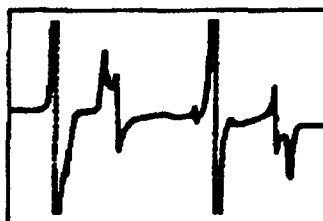




Warsaw, 9-13 September 1996

ELECTRON PARAMAGNETIC RESONANCE OF RADICALS AND METAL COMPLEXES



**2nd International Conference
of the Polish EPR Association**



INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY



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CONFERENCE PROGRAM

SUNDAY, 8 SEPTEMBER

9:00 - 20:00 Registration at Belwederski Hotel

MONDAY, 9 SEPTEMBER

10:00 Opening by Prof. **Andrzej Chmielewski**,
Deputy Director of the Institute of Nuclear Chemistry and Technology
Address by Dr. **Jan Krzysztof Frąckowiak**,
Undersecretary of State, State Committee for Scientific Research
Address by Prof. **Jerzy Niewodniczański**,
President of National Atomic Energy Agency

10:30 **H. Kurreck**
Opening lecture

11:00 Welcome drink

12:30 - 14:00 LUNCH

Session 1: 14:00 - 18:00
Chair: **K. A. McLauchlan**

14:00 **M.C.R. Symons**
Radicals in DNA as seen by ESR Spectroscopy

14:45 **M. Sevilla**
Electron and Hole transfer within DNA and its Hydration Layer

15:30 - 16:00 COFFEE BREAK

16:00 **H. Kurreck**
*Models for Photosynthetic Reaction Center. Steady State and
Time Resolved Spectroscopy*

- 16:45 **K. Gwoździński**
Free Radical Formation in Red Blood Cell Components upon Paraquat Treatment
- 17:00 **Ya. Lebedev**
Very High Field EPR of Multispin Metal Complexes with Semiquinone Ligands
- 17:45 **J. Pedersen**
ESR and Cyclic Voltammetry Studies of the Cations and Anions of α -Aminoanthraquinones Obtained by Electrochemical Oxidation/Reduction

Informal Panel Discussion: 18:30 - 19:30 "New EPR Techniques and Instrumentation"

TUESDAY, 10 SEPTEMBER

Session 2: 8:45 - 12:30
Chair: **D. Goldfarb**

- 8:45 **M. Brustolon**
Electron Spin Relaxation and Dynamics of Radicals in Inclusion Compounds
- 9:30 **K. A. Mc Lauchlan**
Transient Radicals and Spin Polarization
- 10:15 **E. Van Faassen**
Motional Spin Relaxation in Photoexcited EOSIN Triplet States
- 10:30 - 11:00 **COFFEE BREAK**
- 11:00 **F. Gerson**
ESR of Organic Radical Ions: A Personal Account
- 11:45 **A. Davies**
EPR Spectroscopy and Electron Distribution
- 12:30 - 14:00 **LUNCH**

Session 3: 14:00 - 15:30

Chair: M. Brustolon

- 14:00 **S. Schlick**
Electron Spin Resonance Imaging (ESRI) of Transport Processes in Polymeric Systems
- 14:45 **T. Ichikawa**
Electronic Structure of Charge Carriers in Polysilane Quantum Wire
- 15:30 - 16:00 **COFFEE BREAK**

Poster session I

- 16:00 - 17:15 **Odd numbers**

Poster session II

- 17:15 - 18:30 **Even numbers**
- 19:00 **Concert in Palace on Water, Łazienki Park**

WEDNESDAY, 11 SEPTEMBER

Session 4: 8:45 - 12:30

Chair: T. Ichikawa

- 9:45 **L. Kevan**
Pulsed EPR Studies of Transition Metal Ions in Microporous Materials
- 9:30 **E. Reijerse**
A Systematic Analysis of 1D and 2D ^{14}N - ESEEM Spectra; Application to a Nitrogen Coordinated Oxo-vanadium Complexes.

- 10:15 **R. Samoilova**
CW and Pulse EPR Study of Paramagnetic Complexes on the Catalytical Surfaces
- 10:30 - 11:00 COFFEE BREAK
- 11:00 **D. Goldfarb**
2D FT EPR Exchange Spectroscopy of Organic Radicals in Solution
- 11:45 **D. Beckert**
Study of Photoreduction of Quinones by Fourier Transform EPR
- 12:30 - 14:00 LUNCH
- 14:00 - 19:30 Chopin Tour:
- Excursion to Żelazowa Wola - Fryderyk Chopin's Birth Place.
- Piano concert in Ostrogski's Palace.
- 20:00 Meeting of Polish EPR Association

THURSDAY, SEPTEMBER 12

Session 5: 8:45 - 12:30

Chair: **L. Kevan**

- 8:45 **B. Gilbert**
EPR Studies of the Role of Copper in Bio-organic Free Radical Reactions
- 9:30 **A. Plonka**
Free Radical Reaction Patterns in Condensed Media
- 10:15 **G. Grampp**
Kinetics of Electron Self-Exchange Reactions Measured by EPR-spectroscopy and the Application of Marcus Theory
- 10:30 - 11:00 COFFEE BREAK

11:00 **C. Rhodes**
Muon Spectroscopy of Organic Radicals in Biology, Catalysis and Materials Research

11:45 **A. Jezierski**
EPR Monitoring of Plant Degradation, Humification and Coalification

12:30 - 14:00 LUNCH

Session 6: 14:00 - 17:00
Chair: **M.C.R. Symons**

14:00 **A. Alberti**
Phosphavinyls and other phosphorus containing radicals

14:45 **F. Callens**
Comparative EPR and ENDOR Results on Carbonate Derived Radicals in Different Host Materials

15:30 - 16:00 COFFEE BREAK

16:00 **N. Abidi**
Water Complexed Mn^{2+} as a Probe in the ESR Study of Silica Glasses Obtained by the Sol-Gel Process

16:15 **J. Michalik**
Silver Clusters in Zeolite Rho

16:30 **C. Oliva**
 Cu^{2+} O^- Hole Pairs and O^- Spin Bags in $La_{2-x}M_xCuO_4$ Oxide Mixtures

16:45 **D. Attanasio**
Degradation of paper and characterization of white marbles: exemples of ESR applications in the field of cultural heritage

17:00 **A. Romanyukha**
Current State of EPR Dose Reconstruction with Teeth

18:00 Conference Dinner, Belwederski Hotel

FRIDAY, SEPTEMBER 13

Session 7: 8:45 - 12:00

Chair: B. Gilbert

- 8:45 **L. Piekara - Sady**
EPR of Graphite and Fullerene
- 9:30 **A. Lund**
EPR and ENDOR Analysis by Simulation in Disordered and Single Crystal Matrices: Influence of Strong NQI and Microwave Power
- 10:15 **M. Romanelli**
Analysis of Electron Spin Echo Decay and Electron Spin Echo Envelope Modulation of Cu(II) and Mn(II) in D₂O/Perfluoropoly Ether Ammonium Carboxylate Systems
- 10:30 - 11:00 **COFFEE BREAK**
- 11:00 **B. Bales**
Emerging Techniques to Study Compartmentalized Liquids Using EPR
- 11:15 **J. Bednarek**
ESR Investigation of γ -Irradiated Hyperquenched Glassy Water
- 11:30 **J. Vidal - Gancedo**
EPR Study of Metallocene-substituted α -nitronyl Nitroxide Radicals
- 11:45 **A. Petr**
In situ UV-Vis ESR spectro-electrochemistry
- 12:00 **Closing remarks**
- 12:30 **LUNCH**

LECTURES

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RADICALS IN DNA AS SEEN BY ESR SPECTROSCOPY

Martyn C. R. Symons

Department of Applied Science, DeMontfort University, Leicester LE 19 BH

This talk will be a random walk through aspects of ESR studies, mainly of DNA systems, after exposure to ionizing radiation at low temperatures. Under these conditions I suggest that "direct" damage is of major significance, and ESR evidence for the concept of the initial formation of electron-gain and electron-loss centres localised within the DNA bases, and deeply trapped by proton-gain or - loss, will be discussed. It will be stressed that "negative" evidence, showing that various phosphate and sugar centred radicals are not detected, is of major importance since the ESR "fingerprints" for base-radicals are relatively ill defined.

The use of additives that selectively scavenge "holes" and electrons will be outlined, together with the use of strand-break studies as a rough measure of overall damage. This will include a brief diversion on the use of polyammonium cations (polyamines) to enhance the efficiency of "drug" delivery to DNA. How far electrons move within the base-stacks will be discussed, and the use of intercalators outlined.

The links between UV damage and that induced by ionizing radiation will be considered, and the situation that arises at the threshold of ionization will be stressed. A sideways look at the way DNA copes with UV generated thymine dimers will also be touched on.

Finally, I will make an attempt to link these studies with the situation for DNA in cell nuclei.

ELECTRON AND HOLE TRANSFER WITHIN DNA AND ITS HYDRATION LAYER

Michael D. Sevilla, David Becker and Yurii Razskazovskii Department of Chemistry, Oakland University, Rochester, MI 48309

Electron and hole transfer within DNA are processes important to the understanding of radiation damage to DNA as well as its photochemistry and redox properties. Through ESR studies we have investigated electron and hole transfer after γ -irradiation of hydrated DNA at low temperatures. DNA is found to be a good ion radical trap and about 30% of all electrons and holes produced by radiation are trapped and observed by ESR experiments at 77K. Electrons are trapped at the pyrimidine bases, cytosine and thymine, whereas the holes are trapped mainly on guanine with a small yield of hydroxyl radical in the hydration layer (roughly, 40% C \cdot -(protonated), 15% T \cdot -, 40% G \cdot and 5% OH \cdot in the hydration layer). Our results show that all electrons in the hydration layer transfer to DNA and all holes in the first layer of waters transfer to DNA; whereas, subsequent layers form hydroxyl radicals. Electron migration and hole transfer processes within DNA are limited at low temperatures; however, on annealing electron hopping is activated and migration to reactive sites such as thymine, bromine substituted bases or a hole are observed. Specific investigations of long range transfer through DNA have been performed by bromination of thymine in DNA at various average separations. Electron transfer to brominated thymine is measured by the build up of the 5,6 dihydro- 6-hydroxy 5-thymyl radical. Transfer distances are found to be temperature dependent in accord with an activated hopping mechanism. For example at 100K we find transfer of only ca. 7 bases; whereas at 200 K we find transfer of about 45 bases. The effects of the hydration layer on DNA ion radical yields and subsequent product formation will also be discussed.

MODELS FOR PHOTOSYNTHETIC REACTION CENTER: STEADY STATE AND TIME RESOLVED EPR SPECTROSCOPY

H. Kurreck, G. Elger, M. Fuhs, A. Wiehe, J. v. Gersdorff, P. Tian
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The search for an understanding of the factors controlling electron transfer (ET) reactions in the primary events of photosynthesis has led to the development of biomimetic model systems consisting of porphyrins covalently linked to quinones (P-Qs). In these model compounds the porphyrin is photoexcited to the singlet state from which, at room temperature, intramolecular ET occurs to the quinone yielding the charge separated radical pair in its singlet state. Alternatively, ET via spin selective spin-orbit intersystem crossing (ISC) creates the porphyrin triplet state from which ET may then occur to the quinone with spin conservation. Occurrence of triplet states allows observation of the ET processes by time-resolved EPR spectroscopy. Photoredox processes in anisotropic media, such as vesicles, micelles and liquid crystals have attracted attention as mimicking photosynthetic electron transfer (ET) across biological membranes. In this paper we present photochemical investigations of P-Qs (a) in isotropic solutions, (b) embedded in reversed micelles and (c) in nematic phases of liquid crystals.

Reversed Micelles: Using steady state *in situ* lamp irradiation through resonator slits, various P-Qs can be converted to paramagnetic derivatives. The species, generated *via* intra- and intermolecular ET processes, can be identified by EPR spectroscopy. Interestingly, emissive signals can be observed which are indicative of electron spin polarization (ESP). The ESP effects can be interpreted in terms of the radical/triplet pair mechanism.

Liquid Crystals: Steady state illumination of guest P-Qs in liquid crystals, frozen after alignment in an external magnetic field, yields orientation dependent triplet spectra of the porphyrin moiety. Time-resolved EPR studies performed on photoexcited, oriented P-Q molecules in nematic phases of liquid crystals exhibit well-resolved, spin-polarized EPR spectra of the porphyrin triplet and of the charge-separated biradical state, generated by ET.

Acknowledgments: Time-resolved EPR experiments were performed by the groups of Professor K. Möbius (FU Berlin) and Professor H. Levanon (Hebrew University, Jerusalem). Long-standing collaboration with these groups is gratefully acknowledged. This paper was supported by Deutsche Forschungsgemeinschaft (Normalverfahren and Sonderforschungsbereich 337) and Stiftung Volkswagenwerk. H. K. thanks the Fonds der Chemischen Industrie for financial support.

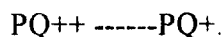
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Free radical formation in red blood cell components upon paraquat treatment.

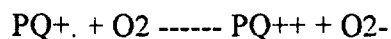
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Paraquat (1,1' -dimethyl-1-4, 4'-bipyridinium dichloride, PQ), a contact herbicide, possesses high toxicity for man and animals. Its redox properties were described in 1933 and since this time paraquat has been used as a redox indicator, known as methyl viologen. It was found that action of paraquat on various tissues is different. It was also suggested that lipid peroxidation is involved in the mechanism of paraquat toxicity in vivo. It is accepted that paraquat can be reduced to paraquat cation radical:



Bipyridylium cation radical is rapidly reoxidized by molecular oxygen with the formation of superoxide anion radical:



The formation of cation radical depends on the presence of reductors for one electron reduction of Paraquat. However, the detailed biochemical mechanism of paraquat toxicity remains unclear. Paraquat role in induction of lipid peroxidation is controversial. In several studies it was reported that paraquat can stimulate lipid peroxidation. On the other hand, it was shown that paraquat does not cause lipid peroxidation in vitro. In vitro effects of bipyridinium herbicides may not be related to the mechanisms of their toxicity in vivo.

Recently we reported the effect of paraquat on human red blood cells and showed that paraquat increased lipid membrane fluidity without lipid peroxidation. We also showed the changes in structure of red blood cells components such as membrane and hemoglobin upon paraquat treatment. In this work we studied the effect of paraquat on free radicals generation in red blood cells components e.g. plasma membrane and hemoglobin using trapping method. We show that paraquat requires the presence of iron ions (Fe^{2+}) for hydroxyl radicals generation. These results confirmed our earlier suggestion that changes in membrane lipid fluidity do not result from lipid peroxidation but rather from the alterations in lipid-protein interactions.

VERY HIGH FIELD EPR OF MULTISPIN METAL COMPLEXES WITH SEMIQUINONE LIGANDS

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The complexes of diamagnetic ions like Al, Ga, Zn, Cd, etc., with the bulky organic ligands like 3,6-di-*t*-butyl-ortho-semiquinones (or similar organic compounds) had appeared to be very convenient models to study magnetic interactions, both intra- and inter-molecular. The very-high-field EPR (around 50 kG) in combination with very low temperature (usually from 5K to 20K, in some cases from 1,2 to 1,8K) was used to observe thermal spin polarization effects for such centers and to determine the sign of zero-field splittings in addition to their values [1]. Such information was for the first time used to detect formation of a number of complexes like Al(semiquinone)₃ in course of mechano-chemical treatment of organic compounds. More over, formation of such complexes was observed just in fluid phase after contact of Al₂O₃ with 1:1 quinone+hydroquinone mixture [2]. It is concluded that traces of Al₂O₃ in organic compounds may be used as analytical tool to check the traces of Al₂O₃ in organic phase. Some other applications of high-field EPR will be discussed as well.

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ESR and cyclic voltammetry studies of the cations and anions of α -aminoanthraquinones obtained by electrochemical oxidation/reduction

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The 1,4-diaminoanthraquinone dyes Disperse Violet 1 and Disperse Blue 14 have been studied by cyclic voltammetry and ESR spectroscopy. The cation radicals, obtained by *in situ* electrochemical one-electron oxidation, can be characterised as aromatic diamino radicals (semiquinonedi-imines), with a spectroscopic pattern similar to those of Wurster's-Blue-type radicals. The anion radicals, obtained by one-electron reduction, are of the semiquinone type. For the cation radicals all amino protons are unequivocally identified by deuterium exchange.

The new data show that single-line spectra observed from the antitumor antibiotics mitoxantrone and ametantrone must have arisen by a process more complex than simple one-electron oxidation of the parent compounds.

Electron Spin Relaxation and Dynamics of Radicals in Inclusion Compounds

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In inclusion compounds molecules of a compound *G* (Guest) cocrystallize with molecules of a compound *H* (Host) accomodating themselves in cavities left by *H*. The cavities are generally large enough to allow large motions of *G*.

The EPR techniques can be used in systems in which radicals $G\bullet$ are formed by γ -irradiation. We are studying the dynamical properties of long chain radicals included in urea. Ketones, organic acids and esthers have been studied, looking for more information i.) on the intra- and intermolecular motions; ii.) on the effects of the guest-host and guest-guest H-bonds; iii.) on the interchannels interaction between guests; iv.) on the effect of the chirality of the channel on the conformation of the guest.

X-band EPR, pulsed EPR and ENDOR have been used to get a picture of the structure and dynamics of the guests. The results obtained so far will be described [1,2,3].

The inclusion of the same guests in another host (Perihydrotriphenilene, PHTP) giving rise to hexagonal channels approximately of the same dimensions, but lacking of the chirality of urea, and of the capability to form H-bonds, produces a strikingly different behaviour of the radicalized guests.

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TRANSIENT FRR RADICALS AND SPIN POLARIZATION

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Free radicals produced by flash photolysis or pulse radiolysis and observed within the first few microseconds of their existence invariably exhibit ESR spectra with hyperfine intensities which are not those expected from radicals in thermal equilibrium with their surroundings, and often with some lines in emission and some in absorption. This arises though processes involved either in the creation of the radicals or in their re-encounters within the geminate cage in which they are formed, in the Chemically Induced Dynamic Electron Polarization (CIDEP) phenomenon. This usually arises through two separate mechanisms, each of which can affect the spectra obtained from radicals produced from triplet state molecular precursors, the Triplet Mechanism (TM), and the Radical Pair Mechanism (RPM). These cause intensity patterns which are, however, qualitatively indistinguishable from those obtained via an alternative mechanism, the Radical-Triplet Pair mechanism (RTPM). Remarkably little firm and conclusive evidence exists for the occurrence of the TM in solution, and in particular of its quantitative implications. Some new studies will be reported on the detailed kinetic test of the theory. Their interest lies also in the way they expose the need to understand the detailed chemistry of a free radical reaction before quantitative conclusions are made, whereas in practice this chemistry is usually assumed, and inadequately assumed.

Spin polarization experiments, together with those performed on the effects of magnetic fields on chemical reactions, exposed the existence of a previously unrecognised reaction intermediate in all radical combination reactions, the spin-correlated radical pair. In turn this provided an uniquely detailed interpretation of how radical reactions proceed, and demonstrated the seminal effects of electron spin. Radicals are produced in pairs with spin conservation, and they react in pairs according to a strict spin selection rule. Vital to the detailed understanding of the reactions is the knowledge of what proportion of radicals created together in a flash then separate only to re-encounter subsequently. This information can be obtained from the relative contributions of the TM and RPM polarizations observed, in method which will be described for the first time. Previous studies have measured the reaction probability within the geminate cage, but our experiments yield an interestingly- different quantity, the proportion which re-encounter with a sufficiently mixed pair wave function in the combined representation to produce spin polarization. It will be interesting to compare the two.

