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Book of Abstracts

Workshop
Dynamics in Soft Matter Probed by Advanced EPR Techniques

Lužnica, near Zagreb, Croatia

5 - 9 May 2014

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Content

Foreword

Dear participants,

On behalf of the Organizing Committee, I have the honor of welcoming you to the workshop Dynamics in Soft Matter Probed by Advanced EPR Techniques.

This workshop is organized in the framework of Alexander von Humboldt Research Group Linkage Programme entitled *The study of soft condensed matter by EPR: dynamics in glassy and crystalline matrices.* The project (2011 – 2014) established the scientific collaboration between Max-Planck-Institut für Chemische Energiekonversion, Mülheim an der Ruhr, Germany (Prof. Dr. Dr. h. c. Wolfgang Lubitz) and Ruđer Bošković Institute, Zagreb, Croatia (Prof. Dr. Marina Ilakovac Kveder).

The main subject of the workshop focuses on relaxation and diffusion processes in soft materials such as biomaterials, supercooled liquids, glasses, polymernanocomposites. The topic involves broad range of length and time scales, which are addressed in the context of application of various advanced electron paramagnetic resonance (EPR) spectroscopic techniques. Although the systems under investigation are widely different, the impact of disorder/frustration/confinement on their fundamental properties is often found to be similar. In this respect the EPR provides an insight into the microscopic picture of the local degrees of freedom of the sites where the spin system is confined. The information about the local frustration of the environment is reflected in the energy exchange between the spin system and the lattice and in the energy exchange within the spin system itself. Since EPR uses the local probe – spin system, this aspect deserves attention in the light of emerging theoretical descriptions of dynamics of amorphous/glassy systems in terms of quasilocalised modes in which the EPR sensitivity to relaxation processes fits the experimental time window ranging from nanoseconds to (milli)seconds.

The workshop aims to bring together investigators who are at the cutting edge of their field while provides opportunities for junior scientists and graduate students to present their work as well as exchange ideas with leaders in the field.

We wish all participants a successful and pleasent meeting in Lužnica and Zagreb.

Marina Ilakovac Kveder

Chairman of the Workshop

Time	Monday 5th	Tuesday 6th	Wednesday 7th	Thursday 8th	Friday 9th
9:00		Registration			Departure
9:30		Opening	Plenary Lecture Matvey Fedin	Plenary Lecture Dariush Hinderberger	
10:00		Plenary Lecture Klaus Möbius	Communications Dijana Žilić Mirta Herak	Communication Damjan Pelc	
10:30		Coffee Break	Coffee Break	Coffee Break	
11:00		Plenary Lecture Dino Leporini	Plenary Lecture Yannis Sanakis	Plenary Lecture Edward Reijerse	
11:30				Communication Srećko Valić	
12:00		Communications Dalibor Merunka Iva Šarić	Communication Boris Rakvin	Group photo	
12:30					
13:00		Lunch	Lunch	Lunch	
14:00			Excursion to Zagreb 14.30		
15:00		Communication Marina Kveder		Plenary Lecture Günter Grampp	
15:30		Plenary Lecture Semion Saikin		Communications Kenneth Rasmussen Nadica Maltar Strmečki	
16:00	Arrival and Registration	Coffee Break		Coffee Break	
16:30		Guided tour of Lužnica manor			
17:00				Free time for discussions	
17:30					
18:00					
18:30					
19:00		Get together Dinner	Dinner	Farewell Dinner	
20:00					
21:00					

Abstracts

Plenary Lectures (PL) and Communications (C) in alphabetical order of authors.

DYNAMICS IN FLEXIBLE METAL-ORGANIC POLYMERS STUDIED BY EPR

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Metal-organic polymers and frameworks are actively investigated with numerous potential applications in materials science, gas separation and storage, catalysis etc. being targeted. Flexible structures, switchable by external stimuli, are of special interest, because, in particular, they can act as sensors, display or data processing units. Among other techniques, EPR plays important role in studies of paramagnetic metal-organic polymers and frameworks. This report overviews recent studies of structural and spin dynamics in two types of flexible materials based on metal-organic polymers.

