play a key role in polymerization catalysis. Upon thermal reduction of the Al₂O₃/TiCl₄ pre-catalyst under H₂ atmosphere, X-band CW-EPR testified the formation of Ti³⁺ species. Reaction with O₂ and subsequent formation of paramagnetic superoxide radicals demonstrated that at least a fraction of the Ti³⁺ sites have pre-existing coordinative vacancies, which may be involved in the coordination of ethylene molecules. Q-band (34 GHz) Hyperfine Sublevel Correlation (HYSCORE) experiments allowed to gain insight into the local surrounding of the Ti³⁺ sites. The HYSCORE spectrum of the catalyst is dominated by an extended ridge signal centered at ²⁷Al Larmor frequency, with maximum extension of 21 MHz, arising from the hyperfine interaction of the unpaired electron localized on the Ti³⁺ with ²⁷Al (*I*=5/2) nuclei of the alumina. This large isotropic coupling provides unique and direct proof for the presence of remarkably strong Ti³⁺-Cl-Al linkages, supporting the existence of a synergistic cooperation between the Ti³⁺ and Al³⁺ sites.



Left: A typical Q-band HYSCORE spectrum of the Al₂O₃/TiCl₄/H₂ catalyst.
Right: schematic representation of the proposed tandem sites.

Protein-support interaction, electron transfer and hydrogen evolution in [Fe-Fe]hydrogenase-TiO₂ hybrid systems prepared using various TiO₂ materials.

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An efficient conversion of solar energy into either electrical power or renewable fuels is one of the most important targets in the last decades. Titanium dioxide, or titania, a cheap, abundant and non toxic semiconductor oxide, has played important role in this area. In spite of the many advantages titania shows two serious drawbacks hampering its direct use in the process of water photosplitting: the large value of the band gap and the electrochemical potential of the conduction band electrons which is only slightly more negative than the H⁺/H₂ potential. Our aim is therefore to overcome these two limitations. On the one hand, to favor the production of hydrogen, the use of an enzyme called [Fe-Fe] Hydrogenase anchored to the surface of TiO₂ could be a valid alternative to typical noble metal co-catalyst. This TiO₂-hydrogenase system is able to produce hydrogen from water, but, so far, it works thanks to the addition of synthetic ruthenium-dyes allowing visible light absorption.¹ On the other hand, among the methods to extend the optical absorption of titania to the visible range, a possible approach consists of exploiting TiO₂ powder materials in which the band gap is engineered by means of alio-valent doping. This type of doping generates intra band gap energetic levels allowing the electron excitation under visible light.^{2,3} The purpose of our work is to investigate hybrids systems prepared coupling doped titanias with a hydrogenase enzyme for hydrogen reduction. Our attention is paid not only to the efficiency of the hydrogenase-TiO₂ materials in hydrogen production but also to the mechanism of interaction of the protein with the solid and to the effect of the irradiation on the hybrid materials. We have followed in particular the electron transfer occurring upon irradiation using Electron Paramagnetic Resonance (EPR).

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Studies of Macro-, Micro- and Nanodiamonds by HF EPR/ENDOR

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Magnetic resonance methods are the basic techniques for studying spin phenomena in condensed matter and biological systems. Spin phenomena are playing a crucial role in the development of devices based on nanostructures. Nanoparticles are also widely used in different kind of technologies and medicine - for transfection, gene silencing, photodynamic therapy, drug delivery, etc. Since 2009 in the EPR division of the Centre of the Shared Facilities of Kazan Federal University we investigate various nanostructures. In this report we present systematically studied representative classes of macro-, micro- and nanodiamonds. Among the results obtained we highlight the following.

Paramagnetic centers of substitutional nitrogen in micro- and nanocrystalline diamond particles have been identified and separated by pulsed EPR at room temperature. A novel approach based on EPR analysis of nanodiamond was suggested for efficient separation of EPR signals from paramagnetic centers within the nanocrystals' core from those localized on the nanoparticle surface. Extremely high concentrations up to 10^4 ppm (1%) of NV centers were observed in sintered clusters of nanodiamond, which allow one to fabricate structures with one NV center per nm³.

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Mechanism operating along C₂H₂ self assembly on anatase TiO₂ and its reduction.

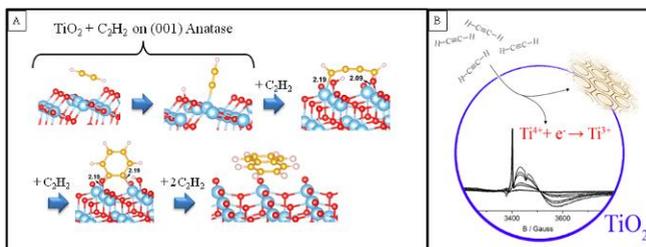
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The interaction of acetylene with the TiO₂ surface at room temperature entails a complex set of self-assembly reactions with the formation of products having relatively high molecular weight. The C₂H₂-TiO₂ has been investigated via both experimental^{1,2} and theoretical approach.³ C₂H₂ was adsorbed on samples submitted to different activation treatments of the surface in order to evaluate the role of the surface hydroxylation in the acetylene/TiO₂ reaction. The reaction has been monitored via Infrared (IR) and optical (UV-Vis) spectroscopy, Thermogravimetric Analysis (TGA) and via continuous wave Electron Paramagnetic Resonance (CW-EPR). The experimental results show the formation of polycyclic aromatic hydrocarbons (PAH) and point towards a crucial role of the more reactive (001) facets of anatase nanoparticles. The self assembly mechanism occurring at the interface is accompanied by the formation of EPR visible Ti³⁺ centres due to electrons injection in the TiO₂ substrate.

Density functional theory (DFT) calculations show that acetylene physisorbs on the anatase (101) surface without activation of the C-H bond. On the contrary, the dehydroxylated (001) anatase surface is very active and leads to the spontaneous splitting of the C-H bond and to the cyclo-oligomerization of the monomer.



A) Reaction profile for the cyclo-polymerization of C₂H₂ to C₁₀H₈ on stoichiometric (001) anatase surface. B) Sketch representing the interaction of acetylene with the TiO₂ surface.

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EPR-monitoring of liver tissues redox state in patients with metastatic rectal cancer

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Introduction: acute liver failure (ALF) in the early postoperative period after extensive resections in patients with metastatic rectal cancer (MRC) is the cause of high mortality in this cohort of patients. Functional state of liver parenchyma after resection is determined by redox homeostasis of mitochondria electron transport chain (ETC) in hepatocytes and superoxide ($O_2^{\cdot-}$) generation level. Dysfunction of ETC can initiate apoptosis/necrosis.

Material and methods: samples of liver tissues and metastases of 23 patients with MRC (pT2-4pN0-2pM0-1) were investigated. Redox state of ETC and CYP450 in liver cells was performed by EPR (77 K). $O_2^{\cdot-}$ generation rate in the mitochondria of hepatocytes was determined by Spin Traps Technology (TEMPONE-H).

Results: pathophysiological changes of liver tissue that is affected by metastasis are presented by wide range of targets and have individual character, which is defined by redox state of mitochondria ETC, differentiation degree of metastasis and neoadjuvant systemic therapy. Quantitative and qualitative changes in redox state of hepatocytes in these patients are determined by decrease of oxidative phosphorylation (OXPHOS) levels in mitochondria and CYP 450 activity of detoxification system, formation of complexes NOFe-S-proteins. Identified disorders are accompanied by changes in oxygen metabolism, cellular hypoxia formation and unregulated increase of $O_2^{\cdot-}$ generation rate.

Conclusions: it was established that the main sources of $O_2^{\cdot-}$ generation in liver stump are mitochondria and CYP 450 of detoxification system, Nox of Kupffer cells and tumor-associated neutrophils. Mitochondrial dysfunction of hepatocytes is a major cause of ALF development and systemic damage of organs in patients with MRC. Monitoring of functional reserves of stump can be achieved via determination of redox state of mitochondria ETL, detoxification system of hepatocytes and markers of oxidation. This opens new possibilities for diagnostic of degree of liver cell damage and definition of response on pharmacological therapy.

Enzymatically Activated Nitroxides for EPR Spectroscopy and Overhauser-Enhanced Magnetic Resonance Imaging

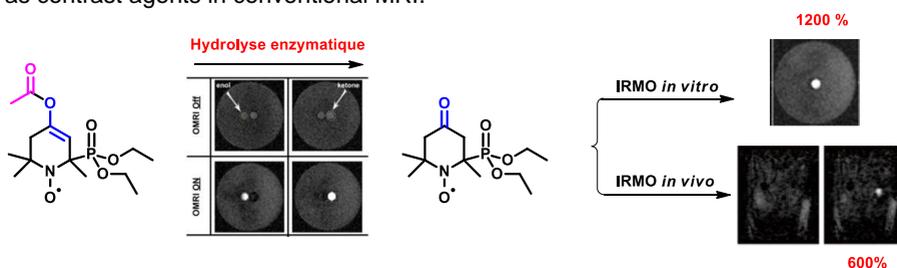
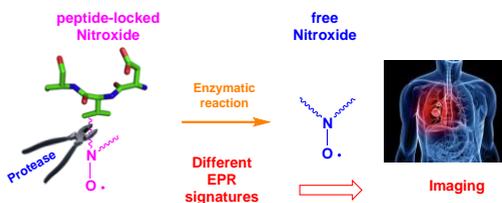
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Herein, we report the development of a new nitroxide sensitive to **non-radical enzymatic activity** and its application as probe for OMRI. Then, an ester linked to nitroxide must upon enzymatic hydrolysis release a new nitroxide exhibiting very different EPR pattern. Hence, a β -phosphorylated nitroxide substrate prototype exhibiting a structural modification upon enzymatic activity affording a large variation of a_N ($\Delta a_N = 4$ G) has been prepared. Then, the enzymatic activities of several enzymes were conveniently monitored using a 0.2 T MRI machine. Finally, ***in vivo* OMRI experiments** were successfully performed **affording a 600% enhanced MRI signal**^[1] compared to the 50% observed with derivatives are used as contrast agents in conventional MRI.



These results nicely highlight the enhanced imaging potential of these nitroxides upon specific enzymatic activity. This nitroxide is actually grafted into different derivatives to detect a specific enzymatic activity for early diagnostic.