Motional Spin Relaxation in Photoexcited Triplet States.

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EPR is widely used to study molecular motions in dilute spin systems, in particular via the spin relaxation induced by the tumbling motion of the paramagnetic molecules. Unless cryogenic temperatures are chosen, relaxation times are often too short for direct measurement with pulsed techniques, and sensitivity is low since Boltzmann polarizations of the spin levels in thermal equilibrium are very low. These problems may be overcome by Transient EPR experiments (TREPR) on photoexcited paramagnetic triplet states in presence of a static Zeeman field and steady state microwave irradiation. Photoexcitation is achieved by irradiation with intense, short laser pulses. Sensitivity is determined by the high spin polarization usually encountered in photoinduced triplet formation, which exceeds by several orders of magnitude the equilibrium spin polarization at room temperature. The method has no instrumental dead time and rapid decay of TREPR signals may be captured with a time resolution determined by the sample cavity (10 ns.). The values of the longitudinal and transversal relaxation times T_1 resp. T_2 may be extracted from analysis of the dependence of the decay rate on the microwave power employed.

Experiments were done on deoxygenized dilute solutions of EOSIN-Y in frozen propan-1-ol at various temperatures and simulated with a model accounting for thermal tumbling motion of the triplets. The model evaluates the photoinduced spin polarization as the cumulative signal of a large number of individual molecules in the triplet state. Each of the molecules undergoes random reorientations in a sequence of discrete steps, separated by short time intervals. The physical observable is computed from the density matrix obtained by averaging over the density matrices ρ_j of the individual molecules

$$\rho(t) = \frac{1}{N} \sum_{j=1}^N \rho_j(t)$$

The density matrix of the j^{th} molecule ρ_j is computed by solving the Liouville equation for the sequence of orientations of this molecule. The starting conditions are determined by the populations of the three triplet sublevels directly after the laser laser flash. The experimental decay curves are described well by the model. In particular, the dependence on time, the Zeeman field, and the microwave field strength is reproduced with a single set of parameters. The analysis allows extraction of the values of T_1, T_2 as well as the correlation time for tumbling motion.

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ESR of Organic Radical Ions: A Personal Account

by F. Gerson (Universität Basel)

The speaker flashes back over 35 years of ESR spectroscopy of organic radical ions. A few examples from five favourite classes of compounds (i)-(v) are presented.

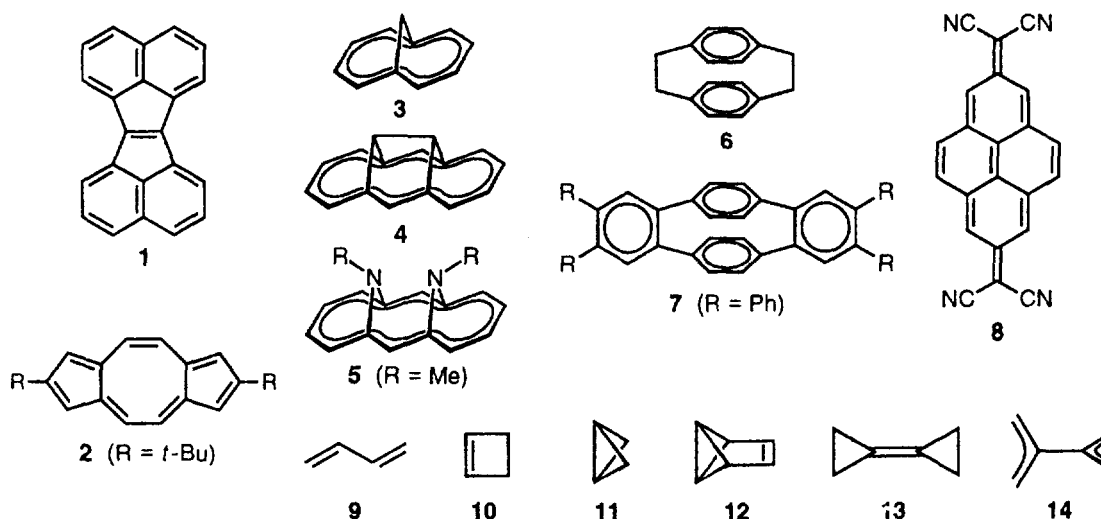
(i) **Nonalternant π -systems:** ¹ acenaphth[1,2-*a*]acenaphthylene (1) and 2,7-di-*tert*-butyldicyclopenta[*a,e*]cyclooctene (2).

(ii) **Bridged annulenes:** ^{1,2} 1,6-methano[10]annulene (3), 1,6:8,13-ethanediylidene-[14]annulene (4), and *N,N'*-dimethyl-*syn*-1,6:8,13-diimino[14]annulene (5).

(iii) **Cyclophanes:** ³ [2.2]paracyclophane (6).

(iv) **Multiple π -electron acceptors:** ⁴ 4',4'',5',5''-tetraphenyl-1,2:9,10-dibenzo[2.2]-paracyclophane-1,9-diene (7) and 11,11,12,12-tetracyanopyreno-2,7-quinodimethane (8).

(v) **Small hydrocarbons:** ⁵ *trans*-buta-1,3-diene (9), cyclobutene (10), bicyclo[1.1.0]butane (11), benzvalene (12), bicyclopropylidene (13), and tetramethyleneethane (14).



While the radical cations and/or radical anions of classes (i)-(iii), as well as the radical anions, dianions, and radical trianions of class (iv), could be generated from the corresponding compounds 1-8 with chemical reagents and/or electrolytically in fluid solution, conversion of the hydrocarbons 9-14 of the class (v) into the radical cations required high-energy irradiation in rigid matrices. The ENDOR technique was amply used to analyse complex or incompletely resolved ESR spectra. The interest focused on structural features of the radical ions, such as lack of pairing properties of frontier orbitals in the class (i), effects of the bridging on the π -perimeters in (ii), lowering of symmetry by association with the counterion in (iii), consequences of passing from mono- to polyions in (iv), and geometry, shape of the SOMO, and rearrangements in (v).

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EPR SPECTROSCOPY AND ELECTRON DISTRIBUTION

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The relation between hyperfine coupling constants and unpaired electron density makes it possible to determine by EPR spectroscopy the electron distribution in a radical, in much the same way as NMR spectroscopy can determine the proton distribution in a closed shell molecule. EPR spectroscopy thus provides the most direct evidence for the various electronic and stereo-electronic effects which can modulate the electron distribution, on which any mechanistic model must depend

This field will be reviewed, taking examples from both the classic and the more recent literature. The various topics which will be dealt with include hyperconjugation, conformational effects, resonance, substituent effects, the Hückel model, anion-cation interaction, solvation, isotope effects, and the Mills-Nixon effect.

ELECTRON SPIN RESONANCE IMAGING (ESRI) OF TRANSPORT PROCESSES IN POLYMERIC SYSTEMS

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ESRI in two dimensions (spectral-spatial) is used in our lab as a method for real-time representation of structural inhomogeneities and dynamics in polymer blends, ionomers, composites and crosslinked polymer gels. Projections taken in a range of magnetic field gradients are used to reconstruct a 2D spatial-spectral image that consists of the ESR spectrum along the chosen spatial coordinate. The method can supply not only the concentration profile of the diffusant, but also the line shape of ESR spectrum of the diffusant in each slice of the sample perpendicular to the direction of the gradient, thus making possible the determination of translational and rotational diffusion in one experiment. Four applications of this method will be presented here. 1. 2D ESRI has been used for measuring the translational diffusion of nitroxide spin probes and spin-labelled poly(ethylene oxide) in hydrogels based on copolymers of 2-hydroxyethyl-methacrylate (HEMA) and 2-(2-hydroxy-ethoxy)ethylmethacrylate (DEGMA).¹ The copolymers are neutral, and have excellent biological tolerance and good mechanical properties even at high water content (> 60 %). For these reasons the gels are especially useful for production of contact lenses. 2. The translational diffusion coefficients of a small deuteriated nitroxide (PDTEMPONE) as tracer were measured in solutions of polystyrene (PS) in toluene and dimethylformamide (DMF), and in cross-linked polystyrene (cPS) networks swollen by the same solvents.² The diffusion coefficients were found to depend on the solvent, temperature and PS concentration in the solutions, and are significantly reduced by cross-linking. The temperature dependence of the diffusion coefficients shows an Arrhenius behavior, and their dependence on the polymer concentration in the solutions is consistent with the free volume theory. 3. ESRI based on paramagnetic Mo^V has been developed in order to avoid problems associated with "hyperfine artifacts". The diffusion coefficients of Mo^V (as MoCl₃) were measured at 300 K in solutions of poly(acrylic acid) in DMF as a function of polymer content,³ and in perfluorinated ionomers swollen by ethanol.⁴ The central position of molybdenum complexes in redox and acid-base catalysis, together with the possibilities opened by this study, suggest that the method of ESRI based on Mo^V could become important for measuring transport properties, and temporal and spatial characteristics of reactions in catalytic systems. 4. The translational diffusion of PDTEMPONE has also been measured in the micellar, hexagonal and lamellar phases of a water-soluble polymeric surfactant consisting of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) segments available as triblocks PEO-PPO-PEO.⁵

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ELECTRONIC STRUCTURE OF CHARGE CARRIERS IN POLYSILANE QUANTUM WIRE

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Polysilanes are σ -conjugated polymers composed of a silicon main chain and organic side chains. Although polysilanes are insulators with band gaps of ca. 4eV, they can be converted to one-dimensional conductors or quantum wires either by photoexcitation or by doping electron donors or acceptors. The electric conductivity of polysilanes depends on the degree of delocalization of the charge carriers in the main chain. The polymer does not show a high electric conductivity if a charge carrier is localized on a small part of the polymer chain. To elucidate the electronic structure of the charge carriers is therefore important for realizing ideal quantum wires.

We have studied the electronic structure of conducting electrons and the holes in polysilanes by analyzing the ESR, ESEEM and optical absorption spectra of their radical anions and cations. Since the ESR takes place between the spin sub-levels of the conducting electron or the hole of the radical anions or cations, respectively, this is especially suitable for determining the ground-state electronic structure of the charge carriers. The absorption spectra, on the other hand, depend on both the ground and the excited electronic states.

The radical anions and cations of polysilanes were generated at 77 K in the glassy matrices of perdeuterated methylcyclohexane with 5 % of perdeuterated tetrahydrofuran and the 1:1 mixture of fluorotrichloromethane and 1,2-dibromo-1,1,2,2-tetrafluoroethane, respectively, by γ -irradiation at 77 K of the matrices containing a small amount of polysilanes. Conclusions obtained from the study are as follows;

- (1) Analysis of the deuterium ESEM of the radical anions revealed that the conducting electron of polysilanes is delocalized not all over the main chain but on a part of the chain composed of only 6 Si atoms.
- (2) Analysis of hyperfine interactions between the hole of the radical cations and the protons in the side chains revealed that the hole is also delocalized on a part of the main chain composed of only 6 Si atoms.
- (3) Analysis of the optical absorption spectra of the radical anions and cations revealed that the delocalization of the charge carriers is induced by pseudo- π conjugation rather than by σ conjugation.
- (4) Comparison of both the ESR and the absorption spectra of the radical cations and anions revealed that the hole can migrate from a main chain to an adjacent polymer chain via the side chains, whereas the conducting electron can not migrate since the side chains act as good intermolecular insulators for the electron.

PULSED EPR STUDIES OF TRANSITION METAL IONS IN MICROPOROUS MATERIALS

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Modern pulsed electron magnetic resonance methods, especially electron spin echo modulation spectroscopy, can give detailed information about metal ion siting and adsorbate interactions in microporous and mesoporous materials which can guide the optimization of their catalytic efficiency. Silicoaluminophosphates (SAPO-n) belong to a new class of microporous (0.5 to 1.5 nm cages and channels) materials which have excellent catalytic potential. The modification of these materials by isomorphous replacement of framework tetrahedral atoms by transition metal ions or by incorporation of such ions into extraframework positions by ion-exchange can lead to improved heterogeneous catalysts for specific catalytic reactions. An even newer class of mesoporous (1.5 to 5 nm cages and channels) MCM-41 silica tube materials have recently been developed which offer new catalytic potential for large molecules. This work describes several applications of pulsed electron magnetic resonance methods to the determination of paramagnetic transition metal ion environments in such catalytically important microporous and mesoporous materials. Examples will be given for palladium(I), cobalt(II), vanadium(IV) nickel(I), and copper(II) ions in medium pore SAPO materials and in MCM-41 materials. These results can aid in the development of improved tailor-made, heterogeneous catalytic materials.

A SYSTEMATIC ANALYSIS OF 1D AND 2D ^{14}N -ESEEM SPECTRA; APPLICATION TO A NITROGEN COORDINATED OXO-VANADIUM COMPLEX.

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A ^{14}N -ESEEM simulation strategy based on first and second order perturbation analysis of peakpositions is presented and applied to the ESEEM data of the complex: Oxobis(2-methylquinolin-8-olato) Vanadium(IV) ($\text{VO}(\text{meox})_2$). This complex acts as a model for the Vanadium containing enzyme Bromoperoxidase¹⁻². Making use of the information in the orientation selection ESEEM and HYSCORE spectra the number of free fitting tensor parameters can be reduced from 9 to 4 (i.e. the α and β Euler angles of both HFI and NQI interaction matrices).

Further constraints based on local symmetry of the complex enable to reduce the number of free parameters to 2. It turns out that the best fit parameter space for this complex is consistent with its crystal structure data. The NQI tensor is near axial and pointing in the ligand plane. The hyperfine interaction is weakly anisotropic and one axis is oriented perpendicular to the ligand plane. The obtained results demonstrate the potential of multifrequency and 2D-ESEEM to obtain structural information about the metal centers in metalloproteins.

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CW AND PULSE EPR STUDY OF PARAMAGNETIC COMPLEXES ON THE CATALYTICAL SURFACES

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CW EPR, Pulsed ENDOR, one- and two-dimensional ESEEM techniques have been applied to study the influence of acid modifications of γ -Al₂O₃ H₂BO₃ on the electron acceptor sites using the adsorbed probe molecules such as anthraquinone and chloranil. After the adsorption of anthraquinone on activated γ -Al₂O₃, the EPR spectra are the superposition of the radicals adsorbed on the surface and three paramagnetic complexes of anthraquinone at coordinatively-unsaturated aluminum sites of different structure. The isotropic hyperfine coupling with aluminum nuclei in these complexes is 3, 21, 28 MHz. The H₃PO₄ treatment of γ -Al₂O₃ decreases the concentration of adsorbed radical and complexes with 3 and 21 MHz hyperfine coupling while H₂BO₃ treatment yields only the complex with 21 MHz hyperfine coupling. The resolved EPR structure arises from two equivalent aluminums in this site. The ESEEM spectra show weak dipole-dipole interaction with ³¹P and ¹¹B nuclei located in the second shell of paramagnetic complexes.

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2D FT-EPR EXCHANGE SPECTROSCOPY OF ORGANIC RADICALS IN SOLUTION

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The two-dimensional (2D) exchange (EXSY) spectroscopy has been used to study slow dynamic processes in solutions of organic radicals. The pulse sequence employed was $\pi/2 - t_1 - \pi/2 - \tau_m - \pi/2 - t_2$, where the FID, acquired during t_2 , is measured as a function of t_1 while the mixing time, τ_m , is held constant. A two-dimensional Fourier transform generates a 2D spectrum with an array of diagonal and cross peaks. The cross peaks link hyperfine components among which magnetization transfer has occurred as a consequence of the dynamic process. Therefore, the cross peak pattern is characteristic of the process involved and 2D EXSY is most useful for mechanistic studies. The rate of the process can be determined by following the cross peaks intensities as a function of τ_m . This method is particularly useful when the rate of the process is too slow to affect the linewidth, but sufficiently fast to compete with the spin-lattice relaxation rate.

Three examples will be presented. The first concerns chemical exchange in the semiquinone ion pair, (di-t-butyl-p-benzoquinone⁻, Na⁺) where the hopping rate of the cation between two polar sites was determined. The second example is of electron transfer between the tetracyanoethylene anion (TCNE⁻) and neutral TCNE, and Heisenberg exchange in this system. The last example involves proton exchange and nuclear relaxation in dihydroxyquinone cation radicals of 2,2',6,6' tetra-butyl-diphenylquinone and duroquinon. In the former the observed cross peaks were a consequence of nuclear relaxation only and the proton exchange with the solvent was very slow, whereas in the latter both processes contributed to the cross peaks.

Study of Photoreduction of Quinones by Fourier Transform EPR

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The photophysical and photochemical reaction pathways of aromatic ketones and quinones are dominated by the singlet-triplet intersystem crossing with a strong spin-polarization mechanism. In alcoholic and aqueous solutions and in the presence of amines the preferred triplet deactivation reactions are electron transfer reactions and / or hydrogen abstraction from the solvent or from the amine ground state molecules. Regarding the general reaction scheme with different benzophenone and anthraquinone derivatives as photoactivated molecules the biphotonic ionization, the electron transfer reaction with different secondary and tertiary amines and the interactions in solvent stabilized radical ion pairs were studied.

With high laser photon fluxes the biphotonic ionization dominates the photochemical behaviour of benzophenone substituted with carboxylic acid groups in different positions. Whereas the emissive spin-polarized photoelectrons disappear by an addition reaction to ground state benzophenones the different benzophenone radical cations decay by nucleophilic addition of OH^- to the aromatic ring generating cyclohexadienyl radicals, and by β -scission of the intermediate alkoxy radicals produced by OH^- additon to the mesomeric cationic keto group. The decay channels of those radical cations depend strongly on the positions of the carboxylic acid substituent. The product radicals of this β -scission are various aryl radicals or phenyl radicals depending on the position of carboxylic acid positions.

The photoreduction of the spin-polarized benzophenone and anthraquinone triplets by different amines generates radical ion pairs with different amount of triplet and/or radical pair polarization. The kinetics of the radical ion pairs, the mechanisms of different secondary reactions and the relaxation behaviour of radical anions and radical cations will be discussed in various polar solvents like alcohols and water. With low amine concentration the lifetimes of the benzophenone triplets are in the microsecond range. In this case the radical-triplet pair mechanism in the free radicals could be detected.

EPR STUDIES OF THE ROLE OF COPPER IN BIO-ORGANIC FREE RADICAL REACTIONS

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EPR spectroscopy is an ideal technique for studying the rates and mechanisms of free-radical reactions involving copper, by combining its ability to identify the role of Cu^{II} complexes (whose structure is revealed by the g -value and hyperfine splittings) and the mediation of short-lived radicals (e.g. via spin-trapping).

Several copper-peroxide systems will be described, including examples relevant to industrial chemistry (e.g. applications in clean technology) and related biological systems. These typically involve the one-electron reduction of Cu^{II} to Cu^{I} (e.g. by thiol or ascorbate) and subsequent rapid reaction with O_2 or H_2O_2 .

The copper-catalysed oxidation of thiols (RSH) to disulphides has been investigated as a function of ligand, solvent and structure of R. The reaction is relatively straightforward in aprotic dipolar solvents in which Cu^{I} can be stabilized and solubilized and in which reoxidation by H_2O_2 and $^t\text{BuOOH}$ is relatively slow: kinetic parameters can be obtained and spin-trapping results confirm the formation of HO^\bullet and $^t\text{BuO}^\bullet$.