The first one, copper-nitroxide based molecular magnets $Cu(hfac)_2L^R$, represents an interesting type of thermo- and photo-switchable materials which exhibit reversible magneto-structural rearrangements with significant changes of the unit cell volume. The unusual type of magnetic switching between weakly- and strongly exchange-coupled states (WS/SS) occurs in spin triads nitroxide-copper(II)-nitroxide. We overview experimental approaches developed for these systems, discuss general trends and characteristics of thermally/light-induced spin state switching and relaxation using continuous wave (CW) and time-resolved (TR) EPR. Dynamic mixing (exchange) processes between multiplets of spin triad can be efficiently studied using multifrequency CW EPR [1]; when these processes are fast enough, simulation of temperature-dependent EPR spectra allows evaluation of temperature-dependent exchange interaction in spin triads. Weaker inter-cluster exchange interactions occurring between spin triads of neighboring polymer chains can also be obtained and studied using orientation dependence of EPR spectra [2]. Finally, structural relaxation from photoinduced WS state to the ground SS state and electron relaxation between spin multiplets of photoinduced WS state can be studied in photoswitching experiments using CW and TR EPR, respectively [3].

The second type of flexible polymeric structures addressed in this work refers to the metal-organic frameworks (MOFs) and is exemplified by MIL-53(Al), which undergoes reversible temperature-induced structural transition between large-pore and narrow-pore crystalline states with a significant hysteresis. Although this MOF is not paramagnetic, we use adsorbed guest molecules of stable nitroxide (TEMPO) as reporters for an EPR study of occurring dynamic behavior in MIL-53(Al). We have found that the mobility of nitroxides in nanochannels of MIL-53(Al) strongly depends on both temperature and crystalline state of the MOF. In addition, guest-host interactions of TEMPO with OH groups of the framework leading to a formation of diamagnetic TEMPOH in narrow pores have been investigated. The "breathing" mode of MIL-53(Al) is suppressed at high concentrations of guest molecules, therefore application of many analytical methods in this mode is impossible. High sensitivity of EPR in conjunction with low concentrations of spin probes makes it an indispensable tool for study of guest-host interactions in MIL-53(Al) and other structurally flexible MOFs [4].

This work was supported by RFBR (14-03-00224) and RF President grant (MD-276.2014.3).

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DYNAMIC ESR-SPECTROSCOPY IN IONIC LIQUIDS: A NEW CLASS OF SOLVENTS

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Ionic liquids are molten salts of mainly organic cations and inorganic or organic anions, liquid at room temperature [1]. They are of interest, not only from scientific point of view but also for chemical industrial productions. Environmental friendly industrial productions based on so-called “Green Chemistry” principles mainly use ionic liquids as solvent to avoid classical toxic organic solvents. The ionic liquid structures, consisting of cations and anions, are completely different from classical organic bulk solvents. But only a few reports exist on ESR-spectroscopic investigations using ionic liquids as solvents.

a) Rotational correlation times τ_{rot}

The temperature dependence of the rotational correlation times, τ_{rot}, of TEMPO, TEMPOL, TEMPAMINE and Fremy’s salt in different ionic liquids is scrutinized. τ_{rot} vary between 54 and 1470 ps at 300K. Within a temperature range of 280-380K, the rotational tumbling is well described by the extended Debye-Stokes-Einstein law. The hydrodynamic radii are smaller than the geometrical radii though. This can partly be accounted for by micro-viscosity effects and deviations from the spherical shape. Our study includes the experimentally resolved proton **super-hyperfine** coupling constants of all nitroxides used. As a consequence, many rotational correlation times reported here are smaller than those found previously. Furthermore the temperature dependence of the nitrogen coupling constants is reported and discussed [2].