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EPR as a unique tool to get deep insight into the redox processes of tetranuclear vanadium phosphonate

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Design and synthesis of functional metal organophosphate hybrid materials are attracting growing attention since interesting properties with relevance to different applications can be obtained. However, there is a general problem of these materials insofar as it is often difficult to characterize them on a molecular level. Recently, we have developed a new highly tunable class of these materials based on fluoride-templated tetranuclear vanadium phosphonate clusters, in which the V/P/O framework assembles around the fluoride template to form an anionic $[(V_2O_3)_2(RPO_3)_4CF]^{n-}$ cage (VPF) that can be balanced by transition metal ions (TMI) such as $[Cu(NCCH_3)_6]$, $[Cu(1,10\text{-phenathroline})_2]$, $[Ni(2,2\text{-bipy})_3]$, and $[Co(NCCH_3)_6]$. In contrast to most mixed-metal organophosphonates, these compounds are soluble and stable in polar organic solvents. Therefore, the intact V/P/O cage structure in solution can be easily proved by multinuclear NMR (1H , ^{19}F , ^{31}P and ^{51}V) while the reduced form ($3xV^{IV}/V^{IV}$) is accessible by EPR due to the facile delocalization of the unpaired electron over the cage structure in solution as well as in solid porous matrices. This is a unique advantage of the $[(V_2O_3)_2(RPO_3)_4CF]^{2-}$ cage, which was used not only to confirm the existence of the cage structure in solutions and solids but also to monitor them *in situ* during redox reaction. Moreover, investigation of the hopping of the unpaired electron in the reduced cage and its tumbling rate derived by EPR (Fig. 1) provided detailed knowledge about the strong interaction between the reduced vanadium cages itself and the surface of different supports such as alumina and Zeolite. For TMI-VPF complexes, the dipolar interactions and spin exchange between localized [such as Cu^{II} , d^9] and localized/delocalized electrons [$3xV^{IV}/V^{IV}$, d^1] and its effect on the spin state and redox properties of these compounds have been investigated by EPR.

In conclusion, EPR investigations of the tetranuclear vanadium phosphonate cages showed for the first time that it is possible to study the redox behavior of these compounds on a molecular level in solution as well as in solids.

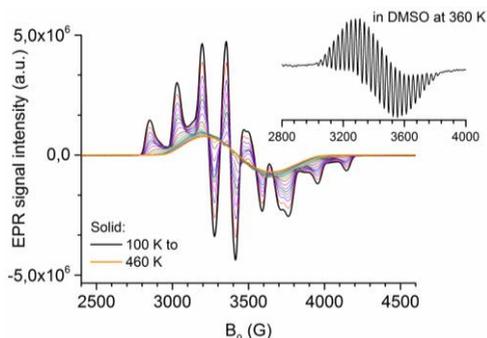


Figure 1. EPR spectra of $Ph_3P(CH_2)_6PPh_3[(V_2O_3)_2(RPO_3)_4CF]$ in solution and solid.

Improved sensitivity for W-band Gd³⁺ - Gd³⁺ DEER measurements with chirp pulses

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Chirp pulses have been recently shown to be highly advantageous for improving sensitivity in DEER (double electron-electron resonance) measurements due to their large excitation bandwidth.^{1,2} The implementation of such pulses for pulsed EPR has become feasible due to availability of arbitrary waveform generators (AWG) with high enough sampling rates to support pulse shaping for pulses with tens of nanosecond durations. Implementations of these pulses for improving DEER sensitivity have been demonstrated for X- and Q-band pulse EPR setups including a recent work focusing on Q-band Gd³⁺ -Gd³⁺ distance measurements.¹ In this work, we demonstrate a setup for obtaining chirp pulses on our home-built W-band spectrometer. Different frequency and envelope functions for shaped pulses were evaluated with respect to inversion bandwidth and -efficiency. DEER with chirp pulses was performed using two types of Gd³⁺ tags differing in zero field splitting (ZFS) parameters and therefore spectral width: (i) A Gd-PyMTA ruler³ (D_{ZFS} ~ 1150MHz) model system with a distance of 3.4 nm; (ii) Ubiquitin, doubly labeled with Gd-DOTA (D_{ZFS} ~ 550MHz) with an average distance of 3.5 nm. An optimization procedure as recently described by Doll et al.⁴ was adapted and used to choose the best conditions for positioning of the detection frequency within the EPR spectrum, the spectral width and the position of the chirp pulse. The optimal conditions were found to depend on the width of the central transition. Additionally, the effect of different pulse types on the DEER results is investigated. A significant improvement in sensitivity was obtained for both samples.

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cw-EPR in DNP. Some examples of new radicals.

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Dynamic nuclear polarization (DNP) has recently revealed its potential to enhance the NMR sensitivity in solids and liquids. DNP allows for the intrinsically large spin polarization of electrons to be transferred to nuclei for detection in a magnetic resonance experiments with a significant signal enhancement for ¹³C and ¹⁵N.

The nature of the polarizing agent, an organic radical, has a crucial role in the efficiency of DNP, in particular in fast dissolution DNP-NMR applications. The water-soluble trityl-based stable free radical OX63 is the most frequently used polarizing agent in dissolution DNP for low- γ nuclei such as ¹³C or ¹⁵N, mainly because it presents a narrow EPR linewidth. However, it is very important to study the behavior of new radicals to understand their performance as polarizing agents.

Herein we present the EPR characterization and their application as DNP polarizing agents of some novel monoradicals derived from 1,3-bisdiphenylene-2-phenylallyl (BDPA): its benzyl alcohol derivative (BA-BDPA), a benzyl amino (BAM-BDPA) and a cyano (CN-BDPA) radicals and a (trans)-4-(2,2,6,6,-tetramethyl-1-piperidinyloxy)-2,3,5,6-(tetrachlorophenyl)bis (pentachloro-phenyl)methyl (PTM=TEMPO) biradical.

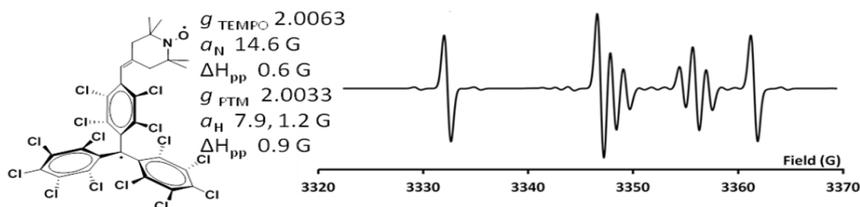


Fig.1: EPR characterization of PTM=TEMPO biradical.

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Time Domain Simulation of Gd(III)-Gd(III) DEER from First Principles with *Spinach*

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The use of Gd(III)-based spin labels as an alternative for nitroxides for intramolecular distance measurements at high fields has been successfully demonstrated on many biological systems¹. However, Double Electron-Electron Resonance (DEER) measurements on rigid model compounds have revealed a spurious broadening of the extracted distance distribution for short Gd(III)-Gd(III) distances even for rigid molecules, and showed the modulation depth to be lower than expected²⁻⁵. As most of the theory of DEER and the commonly used DEERAnalysis⁶ software were developed for a S=1/2 pair, namely nitroxides, it appears that these unexpected observations result from the different spectroscopic characteristics of Gd(III) – the high spin (7/2) and Zero Field Splitting (ZFS), combined with the pseudosecular term in the dipolar coupling Hamiltonian, which is often neglected. This was computationally addressed using perturbation theory in the frequency domain⁴, but such calculations do not consider the modulation depth. An understanding of the factors affecting the modulation frequency and amplitude is essential for the proper data analysis of Gd(III)-Gd(III) DEER and for the educated choice of experimental parameters, such as the type of chelate and the pulses setup.

This work uses time-domain simulations of Gd(III)-Gd(III) DEER by explicit density matrix propagation to assess the effects of ZFS and dipolar state mixing on the DEER traces. The tool applied is *Spinach*⁷, an open-source spin dynamics simulation library. A series of simulations using various input parameters shows that state mixing between the 1/2 and -1/2 states of the two spins, caused by the pseudosecular term in the dipolar Hamiltonian, leads to a major damping of the dipolar modulation, an effect greatly mitigated by a large ZFS or a large spectral separation between the excitation frequencies. The simulation qualitatively predicts the experimentally observed trends of dependences of the modulation depth on the distance, ZFS, and pulses setup, and reproduces the experimental spectral lineshapes to a reasonable degree. It can therefore be used as an aid for experiment design and data analysis.

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ATPase activity of the DEAD box RNA helicases studied by EPR spectroscopy

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YxiN is a DEAD box RNA helicase of *Bacillus subtilis*, which remodels RNA in an ATP dependent manner. It shows high specificity for Hairpin-92 ribosomal RNA (HP92). The RNA interaction mechanism consists of binding of RNA and Mg(II)ATP that results in ATP hydrolysis and RNA remodeling associated with large conformational changes in the protein.^{1,2} While a general idea of this mechanism is known in terms of the kinetics involved, the structural basis for the coupling of the ATPase activity², the protein conformational changes and the RNA remodeling is unknown. In order to follow the steps of the RNA unwinding cycle we have studied the ATPase activity using EPR techniques where we replaced the Mg(II) with Mn(II). This substitution retains the helicase activity. We have focused on the ³¹P hyperfine coupling of the nucleotides with the Mn(II), which is a signature of the changes the Mn(II)ATP undergoes at the ATPase active site during the helicase function. This was determined by high field electron-nuclear double resonance (ENDOR) and electron-electron double resonance (ELDOR) detected NMR.

Understanding the sequence of the structural rearrangement of nucleotides during the reaction of RNA unwinding can give valuable information about mechanism of ATPase activity of the protein. Metal-nucleotide complexes are a complex system for hyperfine spectroscopy. Assignment of spectral lines to specific coordinated nuclei and conformations proved to be a challenge for ENDOR alone. Therefore we have also applied a correlation technique named Triple Hyperfine Correlation Spectroscopy (THYCOS)³.

We looked at various combinations of YixN/HP92/Mn(II)-nucleotides (ADP, ATP and AMPPNP). We found out that the behavior of YxiN is significantly different than that of DbpA, its analog from *E.coli*⁴ and detected a unique state of post hydrolysis Mn(II)ADP binding site that occurs only when the RNA is bound to the protein.

The results of the ENDOR and ED-NMR experiments have led us to a conclusion that Mn²⁺ has several binding modes in nucleotides. The equilibrium between these structures changes during ATP hydrolysis cycles of the YxiN. Based on THYCOS results we have assigned different components of ENDOR spectra to separate conformations of metal-nucleotide complex.