In water, the oxidation of Cu^{I} to Cu^{II} is much faster for examples involving coordinatively unsaturated copper: the reaction is retarded by Cl^- . For a variety of thiol-substituted amino acids (e.g. cysteine, penicillamine), the reverse reaction is clearly retarded, and EPR evidence obtained for (stabilized) Cu^{II} complexes liganded to S and N. For these substrates and some related thiols, including glutathione, evidence is presented for intermediate $\text{Cu}^{\text{I}}\text{-SR}$ complexes whose reoxidation is relatively slow. Again, the influence of ligands (e.g. EDTA, ortho-phenothroline) is important.

FREE RADICAL REACTION PATTERNS IN CONDENSED MEDIA

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The concept of constant specific reaction rate, k , is applicable to only a part of known kinetics¹, for reactions at time scales much longer than those of internal rearrangements in reaction systems renewing the environments of reactants. Only under these conditions the distribution of reactant reactivity remains constant during the reaction course. For reactions at time scales comparable to or shorter than those of internal rearrangements the distribution of reactant reactivity changes during the reaction course and the specific reaction rates do depend on time, $k(t)$. This is the case for free radical reactions in numerous systems²⁻⁴ adequately described with the use of

$$k(t) \sim t^{\alpha-1}, \quad 0 < \alpha \leq 1$$

where the dispersion parameter α is directly related to the dispersion σ of rate controlling parameters like the height of potential energy barrier for thermally activated processes or potential energy surface for quantum mechanical tunnelling, $\sigma \sim (1-\alpha)/\alpha$. The lower the numerical value of α the more dispersive is the kinetics, $\alpha=1$ corresponds to classical limit of single valued barrier crossing parameters, $\sigma=0$. The transition from dispersive to classical kinetics will be shown to be accompanied by a marked increase of apparent activation energy for reaction and, in the classical limit the dependence of specific reaction rate on viscosity will be rationalized.

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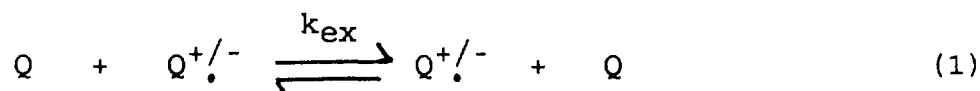
KINETICS OF ELECTRON SELF-EXCHANGE REACTIONS MEASURED BY EPR-SPECTROSCOPY AND THE APPLICATION OF MARCUS THEORY

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We report on different measurements of electron self-exchange rates in solution.

1.) *Homogeneous intermolecular electron self-exchange* rate constants k_{ex} (see eq.1) are measured by EPR-linebroadening effect in 18 different aprotic solvents at various temperatures



for the redox couples: Q=p-phenylenediamines, pyrazines, quinones, TTF, TCNQ, TCNE.

$Q^{\bullet/\cdot-}$ denotes the corresponding radical cations or anions¹⁾.

Rate constants vary between $0.9\text{-}70 \cdot 10^8 \text{M}^{-1}\text{s}^{-1}$ for the different substances in various solvents at $T=293\text{K}$.

On the influence of **solvent dynamical effects** via the longitudinal relaxation time time of the solvent is reported, too.

The limits of application for the so-called "fast" and "slow" exchange regions are discussed in details.

2.) *Intramolecular electron exchange* rates are reported for different 1,3-isodisubstituted benzene radical anions²⁾ and substituted bianthryl radical anions. Rate constants are obtained by computer simulation of the alternating line-width effects.³⁾

3.) Finally simultaneous measurements of both kinetic EPR and UV-VIS spectra are reported. A diode array is coupled directly to an EPR-cavity with light pipes and the kinetics of redox reactions are observed in a stopped-flow mode.

All kinetic and thermodynamic results obtained are interpreted in the sense of **Marcus-Theory of electron transfer reactions**^{1,3)}.

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MUON SPECTROSCOPY OF ORGANIC RADICALS IN BIOLOGY, CATALYSIS AND MATERIALS RESEARCH.

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By implantation of spin polarised, positive muons into matter, free radicals are formed by the formal addition of the light hydrogen isotope, muonium (μ^+e^-) to unsaturated organic molecules. Relevant to radiation biology is the reactivity of hydrogen atoms with nucleic acids; we find that the muon technique may be used to probe the selectivity of hydrogen atoms in their reaction with relevant functional building blocks, specifically imidazoles, purines and uracils.

In heterogeneous catalysis by zeolites, organic radicals are believed to participate as reactive intermediates; by incorporation of unsaturated organic substrates into zeolites such as NaX, Na-ZSM-5 and Na-mordenite, followed by muonium addition, information regarding the surface reorientational dynamics of the resulting free radicals can be obtained.

We have found that radicals PhCHOMu., formed by muonium addition to benzaldehyde, offer significant potential as environmental probes: in particular, when incorporated into zeolite X, the isotropic muon hyperfine coupling is extremely sensitive to the nature of the counter cation which is present; additionally, this coupling provides a probe of solvation effects, and which moreover is particularly influenced by hydrogen bonding, thus acting as a specific probe of this effect.

EPR Monitoring of Plant Degradation, Humification and Coalification

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Stable free radicals are known to be produced during the senescence processes in plants, formation of humic substances in soil, maturation and coalification of organic material. These radicals are generated by red-ox reactions, enzymatic action, thermally induced bond scission, radiation, etc.

Measurements made with the green parts of living plants show that rapid changes in free radical activity can be observed as a result of the polluted atmosphere [1]. Lichens are especially sensitive to sulphur dioxide and nitrogen oxides in the atmosphere; high concentration of semiquinone radicals and, in some cases iminoxy radicals, was detected using quantitative EPR measurements [2].

Production and stabilization of free radicals in humic substances depend on transition metal containing red-ox systems in soil [3]. The EPR monitoring of iron(III) complexes, copper(II) complexes, and semiquinone free radicals was used for strongly contaminated soils and composts. EPR investigations of city refuse composts in different stages of their maturity show distinct correlation between free radical concentration and microbiological activity [4].

Living cells as well as isolated cell wall preparations of some microorganisms (e.g. *Streptomyces* sp.) are characterized by relatively strong free radical signals depending on biosorption of metal ions [5]. These signals are especially intensive for living cells before metal sorption. Copper(II) sorption by living microorganisms and complexation by humic substances results in decrease of the concentration of semiquinone or phenoxy radicals.

During the process of maturation or coalification, the organic material is known to undergo a variety of free radical reactions. Thermally induced bond scission and formation of aromatic radicals is the most likely mechanism for production of the radicals in coal [6]; quantitative EPR technique is necessary for monitoring of the process.

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PHOSPHAVINYLS AND OTHER PHOSPHORUS CONTAINING RADICALS

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EPR studies indicated that the addition of radicals to diaryl-1,3-diphosphallene proceeds with a regioselectivity which varies with the nature of the attacking radical. Thus such electrophilic species as oxygen- or sulphur-centred radicals add to either of the equivalent phosphorus atoms to give spin adducts that can be seen as phosphavinyl radicals, whereas Group 14 organometallic radicals afford spin adducts that are believed to result from addition to the central carbon atom and having a phosphinyl structure. *Ab initio* calculations provided a theoretical basis for the identification of the observed radicals.

Although phosphavinylys proved much less persistent than phosphinylys, both kind of adducts were relatively short-lived, and provided little information as to the nature of the added radical species. Rather persistent adducts were instead characterised by EPR spectroscopy upon addition of a wide variety of different organic radicals to some phosphoryldithioformates. These were identified as alkyl radicals bearing two alkythiyl substituents and a phosphoryl group directly bound to the radical centre. In all cases the adducts are characterised by similar and relatively simple EPR spectra; on this basis the investigated dithioformates can be considered as spin trapping agents of some practical interest.

COMPARATIVE EPR AND ENDOR RESULTS ON CARBONATE DERIVED RADICALS IN DIFFERENT HOST MATERIALS

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When calcified tissues like bone or tooth enamel are exposed to ionizing radiation, the EPR spectrum is dominated by the so-called "asymmetric EPR signal near $g=2$ ". This signal is essentially stable for thousands of years and has applications in EPR dosimetry, EPR dating and detection of irradiated food.

Some ten to twenty years ago this signal was assigned to a single radical, either to CO_3^{3-} or CO_2^- . An extensive comparative EPR study performed in our laboratory on both biological and synthetic apatites, and on carbonate containing single crystals, convincingly proved that the signal is composite and mainly due to two CO_2^- radicals. Moreover, other carbonate derived radicals like CO_3^{3-} , CO_3^- , CO^- , O^- and O_3^- may also contribute to the EPR spectrum. For the spectrum decomposition the applicability of the statistical MLCFA (Maximum Likelihood Common Factor Analysis) technique has been demonstrated.

For some ions it was possible to identify their exact location by means of powder ENDOR studies using the "orientation selection principle" (O^- , CO_3^{3-} , O_3^-). The principal g -values of most radicals discussed in this work depend only weakly on the host lattice. The EPR work on CO_2^- , CO_3^- and O_3^- in alkali halide single crystals is very illustrative in this respect.

The possible consequences of the composite character of the asymmetric EPR signal near $g=2$ for EPR applications in dosimetry, dating and food irradiation, are discussed.

WATER COMPLEXED Mn^{2+} AS A PROBE IN THE ESR STUDY OF SILICA GLASSES OBTAINED BY THE SOL-GEL PROCESS

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Manganese (II) ions have been used as paramagnetic probes for EPR investigation of the local structural changes taking place during the sol-gel-xerogel transformation of silica. In a recent study¹, we have shown that, during the first step of gel formation, paramagnetic signals are ascribed to surface interactions, rather than to substituted species in the forming glassy network. There is a close relation between the linewidths of the hyperfine structure (ΔH_{hfs}) and the nature of pore surface of gel and of the xerogels. The effects observed are ascribed to the interaction of hydrated Mn^{2+} with silanol groups. The linewidths are modified during the aging of the xerogels and this slow phenomenon is ascribed to the reaction of molecular water with the silica network.

The evolution of ΔH_{hfs} has also been studied during dehydration and hydration of xerogels. The experimental laws of variation of ΔH_{hfs} and of the number of paramagnetic species, as a function of pressure, allow to obtain informations on the nature of pore and confirm the microporous character of the samples. The hydration process is characterized by a slow increase of the hyperfine structure with time, t . Two mechanisms are involved during hydration: the first one is diffusional with a \sqrt{t} law for the decrease of ΔH_{hfs} , the second is observed for times longer than about 500 hours (at room temperature) and is again attributed to the effect of aging on ΔH_{hfs} .

These results are analyzed in terms of migration of Mn^{2+} in micropores (drainage) rather than of the diffusion of water.

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TETRAMERIC SILVER CLUSTERS IN ZEOLITE RHO

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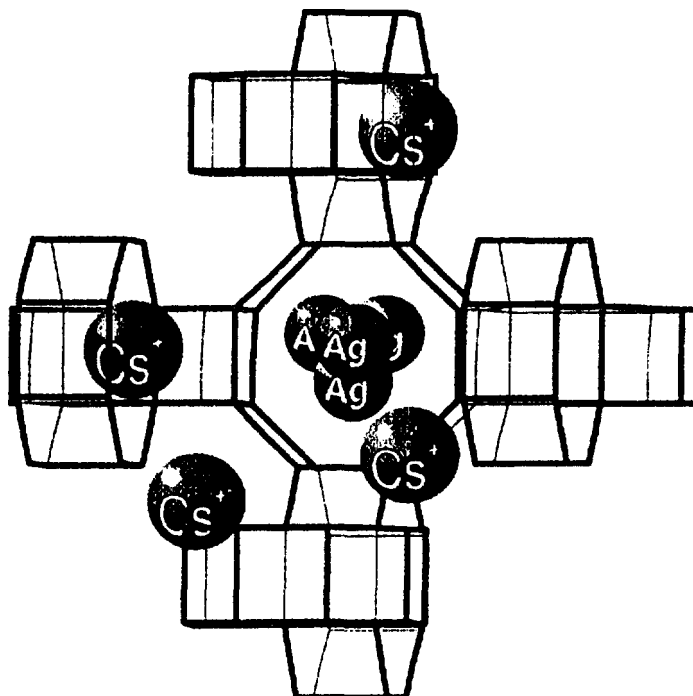
The use of silver containing zeolites as catalysts for water photocleavage¹ and as novel materials for reversible optical data storage² has been proposed. It was postulated that small silver clusters are the active centers in both processes.

We have been studied radiation-induced silver agglomeration process in Ag^+ -exchanged zeolite rho using electron spin resonance (ESR) and electron spin echo modulation (ESEM) spectroscopies.

It turned out that Ag-rho zeolites show remarkable tendency for stabilization of tetrameric silver clusters, Ag_4^{3+} . They are formed in zeolites with silver loadings as low as 0.3 Ag^+ per unit cell and also in zeolites fully exchanged with Ag^+ (12 cations per unit cell). Ag_4^{3+} clusters are stabilized in hydrated and dehydrated rho structures as well as in samples exposed to methanol, ethylene and ammonia. The Ag_4^{3+} clusters are represented by isotropic ESR pentet with hyperfine splitting in the range 103 -141 G depending on the adsorbate molecules present in zeolite cages.

In dehydrated AgCs-rho zeolite Ag_4^{3+} clusters are exceptionally stable - the ESR pentet was recorded two years after γ -irradiation. It was shown based on the electron spin echo modulation (ESEM) results that Ag_4^{3+} are localized in octagonal prisms with Cs^+ cations at hexagonal window sites blocking entrance to the prisms (see figure). It is postulated that such an arrangement of Cs^+ cations together with lattice distortion of dehydrated rho zeolites makes the Ag_4^{3+} trapping site very stable.

ESR results clearly show that radiation-induced silver agglomeration in zeolite rho proceeds by reaction of silver atoms or cationic silver clusters with Ag^+ cations.



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Cu²⁺O⁻ HOLE PAIRS AND O⁻ SPIN BAGS IN La_{2-x}M_xCuO₄ OXIDE MIXTURES

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La_{2-x}Ce_xCuO₄ (0 ≤ x ≤ 0.2) (formed by mixing proper amounts of CeO₂ with La₂CuO₄) shows the usual Cu²⁺ EPR line. However, the x = 0.2 sample, after use as catalyst for NO reduction by CO, shows also an unusual EPR line, with g ranging between 5 and 2.5 when changing temperature from 150 up to 400 K. Ce⁴⁺, substituting for La³⁺, would transform into Ce³⁺ by removing one electron from the CuO₂ plane. However, this, by itself, could not account for the unusual behaviour of the x = 0.2 used sample, as the solubility of cerium dioxide in lanthanum cuprate is very low, and a very small amount of Ce³⁺ would substitute for La³⁺ ions, nearly identical in all of the examined samples. We propose that undissolved CeO₂ partially transforms into Ce₂O₃ also acting as a sink of O²⁻. The last ions would transform into O⁻ by reacting with O atoms brought about by the NO reduction. When CeO₂ is enough concentrated, as for x = 0.2, O⁻ "spin bags" would form upon the catalytic reduction of NO by CO, eventually interacting with Cu²⁺ ions in Cu²⁺O⁻ hole pairs. This could account for the unusual EPR high-g feature.

DEGRADATION OF PAPER AND CHARACTERIZATION OF WHITE MARBLES: EXAMPLES OF ESR APPLICATIONS IN THE FIELD OF CULTURAL HERITAGE.

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The present work deals with the possible use of ESR spectroscopy in the investigation of materials and artifacts of historic or artistic value. It is well known that most natural or man fabricated diamagnetic materials contain measurable amounts of paramagnetic centres either transition ions or organic free radicals or point defects, and are therefore amenable to ESR investigation. The information provided may address problems such as dating, materials origin, copies and forgeries, degradation processes, conservation and restoration procedures and so forth.

Two examples, taken from our recent work and pertaining to entirely different fields, will be used to illustrate the above points. They refer to the study of the ESR properties of ancient paper¹ and of white marbles.²

In samples of antique paper, paramagnetic impurities consist primarily of transition metal ions (Fe^{3+} , Mn^{2+} , Cu^{2+} ..), present in different environments and symmetries. They allow the identification and characterization of the raw materials as well as of the fillers and sizing agents employed. More importantly, their presence is strictly correlated to the phenomenon of degradation, since some of these paramagnets, in specific bonding situations, act as catalysts, promoting the hydrolysis of cellulose, which is, by far, the most important ageing process. Copper and rhombic iron turn out to be particularly effective, whereas the presence of pseudo octahedral iron is almost irrelevant.

Unravelling the provenance of marbles used in ancient architecture and sculpture is still a major task in archaeometry. They have characteristic ESR properties, essentially due to traces of Mn^{2+} which enters the cationic sites of calcite and, eventually, dolomite. It will be shown that information concerning concentration, fraction of dolomite, linewidths, presence of other impurities and anisotropic behaviour may give a valuable and often essential contribution to the identification of the quarries of origin, when compared with the results obtained from a properly constructed database.

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CURRENT STATE OF EPR DOSE RECONSTRUCTION WITH TEETH

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Application of electron paramagnetic resonance (EPR) dosimetry with tooth enamel for external gamma exposure is already done for dose reconstruction of survivors after Hiroshima and Nagasaki bombardment [1] and nuclear workers [2]. However, in the case of internal exposure using of this method is not so obvious especially for Sr-90. First, because Sr-90 is a pure beta emitter with short depth of penetration in bone tissues (~1-2 mm). Second, the metabolism of this radionuclide in tooth enamel of adult persons is practically absent. Therefore, the meaning of dentine (inner tooth tissue) for EPR dose reconstruction after internal exposure has remarkably increased because this tissue shows for Sr-90 a continuing metabolism during whole human life and has direct contact with blood vessels. In the case of Sr-90 dentine would be the main source of irradiation for enamel. The application of dentine as individual EPR dosimeter is possible by using specially developed chemical treatment because of the high concentration of organics.

In the present contribution details of the sample preparation for the EPR measurements, procedure of dose reconstruction and results of individual measurements with tooth enamel and dentine for Russian nuclear workers and population of wasted areas [3] are presented. Analysis of EPR results from persons with mostly internal exposure by Sr-90 (population of wasted areas) is made as compared to mainly external exposure (reactor workers). Comparison are made between individual doses obtained from EPR measurements and individual doses from personal dosimeters (nuclear workers), whole-body counter measurements (persons with incorporated Sr-90).

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EPR OF GRAPHITE AND FULLERENE

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The fullerene conductance on the basis of the additive conductance Dresselhaus-Dresselhaus model for graphite, taking into account the topology of a fullerene molecule in the crystal lattice has been discussed. It has been shown that fullerene conductance is related to the σ_c component of the conductance of graphite through the relation $\sigma_{full} \approx 10^{-2} \sigma_c^{graph}$, because only 1 out of 60 atoms in a fullerene molecule is involved in creating a path of conductance between electrodes and the ratio of fullerene to graphite density is $\rho_{full}/\rho_{graph}=0.74$. Total resistivity of fullerene is determined by resistivities of individual fullerene balls. Doping, like in graphite, causes an increase in the conductivity of intercalated Me_xC_{60} .

Two superconducting phases related to different stoichiometry of K-doped C_{60} will be presented. The evolution of superconductivity related to a different v value of C_{60}^{v-} radicals was examined by means of the MMMA method. Two different and well separated onset T_c temperatures were found: $T_c^{(1)} = (21 \pm 0.5)$ K related to the presence of C_{60}^{1-} EPR signal and $T_c^{(2)} = (18 \pm 0.5)$ K related to C_{60}^{3-} in EPR spectrum. Simultaneous Electrochemical EPR Studies of Fullerene Anion radicals C_{60}^{1-} and C_{60}^{3-} has been presented. Values of the $g=1.9997$ and 2.0008 for frozen solution lead to conclusion that reduced C_{60} molecule should be related to C_{60}^{1-} and C_{60}^{3-} .