Also the kinetics of the inter-molecular spin-spin (Heisenberg) exchange is reported in various ionic liquids [3]. Line shape contributions from Heisenberg-exchange and from electron-electron dipole interactions can be separated based on their distinct temperature dependences.

b) High pressure ESR-results

We shortly report on the pressure dependence of the spin-spin exchange kinetics in various ionic liquids. The experimental activation volumes, $\Delta V^{\#}$, can be explained by the pressure dependence of the ionic liquids viscosities [4,5].

c) Electron-self exchange of the methylviologene redox couple ($MV^{++}/MV^{+\bullet}$)

From ESR-linebroadening experiments rate constants corrected for diffusion vary between $8.2 \text{ x}10^7$ $M^{-1}s^{-1}$ and $1.2\text{x}10^9$ $M^{-1}s^{-1}$, depending on the ionic liquid used [6]. The activation energies range from $\Delta G^* = 27.4 – 42.1$ kJ/mol. These results will be compared with those obtained in different common organic solvents [7]. For the solvent dependent outer-sphere reorganization energy in the sense of Marcus-Theory, there appear some differences.

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MAGNETIC ANISOTROPY OF SPIN TETRAMER SYSTEM $SeCuO_3$ STUDIED BY TORQUE MAGNETOMETRY AND ESR SPECTROSCOPY

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Low – dimensional spin systems present a fertile ground for study of magnetism. Their relatively simple magnetic lattices are ideal for analytical and numerical theoretical investigations. At the same time such systems can be found in real materials thus enabling a comparison of experimental study with theory. Of special interest are spin $S = 1/2$ systems in which the interactions of spins are usually well described by isotropic Heisenberg Hamiltonian and the magnetic anisotropy mostly comes from the *g* factor anisotropy. Presence of small anisotropic exchange interaction can have a profound influence on the ground state and low-energy excitations of these systems.

We present an experimental study of macroscopic and microscopic magnetic anisotropy of a novel low-dimensional spin S=1/2 system $SeCuO_3$ using uncommon experimental approach of combining torque magnetometry and ESR spectroscopy.[1] It was proposed recently that magnetic lattice of $SeCuO_3$ consists of isolated spin tetramers[2] (Fig.1). However, theoretical model[3] failed to describe the measured magnetic susceptibility, and strong temperature dependence of *g* factor and rotation of macroscopic magnetic axes were also reported.[2] We performed detailed measurements of the temperature dependence of ESR spectra which enabled us to compare the rotation of the **g** tensor with the rotation of macroscopic magnetic axes obtained from torque. Rotation of **g** tensor can account for rotation of magnetic axes only below below $T \approx$ 50K (Fig. 2). Temperature dependence of magnetic susceptibility anisotropy we obtain from torque points out importance of including anisotropic exchange interaction in the spin Hamiltonian of $SeCuO_3$, which is corroborated by our ESR linewidth analysis. Our results show that existing theory is insufficient to explain the effects observed in this system and call for further theoretical and experimental investigations of low-dimensional spin systems.

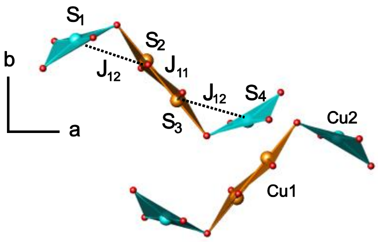

Fig. 1

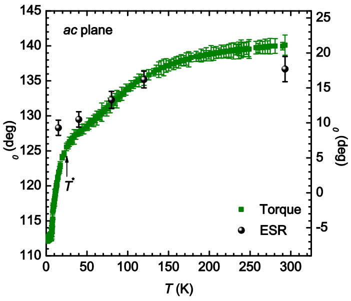

Fig. 2

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APPLICATIONS OF DOUBLE ELECTRON-ELECTRON RESONANCE (DEER) SPECTROSCOPY ON COMPLEX SOFT MATTER SYSTEMS

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An overview of current developments for applications of double electron-electron resonance (DEER) spectroscopy on complex soft matter systems is presented. The examples reach from elucidating self-assembly of intrinsically disordered proteins [1], via characterization of size and shape of charged dendronized polymers in solutions [2, 3] all the way to distirbutions of fatty acids taken up by albumin in solution [4]. These applications all have in common very broad distributions of electron spins and often complex background functions such that the broad radical distribution does not lead to clearly observable dipolar modulations on the DEER time traces, which demands more complex approaches for the respective analyses. Going beyond specific systems, we have furthermore derived analytical pair distribution functions of particles (either identical or distinguished) distributed homogeneously in/on cylinders or any spherical object, including onion-like shell structures [5].
Taking all these examples together it becomes clear that DEER offers a unique approach for the study of soft matter.