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EPR-based long range distance constraints help structure determination of the complex between TAR RNA binding protein and double stranded RNA

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TAR RNA binding protein (TRBP) contains two RNA-binding domains (RBDs) of 10.1 and 8.9 kDa separated by an unstructured loop region. Upon RNA binding, TRBP regulates innate immunity and RNA interference.^{1,2} The two RBDs of TRBP can attach to a double-stranded RNA helix, and the structure of this complex is currently under investigation in our labs. In this presentation we demonstrate how the long-range EPR constraints can be combined with NMR-based information (residual dipolar couplings and nuclear Overhauser effect data) in order to determine the binding sites and mutual arrangement of the subunits in the TRBP/RNA complex. Double electron-electron resonance (DEER) data on doubly iodoacetamido-PROXYL spin labeled TRBP prove the anti-parallel arrangement of the two RBDs in the complex with RNA. Furthermore, the EPR distance measurements with use of singly labeled RNA and singly labeled TRBP reveal binding of the protein in two 'mirrored' conformations with exchanged positions of the two RBDs. In general, the hybrid NMR/EPR approach appears to be particularly powerful in situations when single elements of the complex do not significantly change their conformations between the free and the bound state, which is found to be the case for TRBP/RNA.

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Design and development of a X-band EPR cavity with microwave magnetic field leakage for measurements of intact mobile phone touch screens

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The aim of this work was to design and to build an EPR cavity, compatible with the X-band commercial spectrometers, and with a non radiating slit such that the sample to be measured may be lodged outside the cavity, without being disassembled or altered in any way. In particular, the set up will be adapted to the measurement of radiation induced radicals in the glass of mobile phone displays.

The starting point was a cylindrical cavity, characterized by high unloaded quality factor, Q_u , designed to work with modes such that on one region of the cavity, along the side wall, the magnetic and the electric fields have their maximum and minimum value, respectively (Fig. 1). The slit was realized on this side wall, in order to allow for microwave magnetic field leakage. Different geometrical configurations were simulated. Simulations were performed using the software Microwave Studio (CST) for the 10 GHz field and EM Studio (CST) for the 100 kHz modulation field.

In this work, the criteria used to choose the resonant modes and the sizing of the cavity structures, the results obtained from the simulations, as well as preliminary results of the experimental measurements achieved with the cavities prototypes will be shown.

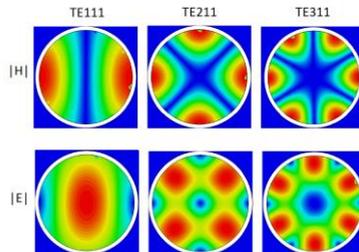


Fig. 1 – Magnetic (H) and electric (E) field distribution for several modes in the cross section of a cylindrical waveguide resonator.

ENDOR-induced EPR of Disordered Systems: Application to X-irradiated Sucrose and Alanine

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Many research fields benefit from EPR-derived techniques that enable decomposition of multicomponent spectra. In particular, in the field of radiation research of organic molecules, one often encounters spectra with multiple largely overlapping contributions. ENDOR spectroscopy is particularly well suited for these problems, because it offers species discrimination and high HF resolution. For crystalline $S = \frac{1}{2}$, $I = \frac{1}{2}$ systems, recording of the intensity of particular ENDOR lines as a function of the magnetic field, yields absorption-like EPR spectra of corresponding spectral components. These experiments are known as field-swept ENDOR or ENDOR-induced EPR (EIE). The technique compliments echo-detected EPR really well, because it is effective even if relaxation properties of different species are identical. In this contribution, we examine how the applicability of EIE can be extended to disordered systems.

The proposed method is put to a test in the case of the stable spectrum of X-ray irradiated sucrose. In recent years, its radical composition was established by single crystal EPR and ENDOR studies, reliable models have been devised and verified using periodic density functional theory calculations^{1,2}. It is now known that four distinct radical species explain the entire stable spectrum of X-irradiated sucrose and that one of them exhibits a HF interaction that is isolated in the ENDOR spectrum. By exploiting this feature, we successfully extracted the radical's EPR absorption spectrum from a multicomponent powder pattern, demonstrating that EIE can be useful in disordered systems. To discuss the potential limitations of the method, we examine the case of X-ray irradiated alanine, which is inherently challenging for EIE due to peculiar cross relaxation mechanisms.

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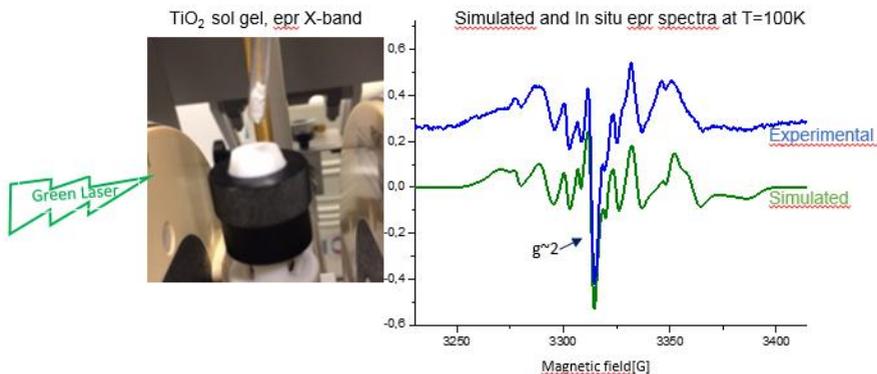
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***In situ* EPR investigation of TiO₂ in sol-gel compositematerial excited underUV and visible light excitation**

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Many methods are described in the literature to optimize TiO₂ photocatalysis. However, the >3 eV bandgap of classical TiO₂ materials requires UV light as excitation source^[1]. Commonly, increasing these materials' ability to use visible light, rather than UV radiation, can be achieved by direct modification of the material through doping, tuning the crystallinity, morphology, etc., which makes synthesis more difficult. Using *in situ* EPR techniques, we show that easily obtained, sol-gel synthesized TiO₂-based composite material,^[2] can be activated by visible light and stabilize paramagnetic species: Ti(III) (anatase, rutile) and radicals (Ti(IV)O[•], OO[•], Me[•], R[•]). The existence and relative stability of the observed species are confirmed by simulation. The developed techniques may open new synthetic routes in photo-organic chemistry^[3].



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Dual molecular probes: reporters for supramolecular interactions in solutions and gels

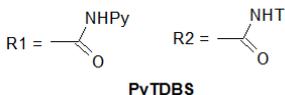
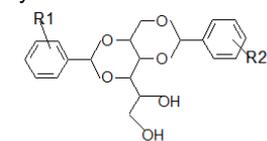
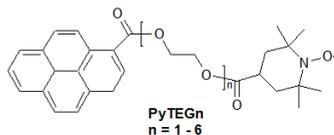
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Molecular probes present structural features sensitive to the local microenvironment, therefore these are often used as reporters for non-homogeneous systems. Non-covalent interactions such as hydrogen bonding, π - π interactions, van der Waals facilitate, or the particular case of host-guest interactions, generate various supramolecular systems, from low molecular stoichiometry assemblies (like in the case of host-guest systems), to supramolecular networks (like in the case of supramolecular gels), resulted by assembly of low molecular weight gelators.

Particularly, spin probes and fluorescence probes can be used individually to investigate non-homogenous systems by electron paramagnetic resonance and fluorescence spectroscopies. Dual paramagnetic and fluorescent molecular probes have the advantage of using two different methods to give comprehensive information on the micro-polarity and dynamic in the same part of a system and interactions with other species.¹ Based on this, we obtained two series of dual molecular probes aiming to investigate supramolecular host-guest systems and gel formation:

i) a series of dual molecular probes (denoted PyTEGn) bearing pyrene and TEMPO moieties, linked by flexible short polyether chains; these compounds have been used to investigate the host-guest complexation with cyclodextrins in solution and in polymeric gels;



ii) a series of dual molecular probes (denoted PyTDBS) with a dibenzylidene-sorbitol backbone, that have the ability to assemble in a supramolecular gel network.

The analyses of EPR and fluorescence parameters evidenced the suitability of using dual molecular probes as reporters for small and large supramolecular assemblies.

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Level crossing analysis of chemically induced dynamic nuclear polarization: towards a common description of liquid-state and solid-state cases

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Chemically Induced Dynamic Nuclear Polarization (CIDNP) is an efficient method of creating non-equilibrium polarization of nuclear spins by using chemical reactions, which have radical pairs as intermediates. The CIDNP effect originates from (i) electron spin-selective recombination of radical pairs and (ii) the dependence of the inter-system crossing rate in radical pairs on the state of magnetic nuclei. The gain from CIDNP is then two-fold: it allows one to obtain considerable amplification of NMR signals; in addition, it provides a very useful tool for investigating elusive radicals and radical pairs and for determining their EPR parameters. While the mechanisms of the CIDNP effect in liquids are well established and understood, detailed analysis of solid-state CIDNP mechanisms still remains challenging; likewise a common theoretical frame for the description of CIDNP in both solids and liquids is missing. We propose to analyze CIDNP in terms of level crossing phenomena, namely, to attribute features in the CIDNP magnetic field dependence to Level Crossings (LCs) and Level Anti-Crossings (LACs) in a radical pair. We have interpreted the CIDNP mechanisms in terms of the LAC concept¹. This consideration allows one to find analytical expressions for a wide magnetic field range, where several different mechanisms are operative; furthermore, the LAC description gives a way to determine CIDNP sign rules. Thus, LCs/LACs provide a consistent description of CIDNP in both liquids and solids with the prospect of exploiting it for the analysis of short-lived radicals. CIDNP analysis can be used for studying short-lived radicals as an alternative tool to conventional EPR methods. The Russian Foundation for Basic Research is gratefully acknowledged (projects Nos. 14-03-00397, 16-33-00590).

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Chlorophyll triplet state in the Water Soluble Chlorophyll Protein: a combined ODMR and EPR investigation.

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An unusual chlorophyll binding protein has been individuated in the flowering plants belonging to the family of *Brassicaceae*. This protein, called Water-Soluble Chlorophyll Protein (WSCP), strikingly differs with respect to the other Chlorophyll containing proteins being not involved in the photosynthetic process. WSCP has been shown to protect its chlorophylls towards photodynamic damage by singlet oxygen and has been hypothesized to be a scavenger of unbound Chl¹, despite it is the only Chl binding protein known so far that does not contain carotenoids. The low binding stoichiometry (each polypeptide subunit binds no more than one chlorophyll molecule), the absence of other bound pigments and its symmetric structure² make WSCP perfectly suitable as a model system for detailed spectroscopic studies. In particular, the possibility of manipulating the number and type of bound porphyrin molecules and the nature of the residues surrounding the pigments in WSCP, seems to be very promising to study the effect of the molecular structure on the magnetic and electronic properties of chlorophylls in a defined protein environment. From a combined approach comprising Optically Detected Magnetic Resonance (ODMR), pulse Electron Nuclear Double Resonance (ENDOR) and time-resolved EPR, a complete characterization of the photo-generated Chl triplet states of WSCP has been obtained. These complementary magnetic resonance techniques, already employed to study different photosystems, lead to a delved description of the triplet states photogenerated in the systems under investigation, both in their magnetic and optical properties. This allowed us to shed some light on the unusual photoprotective mechanism of this chlorophyll-binding protein.