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EPR AND ENDOR ANALYSIS BY SIMULATION IN DISORDERED AND SINGLE CRYSTAL MATRICES: INFLUENCE OF STRONG NQI AND MICROWAVE POWER

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EPR and ENDOR spectra of $S = 1/2$ radicals in single crystal or disordered solids have been analysed by simulation. The analysis is suitable for paramagnetic systems with several interacting nuclei which can be described by the spin-Hamiltonian

$$H = \beta B g S + \sum_{i=1}^n I_i A_i S + I_i Q_i I_i - g_i \beta_N B I_i.$$

There are no restrictions on the relative magnitude of the hyperfine, quadrupolar and nuclear Zeeman interactions, nor on the relative orientation of the principal axes of the tensors.¹ Two recent extensions are described. The aim is (1) to refine hyperfine couplings obtained from powder ENDOR and (2) to take into account spin flip lines occurring in radicals of irradiated alanine and other potential EPR dosimeters.

1. Simulation of ENDOR spectra of radicals with anisotropic hyperfine and nuclear quadrupolar interactions.

ENDOR transition frequencies and intensities are calculated with perturbation theory under the assumption that the electron Zeeman interaction is dominating. A simple formula for first order transition moments, including the effect of the quadrupolar coupling, is presented. The impact on the transition moment of the orientational distribution of the radio-frequency field in single crystal and disordered systems is taken into account. The method is tested against experimental proton- and ^{14}N -ENDOR data of neutral and ionic radicals in disordered solids.² Analysis of ^{23}Na -ENDOR from $\text{Na}^+ \dots \text{CO}_2^-$ trapped in $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ single crystals is in progress.

2. Simulation of EPR spectra under microwave saturation.

EPR transition fields and line intensities are calculated under the same assumptions as in 1. The intensity dependence due to the microwave magnetic field strength is computed with a formula given by Maruani.³ The method is tested on radicals trapped in single crystals and powders of irradiated alanine and oxalate. At saturation the intensity of spin flip lines from distant protons is comparable to the intensity of the main lines.

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ANALYSIS OF ELECTRON SPIN ECHO DECAY AND ELECTRON SPIN ECHO ENVELOPE MODULATION OF Cu(II) AND Mn(II) IN D₂O/PERFLUOROPOLYETHER AMMONIUM CARBOXYLATE SYSTEMS

Sandra Ristori, Maurizio Romanelli, Vadim Kurshev and Larry Kevan

Perfluoropolyether surfactants (PEPE) with general formula:

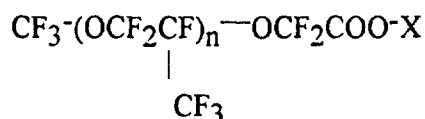


exhibit a strongly enhanced tendency to set up large and anisotropic aggregates and lyotropic smectic phases in aqueous solutions when compared with their straightchain perfluoro-carboxylate analogs¹. In the concentration range 5% - 90% w/w the NH₄PEPE surfactant with n=3 (E.W.=681) gives rise to lamellar phases, whereas at lower concentrations micellar systems are present². The lamellar phases are stable with respect to temperature and concentration changes³.

The Electron Spin Echo has been proven to be a useful technique to obtain structural informations through to interpretation of the nuclear modulation of the echo signal⁴. Moreover, the echo signal decay as a function of the increasing interpulse time can be studied to gain informations on the spin system dynamics, related to the relaxation time and to the spin concentration⁵.

In this study we analyze both the decay and the nuclear modulation of the electron spin echo signal of Cu(II) and Mn(II) ions dissolved in D₂O/PEPE systems at different concentrations of the surfactant and of the metallic ions. The range of used surfactant concentrations lies in the existence domain of lamellar phases. Deuteriated water is used due to the enhanced amplitude and periods of the deuterium modulation with respect to the proton modulation.

Parameters concerning the arrangement of the interacting nuclei around the metallic ions are obtained from the best fit simulation procedure applied to the deuterium modulation in the two-pulse and three-pulse experimental patterns. The analysis of the decays in terms of the Sudden-Jump model⁶ revealed a dependence both on the A-spin and B-spin concentrations. Its interpretation in terms of the different experimental conditions is discussed.

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Emerging Techniques to Study Compartmentalized Liquids Using EPR.

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There are many systems of technological and biological importance that are heterogeneous liquids comprised of regions of relatively low viscosity in which molecules may remain for a significant period of time. One interesting and important aspect of compartmentalized liquids is their ability to concentrate additive molecules into relatively small effective volumes which increases the rate at which such molecules encounter one another. In principle, the collision rate between two additive molecules may be studied by monitoring a measurable quantity that is altered during the act of collision. In practice, since the collisions are frequent, a fast measurement technique is needed and thus far only two have been developed: quenching of fluorescence studied by time-resolved techniques (TRFQ) and spin-relaxation of stable free radicals studied by EPR. TRFQ has been used to study dynamics in compartmentalized liquids for many years, while EPR has only recently been employed for this purpose. Both techniques employ an indicator (fluorescent molecule with a long life time for TRFQ -- nitroxide free radical for EPR) and both rely upon measuring the effect of added molecules (quenchers or paramagnetic broadeners). Since nitroxide free radicals and some other paramagnetic molecules effectively quench fluorescence, it is relatively easy to design experiments to study essentially the same system using both techniques, substantially increasing the information available. The measurement of the bimolecular collision rate is complicated by the fact that a sample contains a statistical distribution of additives among compartments. Thus, the signal is a superposition of signals due to compartments containing zero, one, two, three, etc. additives. Either these component signals must be separated or the superposition must be interpreted under testable assumptions. So far, the separation has been effected in neither the fluorescence nor the EPR experiment; therefore, the superposition must be interpreted and central to this interpretation is an understanding of the statistics of the distribution of additives. Progress to date will be summarized in three areas: (1) combined TRFQ-EPR, (2) EPR techniques using different molecules as broadeners and indicators, and (3) EPR techniques using the same molecule as broadener and indicator.

ESR INVESTIGATION OF γ -IRRADIATED HYPERQUENCHED GLASSY WATER

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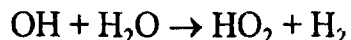
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The ESR spectroscopy has been used to identify the paramagnetic species trapped at 77 K upon γ -irradiation of glassy water prepared by hyperquenching¹ of liquid water at rates exceeding 10^5 K/s. Glassy water is the best existing model² of liquid water.

In addition to OH radicals³, which are the only paramagnetic intermediate of water radiolysis stabilised in irradiated hexagonal ice at 77 K, we have found the comparable amount of HO₂ radicals. Their contribution to the ESR spectra does not depend on irradiation dose in the range 0.8 - 18 kGy. We stress that HO₂ radicals are not detected in irradiated hexagonal ice under these conditions. They are formed, with tiny yields, as secondary products after annealing to destroy OH radicals⁴. Thus the HO₂ radicals seem to be produced with much higher yield and in much earlier stages of water radiolysis than so far expected. We propose formation of HO₂ radicals by single step mechanism for reaction



that occurs at L-defects, present in relatively high concentration in glassy water.

We were unable to detect either trapped electrons nor trapped hydrogen atoms in hyperquenched glassy water irradiated at 77 K. The transformation⁵ of OH radicals into O⁻ anion radicals on cooling of irradiated samples down to 4 K was obscured by excessive line broadening.

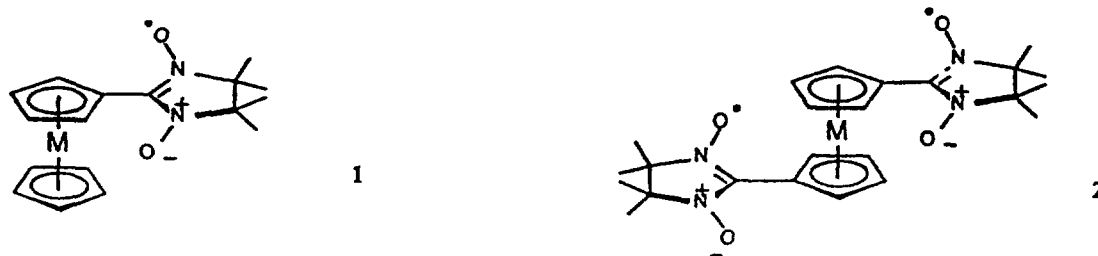
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EPR STUDY OF METALLOCENE-SUBSTITUTED α -NITRONYL NITROXIDE RADICALS.

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The EPR characterisation of a series of α -metallocenyl nitroxide monoradicals (1; M = Fe, Ru, Os) and diradicals (2; M = Fe, Ru) is reported and intramolecular magnetic interactions in this series of compounds have been studied. EPR spectra of monoradicals in diluted solutions under isotropic conditions show small spin densities on the metal centres which are presumably transmitted by a through-space mechanism. This mechanism also seems to be responsible for the antiferromagnetic coupling between the two radical moieties of 2, as ascertained from the spectra in frozen dilute solutions.



Some of the cations and cation-radical derivatives obtained by electrochemical oxidation of these compounds have also been studied by EPR in order to study the magnetic behaviour of the multispin systems and to detect intramolecular electron transfer processes in the mixed-valence derivatives.

In situ UV-Vis ESR spectroelectrochemistry

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Abstract

It is shown for the first time that simultaneous in situ measurements by both ESR- and UV-Vis spectroscopy at the same electrode can be done during one single electrochemical experiment to characterize the electrochemical reaction products by both these spectroscopic methods. The experimental technique including a special T₁₀₂ optical cavity and a transmission spectroscopic electrochemical cell for both ESR and UV-Vis spectroscopy is described. It is shown that the in situ measured UV-Vis absorbance as well as the ESR-intensity behaviour of the electrochemical system under study can be understood in terms of the Faradaic current. The reliability of this system is proved by measuring the organic redox couple of substituted p-phenylenediamine and by comparing the calculated and experimental curves.

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**ESR Characterization of Catalytically Active V Centres Supported on
Titania-, Zirconia-, and Alumina- Pillared Montmorillonite Clays**

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Abstract

Vanadium-doped alumina-, titania-, and zirconia-pillared montmorillonites obtained by various preparative procedures have been investigated with the aid of ESR. Analysis of the spectra shows that localization of vanadium dopant in the pillared clay structure depends on the type of pillared matrix and on the mode of preparation. In V-doped alumina- and titania-pillared clays the vanadyl ions are bound to the pillars. In zirconia-pillared samples, beside the vanadyl centres bound to the pillars, also species associated with the interlayer surface of clay play an important role. In all cases co-pillaring produces species of relatively stronger in-plane π covalency than that observed for other members of the respective series, the effect being most pronounced for (V-Ti)-PILC and (V-Zr)-PILC samples. Catalytic experiments with oxidative dehydrogenation of propane demonstrate superior catalytic properties of these centres. This effect is interpreted in terms of the in-plane π covalency facilitating electron transfer between the electron donor and electron acceptor sites at the catalyst surface.

ESR STUDY OF SOME SOLVENT EFFECTS ON CU(II)-OXAZEPAM COMPLEXES

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Oxazepam (7-chlor-1,3-dihydro-3-hydroxi-5-phenyl-2H-1,4-benzodiazepin-2-one) (L) is one of the drugs used for its tranquillizing, mild hypnotic, anxiolytic and myorelaxant properties.

The CuL_2Cl_2 (I) and CuL_2Br_2 (II) compounds and theirs dimethylformamide (DMF), pyridine (Py), and DMF-Py solutions adsorbed on NaY zeolite were investigated by ESR spectroscopy.

Powder ESR spectra of these complexes obtained at room temperature show the presence of monomeric species with a small rhombic distorsion from the axial symmetry with $g_1 = 2.189$, $g_2 = 2.042$, $g_3 = 2.028$ for the first and $g_1 = 2.232$, $g_2 = 2.067$, $g_3 = 2.027$ for the second compound respectively.

Solutions ESR spectra at room temperature, suggest the presence of the monomeric species with a pseudotetrahedral symmetry.

The anisotropic spectra with four hyperfine lines in the g_{\parallel} region and a strong absorption in the g_{\perp} region were obtained for Cu(II)-oxazepam solutions adsorbed on NaY zeolite. The presence of the half-field resonance (1600 G) due to the forbidden $\Delta M_s = \pm 2$ transitions shows the existence of the dimeric species [1].

Two different monomeric species CuL_2DMF_2 and CuL_2Py_2 were identified from the spectra of 40%Py + 60%DMF solutions of CuL_2Cl_2 and CuL_2Br_2 adsorbed on NaY zeolite [2]. Cu(II) ion is bonded in the last species in a trans square-planar arrangement by two nitrogen atoms from two pyridine molecules and by one carboxylate oxygen atom from each of the oxazepam anions [3].

The appearance of nine superhyperfine lines in the g_{\perp} region of the spectrum of pyridine Cu(II)-oxazepam solution adsorbed on NaY zeolite, suggest the presence of monomeric species with CuN_4 chromophore ($a^N = 18\text{G}$).

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ENDOR AND PULSED ESR STUDY OF GLYCINE RADICALS

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The nature and structure of the radiation induced free radicals in glycine crystals have been studied by several authors during many years. The interpretation of ESR spectra of these radicals has been the subject of some conjecture since the first experiments. Many radicals have been proposed in order to explain the ESR spectra of gamma irradiated single crystals of glycine at different temperatures but two radicals are generally accepted to be formed by irradiation at room temperature [1,2]: $^+\text{NH}_3\text{CHCOO}^-$ (radical A) and CH_2COO^- (radical B).

In this paper we report an ENDOR and ESE investigation on the glycine single crystal irradiated at room temperature. Hyperfine tensors corresponding to radical A are obtained from ENDOR data, in very good agreement with those reported by Collins and Whiffen [2]. The set of tensors obtained for the second species better agrees with the results of Bonazzola et al. [3] for the CH_2^+NH_3 radical and substantially differ from those reported for CH_2COO^- radical [4]. For certain orientations of the crystal in the magnetic field the hyperfine components of radical B in echo-detected ESR spectra show an evident splitting due to the nitrogen nucleus.

We measured also the T_1 values of glycine at different temperatures by saturation recovery method. By fitting the saturation recovery curves with a biexponential expression we have found two sets of relaxation rates, the slower one being attributed to the spin lattice relaxation mechanism. The temperature dependence of $1/T_1$ in the range of 190-290K shows an Arrhenius behavior with an activation energy of 4.1KJmol^{-1} which is not in agreement with the value of $\approx 20\text{KJmol}^{-1}$ obtained for CH_2COO^- radical in other systems [4].

Our results suggest that the radical B is not CH_2COO^- . The species $-\text{COO}-\text{CH}-\text{NH}-\text{R}$ or $\text{CH}_2-\text{NH}-\text{CO}-\text{R}$ are proposed in order to explain our ENDOR and pulsed ESR data, studies on the most probable structure being now in progress.

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**General conclusions on EPR and ENDOR studies
of homogeneous and heterogeneous
diatomic chalcogen defects in alkali halides**

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X_2^- and XY^- defects (X, Y = O, S and Se) have been observed as impurities in several alkali halide single crystals. From the EPR and ENDOR studies of these samples, interesting conclusions concerning the structural and electronic properties of the diatomic chalcogen defects, could be drawn. All X_2^- and XY^- ions were found to be situated in a monovacancy (i.e. replacing a single halide ion on a lattice site).

For the different centres, the measured superhyperfine (SHF) parameters could be correlated nicely. Using the ENDOR data, the occurrence of two ground states observed with EPR, could be fully explained.

SPIN DOSIMETRY IN CATALYTIC RESEARCH

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Advanced chemical methods were applied to prepare the standard samples for solids containing transition metal ions and to determine the concentration of paramagnetic centres by chemical analysis. Standards for d^1 and d^9 ions were prepared by uniform distribution of paramagnetic V(IV) and Cu(II) ions in a diamagnetic, chemically unreactive matrix. The quality of standards was tested by statistical methods considering the following factors: reproducibility of the chemical composition, macro- and microhomogeneity within preparations and precision of EPR measurements. Various aspects of the procedure of preparation of reliable standards are discussed. The means are described which may be employed to resolve complex EPR spectra into separate signals and to determine the concentration of particular paramagnetic species.

Several examples are given to illustrate the importance of the quantitative determination of the number of spins in catalytic studies.

EPR STUDIES OF SYNTHETIC PHEO- AND MIXED TYPE-MELANINS

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Some data, including EPR studies, suggest that human substantia nigra neuromelanin is a mixture of copolymers derived oxidatively from dopamine and its cysteinyl adducts [1]. The exact role of this unique pigment still remains unclear. Under physiological conditions neuromelanin acts probably as a cytoprotective agent, but it also seems to be involved in free radical mediated cytotoxic processes which occur in some neurodegenerative disorders (eg. Parkinson disease) [2]. To perform in vitro studies of these functions, it is necessary to choose optimal synthetic neuromelanin model. The aim of this work was to compare free radical properties of some synthetic model pigments derived from different cysteinyl precursors.

5-S-cysteinylDOPA, 2-S-cysteinylDOPA, 5-S-cysteinyl-dopamine and 2-S-cysteinyl-dopamine were prepared by enzymatic oxidation of DOPA or dopamine in the presence of cysteine. Resulting isomers were separated and purified using ion-exchange chromatography on DOWEX 50W x 4 [3]. To prepare pheomelanins individual or mixed cysteinylDOPAs or cysteinyl-dopamines were incubated at 37°C with tyrosinase. Mixed type-melanins were obtained using DOPA or dopamine and their cysteinyl derivatives in different molar ratios. Eumelanins were prepared by autooxidation of DOPA and dopamine.

Measurements for the melanin samples were performed using an X-band (9.3 GHz) EPR spectrometer connected to IBM computer. EPR spectra were collected by Rapid Scan Unit and analyzed by ELF1 and INTER programs. Microwave frequency was recorded.

For the studied samples concentration of free radicals, lineshape and parameters of the EPR spectra: g-factor and linewidth, were determined. Ultramarine was used as the reference for the paramagnetic centers concentration. A ruby crystal was an inner reference. Double integration of the first-derivative EPR spectra was done to determine the area under the absorption curve. The influence of microwave power on intensities and linewidths of the EPR spectra was studied. The obtained data rendered comparison of contents and types of free radicals, and their spin-spin and spin-lattice interactions in the individual melanin samples.

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EPR OF HIGH-SPIN OCTAETHYLPORPHYRATOIRON (III) ALKOXY COMPLEXES

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The heme group composed of iron-porphyrin complexes is the centre of all the biologically important functions of hemoproteins. Alkoxy groups obtained from methanol and ethanol as well as other alcohols, in competition with other ions and small radicals, interact with the heme group to form some complexes. The nature of the heme-alkoxy bonds and their reaction to the function of hemoprotein molecules have not been satisfactorily explained so far. This communication reports methoxy-[Fe(OEP)OCH₃] and ethoxyoctaethylporphyratoiron [Fe(OEP)OC₂H₅] complexes characterized by EPR spectroscopy. Powder and solution EPR spectra were recorded within 4.2 - 300K temperature range. The powder spectra of the alkoxy complexes exhibit significant rhombic distortion of the axial symmetry in comparison with the one of μ -oxo octaethylporphyratoiron dimer. The rhombic character of the EPR spectra is most noticeable for Fe(OEP)OC₂H₅ and less for Fe(OEP)OCH₃ at liquid helium temperature. Smaller axial-symmetry deformation was observed for corresponding frozen chloroform solutions. This suggests that crystal packing effects and possible suprachemical bonds influence significantly an environment symmetry of the central iron atom in the solid state. Contrary to the glasses, powder spectra were also detectable at room temperature, what is rather unusual feature for iron porphyrin complexes. All spectra were analysed by the use of iterative least-squares fitting procedure for the case $D \gg h\nu$. The EPR spectra were interpreted in the light of earlier obtained results with IR, Resonance Raman, NMR and Mössbauer spectroscopic methods [1].