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MOLECULAR DYNAMICS OF SYSTEMS WITH LATTICE DISORDER PROBED BY LOW-TEMPERATURE EPR

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Systems exhibiting geometrical frustration are ubiquitous in nature ranging from proteins to volcanic glasses. They challenge contemporary condensed-matter physics both in terms of experimental and theoretical aspects due to the fact that they exhibit strange dynamical properties, which deviate from the standard Debye model predictions developed for crystalline solids. Here we present the study of local disorder in terms of energy exchange within the electron spin system and between the electron spin system and the lattice applying electron paramagnetic resonance spectroscopy (EPR) at *X*- and *W*- band frequencies. We focus on the relaxation behavior of paramagnetic centers embedded in the material prepared in the glassy or crystalline state. The specific molecular dynamics due to the local frustration of the environment is compared and the role of spectral diffusion in decoherence of electron spins discussed.

ELECTRON SPIN RESONANCE STUDIES OF SUPERCOOLED WATER

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Using electron spin resonance spectroscopy (ESR), we measure the rotational mobility of probe molecules highly diluted in interstitial supercooled water of polycrystalline ice [1-3]. By changing the thermal history, both weak [1] and strong [2] confinement of the liquid fraction by the ice crystals is studied.

If the confinement is weak, the mobility increases above the glass transition temperature of water, Tg ~ 136 K, and smoothly connects to the thermodynamically stable region by traversing the so called ''*no man's land*'' (the range 150–235 K), where it is believed that the homogeneous nucleation of ice suppresses the liquid water [1]. Two coexisting fractions of the probe molecules are evidenced. The two fractions exhibit different mobility and fragility; the slower one is thermally activated (low fragility) and is larger at low temperatures below a fragile-to-strong dynamic cross-over at ~225 K. The reorientation of the probe molecules decouples from the viscosity below ~225 K, like the translational diffusion of water [4]. The findings are consistent with key issues concerning both the statics and the dynamics of supercooled water, namely the large structural fluctuations [5] and the fragile-to-strong dynamic cross-over at ~228 K [6].

By increasing the confinement of interstitial water of polycrystalline ice, the mobility of probe molecules, surprisingly, increases [2]. We argue that loose confinement allows the presence of ice-like regions in supercooled water, whereas a tighter confinement yields the suppression of this ordered fraction and leads to higher fluidity. Compelling evidence of the presence of ice-like regions is provided by the probe orientational entropy barrier which is set, through hydrogen bonding, by the configuration of the surrounding water molecules and yields a direct measure of the configurational entropy of the same. We find that, under loose confinement of supercooled water, the entropy barrier surmounted by the slower probe fraction exceeds that of equilibrium water by the melting entropy of ice, whereas no increase of the barrier is observed under stronger confinement.

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ENDOR STUDY OF LATTICE INSTABILITY IN GAMMA IRRADIATED L-ALANINE CRYSTAL PROBED BY SECOND STABLE RADICAL

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Studies of dynamical response of amino acids in a wide temperature range attracted considerable attention because of their suitability as model systems and building blocks of proteins and large biomolecules as well as due the fact that their dynamical properties play main roles in regulating protein behaviour. Until now extensive investigations of L-alanine crystal have been undertaken, pointing out very interesting physical properties. Despite the fact that x-ray and neutron single-crystal diffraction measurements support the same crystal structure at low (20 K) and at room temperature, there are several other experimental evidences for lattice instability [1] at around 220 K such as birefringence and light depolarization measurements and 1H NMR measurements around the same temperature.

Radiation induced alanine radicals have been explored extensively using different EPR spectroscopy techniques over many years. Despite of these investigations, molecular environment of the three known radicals and the dynamic processes associated with the radicals motion are still not fully understood [2]. Detailed EPR studies of individual probes, as specific fragments of the radicals, provide additional information on the intermolecular dynamics and help to better understand lattice instability in crystalline L-alanine [3, 4]. Such investigation of local dynamic properties and lattice instability in crystalline amino acids are of interest for understanding dynamic properties of the proteins as well.