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EPR Study of Stable Radicals: Di- and Polynitroxides

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Nitroxide multiradicals as members of the organic polyradical family play important roles in the fields like organic magnetism, molecular charge transfer and multiple spin labeling. The basis of these phenomena is the electron spin-spin exchange coupling between unpaired electrons localized on the different centers. Despite an intensive research, the scope of many investigations still remains the correlation between the structural parameters and the exchange coupling, accomplished *via* a direct (through bond) or an indirect (through space) mechanism. The latter is significantly affected by the nature of surrounding medium, e.g. polarity and viscosity of the solvent.¹

The analysis of EPR spectra obtained for a synthesized series of amidic dinitroxides and polynitroxides containing 2,2,6,6-tetramethylpiperidine 1-oxyl (Tempo) or 2,2,5,5-tetramethylpyrrolidine 1-oxyl (Proxyl) subunits in dichloromethane or toluene solutions under argon atmosphere was the main aim of our study. Tempo/Proxyl dinitroxides possessing a different type of spacer between the paramagnetic units were studied and the experimental EPR spectra were interpreted by the simulation analysis. The obtained results revealed a significant effect of the nitroxide heterocycle ring size, as well as of the spacer character on the value of the exchange coupling constant (J). Changes in the nature of the spacer and the decreased steric demands can lead to significant differences in the EPR spectra reflecting the current J value. We can propose that the interaction between the electrons of the nitroxide subunits for the dinitroxides reflects the interaction through space rather than through bonds.² Additionally, mobility of the spacer can lead to the formation of the loop conformations with interacting/non-interacting paramagnetic centers.³ EPR spectra for the structurally similar dinitroxide couples were measured in toluene solutions in the temperature range 190–360 K. The observed changes in the EPR spectra reflect the conformational dynamics between the interacting and non-interacting loop-conformations of dinitroxide and the thermodynamic parameters for transition from open (non-interacting) to closed (interacting) loop conformations were evaluated.

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EPR-spectroelectrochemical study of tris-(tetrathiafulvaleno)dodecadehydro[18]annulene

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The incorporation of the redox-active tetrathiafulvalene (TTF) units into π -conjugated cyclic oligomers leads to both the enforcement of self-assembly properties and conductivity improvement.¹ Recently, a special tetrathiafulvalene-fused dodecadehydro[18]annulene molecule containing three redox active TTF units connected together by cyclic π -conjugated bridge was studied in our laboratory in detail by EPR spectroelectrochemical methods.² Each TTF unit can be first oxidized to the monocharged EPR active radical cation and then to the EPR silent dication state.³⁻⁵ Cyclic voltammetric studies of tris-(tetrathiafulvaleno)dodecadehydro[18]annulene revealed three oxidation peaks with strongly concentration dependent shapes.² Using EPR/UV-Vis-NIR spectroelectrochemistry the presence of mixed-valence complexes consisting of TTF units in different charge states was confirmed. Inter-valence charge transfer transition (IVCT) band at 2000 nm was detected during oxidation in the potential region of the first oxidation step. The singlet EPR spectrum simultaneously measured at the first anodic peak with g-factor of 2.0072 is characteristic for TTF-centered cation radical.³ During oxidation in the potential region of the second oxidation peak, where the corresponding trication is formed, a new radical species exhibiting singlet EPR line with slightly higher g value 2.0075 was observed. In this case all three TTF redox sites exist as radical cations and an IVCT band disappears. At the third anodic peak, where the hexacation is formed, a substantial decrease of the EPR intensity confirmed the EPR silent nature of the hexacation.

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ONE STEP HYDROXYLATION OF BENZENE TO PHENOL AND AN OBSERVATION OF FORMATION OF BENZENE CATION RADICAL AT AMBIENT CONDITIONS

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Abstract: Phenol is one of the most demanding commodities in industry because of its variety of applications as resins, in pharmaceuticals, disinfectants and precursor to many organic chemicals. Currently, phenol is produced in industry in two steps: (a) conversion of benzene to cumenehydroperoxide with propylene in presence of molecular oxygen followed by (b) acid hydrolysis.¹ The one step hydroxylation of benzene to phenol is a major challenge for industries for decades. The C-H bond dissociation energy of benzene is around 111 kcal/mol. We demonstrate here a mechanistic study of hydroxylation of benzene in 50% H₂SO₄ as reaction media at elevated temperature in presence of 10 atm of oxygen. The catalyst was recovered by electrolysis with the release of hydrogen as byproduct. Hydroxylation of benzene to phenol is a two-electron oxidation process and H₅PV₂Mo₁₀O₄₀.32H₂O being a two-electron oxidant, stoichiometric reactions between benzene and H₅PV₂Mo₁₀O₄₀.32H₂O were carried out in 1:1 ratio for the formation of phenol. CW X-band and high field (95GHz) EPR, ENDOR and ELDOR detected NMR were used to identify and characterized the presence of benzene radical catio

Identification of Paramagnetic Centers in Doped Anatase Nanosheets

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Information on the character and amount of paramagnetic centers present in the nanomaterial before and upon photoexcitation with the light of differing photon energy can bring valuable insight into the structure–reactivity relationship of the studied photocatalyst. High photoactivity of anatase foams synthesized previously^{1,2} and the effort to develop a visible-light active photocatalyst motivated the preparation of metal and non-metal doped anatase nanostructures. Series of lamellar TiO₂ nanosheets possessing Nd, Ag, Au or N as a dopant annealed at different temperatures (300–900 °C) was studied by EPR spectroscopy. EPR signals of paramagnetic centers monitored by the X- and Q-band experiments at 100 K in all samples already before irradiation were assigned to Ti(III) and F-centers, often generated during the synthesis of nanocrystalline TiO₂ materials *via* high-temperature treatment under specific atmosphere.³ The samples annealed at temperatures lower than 500 °C, both metal- and nitrogen-doped, revealed the EPR spectra typical for N-doped titania. The presence of paramagnetic nitrogen species assigned on the basis of literature data^{5,6} to *N_b ($g_1 = 2.005$, $g_2 = 2.004$, $g_3 = 2.003$; $A_1 = 0.23$ mT, $A_2 = 0.44$ mT, $A_3 = 3.23$ mT) in the samples annealed at 350 and 400 °C, and to NO ($g_1 = 2.001$, $g_2 = 1.998$, $g_3 = 1.927$; $A_1 < 0.1$ mT, $A_2 = 3.22$ mT, $A_3 = 0.96$ mT) in the samples annealed at 450 and 500 °C, can be explained by the application of ammonia for the precipitation during the synthesis of all nanostructures. The identified nitrogen species incorporated in the bulk of the TiO₂ precursor (*N_b)^{5,6} are responsible for the photocatalytic activity in the visible region, confirmed by the increase of *N_b EPR signal upon visible-light irradiation, rather than the presence of a metal dopant in the structure.

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EPR and DFT Study of O⁻ Radicals Formed on the MgO Surface after Illumination in Oxygen and N₂O

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Long-distance separation of electron-hole pairs is commonly assumed to be the first stage of various thermal and photochemical processes resulting in the formation of ion radicals on the surface of oxides. However, long-distance charge separation with participation of the conductivity or valence bands is unlikely for wide band-gap dielectrics, such as MgO with the band gap 7.8 eV. Still, the experiments show that the radicals can be effectively generated under illumination with soft UV light with 4.1 eV (303 nm) photon energy.¹ A viable alternative to the physical charge separation mechanism is a "chemical" mechanism ascribing the generation of the ion radicals to the formation of mobile radical species.^{1,2} Radicals H[•] and OH[•] formed from the fragments of chemisorbed water H⁺ and OH⁻, respectively, are the most likely candidates for such species.

In this communication we shall demonstrate that the chemical and spectroscopic properties of O⁻ radicals formed as hole and electron sites seem to be exactly same. Quantum-chemical simulations supporting this hypothesis will be discussed.

MgO illumination by UV light in the presence of N₂O was found to result in the formation of spectroscopically indistinguishable O⁻ radicals both on electron and hole sites. So, the total concentration of such radicals proved to be higher than after illumination in oxygen when such radicals are formed only on hole sites. Chemical properties of the O⁻ radicals formed on the electron and hole sites in reactions with O₂, CO and ethylene were found to be the same as well.

This is possible only if these species are formed by the transfer of uncharged radical species formed from homolytic splitting of water. According to quantum-chemical simulations, the homolytic water dissociation on the oxide surface has the energetic barrier 2.75-3.39 eV, depending on the nature of radical stabilization sites. Thus, it becomes clear why soft UV illumination with photon energy about 4 eV is sufficient for generation of the radicals.

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Inverted Spin Trapping – Fluorine Spin-Adducts Generated upon UVA Exposure of Titania in Acetonitrile

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The photoexcited titania dispersed in different solvents represent a complex system, in which the primary photogenerated charge carriers (electrons and holes) are involved in the consecutive redox reactions producing the non-persistent paramagnetic intermediates reflecting the actual experimental conditions (solvent, presence of molecular oxygen and additives). The EPR spin trapping experiments using a variety of spin trapping agents were performed to identify reactive intermediates formed upon irradiation of TiO₂ suspended in water and organic solvents.¹ The paramagnetic spin-adducts detected in a specific system should be evaluated carefully, as their formation may reflect not only the genuine spin trapping of non-persistent free radicals, but also the alternative reaction pathways including the inverted spin trapping or Forrester-Hepburn mechanism.² In order to monitor the role of surface hydroxyls on the photoinduced generation of hydroxyl radicals, the spin trapping experiments with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) were performed under argon in the dried acetonitrile (ACN) using Ag(I) as the electron acceptor and the production of ^{*}DMPO-OH was confirmed.³ However, the repetition of these photocatalytic experiments in the presence of fluoride ions led to the generation of unique ^{*}DMPO-F spin-adduct.³ Since the formation of fluorine radicals ($E^{\circ}(F^{\bullet}/F^{-}) = 2.7$ V vs. SCE in ACN) is not presumable in the irradiated titania (valence band-edge position of 2.2 V in ACN vs. SCE), the generation of ^{*}DMPO-F can be adequately interpreted considering the inverted spin trapping mechanism *via* the photogenerated radical cation DMPO^{•+} ($E^{\circ}(\text{DMPO}^{\bullet+}/\text{DMPO}) = 1.63$ V vs. SCE) with a subsequent nucleophilic attack of the fluoride anions adsorbed on the titania surface. Recently, we performed further spin trapping experiments in the deoxygenated TiO₂ suspension in acetonitrile containing AgBF₄, with silver ions serving as an electron acceptor and BF₄⁻ acting as a nucleophilic agent, using DMPO and four its analogues. For all pyrroline *N*-oxide derivatives under study, the TiO₂ irradiation in the presence of AgBF₄ results in the formation of unique EPR signals of corresponding fluorine spin-adducts characterized with the hyperfine coupling constants of fluorine atom in the range of 4.93–5.79 mT.