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EFFECT OF EPR SPECTRA RESOLUTION DEGREE ON ACCURACY OF HYPERFINE STRUCTURE PARAMETERS DETERMINED FOR ISOTOPE SUBSTITUTED Zn-CHLORIN RADICALS

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The degree of hyperfine structure resolution in EPR spectra can be described by the ratio $hfcc/\delta H$, where $hfcc$ denotes values of hyperfine coupling constants and δH - linewidth. It follows from the above ratio that the greater $hfcc$ parameters or the smaller δH the better resolution. EPR spectra of Zn-octaethylchlorin [ZnOEC] anion radicals show different resolution for unsubstituted and successively substituted deuterium and ^{15}N analogues [1]. These spectra were used as the suitable ones for estimation of the effect of a resolution degree on the accuracy of $hfcc$ parameters. Resolution of the hyperfine structure from deuterium substituted [ZnOEC]⁻ at α, β and γ, δ -meso-positions was improved by using a method of computer enhancement of complex spectroscopic spectra resolution described earlier [2]. An analysis of $hfcc$ parameters obtained for the spectra before and after resolution has shown that the enhancement resolution method [2] can be successfully applied even then when EPR spectra display hyperfine structure in outline. However, the use of this method for the completely unresolved spectrum, detected for [ZnOEC]⁻ with deuterium substituted at all meso-positions, did not give a satisfactory result. The accuracy of $hfcc$ parameters has been considered taking into account multi-extremal character of the least-squares function optimized. The simplex and Marquard algorithms were used for fitting theoretical to experimental spectra and their Fourier transforms.

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ELECTRON SPIN ECHO SPECTROSCOPY OF THE GLYCINE RADICAL IN DIGLYCINE NITRATE SINGLE CRYSTAL

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In X-ray irradiated diglycine nitrate $(\text{NH}_2\text{CH}_2\text{COOH})_2\text{HNO}_3 = \text{DGN}$ crystals a stable free radical appears which we have identified by single crystal cw-EPR as $\text{NH}_3^+-\text{CH}-\text{COO}^-$ with g-factors $g_{\parallel}=2.0053$ and $g_{\perp}=2.0012$ and isotropic hyperfine splittings from protons: $H_{\alpha}=2.18$ mT, $H(\text{NH}_3)=1.71$ mT and nitrogen 0.3 mT at room temperature. This radical was used as a paramagnetic probe for studying the crystal and molecular dynamics by electron spin echo methods.

Pulsed EPR measurements were performed in the temperature range 4.2-300 K with magnetic field along the crystal c-axis using a BRUKER ESP380E FT/CW spectrometer. At this crystal orientation a well resolved five hyperfine component spectrum is observed and the relaxation measurements were performed for every of the five line separately, using nonselective pulses of spectral width exciting the each line.

The spin-lattice relaxation time T_1 was measured by saturation recovery method with a sequence of eight saturation pulses and two 48 ns reading pulses. The recovery of the magnetization was described by two-exponential function with both components being temperature dependent. The spin-lattice relaxation time is relatively long at helium temperature with $T_1=0.83$ s for longer component and decreases monotonically on heating. The T_1 has the same value for all five hyperfine structure lines.

The phase memory time T_M was measured by Hahn method using two 48 ns pulses. T_M varies with temperature. The echo amplitude decay was monoexponential and strongly modulated by interactions with surrounding protons and nitrogens. The five hyperfine lines relax with different T_M values. There exist two minima in $T_M(T)$ dependence indicating a resonance type phase relaxation acceleration by molecular dynamics. In the high temperature minimum ($T=170$ K) $T_M=400$ ns and all hyperfine components have the same relaxation rate. This minimum seems to be related to the hindered rotation of the NH_3 groups. At low temperature minimum at $T=17.5$ K the lowest relaxation rate appears for the low-field hyperfine line with $T_M=4$ μs . This minimum we relate to the flipping motion of the glycine molecules between two crystallographical positions.

Neither the T_1 nor T_M exhibit an anomaly at ferroelectric order-disorder phase transition at $T_c=206.5$ K.

ESEEM data were collected at room temperature using both two and three-pulse sequences. ESEEM spectra were obtained by Fourier transformation proceeded by a removal of the decay function. Except the proton matrix lines the very sharp lines were observed at nitrogen frequency region. They are interpreted as quadrupole frequencies under „cancellation conditions”. The quadrupole coupling constants was estimated as 2.10 MHz with the asymmetry parameter 0.7, and the isotropic nitrogen hyperfine couplings was found as $a_{\text{iso}}=2$ MHz.

This work was supported by the Research Project KBN 2-P03B-038-08 of the Scientific Research Committee.

ESR STUDIES OF Cu(II) AND VO(IV) IONS IN ORGANICALLY MODIFIED AND DOPED OXIDE GELS

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ESR spectroscopy is a powerful tool for identifying changes of the coordination environment of Cu(II) or VO(IV) ions in gel materials received by the sol-gel process. This process is a useful method for preparation of two series of organically and simultaneously coordinatively modified gels. It is owing to amino groups that the gels are coordinatively active and create crosslinking points with transition metal ions.

Changes of the coordination sphere were determined during gelation, temperature increasing as well as in the dried gels with composition changes. The results of ESR and thermal decomposition of the gels are summarized in identified models of the coordination sites in the gels.

ESR spectroscopy was also used in our studies to identify Cu(II) or VO(IV) complexes with supramolecular ligands as crown ether derivatives encapsulated in silica gel prepared by the sol-gel method.

ESR SPECTROSCOPIC INVESTIGATION OF AN ELECTRON TRANSFER FROM HYDROGEN TO PLATINUM

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The nature of the active hydrogen species (spilt-over hydrogen) which are formed in metal-containing catalysts is still not completely clear : radical, ionic and bound species are discussed in the literature [1]. Until now, the application of several spectroscopic methods (e.g. IR, NMR, and ESR spectroscopy) did not allow the direct and unambiguous detection of the active species. Nevertheless, their presence could be clearly shown by means of different test reactions (e.g. the reaction with organic radicals [2] and the H-D exchange of hydroxyls [3]).

In the present work we have studied the hydrogen spillover process on a Pt-containing alumina catalyst. The Pt content was 0.5 wt.-%. The metal was introduced by impregnating γ -Al₂O₃ with an aqueous H₂PtCl₆ solution and subsequent washing and drying. A Varian X Band spectrometer (V-4502-15) equipped with a double cavity TE₁₀₄ has been used for the ESR measurements.

The exposure of the activated Pt/ γ -Al₂O₃ catalyst to hydrogen (13.3 kPa) at room temperature followed by cooling down to 77 K led to the immediate formation of a broad line (g-values 1.995 and 1.997) and subsequently to the appearance of three relatively narrow lines with one g factor of 1.995. An identical behaviour was observed after the same treatment with deuterium instead of hydrogen. Therefore, the lines can be clearly correlated with paramagnetic Pt species. In detail, the broad line should be due to a partial charge transfer from adsorbed hydrogen to the Pt clusters and the narrow lines that are formed in the course of about 30 min can be correlated with an electron transfer from spilt-over hydrogen to atomic platinum. The observed ratio of the hfs line intensities is in good agreement with the natural abundance of the different Pt isotopes. The behaviour described above was reversible upon heating to room temperature and cooling down to 77 K again.

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ELECTRON SPIN ECHO MEASUREMENTS OF THE FREE RADICAL SPIN RELAXATION IN $\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$

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At room temperature, lithium hydrazinium sulphate, $\text{Li}(\text{N}_2\text{H}_5)\text{SO}_4$ is orthorhombic, space group $\text{Pbn}2_1$. The crystal structure of lithium hydrazinium sulphate (LHzS) consist of LiO_4 and SO_4 tetrahedrons forming a three- dimensional network containing channels running parallel to the c -axis.

ESR measurements were on free radicals produced by gamma irradiation. ESE measurements were performed on a pulse BRUKER ESP 380E FT/CW operating at X - band spectrometer in the temperature range 4.2 - 300 K, equipped with OXFORD CF935 flowing helium cryostat. The temperature was controlled by OXFORD ITC4 controller and measured by the thermocouple located in the close vicinity of the sample. For ESE measurements the crystals were oriented with a -axis parallel to the magnetic field. The orientation of the crystals was verified by recording continuous wave spectrum..

The phase memory time T_M (for three crystals irradiated with differents doses) was determined from spin - echo amplitude decay in two - pulse experiments.

In order to obtain phase memory time T_M the two pulse echo was generated. Two 120 ns microwave high power pulses were applied. The amplitude of the pulses was adjusted to obtain maximum echo intensity and the duration of the pulses was chosen experimentally to suppress the echo amplitude modulations. The initial separation of the pulses was set to 240 ns and then increased by 8 ns steps. The pulse sequence repetition time was set to $5T_1$, where T_1 denotes the electron spin lattice relaxation time, and was estimated by „saturation recovery” method.

The measurements were done for one central line of hyperfine lines in the chosen orientation. The peak-to-peak linewidth for this line is less than 0.3 mT thus the 120 ns pulses were wide enough to excite the whole line. The temperature dependencies of the phase memory time T_M for the irradiated crystals (the dose respectively 3.3 kGy, 4.8 kGy, 12.8 kGy). At about 115 K for every crystals minima in temperature dependence of T_M appear. For crystal with dose 4.8 kGy at temperature about 175 K second minimum is observed. It is very possible that second minimum appear in other crystals, but signal ESE was too weak. The minima in $T_M(T)$ dependence can be related to molecular motions in the crystals, probably these minima can be ascribed to the rotation of NH_3 group. An origin at the difference in T_M - values for differents crystals and second minimum is not clear, but the effect of concentration of defects is visible. The T_1 varies with temperature from 400 ms at 4.2 K to 60 μ s at 170 K.

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EPR OF Mn^{2+} IN LOW TEMPERATURE PHASE OF K_2ZnCl_4

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K_2ZnCl_4 belongs to the large group of A_2BX_4 crystals which exhibits incommensurate phases. Above $T_I = 553$ K it has the paraelectric phase with orthorhombic space group Pcmn with four formula units ($Z = 4$) per unit cell [1]. Between T_I and $T_{C1} = 403$ K it is modulated along c axis with the wave vector $q = (1-\delta)c^*/3$, where δ decreases almost linearly from 0.08 at T_I to 0.03 at T_C . Another phase transition, with a nature still not clear, to a ferroelectric phase takes place at $T_{C2} = 145$ K [2]. The unusual feature of K_2ZnCl_4 is the presence of quite large thermal hysteresis, memory effects and extremely slow relaxation of the dielectric constant.

Structural phase transitions in many systems of the group have been extensively studied up to now by different physical methods. In order to throw some light on the microscopic origin of above mentioned effects we decided to study of phase transition by the EPR spectra of Mn^{2+} ($3d^5$) ions. The Mn^{2+} ions have already been employed successfully in studies of the incommensurate phases in isomorphous $[\text{N}(\text{CH}_3)_4]_2\text{ZnCl}_4$ [3], and Rb_2ZnCl_4 systems [4],[5]. We focus our attention on critical behaviour of the system in low temperature phase close to T_{C1} . In the analysis of the EPR spectra, emphasis is laid on the outermost lines of various hyperfine group due to the spectrum complexity and the extensive overlapping of the neighbouring lines. The analysis relies on the well-established spin Hamiltonian of Mn^{2+} ions in a crystalline fields of rhombic symmetry. The shifts and splittings of the EPR lines are calculated on the basis of a microscopic model of the incommensurate modulation.

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DOUBLE-STACKED DIELECTRIC RING RESONATOR FOR EPR MEASUREMENTS OF BIOLOGICAL SAMPLES

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Abstract

We discuss the microwave properties of a newly developed double-stacked dielectric ring resonator (DR) for applications in Electron Paramagnetic Spectroscopy (EPR). This design leads to a substantial improvement of the signal-to-noise ratio (S/N), as well as enables one to measure biological samples characterized by high dielectric losses and often limited in supply. The paper presents a new theoretical approach for calculating the resonant frequency, resonator filling factor (η) and resonator Q -factor for the double DR system. The comparison of experimentally and theoretically determined technical parameters reveals a very good accuracy that is better than 1% for the resonant frequency.

Paramagnetic Resonance and Magnetism of Binuclear Copper(II) Complexes with Octadentate Ligand

N,N',N'',N'''-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc)

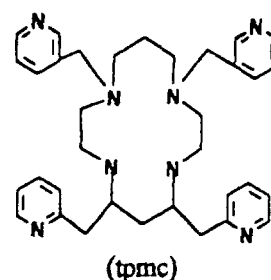
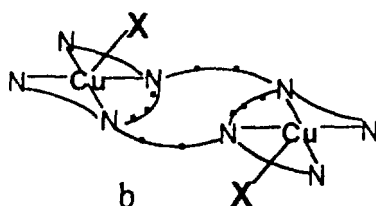
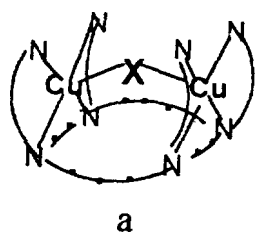
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Intra- and intermolecular spin-spin interactions were studied using EPR (X- and Q-band) and magnetic susceptibility measurements over the temperature range 4.2-300 K for $[\text{Cu}_2\text{Xtpmc}](\text{ClO}_4)\cdot\text{L}$ complexes ($\text{X}=\text{N}_3, \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{NO}_2, \text{OH}$; and $\text{L}=\text{nH}_2\text{O}$ or CH_3CN) having a boat configuration of a binuclear fragment where X bridges two copper ions (Fig. a) and for $[\text{Cu}_2\text{tpmc}(\text{ClO}_4)_4]$, $[\text{Cu}_2\text{X}_2\text{tpmc}](\text{ClO}_4)_2$ complexes with a chair type of the binuclear fragment configuration (Fig. b) and X at the apical positions.



The EPR and magnetic properties observed for a majority of the complexes are affected by intramolecular interaction (estimated as $J \sim 2-4 \text{ cm}^{-1}$) and by a weak intermolecular interaction leading to average of the EPR fine structure. The exceptional behaviour exhibits $[\text{Cu}_2(\text{OH})\text{tpmc}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ for which extremely strong influence of lattice perturbations on magnetic exchange properties were recognized. An antiferromagnetic exchange interaction of about 70 cm^{-1} and EPR spectrum associated with spin-Hamiltonian parameters $g_z=2.25$, $g_y=2.05$, $g_x=2.04$, $D=0.06 \text{ cm}^{-1}$, $E=0.005 \text{ cm}^{-1}$ transforms into the weak ferromagnetic and antiferromagnetic interactions at temperature range 4.2 K - 50 K corresponding to a new EPR spectrum with different values of anisotropic spin-spin interaction parameters ($D=0.172 \text{ cm}^{-1}$, $E=0.015 \text{ cm}^{-1}$). These additional magnetic interactions are consistent with the structural perturbations due to the binuclear fragments resulting from a partial loss of the crystalline H_2O by a parent $[\text{Cu}_2(\text{OH})\text{tpmc}](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ complex.

EPR of the frozen solution spectra of all the complexes in NMF and DMF are typical for a triplet state with distinctly resolved hyperfine structure for $\Delta M_S=1$ and $\Delta M_S=2$ signals and show very similar values of g-factors, hyperfine and fine structure parameters ($g_z=2.206$, $A_z=0.009 \text{ cm}^{-1}$, $g_{xy}=2.056$, $D=0.028 \text{ cm}^{-1}$). The results reveal the same molecular structure of binuclear complexes formed in the solutions due to the loss of one bridging X or two apical X anions.

THE EFFECT OF NEAR INFRARED RADIATION ON THE ERYTHROCYTE MEMBRANE.

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Near infrared absorption (NIR) has been known to activate proton transfer in molecular crystals containing intermolecular hydrogen bonds [1]. The same process has been observed in solution of aminoacids in presence of spin probe TEMPO [2]. Weak intermolecular hydrogen bonds play a significant role in biological structures, hence the NIR radiation is supposed to affect strongly the structure and properties of erythrocyte membrane. The spin probe technique was applied to study the structural changes in lipids area of membrane which are caused by NIR radiation.

After exposition of erythrocyte cells to NIR radiation a polarity, a microviscosity, an order parameter and a ratio of a spin probe reduction inside the membrane were monitored.

Major conclusions have been established.

- The structure of erythrocyte membrane is very sensitive to NIR radiation.
- Changes are observed on different depths of cell membrane.
- The degree of changes is strongly dependent on irradiation time.

Observed effects may be explained by model of proton transfer caused by NIR radiation.

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RADICALS AS PROBES OF PHASE TRANSITIONS IN EPR INVESTIGATION OF PYRIDINIUM TETRAFLUOROBORATE SINGLE CRYSTALS.

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The EPR technique was used to study γ - irradiated single crystals of pyridinium tetrafluoroborate in three perpendicular planes. EPR measurements were performed in the X - band at room temperature and also, for a few chosen orientations of the single crystal in a magnetic field, in the temperatures ranging from 158 K to 254 K, in cycles of cooling and heating.

Pyridinium tetrafluoroborate crystallizes in the trigonal space group $R\bar{3}m$ with $a = 5.669$ Å, $\alpha = 97.28^\circ$ and $Z = 1$ [1].

It was established that the radical appearing under the effect of γ - irradiation is formed by attachment of hydrogen atom to the carbon atom in the pyridine ring.

Analysis of the complex EPR spectra was possible by the use of a special computer resolution enhancement method (CREM) [2,3].

The g - tensor components were found to be $g_{xx} = 2.0017(8)$, $g_{yy} = 2.0028(8)$ and $g_{zz} = 2.0032(8)$, the components of hyperfine splitting tensor describing interactions between unpaired electron and nitrogen atom were $A_{xx} = 0.00(6)$ mT, $A_{yy} = 0.44(6)$ mT, $A_{zz} = 2.07(6)$ mT.

The CREM method based on Fourier transform and the methods of convolution and deconvolution was applied for analysis of the temperature changes of EPR linewidths in the spectra of single crystals of pyridinium tetrafluoroborate, which is known to undergo solid - solid phase transitions [4].

Analysis of the obtained results has proved that both the strength of the hyperfine interaction and the linewidth of individual components of the pyridine radical EPR spectra can be reliable parameters providing the information about the nature of phase transitions.

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INFLUENCE OF PRESSURE AND TEMPERATURE ON b_4^o SPIN-HAMILTONIAN PARAMETER FOR Gd^{3+} ION IN $Cs_2NaLaCl_6$ SINGLE CRYSTAL

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The elpasolite $Cs_2NaLaCl_6$ crystal has been already studied by means of various methods [1]. Our supplementary studies are devoted the influence of temperature and hydrostatic pressure on the b_4^o spin-Hamiltonian parameter of Gd^{3+} ion in $Cs_2NaLaCl_6$ performed by the electron paramagnetic resonance (EPR) method. The single crystal of $Cs_2NaLaCl_6:Gd^{3+}$ was prepared in the Zavoisky Physico-Technical Institute in Kazan, and EPR measurements in X-band under hydrostatic pressure were carried out in the Institute of Molecular Physics in Poznań.