In this study second stable L-alanine radical, R2, was use as a probe for investigation of the lattice instability. The ENDOR study focuses on the dynamical properties of three amino protons of R2 radical in the temperature range from 120-300 K. The motional dynamics of the amino group is important due to its involvement in intermolecular interactions through the hydrogen bond network in the crystal lattice.

The results of the temperature dependence ENDOR study show phase transition around 220 K for all three amino protons and additionally confirm the strong dynamic Jahn-Teller effect in the L-alanine lattice and support evidence for properties related to lattice instability at around 220 K.

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TRANSLATIONAL DIFFUSION OF NITROXIDE RADICAL IN WATER

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The X-band electron paramagnetic resonance (EPR) was applied to study translational diffusion of perdeuterated nitroxide radical 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl (pDTEMPONE) in water.[1] The measured temperature interval −18-30°C lies in both normal (T>0°C) and supercooled (T<0°C) regions. At each measured temperature, the EPR spectra were recorded for various concentrations C of pDTEMPONE, with C<70 mM. The spectra were fitted to theoretical expression based on modified Bloch equations, which describe motion for transversal magnetizations of three subensambles of radicals with different projections of ^{14}N nuclear spin (I=1). In these equations, the spin dephasing rate W_2C and the coherence transfer rate V_2C are introduced to take into account the effect of Heisenberg spin exchange (HSE) and dipole-dipole interaction (DD) between radicals.[2] The best-fit values of the spin dephasing and coherence transfer rates obtained from the spectra were subsequently fitted to theoretical linear concentration dependence. Thus, we found total rate constants of spin dephasing $W_2=W_2^{\mathrm{HSE}}+W_2^{\mathrm{DD}}$ and coherence transfer $V_2=V_2^{\mathrm{HSE}}+V_2^{\mathrm{DD}}$. Using the facts that $V_2^{\mathrm{HSE}}/W_2^{\mathrm{HSE}}=1/2$ and that $V_2^{\mathrm{DD}}/W_2^{\mathrm{DD}}\approx-4/19$ holds when correlation times of DD are much longer than inverse Zeeman frequency, the HSE and DD contributions to the rate constants were separated. Then, applying theoretical equation for W_2^{HSE} and W_2^{DD} in the continuous-diffusion model, the long-time diffusion constants D_{HSE} and D_{DD} of the radical were obtained as a function of temperature.

Additionally, we analyzed the effective ^{14}N hyperfine splitting frequency a_{eff}, which is expected to vary with concentration as $a_{\mathrm{eff}}=a_0-b_2C$ due to HSE.[2] This concentration dependent shift in frequency is induced by spin precession during the time τ_c spent by two colliding radicals in the HSE interaction zone and the total time τ_{RE} between their re-encounters. Using the best-fit values of a_{eff} obtained from the EPR spectra, we found the rate constants b_2 from the concentration dependence of a_{eff} and the re-encounter times τ_{RE} from the equation $b_2/W_2^{\mathrm{HSE}}=0.43(a_0\tau_{RE})^{1/2}$. This equation follows from the continuous-diffusion model when $\tau_c<<\tau_{RE}$ and it is expected that $\tau_{RE}\approx 2r^2/D$, where $2r$ is the closest distance between colliding radicals.[2]

The results show that the long-time diffusion constants D_{HSE} and D_{DD} correlate well with each other, which justifies the separation method of HSE and DD contributions and the continuous-diffusion model. By comparing temperature dependence of diffusion constants with hydrodynamic Stokes-Einstein equation, we found that the effective hydrodynamic radius varies within 15% from the van der Waals radius of pDTEMPONE (~3.5 Å). Temperature dependence of hydrodynamic radius is somewhat stronger in the supercooled than in normal region. On the other hand, the temperature dependence of re-encounter time τ_{RE} is unusual. In the normal region τ_{RE} increases with decreasing temperature, as expected, but in the supercooled region it starts to decrease with decreasing temperature. This indicates that the re-encounter dynamics of radicals after first contact within the solvent cage differs markedly from the continuous diffusion in the supercooled region.