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Nonpareil Yb Magnetic Properties in YbMn₆Ge_{6-x}Sn_x As Studied by ESR

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In intermetallic solids, the *4f* states of ytterbium, the non-magnetic divalent Yb (*4f¹⁴*) and the magnetic trivalent Yb (*4f¹³*), can hybridize more or less strongly with other valence electrons (*f-sp*d hybridization) to yield a wealth of interesting physical phenomena including heavy fermion behavior, Kondo effect or intermediate valence.¹

We have investigated the YbMn₆Ge_{6-x}Sn_x compounds ($x = 4.2$ and 4.4) by means of magnetic measurements, resonant inelastic x-ray scattering², and electron spin resonance (ESR) spectroscopy over the temperature range $4.2 - 300$ K. Substituting Sn for Ge in YbMn₆Ge₆ allows us to observe a Yb valence change. The temperature evolution of ESR parameters clearly reflects the unusually high magnetic ordering temperature of Yb (60 and 90 K for $x = 4.2$ and 4.4 , respectively), a co-existence of ESR signals which can be ascribed to the Yb³⁺ and manganese ions, and ordering of Mn moments with increasing temperature. The hybridized character of the Yb *4f* states might play an important role in the unusually high Yb magnetic ordering temperature. The strong Mn-Yb exchange interaction which enhances the intermediate valent Yb magnetic ordering temperature and allows for extending the stability domain of the Yb magnetic order towards lower Yb valence³ is discussed.

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Nanocarriers vs conventional transport vehicles – investigations of the penetration of Dexamethasone into skin using EPR spectroscopy

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Introduction: In the last decades different carrier systems have been developed, ranging from macromolecules to nanocarriers to improve the penetration of topical applied drugs into the skin. Pharmaceutically used drugs show various physical and chemical properties, thus the use of carrier systems is depending on the respective drug and its application. For systematic improvement of the drug-carrier system the localization of the drug within the carrier should be known. To study this in more detail the synthetic glucocorticoid Dexamethasone (Dx) was loaded to various carriers and the localization within the carrier, the release and the penetration efficacy was investigated.

Methods and Materials: For these investigations electron paramagnetic resonance (EPR) spectroscopy was performed. Therefore, the drug was covalently labeled with the EPR marker PCA. As nanocarriers, core multi shell systems, nanolipid and polymer-based carriers were investigated. They were applied onto porcine ear skin and the absorption after different penetration times was determined. A depth resolution of penetration within the *stratum corneum* was realized using tape stripping.

Results: By multi frequency EPR it could be shown that Dx-PCA was loaded to the particles and the location could be determined by analyzing the microenvironment properties polarity and viscosity. Dx-PCA loaded to all investigated carrier systems penetrates enhanced and deeper into the skin compared to Dx-PCA incorporated to a standard base cream formulation or an aqueous solution.

Conclusion: It could be shown that nano-sized carrier systems are very suitable to increase the penetration of Dx into the *stratum corneum* and can have a reservoir function. The application of EPR spectroscopy permits to analyze the microenvironment of the drug Dx in nanocarriers in more detail and its possible release in the skin after topical application.

ENHANCED CHARGE TRANSFER AND SEPARATION IN PCBM/CdSe QUANTUM DOTS PHOTOACTIVE FILMS

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Introduction

Colloidal Quantum Dots (CQDs) are actively investigated as additional component capable to enhance organic solar cells performances thanks to their band gap tunability, high absorption coefficient and easy processability.¹ It was demonstrated that small amounts of CQDs in polymer/fullerene blends contribute to increase the cell efficiency. This enhancement was attributed mainly to morphological changes on the nanoscale. Nevertheless, it is likely that CQDs strongly influence also electronic properties of the active layer.

Materials and Methods

We focused our work on binary blends containing fullerene derivative PCBM and CdSe QDs. Light induced EPR, Time Resolved EPR and pulsed EPR were used to check the capabilities of CdSe QDs to induce photoinduced electron transfer (PET) towards PCBM and to investigate the photophysics of the blend. Absorption, fluorescence and pump and probe techniques were used to study the PET process more in detail, confirming EPR results. By modification of ligand shells, we synthesized CdSe QDs with strongly enhanced electron transfer and charge separation capabilities.

Results

Using LEPR we detected strong photoinduced formation of charges (radical anion of PCBM) demonstrating the efficient PET from CdSe QDs to PCBM. Using TREPR we identified a fast charge separation within the blends, attributed to the high dielectric constant of QDs that decreases the binding energy of the initial charge transfer state. Spin Relaxation time analysis on the PCBM anion shows that the addition of QDs drastically decreases magnetic relaxation times underlining an interaction between the anion and the magnetic nuclei of the nanocrystals within the blends.

Finally, using EPR and optical spectroscopy, the effects of the ligand size and binding groups (amines or thiols) are investigated: both the decrease in the ligand chain length and the thiol as binding group enhance the electron transfer from nanocrystals to PCBM.

Conclusions

The combined optical and EPR analysis and the tailored QD synthesis has allowed to investigate in depth the multiple effects of the CQDs embedded in organic solar cells materials.

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The tungsten-nitrogen paramagnetic system in anatase titanium dioxide

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Tungsten-nitrogen co-doped TiO₂ may contain three types of paramagnetic extrinsic defects, all of them exhibiting well-resolved EPR spectra. The first centre consists of an interstitial N chemically bound to a lattice O forming a $[N_iO]^{\bullet}$ group carrying one electron in the SOMO. Formally an intra-band gap NO²⁻ state, this species is well known in N-doped TiO₂^{1,2}. The second centre is identified as $[N_iO]^{\bullet}(W)$. It is the same N-O adduct but exhibiting a specific close range interaction with a neighboring W. Its spectrum shows a higher spin density in N 2p orbital when compared to the previous species and it is characterised by hyperfine coupling with the ¹⁴N nucleus as well as super-hyperfine coupling with the ¹⁸³W nucleus (natural abundance 14.31 %), i.e. the only naturally occurring nuclide of W with nonzero nuclear spin. Finally, the third centre consists of paramagnetic W(V). Its spectrum is characterised by a highly rhombic signal with principal g-values lower than 1.6 and hyperfine structure due to the ¹⁸³W nucleus.

All these centres introduce new energy states in the band gap, which permit visible light sensitisation of the semiconductor material. The W centre is also involved in multi-electron transfer processes that can be followed and interpreted combining EPR with electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). The feasibility of multi-electron transfer is responsible for an exceptionally high selectivity towards nitrate, when (W,N)-TiO₂ is used as a photocatalyst to oxidise nitrogen oxides.

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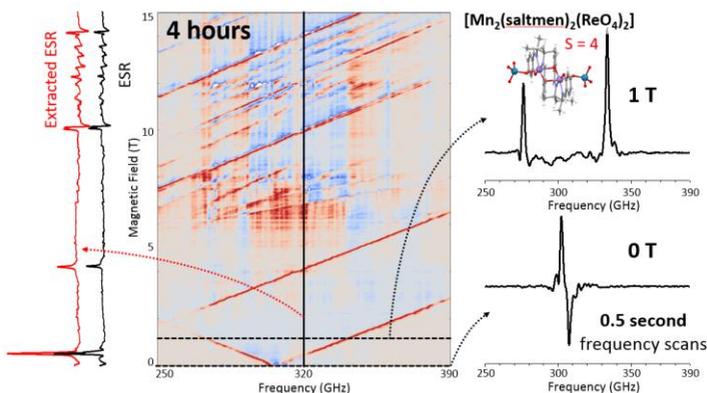
High Frequency EPR Spectroscopy in Field and Frequency Domains

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Electron Spin Resonance (ESR) is a powerful technique to investigate electronic and magnetic properties of various materials. ESR at THz frequencies is of great interest in view of the large inherent spectral resolution and the possibility to investigate molecular systems with large magnetic anisotropies. We will present the recently developed combined High Frequency Field and Frequency Domain THz Electron Spin Resonance (HFESR/FDMR) spectrometer capable to investigate for the first time the electronic and magnetic properties of molecular systems, thin films and bulk materials in the very broad frequency range of 85-1100 GHz. The HFEPFR/FDMR spectrometer operates at high magnetic fields up to 17 T and temperatures from 300 K down to 1.8 K. For the microwave radiation an amplifier multiplier chain is used which gaplessly covers the entire frequency range. A quasi-optical bridge in combination with corrugated waveguides guarantees the propagation of the microwave with only minimal losses, where special care was given to eliminate any standing waves in the system. For very sensitive measurements we developed a tunable Fabry-Pérot resonator, which allows a sensitivity of only 10^7 spins/Gauss. Furthermore, samples can be oriented with respect to the applied magnetic field by using single crystal rotator. The performance of the spectrometer will be demonstrated on molecular systems, thin films and bulk materials.



The EPR Study of Photoinduced Processes of Composite g-C₃N₄/TiO₂ Photocatalysts

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Nowadays, one of the main efforts in the heterogeneous photocatalysis is preparation of materials more active in visible region. Recently, the graphitic carbon nitride (g-C₃N₄) was identified as a novel form of organic polymer-like photocatalysts due to its visible-light activity (band-gap ~ 2.7 eV/460 nm). However, the small surface area and rapid electron-hole recombination hinder its practical application. The combination of g-C₃N₄ with titanium dioxide can utilize the advantages of both materials and thus an improved photocatalytic activity can be obtained.¹ In our laboratory composite photocatalysts g-C₃N₄/TiO₂ with various ratios of g-C₃N₄ and TiO₂ were synthesized.² Due to the stronger reduction ability of the conduction band electrons of g-C₃N₄ can effectively react with molecular oxygen forming superoxide radical anions, in addition, the position of valence band of TiO₂ is suitable for effective generation of hydroxyl radical *via* photogenerated holes. The unstable paramagnetic intermediates can be monitored *via* indirect EPR techniques.³ The EPR spin trapping was applied to test the photocatalytic activity of composite photocatalysts upon UVA ($\lambda_{\text{max}} = 365 \text{ nm}$) and visible light exposure in aqueous and dimethylsulfoxide suspensions. The results showed that paramagnetic species formed upon exposure sensitively reflect the reaction conditions and the influence of weight ratio of g-C₃N₄ and TiO₂ in photocatalysts. The better photocatalytic activity upon UVA and visible-light exposure was found for composites with lower amount of g-C₃N₄. The photogenerated charge carriers in g-C₃N₄/TiO₂ were also monitored in solid state in the temperature range 100-293 K.