The temperature dependence of the b_4^o parameter in the cubic phase of $Cs_2NaLaCl_6:Gd^{3+}$ were measured at two constant pressures: 100 and 600 MPa. In the observed range between the phase transition temperature T_c and 350 K the dependence $b_4^o(T)$ is linear with the slope: $(\partial b_4^o / \partial T)_p = -(68.1 \pm 0.5) \cdot 10^{-8} \text{ cm}^{-1} \text{ K}^{-1}$.

The room temperature measurements of b_4^o as a function of pressure up to 700 MPa show a linear dependence with the coefficient: $(\partial b_4^o / \partial p)_T = (15.5 \pm 0.5) \cdot 10^{-8} \text{ cm}^{-1} \text{ MPa}^{-1}$.

Thermal expansion and spin-phonon contributions are separated by the thermodynamic relation: $(\partial b_4^o / \partial T)_{p,T} = (\partial b_4^o / \partial T)_p - (\beta / \kappa) (\partial b_4^o / \partial p)_T$

with the volume thermal expansion coefficient $\beta = (9.3 \pm 0.5) \cdot 10^{-5} \text{ K}^{-1}$ and volume compressibility coefficient $\kappa = (48 \pm 2) \cdot 10^{-3} \text{ GPa}^{-1}$.

Inserting these experimental values into the above relation the following spin-phonon (vibronic) contribution to b_4^o is obtained: $(\partial b_4^o / \partial T)_v = -(38 \pm 3) \cdot 10^{-8} \text{ cm}^{-1} \text{ K}^{-1}$. It is 56% of the total temperature changes in $b_4^o(T)$ and the rest 44% is related to the thermal expansion of the crystal. This result is compared to that one obtained for Gd^{3+} ions in fluoroperovskite crystal [2]. On the assumption that b_4^o depends on the metal-ligand distance according to a law $b_4^o \propto r^k$ the value of $k = -6.6$ is obtained that is 3 - 4 times less than for fluoroperovskite crystals [2], and it is comparable with the value of k for Gd^{3+} in the simple fluorides MF_3 and $CsCaCl_3$.

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POTENTIAL DEPENDENCE OF A NUMBER OF THE PARAMAGNETIC CENTERS IN THE ELECTRONICALLY CONDUCTING POLYMER MATRIX.

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Electron paramagnetic resonance (EPR) coupled with electrochemistry is one of the powerful tools for studying electroactive polymers. The shape of the EPR intensity versus potential plots is usually interpreted on the ground of a process with two one-electron steps (polaron/bipolaron model). In the first step (1) paramagnetic species (polarons) are created, that give rise to the EPR absorption. In the second step (2) polarons are transformed into a spinless species (bipolarons), destroying the EPR intensity.



The process of recombination of two polarons is also possible:



We carried out the EPR and electrochemical measurements on poly(1,5-diaminonaphthalene) prepared by monomer electrooxidation. The EPR intensity vs. electrode potential dependence is quite different from the dependence predicted by the polaron/bipolaron model. In the case of poly(1,5-diaminonaphthalene) the maximum of EPR signal was observed for fully reduced form while usually it was observed for oxidized polymer. We suppose that this EPR signal can be ascribed to the residual paramagnetic centers. In this paper we described this unusual dependence of the EPR intensity on the electrode potential by calculating of the probability of recombination between the "residual" spins.

EPR OF DIVALENT MANGANESE IN NON-KRAMERS' HOSTS

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In spite of early expectations that, due to the dipolar and exchange interactions between a paramagnetic dopant (guest) and an ion of paramagnetic host, lines in an EPR spectrum of the dopant should be so broadened that any fine or hyperfine structure could not be observed, reasonably sharp and well resolved EPR spectra of divalent manganese ($S=5/2$, $I=5/2$) have been taken in certain paramagnetic hosts at room temperature; see, for example [1-4] and papers cited therein.

We have studied EPR of Mn^{2+} in paramagnetic hosts with integer spins, i.e. in so-called non-Kramers' hosts. Studies have been carried out on the basis of data extracted from experimental spectra of Mn^{2+} in single crystals of Fe^{2+} ($S=2$) and Ni^{2+} ($S=1$) perchlorate hexahydrates. The spectra have been taken at X-band ($\nu \approx 9.4$ GHz) in a temperature range from 77 to 380 K for $Fe(ClO_4)_2 \cdot 6H_2O$ (FePH - for short) and from 77 to 450 K for $Ni(ClO_4)_2 \cdot 6H_2O$ (NiPH). We have considered various interactions which lead to the observation of sharp spectra in these crystals. We have taken into account interactions in three spin systems: (i) the host system, i.e. $Fe^{2+} - Fe^{2+}$ or $Ni^{2+} - Ni^{2+}$; (ii) the impurity system $Mn^{2+} - Mn^{2+}$; and the host - impurity system: $Fe^{2+} - Mn^{2+}$ or $Ni^{2+} - Mn^{2+}$. We have also studied effects of lattice dynamics.

It has been concluded that the dipolar host-host and host-guest interactions broaden resonance lines of Mn^{2+} . Narrowing of the lines in both the crystals can be attributed to the host-guest exchange interactions and to the quenching of the host spins. In the $Fe^{2+} - Mn^{2+}$ system a strong narrowing of the Mn^{2+} lines observed at room temperature can be caused by fast Fe^{2+} spin-lattice relaxation. Motions of molecular groups, particularly motions of molecules H_2O , also reduce widths of the lines in EPR spectra of Mn^{2+} ions.

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METALLOPORPHYRIN (Cd, Hg) RADICALS.

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Interest in metalloporphyrins probably originated in the biological implications, but these compounds are chemically important in their own right. The complexes have a square-planar (D_{4h}) or, in some cases, squarepyramidal (C_{4v}) structures, but are unique in that the ligand is a fairly rigid cyclic tetradentate and the metal-ligand distances therefore are very much constrained. The chemically important electrons of the porphinato ligand are those belonging to the conjugated π -electron system. There are two somewhat isolated electronic systems, one belonging to the metal and the other to the ligand. In this study we have synthesized meso-tetra piperonyl phenylporphyrin and its cadmium and mercury complexes according to procedure described before [1]. EPR spectra were measured in room temperature for porphyrins in powder state. In the EPR spectrum dominates strong line around $g \approx 2.0026$ belonging to free radical with electron delocalized in chain of conjugated bonds of porphyrin ring. Remaining part of the spectrum originates from metal ion and is more complex due to hyperfine structure.

Acknowledgements.

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A PC-CONTROLLED KINETIC ESR-EXPERIMENT WITH 10 μ s TIME RESOLUTION

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ESR investigations of the kinetics of transient radicals with millisecond lifetimes are often performed with time resolved experiments, i.e. the ESR signal is recorded as a function of time after a sudden change of radical initiation. We generate the radicals photochemically interrupted by a rotating sector which also provides the triggering. The signal is taken from an output of the ESR spectrometer *EMX* with a time constant smaller than 10 μ s. It is fed into a PC with a programmable AD-Converter board with high time and bit resolution. To obtain a sufficient signal-to-noise ratio 50'000 to 500'000 traces are added coherently to the PC memory. The analysis requires baseline-free signals, hence, we apply the following PC-controlled procedure to eliminate a general off-set. Firstly, a fixed number of signal vs. time profiles, e.g. 30 traces, is taken in one block on the maximum of an ESR line ($-\frac{1}{2} \Delta H_{pp}$) and accumulated in an intermediate storage. Then, the magnetic field is changed to the minimum of the ESR line ($+\frac{1}{2} \Delta H_{pp}$). The next one or two sector periods are rejected, and during this time the data taken at $-\frac{1}{2} \Delta H_{pp}$ are dissected into the individual traces and added to the memory. Subsequently, the same number of profiles is taken at $+\frac{1}{2} \Delta H_{pp}$ and accumulated in the intermediate storage. After the next field jump to $-\frac{1}{2} \Delta H_{pp}$ these data are dissected as before but subtracted from the memory. This gives a baseline corrected profile. The loop stops after every 30 seconds, and the kinetic curve is monitored on the computer screen. Then the process is repeated until the desired quality of the data is reached. A crucial point is time-jitter. Therefore, the stability of the sector frequency is regulated by a digital frequency check system employing a *zero counter lock loop*. The detailed experimental setup and applications are presented. The PC-based concept could be a solution for other acquisition problems, since it avoids the time delays during fast repetitive data acquisition encountered with modern digital oscilloscopes and is more flexible with respect to acquisition times and the number of data points per trace. It allows to utilize at least 90% of the total measuring time.

PHASE TRANSITIONS IN DOPED SYSTEMS

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The doped crystals or crystals containing the paramagnetic host material are most frequently used for EPR investigation, as well as for laser action. On the other hand, the properties of doped crystals, e.g. phase transition temperature (T_c), are often different than the undoped crystals investigated by other methods. EPR is useful tool to study structural phase transitions because dynamic effects which are associated with the phase transitions can be detected using EPR zero-field splitting, linewidth and intensity data. The spin-Hamiltonian parameters are also very sensitive to the strength and the symmetry of the local crystalline electric field. This method requires the doping of host crystal by paramagnetic impurity ions.

The phase transition temperature could be influenced by isotope effect, by the interchanging of protons/deuterons in water molecules, by the incorporation of different impurity ions into host lattice, as well as by changing the host ions in the series of isostructural host lattices. The almost negligible isotope effect on the phase transition temperature T_c in ammonium, lithium, and rubidium sulphates shows that in these crystals the structural phase transitions are pure order-disorder of second order transitions [1]. On the other hand, the isotope effect is quite big in BaTiO_3 crystals, where T_c is 20°C higher for light isotope-enriched sample [2], contrary to the classical lattice-dynamics theory, which predict that T_c should decrease with the introduction of lighter isotope because of the larger thermal fluctuations.

The impurities play an important role (except in the case of LiCsSO_4 family of crystals) in modifying the value of T_c , as well as spreading of the phase transition over a longer temperature interval, e.g., in Mn^{2+} and Cu^{2+} -doped NH_4Br T_c is lower by 4-5 K than in pure NH_4Br . The impurities of VO^{2+} type can even removed the phase transition. Concluding, the phase transition is better to observe using similar impurity ions, the same charge and isostructural to host lattice ions, because their influence on phase transition is minimum, e.g., Gd^{3+} ion substituted for rare-earth ions.

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EPR STUDY OF Gd^{3+} IN $\text{La}_{0.9}\text{Nd}_{0.1}\text{F}_3$ SINGLE CRYSTAL

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Abstract

EPR (X-band) study of Gd^{3+} -doped (0.1 mol%) $\text{La}_{0.9}\text{Nd}_{0.1}\text{F}_3$ single crystal at liquid helium, liquid nitrogen and room temperatures has been made in order to investigate crystal field effects in $\text{La}_{0.9}\text{Nd}_{0.1}\text{F}_3$ and to estimate exchange interaction between Gd^{3+} - Nd^{3+} ions. From the angular variation of spectra in the ZX plane, the eleven spin-Hamiltonian parameters have been evaluated, using spin-Hamiltonian of rhombic symmetry C_{2v} . The fitting parameters were performed with g_z, g_x, b_l^m ; $l = 2, 4, 6$; $m = 0, 2, 4, 6$; $m \leq l$.

The sample was prepared using a modified Bridgman-Stockbarger method. The Z axis, along which the splitting of the EPR lines is maximum, lies in the cleavage plane (002) and is perpendicular to the (110) plane. The Z and Y axes are found to be coincident with the crystallographic a and c axes, respectively. The EPR spectra of the Gd^{3+} ions in $\text{La}_{0.9}\text{Nd}_{0.1}\text{F}_3$ single crystal were recorded with the external magnetic field B oriented perpendicular to the Y axis, being perpendicular to the cleavage plane (002). Thus the magnetic field B was applied in the plane (002) and rotated in the ZX plane.

The angular variations in the ZX plane at room and liquid nitrogen temperatures were found to display three maxima and minima of three centers. The six ions are found to be magnetically equivalent in pairs, so that there are three magnetically nonequivalent sites of Gd^{3+} ions in the unit cell. Thus the EPR spectra are consistent with a C_2 site symmetry for the Gd^{3+} ion in the D_{3d}^4 trigonal symmetry with a hexamolecular unit cell. At liquid helium temperature Gd^{3+} (1) center exhibit the two-fold repetition pattern about the c axis (Y axis). The other Gd^{3+} center exhibit the symmetry more close to monoclinic.

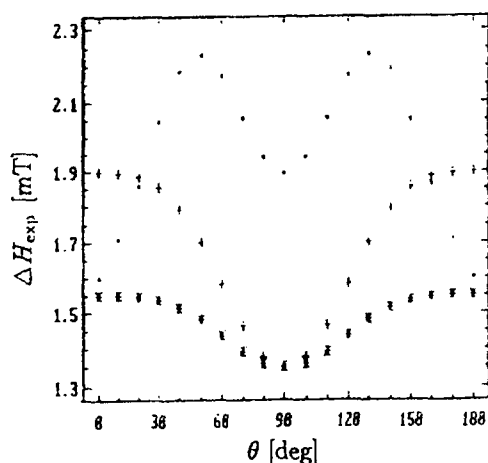
It is interesting that with decreasing temperature there is observed the symmetry distortion, when compared angular variations at room temperature and liquid nitrogen, as well as liquid helium temperatures.

EPR STUDY OF COPPER (II) DIPYRIDINE HALOGENIDE SINGLE CRYSTALS

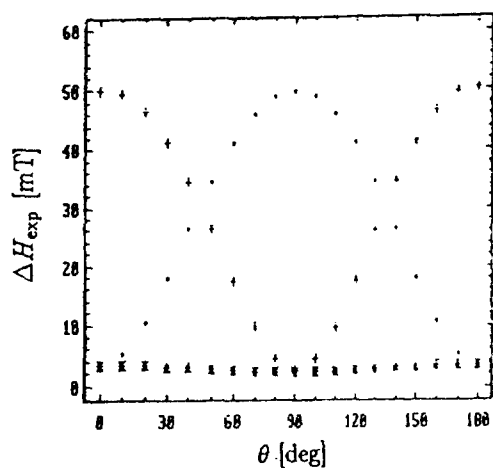
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Angular measurements of EPR spectra in the X band were performed at room temperature for single crystals of two isomorphous complex compounds $\text{Cu}(\text{py})_2\text{Cl}_2$ (CPC) and $\text{Cu}(\text{py})_2\text{Br}_2$ (CPB) of the monoclinic structure and space group $P 2_1/n$. For CPC crystal the Cu-Cu distance along the chain of molecules is 3.84 Å and between two chains 8.560 Å whereas for CPB the corresponding distances are 4.050 Å and 8.424 Å. An elementary cell contains two magnetically inequivalent Cu ions and the exchange interactions between them are so strong relative to the Zeeman energy, that two separate EPR lines fuse into a single absorption line for the microwave frequency used in the studies. For CPC the EPR line takes a lorentzian shape and its width is poorly dependent on orientation, while for CPB the EPR line is characterized by a large anisotropy of width.



The angular dependence of ΔH_{pp} [mT] taken for a CPC single crystal in the three planes : $yz\gamma$ (·), zxz (+), yxy (*).



The angular dependence of ΔH_{pp} [mT] taken for a CPB single crystal in the three planes : $yz\gamma$ (·), zxz (+), yxy (*).

The exchange interactions in CPC have a 1-D character with distinct paths of hyperexchange transmission, whereas in CPB they are isotropic. The ground state of the wave function of Cu^{2+} in both complexes studied is $d_{x^2-y^2}$ which means that this ion forms a complex of the coordination number 4 with a square planar configuration of ligands.

EFFECTS OF ULTRASOUND IRRADIATION ON THE PROPERTIES OF BIOLOGICAL HOMOGENATES

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The effects induced in biological samples by free radicals generated during short periods (≤ 5 min) of ultrasound irradiation have been investigated by following the decay kinetics of the EPR signal of the piperidine nitroxide 4-hydroxy-2,2,6,6,-tetramethylpiperidine-N-oxyl (TEMPOL) in rat heart homogenates. Different kinetic models have been evaluated in order to identify the reactions involved in nitroxide decay. The results obtained indicate that sonication, however short its duration, significantly alters components of the homogenate playing a major role in nitroxide decay, thus substantially modifying the kinetics of the process.

Furthermore, "dispersive" and "non-dispersive" kinetic models, as defined by Płonka, are compared in the different experimental conditions. The "dispersive" nature of decay kinetics is typical of situations in which reaction rates approach those of the host structural relaxation or reorganization, as reported in a number of microheterogeneous systems like micellar solution. A 2nd order "dispersive" kinetic decay has been observed in this work also with 0.1mM TEMPOL non-sonicated sample, while a normal 2nd order kinetic decay was observed after sonication of the same sample. This suggest that the the sample is no more microheterogeneous after that procedure.

A COMBINED EPR AND QUANTUM CHEMICAL APPROACH TO THE STRUCTURE OF SURFACE $F_2^+(H)$ CENTERS ON MgO

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Two types of surface colour centers can be localized on the surface of alkali-earth oxides. These are F_2^+ and F_2 centers consisting in one or two electrons respectively, which are trapped in suitable anionic vacancies at the surface (1-3). However when the oxide is irradiated by UV rays in the presence of H_2 in the gas phase, the surface F_2^+ centers are generated. These can be regarded as F_2^+ colour centers characterised by distinctive superhyperfine interaction between the trapped electron and a proton of a nearby hydroxyl group.

Most of the current knowledge of these $F_2^+(H)$ centers is based on the interpretation of the experimental data obtained years ago by Tench and coworkers (4,5).

In the present contribution a new insight in the $F_2^+(H)$ center structure is provided by means of EPR spectra simulation and theoretical calculation. New interpretations of the 1H and ^{25}Mg hyperfine structures as well as of the localisation of the centers are proposed.

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ESR STUDY AND MM⁺ CALCULUS OF SOME ASYMMETRIC-TRIAZINES COPPER(II) COMPLEXES HAVING HIGH ANTI-VIRAL ACTIVITY

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There is considerable interest in the use of synthetic Cu-complexes with low molecular weight ligands in order to serve as mimics for the Cu-proteins biological functions during the pathological period.

Recent studies have shown that a group of complexes with asymmetric-triazines ligands have high superoxide-dismutase and strong anti-viral activities [1]. Some of them have been studied by EPR spectroscopy in order to investigate the environment of the Cu ion and to correlate it with their biological activities [2].

The present paper describes the use of EPR spectroscopy as well as the molecular mechanics force-field calculations to compare the structure of the most active complex of the analysed group [complex I from ref.2] with other new ones in order to confirm the hypothesis concerning the biological active structure.

The analysis of the polycrystalline powder EPR spectra at room temperature showed the presence of monomeric Cu(II) species for all complexes and a very small concentration of dimeric species too for the new analysed complexes.

The simultaneous presence of more than one species in the fluid solution preparations was established. The structure previously assumed to be biological active for complex I is a distorted square-planar one with 6 member chelate ring and is present in complex II too, but in different concentration. The difference between the activities of these complexes can be linked to the difference in the concentration of this species. The others two complexes have a pseudo-tetrahedral structure for the first sphere of coordination around the copper which can explain the difference of activity compared with that of complex I. The EPR parameters derived from the frozen solutions spectra point out the presence of different monomeric species and some changes in the coordination polyhedra symmetry were evidenced.

Bonding parameters calculated from EPR data were used to determine the covalent character of the metal-ligand bonds, in all cases the in-plane σ bonds having a substantial degree of covalence.

The MM⁺ molecular dynamic calculus showed that there are possible more than one type of structure with 2N2O coordination environment around the copper ion for all the complexes. The square planar arrangement with 6 member chelate ring, previously assumed to be biological active is present only in complexes I and II.