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MATRIX EFFECTS ON PROTEIN DYNAMICS - THE MAGIC OF THE TREHALOSE MATRIX DECODED BY HIGH-FIELD EPR

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The biological function of many water-soluble and membrane proteins depends not only on the three-dimensional structure of the protein and its cofactors but also on the matrix properties of its micro-environment under the specific conditions of temperature and hydration degree. Remarkably, some organisms in the kingdoms of plants, animals and micro-organisms can survive long periods of complete dehydration and high temperatures transforming into an *anhydrobiotic state* of suspended metabolism. By adding some water they resume their metabolism again (like the "resurrection plants"). In the anhydrobiotic state, the intracellular medium contains large amounts of the non-reducing disaccharides *trehalose* or *sucrose*. Trehalose is most effective also in protecting isolated *in vitro* biostructures [1] which to exploit is a common technique in food preservation. However, the molecular mechanism of the anhydrobiotic biostability is largely unknown up to now.

To clarify the molecular mechanisms of disaccharide bioprotection, we studied the structure and dynamics of spin-labelled molecular systems and photosynthetic reaction centers (RCs) in sucrose and trehalose matrices at different hydration levels by cw and pulse high-field W-band (95 GHz) EPR as well as by FTIR [2,3]. Analysis of the EPR spectra showed that the structural organization and dynamics of the dehydrated matrix as well as their evolution upon re-hydration differ substantially between trehalose and sucrose. The dehydrated trehalose matrix is homogeneous in terms of distribution of the residual water and nitroxide probe molecules, which are equally immobilized at room temperature and at 150 K. In contrast, dehydrated sucrose forms a heterogeneous matrix. The different solvent-solute interaction characteristics account for the different protein-matrix dynamical coupling observed in dried sucrose and trehalose matrices and their different efficacy as a bioprotectant.

We conclude that the anhydrobiotic state of the RC-trehalose system (i) *is not* the result of matrix-induced changes of the local structure of the charge-separated radical-pair cofactors and (ii) *is not* the result of changes of local dynamics and local hydrogen bonding of Q_A in its binding pocket. Rather, the stability of the charge-separated radical-pair state originates in the high rigidity of the dry trehalose glass matrix coating the RC protein surface by hydrogen-bond networks already at room temperature. This shifts the correlation time of thermal conformational fluctuations into the *non-biological* time domain.

This work has been done in collaboration with M. Malferrari, F. Francia and G. Venturoli from the University of Bologna, Italy, and with A. Savitsky, A. Nalepa and W. Lubitz from the Max Planck Institute in Mülheim (Ruhr), Germany.

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MESOSCOPIC DYNAMICS AND THE MECHANISM OF GELATIN SOL-GEL TRANSITION

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We present an experimental investigation of mesoscopic dynamics of gelatin molecules in gelatin water solutions at the micron scale, revealing an emergent length scale and slow cooperative diffusion. Combining pulsed field gradient NMR diffusometry and specially designed low frequency conductivity spectroscopy exoeriments[1] we are able to closely track the motion of polypeptide chains during the transition from sol to gel, resolving two distinct diffusion regimes.

At short timescales we observe an effective diffusion coefficient which is shown to correspond to single chain diffusion. This effective diffusion survives down to a characteristic, temperature-independent length, playing the role of a pore size. Simultaneous measurements of diffusion and conductivity also directly provide the number of non-bound chains in the solution, enabling us to follow chain aggregation and gel network formation, and yielding a concentration master curve for the aggregation process. However, no abrupt change is detected when going from sol to gel, indicating that the local dynamical surrounding of the free molecules remains the same in both phases. This strongly suggests an aggregation scenario for the gelation process[2], driven by emergent interaction between molecules.

At longer times (~1 s) both NMR and conductivity measurements detect an additional diffusion process, related to cooperative motion of chains and similar to dynamics observed in glasses[3] and coloidal gels[4]. The slow process abruptly transforms from elastic to dissipative at the sol-gel transition.