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Time-Resolved EPR and Theoretical Investigations of Metal-Free Dual Singlet-Triplet Emitters in OLEDs

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Organic light-emitting diodes (OLEDs) have attracted significant attention for the application in next generation display technologies. In OLEDs using fluorescent emitters, internal quantum efficiency is limited to about 25%. Introduction of phosphorescent emitters allows to take advantage of spin statistics and to raise this limit. Recently, triplet harvesting without heavy atoms has also been explored. Thiophene-decorated phenazines are an example for this, which are promising candidates as metal-free organic compounds for OLEDs. They showed both fluorescence and phosphorescence even at room temperature.¹

A series of such phenazines in the first excited triplet states have been investigated by time-resolved EPR (tr-EPR) and quantum chemical calculations. For all of the molecules including the non-phosphorescent ones, excited triplet states could be generated by optical excitation, and monitored by tr-EPR. The TR-EPR measurements clearly showed the energy gap law for the decay rates from the excited states at 10 K, demonstrating that the non-radiative decays are tuned by the number and orientation of the thiophene. For example, phosphorescent molecules have spin distribution localized on the phenazine unit, whereas non-phosphorescent ones have spin distribution delocalized to the thiophene unit. The EPR-derived zero-field splitting parameters also showed the influence of the spin delocalization on the luminescent properties, which were supported by quantum chemical calculations.

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Optically driven Overhauser DNP in aqueous solution

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We present for the first time a demonstration of optically generated nuclear polarization in aqueous solution based upon the radical triplet pair mechanism (RTPM).^{1,2} NMR is intrinsically less sensitive than EPR due to the significantly lower Boltzmann polarization of nuclei compared to electrons, hence electron-nuclear polarization transfer can significantly boost NMR sensitivity. Conventional approaches to such Dynamic Nuclear Polarization (DNP) use microwave pumping of electrons, with enhancements limited by the ratio of thermal electron and nuclear polarizations. Optical pumping to hyperpolarize electrons removes this cap making much larger nuclear polarizations a possibility.

In the Shuttle-DNP method NMR detection at high magnetic field (maximal chemical shift dispersion) is combined with polarization at low field (greatest Overhauser efficiency). The Boltzmann factor penalty limits the gains of this approach, but with optically polarized electrons a route to boost sensitivity in high resolution liquid-state NMR may be realised.³ In contrast to the existing single-shot dissolution-DNP method a combined optical and shuttle approach will boost NMR sensitivity in multi-dimensional experiments.

There are a number of chemically induced dynamic electron polarization mechanisms which lead to spin-polarized radicals as observed by transient EPR spectroscopy.² However, the majority of these polarize only transient radicals whose concentration decays rapidly due to radical recombination or other chemical reactions, hence they are unsuitable as general polarizing agents for nuclear spins. In the under-exploited RTPM, a transiently generated triplet state produces a large net polarization of a stable radical. As this hyperpolarized radical persists in solution we have been able to observe polarization transfer to solvent nuclei via the Overhauser effect without any microwave pumping (Figure 1). We present our proof-of-principle demonstration of RTPM generated nuclear polarization at X-band, and discuss the route to high-field NMR enhancements.

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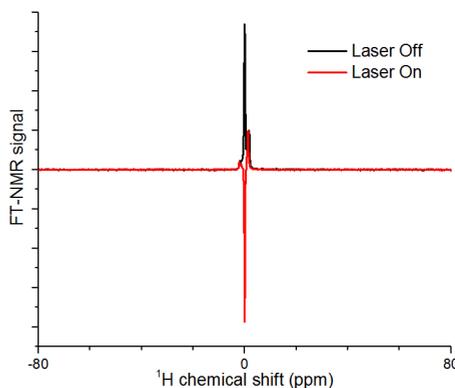


Figure 2 ¹H NMR at 0.34 T of water containing Rose Bengal / TEMPO with and without 532 nm illumination.

Sterilization by γ -Irradiation: Evaluating the Effects on Pharmaceutical Excipients

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Sterilization by γ -irradiation is emerging as an alternative technique to classic sterilization methods that are inapplicable to heat- or moisture-sensitive products, as a result of being easy to control, secure, reliable, fast, and having a high penetrating power.¹ The radiolytic effect of such ionizing radiation is however difficult to predict and can lead to the formation of radical species.² The process can thereby induce degradation of the product, affecting the efficacy of sterilized pharmaceuticals. Excipients are substances other than the pharmacologically active drug or prodrug which are included in the manufacturing process or are contained in a finished pharmaceutical product dosage form³ to improve the properties of the drug, such as enhancing the therapeutic effect of Active Pharmaceutical Ingredients (APIs) or facilitating the manufacturing process.⁴ Not only could direct degradation of the APIs diminish the action of the product, but also degradation of pharmaceutical excipients included in the formulation can affect the efficacy of the drug by either altering its chemico-physical properties or reacting with APIs. EPR can provide both qualitative and quantitative information on irradiated pharmaceutical products, allowing the identification and quantification of the radical species formed.

In this work we analyse the effect of γ - and X-irradiation on pharmaceutical excipients such as L-histidine and D-mannitol by means of EPR techniques, identifying the primary radical species generated at low temperature and following their evolution into the stable room temperature species. Using spin-trapping experiments we assess the reactivity of such radicals in solution. Our studies represent the first step in the evaluation of γ -sterilization effects on complete pharmaceutical products, providing an increased mechanistic understanding of the sterilization process which will allow mitigation against radical induced degradation.

We acknowledge funding from the European Union under a Marie Curie Initial Training Network FP7-PEOPLE-2012-ITN Grant Agreement Number 316630 CAS IDP.

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Structural, EPR and optical studies on Cu-doped ZnO nanoparticles synthesized by the sol – gel method

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In this work, pure ZnO and Cu-doped ZnO nanoparticles ($Zn_{1-x}Cu_xO$, $x=3$ mol%) were synthesized using the sol-gel method at three different calcination temperatures ($T_C=773K$, $823K$ and $873K$). The nanoparticles were analysed by atomic absorption spectroscopy (AAS), X-ray diffraction (XRD), electron paramagnetic resonance (EPR), at different measurement temperatures, and diffuse reflection spectroscopy (DRS). All samples have wurtzite structure. The Cu-doped nanoparticles have smaller size than the pure ZnO particles. EPR analysis shows that in samples of ZnO prepared at $873K$ there is presence of superficial defects, with g values of $g=2.036$, $g = 1.967$ and $g = 1.958$. For sample synthesized at $773K$ a simulation of the Cu EPR experimental signal, using an anisotropic Spin Hamiltonian, was performed, and showed good coincidence with the experimental spectrum for g -values of $g_x = 2.084$, $g_y = 2.092$, $g_z = 2.336$. For these samples Cu^{2+} ions enter interstitial on octahedral sites of orthorhombic symmetry, in the wurtzite crystal structure (Figure 1). The same was made for sample calcinated at $873K$ and $g_{\perp}=2.082$ and $g_{\parallel} = 2.320$ were obtained in the fit. Temperature dependence of the EPR linewidth and signal intensity shows a paramagnetic behaviour of the samples calcinated at $773K$ and $823K$ in the measurement range. A Néel temperature were determined, giving values of $T_N = 78K$ and $139K$ respectively. In case of sample calcinated at $873K$, Curie temperature of $137K$ was obtained. Cu doped samples revealed a smaller band gap for the Cu-containing samples than for pure ZnO samples. Additionally, the gap of the Cu-containing samples decreases with calcination temperature increase.

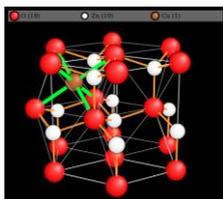


Figure 1. Schematic position of the Cu^{2+} ions in the ZnO matrix.

Keywords: Atomic Absorption Spectroscopy (AAS), Diffuse Reflectance Spectroscopy (DRS), Electron Paramagnetic Resonance (EPR), magnetic semiconductors, sol-gel processing, superficial defects, X-ray diffraction, Zn vacancies.

Overview of recent advancements in EPR dosimetry

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EPR spectroscopy has been used over the last sixty years for estimating ionizing radiation doses in various types of application: fossil dating, radiological accident dosimetry, retrospective dosimetry, metrology of dose.

For these different applications, we will present an overview of recent advancements. For all these applications, the development of the use of CW Q-band, instead of the classical CW X-band, has allowed new possibilities in application of EPR dosimetry. Thus, samples of a few mg are sufficient for EPR analysis with performances similar to the gold standard method of X-band. For example, in the case of radiation accident, collection of mini-biopsy of calcified tissue (tooth enamel) can be made with no detriment to the overexposed person allowing dose evaluation with better performances than in vivo EPR techniques. Detection limit is estimated at 0.4 Gy against 2 Gy in the best case for in vivo dosimetry. This approach has been already used for about a dozen of expertises for actual or suspected overexposures. Recently, it has been also applied to dating of teeth fossil. In dose metrology, it can be used to measure new generation of small size dosimeters (< 1 mm) for application in radiotherapy.

For radiation accident dosimetry, one of the major recent advancement is the identification of stable radio-induced radicals in fingernails. It offers new possibilities of dose estimation, which is particularly pertinent for localized irradiation to hands, as for example for accidental radioactive source handling. We will present recent examples of expertise of actual radiological accident based on fingernails dosimetry.

V^{IV} IONS AS PARAMAGNETIC PROBES FOR MONITORING THE STRUCTURAL FLEXIBILITY OF V-DOPED MIL-53(AL)

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Their tunability in porosity and in functionalization of the internal surface makes metal-organic frameworks (MOFs) an important class of materials with potential major impact in catalysis, gas sensing and gas storage. These three-dimensional crystalline porous materials are constructed from metal moieties connected by organic ligands. MIL-53(Al) [Al(OH)(BDC), BDC = terephthalate or 1,4-benzenedicarboxylate] is a characteristic example, that features channel-like pores parallel to the crystallographic c-axis. This MOF exhibits a structural flexibility, referred to as breathing: the structure can reversibly change from a large open pore (LP) to a narrow pore (NP) form without any loss of crystallinity.

In this work we have monitored the temperature-induced breathing of V-doped MIL-53(Al) with a combination of *in situ* EPR and powder X-Ray Diffraction (XRD), recording spectra as a function of temperature in air and in vacuum. The EPR spectra of the paramagnetic V^{IV} probe ions in the LP and NP forms are clearly distinguishable (see Figure 1). These two V^{IV} centers exhibit the typical EPR characteristics of vanadyl molecular ions ((VO)²⁺, S=1/2, 2 > g_x ≈ g_y > g_z, I(⁵¹V)=7/2, A_x ≈ A_y ≈ 150 MHz ; A_z ≈ 500 MHz). Determining their spin Hamiltonian parameters requires a multi-frequency approach.