Further purification is necessary in order to establish the role of all possible species in the biological activity of these compounds.

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EPR STUDY OF CONFIGURATION OF DIVALENT COPPER ION

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In this paper we analysed the values of g-factor of cupric compounds obtained by EPR measurements. EPR studies of powdered and single crystal samples of $\text{Cu}(\text{NO}_3)_2(\text{C}_4\text{H}_4\text{N}_2)$ proved that the values of g-factor the corresponding of their g-factor are similar. On the basis of this observation we suggest that the values of g-factor components can be determined from the powdered as well as single crystal samples. Two groups of compounds have been studied for which the relations between the g-factor components were $g_z > g_x, g_y$ for compounds including cyclic ligands and $g_z < g_x, g_y$ for those including linear ligands.

The values of components of the molecular g-factor for $\text{Cu}(\text{NO}_3)_2(\text{C}_4\text{H}_4\text{N}_2)$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were calculated following the method from [1]. For both compounds the relationship between the values of their g-factor components is the same: $g_z > g_x, g_y$.

Analysis of lengths of bonds formed by Cu^{2+} ion revealed that four of them are short and of covalent or ionic nature and the others are long and of weakly bonds. This results are in agreement with the VB data as Cu^{2+} ion has only four empty orbitals which can form only four bonds, [2], and have been confirmed by EPR studies. This four bonds determine the interactions between the copper ion and its ligands, hence, these four bonds specify the character of coordination of the divalent copper ion and the configuration of Cu^{2+} environment can only be tetrahedral or planar.

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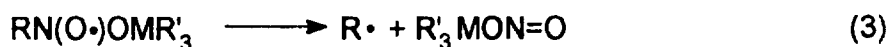
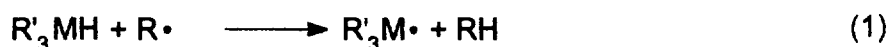
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REACTIONS OF SUBSTITUTED BORYL RADICALS WITH NITROALKANES. AN EPR STUDY.

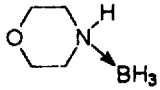
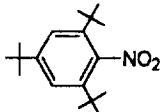
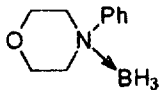
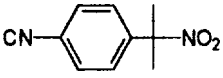
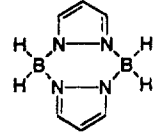
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The reduction of tertiary aliphatic nitro compounds to the corresponding alkanes using tributyltin hydride in the presence of radical initiators has been extensively used for synthetic purposes. Mechanistic studies based on spectroscopic, kinetic, and electrochemical data are consistent with a free-radical chain reaction where the key propagation steps are the addition of $\text{Bu}_3\text{Sn}\cdot$ to the nitro group and the subsequent elimination of an alkyl radical (eqs 1-3).



Cleavage at the carbon-nitrogen bond is peculiar to tin adducts of nitro compounds, since fragmentation takes place preferentially at the nitrogen-oxygen bond in the analogous adducts of carbon-centred radicals. Searching for a possible substitute of the very toxic tin hydride we have examined the possibility of using, as reducing agent of aliphatic nitro derivatives, several boranes complexed by amines or phosphines. We report here an EPR and kinetic investigation on the radical initiated reaction of boranes LBH_3 , complexed with amines and phosphines, with the nitroalkanes, RNO_2 .

	RNO_2		LBH_3
1a	MeNO_2	2a	Me_3NBH_3
1b	EtNO_2	2b	Et_3NBH_3
1c	$\text{Me}_2\text{C(H)NO}_2$	2c	Bu_3PBH_3
1d	Me_3CNO_2	2d	$\text{Me}_2(\text{H})\text{NBH}_3$
1e	$\text{CH}_3(\text{CH}_2)_5\text{NO}_2$	2e	
1f		2f	
1g		2g	

EPR CHARACTERISTICS OF METAL IONS-FUNGAL MELANIN COMPLEXES

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The important role of soil fungi melanin biopolymers in adaptation process is suggested [1]. Biological activity investigations of Karkonosze soils have shown that the metabolic activity of dark pigmented soil fungi is higher than that of light pigmented species. In the presence of pollution by metals only organisms with high melanin content survive. On the other hand domination of dark soil fungi in the regions with high metal content leads to the detoxification process.

o-Semiquinone free radicals play an important role in the interactions melanin-metal. The aim of the presented work was to examine free radical properties of melanin isolated from soil fungi of the Karkonosze Mountain, compare them with synthetic model melanins, and characterize complexes with metal ions.

EPR measurements at the X-band (9.3 GHz) were performed for synthetic DOPA-melanin, natural soil fungi melanin and for their complexes with Cd^{2+} , Pb^{2+} and As^{3+} ions. Free radical concentration in the samples, g-factor and linewidths of EPR spectra, were measured. Microwave saturation behaviour of the EPR signals were studied.

Single-line EPR spectrum and EPR spectrum with marked hyperfine splitting are characteristic for DOPA-melanin (eumelanin) and cysteinyl-dopa-melanin (pheomelanin), respectively [2]. The weak hyperfine splitting observed in the EPR spectra of fungal melanin suggests that these biopolymers contain mainly eumelanin units than pheomelanin ones. The concentrations of free radicals (10^{19} spin/g) in soil fungi melanin and its complexes with Cd^{2+} , Pb^{2+} and As^{3+} are higher than in synthetic DOPA-melanin samples. Metal ions increase the concentration of paramagnetic centers in the order: $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{As}^{3+}$. Free radicals interactions with metal ions changes the melanins EPR linewidths, but their influence on spin-lattice relaxation process was not observed. The performed EPR analysis proved that the metal ions-melanin interactions are similar in model DOPA-melanin and natural fungal pigment.

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THE EFFECT OF CHLOROQUINE ON FREE RADICAL PROPERTIES OF METAL IONS-DOPA-MELANIN COMPLEXES

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Stable paramagnetism of melanin biopolymers permit the application of electron paramagnetic resonance technique to investigate these pigments and their complexes with some small molecules (metal ions, drugs). Melanin-metal complex formation depends on the magnetic (dia- or para-) and chemical (ionic radius, valency) properties of the analyzed metal ion [1]. The ability of some drugs accumulation by melanin pigments may modify metal ion-melanin interactions [2].

The aim of this work was to compare the free radical properties of DOPA-melanin-Zn²⁺ and DOPA-melanin-Co²⁺ complexes in the presence of model drug-chloroquine.

Measurements were performed using an X-band (9.3 GHz) EPR spectrometer. EPR spectra were collected by Rapid Scan Unit, and analyzed by ELF1 and INTER programs. The microwave frequency was recorded. Free radical concentration in the samples, g-factor and linewidths of EPR spectra, were measured. The influence of microwave power on parameters of EPR signals was determined.

o-Semiquinone free radicals (10^{18} - 10^{19} spin/g) with g-factor of 2.0036-2.0042 and single broad (0.45-0.51 mT) EPR lines, occur in the studied samples. Free radical concentration in DOPA-melanin-chloroquine complexes was higher than in DOPA-melanin. Paramagnetic Co²⁺ ions reduce the free radical concentration in melanin, whereas diamagnetic Zn²⁺ ions increase the EPR signal. The EPR signals of metal ion-melanin complexes were modified in the presence of chloroquine, depending on the concentration used.

Homogeneous broadening was detected for the all measured EPR spectra. The strong influence of Co²⁺ on spin-lattice interactions of unpaired electrons in DOPA-melanin and its chloroquine complexes was observed.

The obtained results indicate that in melanin-metal ion-chloroquine complexes, besides chemical, also some magnetic interactions exist.

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MULTICOMPONENT STRUCTURE OF THE EPR SPECTRA OF BITUMINOUS COAL MODIFIED IN POTASSIUM-LIQUID AMMONIA SYSTEM

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Complex chemical structure of coal and petrographic constituents indicate multicomponent character of their EPR spectra [1]. Unpaired electrons of units consisting of a few aromatic rings are responsible for the broad lines. The dipole interactions of unpaired electrons and unresolved hyperfine structure of unpaired electrons-neighbouring protons interactions are the reasons for the broadening of these signals. Unpaired electrons of large aromatic structures, mainly delocalized π -electrons with strong exchange interactions, are responsible for narrow lines. The aim of the present work was to determine the number and behaviour of different groups of paramagnetic centers existing in medium metamorphosed coal and its reductive alkylation products.

Reduction and reductive alkylation of medium-volatile bituminous coal (85.7 wt% C, d.a.f.) were carried out using potassium in liquid ammonia, and using ethyl and butyl iodides to alkylate the resultant polyanion [2]. Multistage ethylation was carried out until a high conversion of coal organic substance to product soluble in dichloromethane was reached. The soluble products of the reductive alkylation reaction were isolated by extraction with dichloromethane.

EPR measurements were performed using an X-band spectrometer (9.3 GHz, magnetic modulation 100 kHz). The experimental spectra were approximated by different superpositions of Gauss and Lorentz lines, using a numerical algorithm given by Opfermann [3]. The parameters of the best fitted lines: linewidths and abundances of the components of the total spectrum, were evaluated.

The EPR spectrum of the studied coal is superposition of broad Gauss (0.86 mT) and two Lorentz (L1, L2) (L1: 0.22 mT, L2: 0.06 mT) lines. Percentage fractions of paramagnetic centers with Gauss and Lorentz (L1, L2) lines in the coal are: 66.5%, 28.3% and 5.2%, respectively. All the paramagnetic centers actively interact with atmospheric oxygen. Protonation and alkylation of the studied coal reduces the amount of paramagnetic centers with Gauss curve. The obtained EPR results were correlated with chemical analysis data [2].

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EPR STUDIES OF THERMAL DECOMPOSITION OF COAL SAMPLES

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Electron paramagnetic resonance (EPR) spectroscopy was used to study the evolution of the total free-radical system in heated coal and macerals [1-3]. The weak changes in concentration of paramagnetic centers in heated exinite and vitrinite were measured, whereas a strong increase above 400 °C was noticed for inertinite [1]. The influence of an increasing temperature on the number of free-radicals in coals depend on carbon content [2] and chemical treatment of the sample [3].

Several groups of paramagnetic centers belonging to different chemical structures, which give EPR lines with different values of linewidths and g-factor, exist in coal samples [4]. The aim of the present study was to determine changes in the amount and behavior of the individual groups of paramagnetic centers during thermal decomposition of macerals and complex coal samples, and check the hypothesis about independent progress of reactions in macerals during heating of coal.

Polish coal with carbon content of 85.6 wt% C, its macerals and petrographically complex samples, were studied. The coal contained 9 vol.% exinite, 77 vol.% vitrinite and 14 vol.% inertinite. The coal samples were separated by centrifugation of demineralized durain, vitrain and clarain in toluen-CCl₄ mixtures. The studied samples were heated in an inert atmosphere at 300-650 °C in 50 °C intervals.

The measurements were performed using an X-band (9.3 GHz) EPR spectrometer with magnetic modulation 100 kHz. The microwave frequency was recorded. EPR spectra were obtained with wide range of microwave power attenuation of 20.0-0.5 dB. The lineshape of the EPR spectrum was analysed using a numerical algorithm given by Opfermann [5]. The following parameters of the best-fit lines were calculated: g-factor, linewidths ΔB_{pp} and fraction of each component in the total spectrum. The concentrations of paramagnetic centers were determined.

The visible strong changes of total concentration of paramagnetic centers in all the samples above 450 °C were observed. The changes in EPR parameters confirm the important role of paramagnetic centers with the broad Gauss and broad Lorentz lines in the process of thermal decomposition of exinite and vitrinite. Heat-treatment changed the concentration of each of the two groups of paramagnetic centers in inertinite. The spin-spin and spin-lattice interactions of unpaired electrons in coal samples depend on temperature of heating. The EPR results indicate interactions between individual macerals during thermal decomposition of coal.

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Cysteamine as radical scavenger in frozen aqueous matrices containing dCMP and TMP.

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EPR spectroscopy was used for evaluation of cysteamine reactivity towards primary and secondary radicals of dCMP and TMP induced by ionizing irradiation. To investigate the influence of environment on these processes, frozen aqueous solutions and glasses of H₂O and D₂O were applied as matrices. The results indicate that at 77K for both nucleotides in frozen aqueous solutions hole transfer to cysteamine or reaction with mobile OH[•] is possible since no C1' sugar radicals characterized by a quartet and the reduced amount of TMP allyl radicals have been detected. dCMP molecules which gain an electron, after protonation, react with cysteamine depending on matrices. The TMP radical anion in frozen aqueous solution of H₂O first undergoes protonation at C6 position and then, in presence of thiol, hydrogen addition to C5 site. The use of D₂O reduces the conversion into corresponding C6-D species to only a few percent, leaving well defined radical anion spectrum. In spite of this difference, the effectiveness of the reaction between cysteamine and TMP radical anion remains high and unchanged in comparison with yield in H₂O matrix. Consequently protonation (or addition of D⁺) is not a necessary condition for transformation into sulphur center radicals or other mechanisms must be considered.

TETRAGONAL SITE OF TRANSITION METAL IONS IN CHRYSOCOLLA

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Chrysocolla is a naturally occurring mineral with general formula $\text{Cu}_2\text{H}_2\text{SiO}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$. The spectrum of a sample from the unknown origin recorded on low dispersive medium quartz spectrograph was reported [1]. The spectrum was explained as due to Cu^{2+} in tetragonal symmetry associated with spin-orbit interaction. Since the origin was not reported and the bands were also not well defined, two samples from (Katanga) Zaire and (Arizona) USA are chosen for the present spectroscopic studies.

The optical absorption spectra of the powder samples are recorded on Hitachi U-3400 spectrophotometer in the region 350-1350 nm. The EPR spectra are recorded on x-band Jeol Fe-1X ESR spectrometer. The spectra of both the samples are similar to each other. The EPR spectra exhibit the characteristic six line pattern attributable to Mn^{2+} with g-value around 2.004. The optical absorption spectra reveal three bands in the regions 1230-1275, 935-940 and 885-895 nm. One more weak band with two components is observed in the region 555-590 nm. The three bands in the longer wavelength region are characteristic of Cu^{2+} in tetragonal site symmetry and accordingly the bands are assigned to transitions from ${}^2\text{B}_1$ to ${}^2\text{A}_1$, ${}^2\text{B}_2$ and ${}^2\text{E}_2$ respectively. Since Mn^{2+} impurity is identified in EPR spectrum, the band with two components is attributed to ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$ transition of Mn^{2+} . These two components are attributed to tetragonal distortion. The tetragonal distortion of Mn^{2+} suggests that the impurity enters into the crystal by substitution of Cu^{2+} . The crystal field parameter (Dq) and tetragonal parameters (Ds, Dt) are evaluated:

Zaire sample : Dq = 1069 Ds = 1678 and Dt = 228 cm^{-1}

USA sample : Dq = 1063 Ds = 1697 and Dt = 268 cm^{-1}

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EPR AND OPTICAL ABSORPTION SPECTRAL INVESTIGATIONS ON Cr-TREMOLITE

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The natural mineral, Cr-tremolite originated from Gouverneur talk mine, Balmat, New York, USA was investigated by EPR and optical absorption spectra. Cr-tremolite has general formula $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ with greenish yellow in colour.

Polycrystalline sample was taken into the quartz tube and EPR spectrum recorded on varian E112 EPR spectrometer at room temperature. The spectrum exhibited the characteristic of Mn^{2+} impurity with g-value close to 2.0 and hyperfine splitting value $A = 92 \pm 3$ G. We could not observe any resonance line corresponding to Cr^{3+} ion in the mineral.

Optical absorption spectrum of Cr-tremolite recorded at room temperature on Hitachi U-3400 spectrophotometer in null form exhibited different absorption bands in UV-VIS region indicating trigonally distorted octahedron of Cr^{3+} ion. The following crystal field(Dq) and interelectronic repulsion(B & C) parameters evaluated are:

$$Dq = 1980, B = 740 \text{ and } C = 3060 \text{ cm}^{-1}$$

The results of EPR and optical absorption studies of Cr-tremolite revealed the presence of Cr^{3+} and Mn^{2+} impurities in the mineral that replaces one of the sites of Ca or Mg site, otherwise they may occupy interstitial site in distorted octahedron.

TIME - RESOLVED ESR-SPECTROSCOPY OF TRANSIENT RADICALS GENERATED BY LASER FLASH PHOTOLYSIS

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Recently mono- and bisacylphosphine oxides have received attention as a new commercially available type of photoinitiators for photocuring of polymer resins. This process involves short-living transient radical species impossible to observe by conventional ESR experiments. Therefore, several research groups applied faster techniques of ESR detection e.g. CW Time-Resolved ESR detection.

In this work, we applied laser flash photolysis (LFP) and time-resolved ESR spectroscopy combined with laser pulse irradiation to determine the rate constants for the addition reactions of the phosphonyl radicals (produced by photolysis of the above mentioned photoinitiators) to vinyl monomers and estimated directly the addition rate constants to monomers.

ENDOR OF HUMAN TOOTH ENAMEL HEATED AT 400°C

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Upon irradiation human tooth enamel exhibits a well-known "asymmetric EPR singlet near $g=2$ ". It has been shown recently that this EPR signal is clearly composite and mainly due to CO_2^- radical. Moreover, it was shown that heating the enamel before irradiation causes specific changes in the spectra. From the above observation it was concluded that in unheated and subsequently irradiated enamel samples, two very similar but clearly distinguishable CO_2^- paramagnetic components appear. In addition, CO_3^{3-} , CO_3^- and CO^- species are also present but in lower concentrations.

As some EPR components are different from those identified in earlier EPR and ENDOR studies on heated synthetic apatites, we started an ENDOR study on heated enamel in the field region close $g=2$, where all carbon containing radicals mentioned above, contribute to the EPR spectrum. In the temperature range 4-30 K strong ENDOR signals due to ^{23}Na , ^{19}F , ^{31}P and ^1H were detected. Only the ^1H and ^{31}P signals show substructure while their anisotropy is surprisingly weak. Therefore, it was immediately checked whether the ENDOR resonances are not due to an O^- centre, which is more anisotropic and was thoroughly studied in synthetic apatites ($g_{\perp}=2.063$, $g_{\parallel}=2.001$). Indeed, there is an excellent agreement between the ^{31}P ENDOR resonances in enamel and the ones due to O^- in synthetic apatites; the agreement between the ^1H lines can also be called striking. It is concluded that an O^- ion in the same crystallographic environment is present both in enamel and synthetic apatites. Minor differences in the O^- EPR and ENDOR spectra and the absence of ENDOR from carbon containing radicals will be discussed.

EPR Investigation of the Activation of N₂O on Mo/SiO₂ Catalysts

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EPR spectroscopy supported by computer analysis and simulation of the spectra has been used to monitor changes occurring at the molecular level upon adsorption of N₂O on grafted Mo/SiO₂ catalysts using naturally abundant and ⁹⁵Mo-enriched molybdenum.

The tetracoordinated Mo_{4c}⁵⁺ surface species produced upon reduction with d_{x²-y²} SOMO coordinates N₂O at 298 K and rearranges into a pentacoordinated complex of apparent C_{4v} symmetry with d_{xy} ground state indicating attachment of the N₂O ligand in equatorial position. Upon temperature induced metal to ligand electron transfer (MLET) between 3π* and d_{xy} redox orbitals, O⁻ radicals are produced with an activation energy of 20 ± 4 kJ/mol measured in the 323-393 K range. The mechanism of this process and the hindrance to electron transfer is discussed in terms of intrinsic barriers and within the framework of potential energy surfaces.

The EPR spectra were analyzed taking into account the noncoincidence of the principal axes of g and ⁹⁵Mo superhyperfine tensors. From the spin Hamiltonian parameters of O, the unpaired electron density on molybdenum and the splitting of energy levels of O species were calculated to be 4.3% and ΔE_{x,y-z} = 1.5 eV respectively. The crystal field approach was used to discuss the O⁻-Mo⁶⁺ bonding.

EPR DETECTION OF IRRADIATED MUSHROOMS AND CONDIMENTS

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Epr spectroscopy is successfully used for the detection of irradiated bone containing meats, fish, dried fruits, nuts, strawberries. The epr methods on the detection of irradiated foods containing bone and cellulose are actually used for professional control the foodstuffs in several countries and will become European Standards probably this year (1996).

Recently it has been proved by us that epr technique can be also useful for the detection of irradiated mushrooms (*Agaricus biosporus*, *Boletius badius*), flavour additives used in food industry and some condiments. Samples of investigated products were irradiated with gamma rays and 10 MeV electron beams (EB) with doses as recommended for given group of food by ICGFI. The epr signals observed with the above mentioned products around $g = 2,000$ several days, weeks and months after their exposure to ionizing radiation are specific (multicomponent spectra) and stable enough to be the reliable proof of irradiation. The kinetic study as done with irradiated mushrooms has shown that epr signals observed at different time intervals are very different. Spectral analysis of a complex signal in mushrooms proved the appearance of two paramagnetic species: (1) a strong but less stable singlet and (2) a middle strong while stable multicomponent signal. The latter can be successfully used for the detection of irradiation. The signals observed with flavour additives can be probably assigned to radicals derived from irradiated sugars; they exhibit in epr a complex characteristic hyperfine structure. The epr signal observed with irradiated gelatin is a doublet and resembles the signals registered by us earlier with degassed bone samples exposed to radiation (bone contains collagen which is the basis for the production of gelatin). The epr signals recorded with unirradiated products are weak single lines which do not interfere the detection of irradiation.

ESR ANALYSIS OF MICROCRYSTALLINE L- α -ALANINE AND STANDARD BONE POWDER IRRADIATED WITH Co-59 ION BEAM

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Microcrystalline L- α -alanine and standard bovine bone powder were irradiated with intermediate energy ion beams from 4-metre U-400 cyclotron (JINR, Dubna, Russia) and analyzed on ESP-300 Bruker spectrometer at X-band. Because of vertical direction of the ion beam, the samples could be irradiated in air, in ambient conditions and without any binders and additives. The main experiments were done using 3.4 MeV/amu Co-59 ions (LET in alanine 5500 eV/nm). The bone powder was not deproteinized and because of that it was measured only after a decay of unstable, organic radicals.

The shape of EPR-signals generated by cobalt ions in bone powder was identical to gamma irradiated samples. Any decay was observed in the time period 16 - 150 days after irradiation. In the case of L- α -alanine the situation was more complicated. We observed the characteristic quintet, well known from gamma radiolysis, to change, especially on its borders. The changes were observed even for very low total fluences, when each latent track had to be treated as a separate entity and it is concluded that they are connected with tracks phenomena. Thus, the shape of outer lines of the alanine ESR spectrum allows one to distinguish quickly between

For low fluences (up to $\sim 3 \times 10^{10}$ ions/cm²) the concentration of paramagnetic centers in both media increased linearly. G-value of paramagnetic centers calculated from linear part of the dose-effect curve was found to be 1.1 ± 0.3 for L- α -alanine and 0.008 ± 0.002 for bone powder. It gives the relative effectiveness in comparison to gamma irradiated samples of 0.28 for alanine and 0.1 for bone powder. For the fluences higher than 1×10^{11} ions/cm² (mean dose about 600 kGy) the colour of irradiated samples changed from white to yellow. Simultaneously the G-value of paramagnetic centers decreased in both materials to about half of the initial value and the saturation of dose-response curves appeared.

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KINETIC BEHAVIOR OF PHOTOPRODUCED RADICAL-CATIONS IN ANIONIC MICELLES

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Radical cations produced by monophotonic UV ionization of N,N,N',N'-tetramethylbenzidine (TMB) in dilute solutions of sodium dodecylsulfate (SDS) micelles are stable for a few hours at ambient temperature. Kinetics of their decay was examined by ESR in the 1980s [1-4], and described by the pseudo first order kinetic equation with the time-dependent rate coefficient

$$k(t) = Bt^{\alpha-1}$$

where B and α ($0 < \alpha < 1$) are parameters, the latter related to the distribution width of reactant lifetimes. It was suggested that the rate determining step is an internal cooperative process involving interactions of $\text{TMB}^{+\cdot}$ with the hydrophobic surfactant chains, which enable the radical cation to reach the configuration needed for subsequent disproportionation. The effective lifetime of $\text{TMB}^{+\cdot}$

$$\tau_0 = (\alpha / B)^{1/\alpha}$$

was correlated with the strength of the radical cation interaction with water molecules, determined from electron spin echo modulation (ESEM) [5].

In this work the ESR studies are extended for a wide range of SDS concentration, in which spherical micelles grow in size and then transform into cylindrical aggregates. We have found that these structural changes lead to a slower decay of $\text{TMB}^{+\cdot}$ and a markedly wider distribution of its lifetime (lower α values). According to the previous interpretation of the kinetic parameters, such behavior reflects tighter molecular packing in the hydrophobic micellar core and lower hydration of the interface region in the case of larger aggregates. $\text{TMB}^{+\cdot}$ may be considered as a promising ESR probe of the structure of micelles.

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EPR AS A TOOL FOR STUDYING SLAGS AND SLAG - LIKE SYSTEMS

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Some results of investigations on possibility of application of the EPR method for studying some properties of steelwork slags or sintering processes involving some slag components are presented. Comparative experimental studies have been carried out at X-band (9.4 GHz) both with industrial slags and synthetic slag-like systems obtained through sintering mixtures of pure reagents of the Ca - Al₂O₃ - Fe₂O₃ phase diagram. Tests on evolutions of EPR spectra during sintering processes have also been done, including sintering raw mixtures currently used in cement industry. EPR spectra of Mn²⁺ ions, which have been observed quite resolved in nearly all studied samples, have been established very useful for studying kinetics of sintering processes in systems involving the slags and components of the CaO - Al₂O₃ - SiO₂ diagram.

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STABILIZATION OF POLYMER RADICALS IN AQUEOUS SOLUTION BY ELECTROSTATIC REPULSIVE FORCES

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Simple alkyl radicals, when generated at room temperature in deoxygenated aqueous solutions, if they are not stabilized by the presence of aromatic, allyl etc. structures, are highly reactive and disappear within a fraction of second. This necessitates the use of pulse methods with time-resolved EPR detection or spin trapping techniques to investigate these species. If the radicals are localized at charged molecules, like carboxylic acid anions, their mutual reactions are slowed down by the action of coulombic repulsive forces between the ions of the same sign. For low-molecular-weight compounds this may result in the prolongation of radical lifetime by approximately an order of magnitude (depending on the charge) [1,2], so even the radicals on small charged molecules are relatively unstable.

This seems to be no longer true for the radicals generated on the chains of hydrophilic, charged polymers in aqueous solution. It has been shown by Görlich and Schnabel [3], that incorporating a low fraction of charged monomer units into the chain of a non-ionic, water-soluble polymer, causes pronounced decrease in the rate constant of bi-radical termination reactions. A fully charged polyelectrolyte, poly(styrene sulfonate), was tested with this respect by Behar and Rabani [4], who reported a very stable radical intermediate ($t_{1/2} \approx 3.5$ h). This effect was, however, interpreted in the terms of stabilizing influence of aromatic rings.

In our studies on an aliphatic synthetic polyelectrolyte, poly(acrylic acid) - PAA, we found that the presence of stabilizing substituents is not necessary to obtain long-living radicals. Macroradicals of fully ionized PAA, when generated by γ - or electron-irradiation in dilute, deoxygenated aqueous solution at room temperature, have a lifetime of *ca.* 80 min. (for the radiation dose of 100 Gy). This corresponds to the recombination rate constant of *ca.* $5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Stability of these macroradicals is, as expected, strongly influenced by the charge density on the chain. In acidic solutions, when the carboxylic groups of PAA are fully protonated, radical lifetime falls to the range of milliseconds. Thus we suggest, that the main factor causing the high stability of radicals localized on charged macromolecules are the repulsive electrostatic forces between the chains, that prevent the approach of the radicals into the reaction distance. In our study we report and discuss also the results on the stability of PAA peroxy radicals.

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NUMERICAL METHODS IN RESONANCE LINE SHAPE ANALYSIS

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When an EPR spectrum given in the form of the first derivative of absorption consists of a single symmetric line, the investigation of the existing interactions between paramagnetic centres can be carried out by an analysis of the width and the form of the resonance curve. In the case of solids, when the dipolar and exchange interactions are present, the EPR profile is known to consist of the Lorentzian centre part and the wings of Gaussian form. Until now the method of linear anamorphosis proposed by Tikhomirova and Voevodskii [1] was used for analysis of the shape of an EPR line narrowed by exchange interaction. A method for fitting an EPR line by linearization is presented.

With the aim to apply numerical methods for EPR line shape analysis, one can describe the most often used line shape functions in the form: $y = a/(1 + bx^2)$ for Lorentz line, and $y = a \exp(-bx^2)$ for Gauss line, where y - absorption ordinate, x - magnetic field abscissa, a - amplitude of absorption, b - parameter proportional to the reciprocal of the square of linewidth.

In the coordinate systems:

$$\begin{aligned} Y &= y'/y^2, & X &= x, \\ Y &= y'/y, & X &= xy^2, \\ Y &= y', & X &= xy^2, \\ Y &= (y''/y' - 1/x)^2/y', & X &= x, \end{aligned}$$

the Lorentz function gives a straight line, and the Gauss function gives a curve.

In the coordinate systems:

$$\begin{aligned} Y &= y'/y, & X &= x, \\ Y &= y', & X &= xy^2, \\ Y &= y'y, & X &= xy^2, \\ Y &= (y''/y' - 1/x), & X &= x, \end{aligned}$$

the Gauss function gives a straight line, and the Lorentz function gives a curve.

For carrying out the linear anamorphosis, an integration or a differentiation of the first derivative spectrum is needed. For differentiation of the spectrum in the presence of noise a simple method of differentiation with simultaneous smoothing can be applied [2-3]. This method is also effective for resolution enhancement by numerical narrowing [4].

The exchange-narrowed line shape function for the computer-assisted fitting can be approximated by the following formula:

$$f(x) = (2\pi)^{-1/2} \left[\omega_e^2 (\omega_e^2 + x^2)^{-1} \left[(\pi/2)\sigma^2/\omega_e^2 + x^2/\sigma^2 \right]^{-1} (1/\omega_e) \exp(\sigma^2/\omega_e^2) + \right. \\ \left. + x^2 (\omega_e^2 + x^2)^{-1} (1/\sigma) \exp(-x^2/2\sigma^2) \right],$$

where σ - linewidth of the Gauss curve, ω_e - exchange field.

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ELECTRON PARAMAGNETIC RESONANCE STUDIES OF PROTEINS IN OZONE TREATED ERYTHROCYTE MEMBRANES

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The sulfhydryl group specific spin labels have been used to study the membrane proteins in the bovine and human erythrocyte membranes treated with ozone (0.5-3.0 % by weight in ozone/oxygen mixture). The ratio h_w/h_s , determined from the respective peak amplitudes of the resulting EPR spectra of 5-MSL bound to the ozone treated membranes, was shown to be elevated following an increased ozone concentration. The ratio of the central to high-field peak amplitude h_0/h_{-1} , a measure of the rotational correlation time, determined from EPR spectra of ozonized membranes covalently labeled with 5-IASL was shown to be diminished. These changes in the erythrocyte membranes treated with ozone, observed for both spin labels, indicate a dose dependent increase in the mobility of membrane proteins. Our preliminary study of the membrane lipid fluidity carrying out by means of spin labels incorporated into lipid bilayer (16 DSA and 5DSA) indicate much smaller changes in the lipid phase of the ozonized membranes compared to those showed by sulfhydryl spin labels. This fact seems to confirm the thesis, that in the reaction of ozone with cell membrane the proteins play a significant role and it also suggests that the changes in the physical state of proteins are likely not due to secondary effects of alterations in the physical state of membrane lipids.

ESR STUDY ON MOLECULAR DYNAMICS OF NO₂ ADSORBED ON CATION-EXCHANGED MORDENITES

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NO₂, one of the rare stable paramagnetic gaseous molecules, can be used as a spin-probe to study molecular dynamics of molecules adsorbed on porous solid surfaces by ESR spectroscopy[1,2] Recently, we have demonstrated that the main dynamic process of NO₂ adsorbed on Na-mordenite (Na-MOR) is Heisenberg type of spin exchange [3]. The present study was aimed to elucidate effects on water adsorbed and cations exchanged for molecular dynamics of NO₂ adsorbed on mordenites.

The cation (H⁺, Li⁺, Na⁺, K⁺, Cs⁺, Ca²⁺, Sr²⁺, and Ba²⁺)-exchanged mordenites were prepared and subjected to the study. After keeping the zeolites in a certain amount of gaseous NO₂ at room temperature for 24 h, the ESR spectra were recorded in the temperature range from 77K to 200K with a Bruker ESP300E spectrometer.

First, heat-treatment effects of Na-MOR on the motional dynamics of NO₂ were studied. The ESR spectral line shapes were found to strongly depend on both measurement temperature and heat-treatment temperature of the zeolites. The observed ESR spectra were rather well simulated by the theoretical ones using the Heisenberg spin exchange model [4]. The spin exchange rates decreased with increasing heat-treatment temperature up to 473 K, and then became constant: for example, the exchange rates obtained at 273, 423, and 473-773 K of heat-treatment temperature were 300×10^6 , 250×10^6 , and $200 \times 10^6 \text{ s}^{-1}$, respectively (measurement temperature, 200 K). Thermogravimetric analysis suggests that the larger rates at lower heat-treatment temperature are due to waters adsorbed on Na-MOR.

Second, the cation effects on the molecular dynamics of NO₂ in mordenite were investigated. The spin exchange rates were found to decrease gradually with increasing ionic radius: for example the rates of H-, Na-, and Cs-MOR were 250×10^6 , 140×10^6 , and $125 \times 10^6 \text{ s}^{-1}$, respectively (measurement temperature, 160 K). The rates could be predominately caused by molecular collisions at which the unpaired electrons of two NO₂ molecules exchange their spin states, then the cations with larger ionic radius in the zeolite cavity are explained to give the lower collision frequencies because of higher steric hindrance.

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**Electron Spin Resonance and Electron Spin Echo Modulation Spectroscopic
Analysis of Cupric Ion Species in Cu(II)-Exchanged K-Offretite
Gallosilicate and Cu(II)-Exchanged K-Offretite Aluminosilicate**

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Abstract

Gallium and aluminum analogs of offretite were synthesized and Cu(II) was exchanged into them. The location of Cu(II) and its interaction with deuterated adsorbates in Cu(II)-exchanged gallosilicate with the offretite channel-type structure were investigated by electron spin resonance (ESR) and electron spin echo modulation (ESEM) spectroscopies, and compared with those in Cu(II)-exchanged offretite aluminosilicate zeolite. Similar results are observed for both CuK-offretite gallosilicate and CuK-offretite aluminosilicate. It is suggested that in the fresh hydrated sample Cu(II) is in the main channel coordinated to three water molecules and three framework oxygens in a six-ring window of an ϵ -cage to form distorted octahedral coordination. Upon evacuation at increasing temperature Cu(II) ion selectively moves from the main channel through an ϵ -cage to a hexagonal prism. The changes of ESR profile during evacuation in CuK-offretite gallosilicate are similar to those in CuK-offretite aluminosilicate. However, it appears that water in Cu(II)-exchanged K-offretite gallosilicate is more easily removed than in Cu(II)-exchanged K-offretite aluminosilicate. This may be verified by the temperature at which no further change of the ESR signal is observed during evacuation, which may indicate the point of complete dehydration. This is about 350 °C or higher for CuK-offretite aluminosilicate and about 200 °C for CuK-offretite gallosilicate. Dehydration produces one Cu(II) species located in recessed sites in the gallosilicate while two different Cu(II) species in the aluminosilicate, both located in recesses sites based on a lack of broadening of their ESR lines by oxygen. The ESR parameters of Cu(II) species which is predominant in dehydrated sample are rather different from each other in aluminum and gallium analogs of CuK-offretite ($g_{\parallel} = 2.366$, $A_{\parallel} = 137 \times 10^{-4} \text{ cm}^{-1}$ and $g_{\parallel} = 2.335$, $A_{\parallel} = 156 \times 10^{-4} \text{ cm}^{-1}$, respectively). Adsorption of polar molecules such as water, alcohols, dimethyl sulfoxide and ammonia causes changes in the ESR spectrum of the Cu(II) indicating migration into cation positions in the main channels where adsorbate coordination can occur in both gallosilicate and aluminosilicate. However, nonpolar ethylene doesn't cause migration of Cu(II). No interaction of Cu(II) was observed with benzene and pyridine due to their bulky size. Cu(II) forms complexes with two molecules of methanol, ethanol and propanol, and one molecule of dimethyl sulfoxide based on ESEM data. Cu(II) is suggested to form a trigonal bipyramidal complex with two ammonias in axial positions and three framework oxygens in a six-ring window of an ϵ -cage based on ESR parameters and ESEM data.

Optical properties of the anion radical derived from α -alanine by deamination

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The anion radical $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ derived during high energy irradiation from α -alanine by deamination, has been investigated mainly by EPR, on irradiated single crystals for basic research or on completely randomized polycrystalline material for dosimetric purposes. The average EPR spectrum, measured qualitatively "peak to peak" became a standard method for γ -processing dosimetry. Alanine crystals in thin layers, necessary for EB dosimetry, cannot be fully randomized to yield characteristic average standard EPR spectrum. Therefore the search for other methods of the radical measurement started. It has been shown that the anion radical shows well defined absorption spectrum with the maximum at 350 nm. The absorption does not depend on the orientation of alanine crystals in the layer of polymer matrix. The same optical spectrum has been obtained from the same radical, but produced in aqueous solution by pulse radiolysis. The molar extinction coefficient (ϵ) of the anion radical in the single crystal of irradiated alanine is identical with the ϵ of the radical in the solution. The time of life of the radical is different in the solid and liquid states, but it does not influence the identity of that species.

Conclusions: The free anion radical $\text{CH}_3\dot{\text{C}}\text{HCOO}^-$ formed by radiation induced deamination, inside of crystals of α -alanine absorbs light with $\lambda_{\text{max}} = 350 \text{ nm}$ and $\epsilon = 1100 \text{ M}^{-1} \text{ cm}^{-1}$ (probably by $\pi \rightarrow \pi^*$) and shows a shoulder starting at 270 nm towards deep UV (probably by $\sigma \rightarrow \sigma^*$). The same spectrum is shown by single crystals, as well as by randomized array of polycrystalline material. The spectrum and the oscillator strength is not influenced by the orientation of crystals in the sample, and thus is preferred for thin layer dosimetry in electron beam processing. The same anion radical is observed by pulse radiolysis in aqueous solutions by Cl-abstraction from the α -chloropropionic anion or H-abstraction from the α -alanine anion. The molar extinction coefficient (900) is the same (in the confidence limits) as in the case of solid state matrix of the radical. The similarity of properties indicates the absence of hydration phenomena, and the radical seems to be as naked as in the solid matrix.

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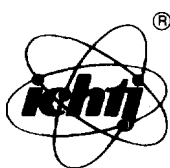
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