Although VCl₃ was used as dopant salt, V-doped MIL-53(Al) samples exhibit an intense vanadyl EPR spectrum, even before high-temperature treatments. In order to elucidate the oxidation state of V in these samples, quantitative EPR measurements are compared with the results of X-ray Adsorption Near Edge Structure experiments, performed at the European Synchrotron Radiation Facility.

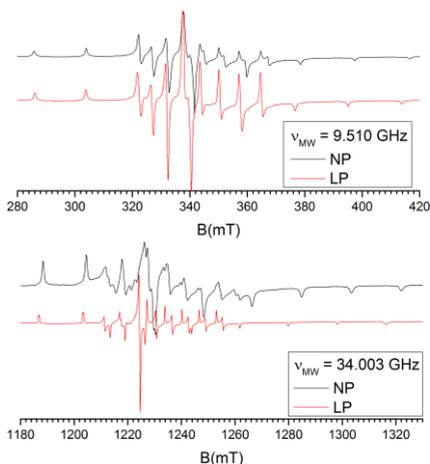


Figure 1 – Room temperature powder EPR spectra of V-doped MIL-53(Al) recorded in X-band (top) and Q-band (bottom) in NP and LP form.

WavPDS: A Wavelet Approach in Denoising Pulsed Dipolar Spectroscopy

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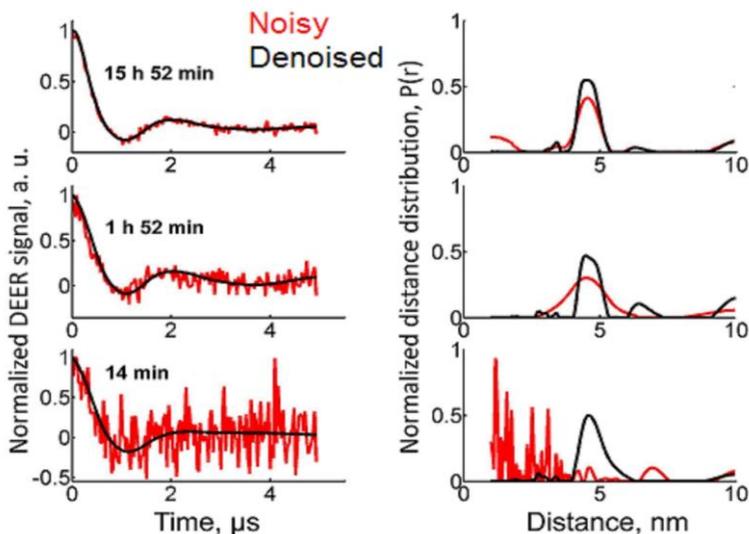
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Studying biological systems using Pulsed Dipolar Electron Spin Resonance Spectroscopy (PDS) is challenging due to the short relaxation times and low protein concentrations typically used. These frequently result in a low Signal to Noise Ratio (SNR), complicating the analysis. Even if the average distance between spin probes can be estimated, the determination of the distance distribution (DD) is likely to be corrupted by noise. To address the challenge of noise removal in Pulsed Dipolar ESR in order to obtain reliable information, we developed a new wavelet denoising method (WavPDS) to remove/reduce noise. Our method improves the stability and reliability of the DD reconstruction, and reduces the signal acquisition time by an order of magnitude. This enables the study of biomolecular structures at low SNR signals with accuracy. We believe that studies in a wide variety of disciplines will greatly benefit.



Intrazeolite Ni(I) complexes with O₂ and CO in ZSM-5 - CW EPR and HYSORE investigations

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Interaction of non-innocent O₂ and innocent CO ligands with transition-metal cations can lead to various paramagnetic and diamagnetic complexes. In case of paramagnetic adducts, CW and pulse EPR spectroscopy has been widely used to elucidate their nature. Yet, quantitative molecular interpretation of the corresponding EPR parameters (*g* and *A*(¹⁷O, ¹³CO) tensors) is not a trivial task, taking into account an intricate nature of the magnetic interactions within the metal-O₂ and metal-CO units.

This contribution deals with the activation of O₂ and CO on Ni(I) ions dispersed inside the ZSM-5 zeolite. The side-on coordination of the nickel-superoxo adduct was ascertained by detailed analysis of the EPR spectra of both ¹⁶O₂ and ¹⁷O₂ species (Figure 1) supported by computer simulations of the spectra and relativistic DFT calculations of the EPR signatures. Molecular analysis of the *g* and *A*(¹⁷O) tensors (*g*_{xx} = 2.0635, *g*_{yy} = 2.0884, *g*_{zz} = 2.1675, and |*A*_{xx}| ~ 1.0 mT, |*A*_{yy}| = 5.67 mT, |*A*_{zz}| ~ 1.3 mT) and quantum chemical modelling revealed an unusual electronic and magnetic structure of the observed adducts. Interaction of nickel(I) centers with ^{12,13}CO led to the formation of T-shaped, top-on monocarbonyl adducts with a unique trigonal nickel core, supported by two oxygen donor ligands (*g*_{xx} = 2.018, *g*_{yy} = 2.380, *g*_{zz} = 2.436, *A*_{xx} = +1.0 ± 0.3 MHz, *A*_{yy} = -3.6 ± 0.9 MHz, *A*_{zz} = -1.6 ± 0.3 MHz) and *Q*(²⁷Al) parameters (*e*²*Qq*/*h* = -13 MHz and *η* = 0.8), as revealed by HYSORE and DFT studies. The mechanism of the formation of the these adduct was accounted for by a quantitative molecular orbital correlation diagram of O₂ and CO ligation. By means of the ETS-NOCV population analysis, three distinct orbital channels (associated with σ, π, and δ overlap shown in Figure 1) of congruent and incongruent charge and spin density flows within the metal-O₂⁻ and CO units were identified. The nature of the *g* tensor was rationalized in terms of the contributions due to the magnetic couplings of the relevant molecular orbitals that control the *g* tensor anisotropy.

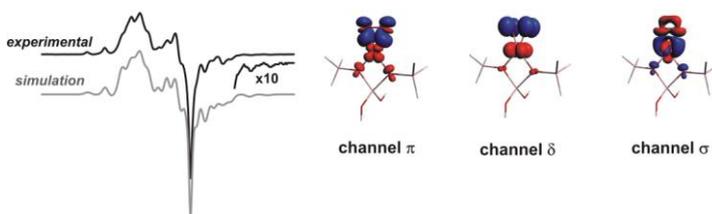


Figure 1. CW-EPR spectrum of O-17 labelled Ni(II)-O₂⁻ adduct in ZSM-5 zeolite and calculated orbital channels of charge and spin flow between O₂ and Ni(I)-zeolite fragments.

Molybdenum cofactor reactivity studied in nitrate reductases by EPR, HYSCORE and theoretical modeling

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Mononuclear molybdo-enzymes are found in virtually all living organisms. In Prokaryotes, most of these enzymes harbour a large Mo-bis pyranopterin guanosine dinucleotide cofactor (figure 1) and catalyse a wide diversity of redox reactions involved in major biogeochemical cycles. In spite of the similarity of their Mo-bisPGD cofactor, these enzymes are able to use a broad diversity of substrates, but the molecular factors which trigger their reactivity remain largely unknown^{1, 2}. During catalysis, the molybdenum ion cycles between the +IV and +VI redox states, the intermediate Mo(V) state being EPR-active (S=1/2). Several Mo(V) species have been identified, but their structure and catalytic relevance is still strongly debated¹⁻⁴.

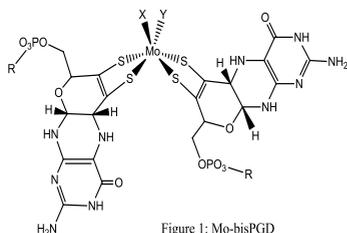


Figure 1: Mo-bisPGD

To address these questions, we used several bacterial nitrate reductases as model Mo-enzymes. By combining site-directed mutagenesis, EPR and DFT calculations, we brought new insights on the catalytic process of these enzymes and on the role of the various spectroscopically detected Mo species. Notably, by using specifically isotopically enriched enzymes (⁹⁸Mo, ¹⁵N) and high resolution EPR techniques (ESEEM, HYSCORE), the nuclear environment of the Mo ion could be studied in details. In addition, the analysis of magnetic coupling between Mo(V) ion and neighbor FeS cluster of the enzyme enable to identify long range modification of the Mo-cofactor during enzyme activation processes⁵.

The results emphasize the role of the second coordination sphere of Mo ion in the stabilization of catalytic intermediates^{5, 6} and provide some clues for the design of new bioinspired catalysts.

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**DETERMINATION OF LARGE ZERO FIELD SPLITTINGS IN
“EPR SILENT”
HIGH SPIN TRANSITION METAL IONS
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Zero field splittings (ZFS) provide important information about functional high spin states in e.g. proteins, synthetic catalytic complexes as well as single molecule magnets. Interest in ZFS is mainly triggered by two reasons. First they determine the magnetic properties of molecular nanomagnets. Secondly, they can be employed as structural probes in transition metal ion complexes. ZFS may range from $\sim 10^{-2} \text{ cm}^{-1}$ (hundreds of MHz, e.g., in highly symmetric Mn^{II} complexes) to $\sim 10^2 \text{ cm}^{-1}$ (several THz, e.g., in octahedral Co^{II}). As a result, it can induce spin energy level splittings that are too large to be detected with conventional EPR techniques. We recently demonstrated that this limitation can be lifted by synchrotron-based Frequency Domain Fourier Transform THz-EPR (FD-FT THz-EPR). This method allows for mapping of the EPR transition energy/magnetic field landscape, in the range from 3 to 200 cm^{-1} (100 GHz – 7 THz) and from -11 T to 11 T.

Herein, we demonstrate for a Mn^{II} and a Co^{I} , both in $S = 1$ state, how very large ZFS can be determined based on advanced FD-FT THz-EPR measurements in combination with frequency domain EPR simulations. In addition, we will discuss how FD-FT THz-EPR can be employed to yield information not only on ZFS but also exchange couplings between neighbouring ions.

Conformational changes of mVDAC1 upon tBid binding studied by pulse EPR

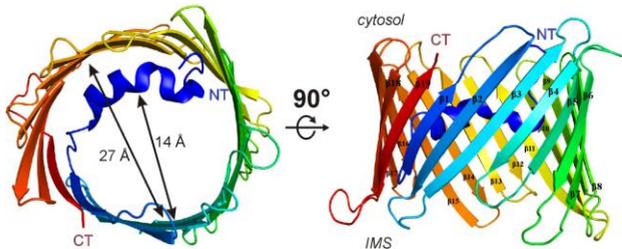
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Voltage-dependent anion-selective channels (VDACs), also known as mitochondrial porins, are the major proteins of the outer mitochondrial membrane of eukaryotes. They form membrane-spanning β -barrels and act as general diffusion pores for small hydrophilic molecules, adopting an open conformation at low or zero membrane potential and a closed conformation at potentials above 30-40 mV. VDACs facilitate the exchange of ions and molecules between mitochondria and the cytosol and are regulated by the interactions with other proteins and small molecules.¹ Furthermore, it is known that VDACs are conserved mitochondrial elements of the apoptosis pathway in both plant and animal cells.²

The high resolution structures of human³ and murine⁴ VDAC1 (h/mVDAC1) revealed a 19-stranded β -barrel with an α -helix located in the middle of the pore (see Figure) which is thought to be the key element for regulating the conductance of ions and metabolites through the channel.



We applied site directed spin labeling and distance measurements by double electron-electron resonance (DEER) spectroscopy to study the influence of tBid (truncated Bid), an activated BH3-only pro-apoptotic member of the Bcl-2 protein family, on mVDAC1. The results from pulse EPR spectroscopy are compared to simulated distance distributions obtained from molecular dynamics simulations of mVDAC1 in a lipid bilayer. We observed a clear influence of tBid binding on the inter spin distance distributions obtained for spin labeled mVDAC1, suggesting that interaction with tBid “closes” the anion channel by fixing the N-terminal α -helix within the pore.

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Q-band ELDOR detected NMR of Mn²⁺ coordination spheres

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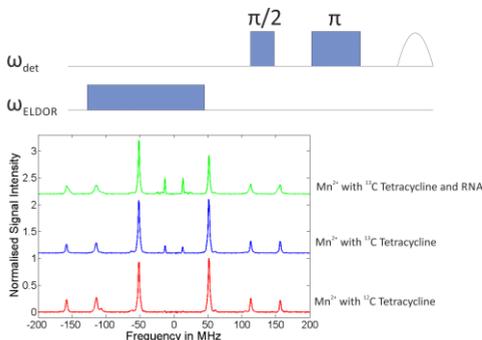
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ELDOR detected NMR (EDNMR)¹ probes hyperfine interactions. It relies on the excitation of simultaneous (forbidden) transitions of the electron and nuclear spins. Two microwave frequencies are used; one fixed frequency (ω_{det}) to observe an allowed transition and another variable frequency (ω_{ELDOR}) to excite forbidden transitions. When ω_{ELDOR} matches the frequency of a forbidden transition, population is removed from one nuclear spin manifold and the intensity of the echo detected at ω_{det} is decreased.

EDNMR is more sensitive than ENDOR for the detection of nuclei with low gyromagnetic ratios. It is possible to observe natural abundance ¹³C signals.² However, due to the spectral blind-spot, which occurs as ω_{ELDOR} approaches ω_{det} and the ELDOR pulse excites the allowed transition, most EDNMR studies of low gyromagnetic nuclei have been carried out at ≥ 95 GHz, where the Larmor frequencies of nuclei are higher and signals lie outside the blind-spot.

In this study we have used EDNMR to detect hyperfine couplings from ¹H, ¹³C, ³¹P, ¹⁷O and ⁵⁵Mn at Q-band (34 GHz) for Mn²⁺ centered spin systems. We compare results using both rectangular and Gaussian shaped ELDOR pulses. Results were collected for the [Mn(H₂¹⁶O)₆]²⁺ and [Mn(H₂¹⁷O)₆]²⁺ model systems, and the technique was used to study the interactions of Mn²⁺ with the antibiotic Tetracycline and the Tetracycline binding RNA aptamer (1-D EDNMR data shown in figure). To probe the correlations between different nuclei in the binding spheres of Mn²⁺ we have used 2-D EDNMR,³ initial results from these investigations are also presented.



Upper figure – EDNMR pulse sequence. **Lower figure** – EDNMR results; signals have been inverted and the blind spot subtracted. In all traces, signals in the region ± 200 to ± 100 MHz correspond to ⁵⁵Mn hyperfine

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Advanced EPR characterization of photosynthetic cytochrome c_{550}

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Cytochrome c_{550} (Cyt c_{550}) is a c-type heme protein with a bis-histidinyl axial coordination adscribed as an extrinsic component in the luminal side of photosystem II (PSII), although its role within this complex is not yet well established. Cyt c_{550} is present in cyanobacteria as well as in eukaryotic algae from the red photosynthetic lineage, which includes diatoms. However, the protein is absent in the green lineage, which comprises green algae and plants.

In this contribution, we show the characterization by means of EPR techniques of two Cyt c_{550} from different Kingdoms, Cyt c_{550} from the diatom *Phaeodactylum tricorutum* and Cyt c_{550} from the cyanobacterium *Synechocystis* sp. PCC 6803. This includes CW-EPR and ESEEM (HYSCORE) techniques, both at X-band and Q-band.

Experimental results are compared and discussed on the basis of structural and functional similarities and differences of both proteins. This study shows how advanced EPR characterization is a powerful tool for revealing structural details in heme proteins.

Wild life dosimetry: Evaluation of EPR analysis of Wolf and Wild boar tooth enamel

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EPR dosimetry on human teeth enamel has been largely used to evaluate the past exposure to ionizing radiation in case of accidental exposure: short and acute exposure or prolonged exposure due for example to contamination from radioactive fall out of nuclear accidents (cf. Chernobyl and Fukushima). The study of the effect of radiation is not limited to the human organism, numerous research programs also investigate the effect of radiation on different non-human living organism, such as mamifer. Few studies have been conducted to determine the received dose by using EPR spectroscopy on animal teeth enamel living closely to humans but were limited to herbivor animals like cows and goats¹.

We will report the possibility to perform EPR dosimetry on tooth enamel collected from wolf and wild boar. Analysis were performed in Q-band in order to limit the quantity of enamel collected on living animal to a few milligrams. Samples were collected from animals in the Chernobyl area.

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Contribution of free radicals to cucurbiturils: allostery, guest rotational speed and controlled reactivity toward new species

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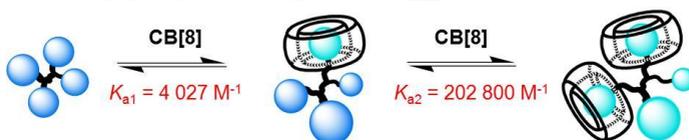
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Free radicals and especially nitroxides have shown interesting properties toward the study of inclusion complexation regarding cucurbiturils using EPR spectroscopy.^[1] Beside 1:1 complexes,^[2] the combination of nitroxides with EPR enabled the characterization of odd structures for examples very strong 1:2 complexes^[3] or 3:3 guest:CB[8] complexes.^[4] Recent results on the contribution of EPR for the study of (i) the strong allosteric complexation of a tetraradical by two molecules of CB[8]^[5] and of (ii) the accelerated rotation of a paramagnetic guest inside CB[7] will be presented. Eventually, recent results concerning the reactivity of cucurbiturils in the presence of highly reactive free radicals for the preparation of cucurbituril derivatives will be shown.

Highly cooperative recognition: $\Delta\Delta G_{\text{alllost}} = 13 \text{ kJ.mol}^{-1}$



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Sunday, 2016/09/04		Monday, 2016/09/05		Tuesday, 2016/09/06		Wednesday, 2016/09/07		Thursday, 2016/09/08	
	8.45	Opening Session							
		Chair: Wolfgang Lubitz		Chair: Zbigniew Sojka		Chair: Mario Chiesa		Chair: Etienne Goovaerts	
	9.00	PL01 Stefan Stoll	9.00	PL02 Damien Murphy	9.00	PL04 Vincenzo Barone	9.00	PL06 Thomas Prisner	
	9.45	KN01 Stefan Weber	9.45	KN05 Herve Vezin	9.45	KN08 Sergei A. Dubba	9.45	KN10 Marina Bernati	
	10.15	OP01 Graham Smith	10.15	OP08 Elisa Albanese	10.15	OP16 Oleg Poluektov	10.15	OP19 Gunnar Jeschke	
	10.35	Coffee Break	10.35	Coffee Break	10.35	Coffee Break	10.35	Coffee Break	
		Chair: Marco Lucarini		Chair: Klaus-Peter Dinse		Chair: Edgar Groenen		Chair: Hiroshi Ohta	
	11.05	KN02 Olivier Quari	11.05	KN06 Marc Newton	11.05	PL05 Carole Duboc	11.05	IES1 Sanjayan Subramanian	
	11.35	OP02 Klaus Moebius	11.35	OP09 Stefano Paleari			11.30	IES2 Sergey Veber	
	11.55	OP03 Anna Ebel	11.55	OP10 Piotr Pietrzyk	11.50	KN09 George Mitrikas	11.50	IES3 Edgar Groenen	
	12.15	OP04 Antonio Barbon	12.15	OP11 Alexander Bedlio	12.20	OP17 Aharon Blank	12.15	IES4 Charles P. Scholtes	
	12.35	Buffet Lunch/Posters	12.35	Buffet Lunch /Posters	12.40	OP18 Bela E. Bode	12.40	General Assembly of IES and Awards presentation	
				Chair: Charles P. Scholtes	13.00	Buffet Lunch/Poster	13.30	Buffet Lunch /Poster	
	14.30	Chair: Bruno Guigliarelli	14.15	PL03 Anton Savitsky	14.30		14.30	Chair: Alexander Schuegg	
		KN03 Sabine van Doorsler							
	15.00	OP05 Sara Della Monaca	15.00	KN07 Ines Garcia-Rubio			14.30	PL07 Daniela Goldfarb	
	15.20	OP06 Elisabetta Millo					15.15	OP20 Dmitry Azamat	
	15.40	OP07 Martina Huber	15.30	OP12 Hiroshi Ohta			15.35	OP21 Peter Rappia	
	16.00	Coffee Break	15.50	OP13 Malte Drescher			15.55	Conclusive Remarks	
	16.30		16.10	Coffee Break					
		KN04 Lorenzo Sorace		Chair: Donatella Carbonera					
	17.00		16.40	Segre Prize: C.E. Tait					
		Braker presentation	16.55	Segre Prize: G. Cutsail					
			17.10	OP14 Olav Schlemann					
			17.30	OP15 Marilena Di Valentin					
	18.00	Braker Reception	17.50	Poster Session					
19.00									
		Registration & Welcome Party			20.30	Gala dinner			