Our results prove that the gelation process of gelatin is significantly more complex than simple percolation or phase separation models indicate, with emergent interactions playing an important role.

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MAGNETIC PROPERTIES OF POLYANILINE STUDIED BY EPR SPECTROSCOPY

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The magnetic properties of the conductive polymer polyaniline (PANI) and its derivatives have been studied extensively during the past decades. These properties are relevant for a better understanding of the nature of the charge carriers in the polymer structure. It can be noted that most of the studied PANI derivatives showed a nearly linear temperature dependence of the magnetic susceptibility multiplied by temperature (χT *vs* T) which was attributed to disorder-induced localised polaron pairs (radical cation with S=1/2) [1]. A further study of the magnetic susceptibility suggests the coexistence of polarons and spinless bipolarons and the possible formation of bipolarons upon changing the temperature or doping level [2]. A slight deviation from the linear dependence of χT *vs* T usually was detected by SQUID at low temperature intervals, at $T < 10$K, for various PANI samples. In this low temperature region, the presence of magnetic field dependence of the magnetic moment was also noted. Both of these magnetic properties were described by employing a “triplet'' model which used the distribution of the singlet-triplet splitting (E) with the density distribution function having a narrow peak near $E=0$ [3]. Recently[4], the EPR obtained orientation dependent susceptibility of the polymer film was described by localised state in which spin ½ polarons behave as spin ½ dimmers.

In this presentation local triplet states in two different types of PANI samples (commercial PANI emeraldine salt sample (PANI ES) and newly enzymatically synthesized polymer samples obtained in the presence of submicrometer-sized vesicles formed from sodium bis(2-ethylhexyl)sulphosuccinate (AOT) as templates for polymerisation[5, 6]) will be addressed in order to more closely examine the nature of their distribution in these samples. It was expected that a characteristic EPR spectrum could be found and attributed to the excited triplet state with corresponding energy at low temperatures. Evidence for the presence of thermally activated states was obtained by studying the temperature dependence of EPR spectral intensities and line widths in the low temperature region[7]. The obtained activation energies for the thermally activated process are discussed in terms of expected energies for single-triplet transitions and possible exchange interactions. The obtained exchange interactions are correlated with different distributions of the polaron pairs in the PANI samples.

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IN-SITU ESR STUDIES OF THERMAL AND UV DEGRADATION OF SPACE-GRADE POLYMERS

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Recently, the European Space Agency (ESA) has expanded their testing laboratories by several facilities for in situ investigation of samples submitted to simulated space environments. One of these incorporates an ESR spectrometer[1].

In the present contribution, the radicals formed during thermal and VUV degradation of several common space-grade polyimide and silicone materials were studied using ESR spectroscopy. The stability of the materials was assessed and by recording subsequent spectra at a sufficient rate, the degradation kinetics could be followed.

The silicones used included optical adhesives such as DC 93-500 and Elastosil S 690, all which have no inherent ESR signal. Thermal degradation at up to 350°C showed only a slight concentration of radicals for all silicones. UV degradation on the other hand led to different responses of the materials. All exhibited a significant rise in ESR signal over a relatively short period of intense radiation and in some cases hyperfine interactions could be observed.

Several polymer films, including Kapton HN and Upilex S, were also studied [2] and the obtained ESR spectra were in good accordance with previous reports [3,4]. Most of these films exhibited a very good thermal stability, which is in accord with findings from other methods [5]. Kapton, however, showed a complex behaviour with at least two separate mechanisms taking place during the thermal treatment. VUV exposure showed an even more rapid degradation of the materials.

Mechanistic insights of the in-situ response of silicone adhesives and polyimide films to thermal and VUV exposure will be presented and the suitability of ESR spectroscopy for fast screening of materials will be discussed.

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PULSED EPR STUDIES OF AN [FeFe] HYDROGENASE WITH A NON-NATIVE COFACTOR

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Hydrogenases are enzymes which catalyze the oxidation of H_2 as well as the reduction of protons to produce H_2. The active site of [FeFe] hydrogenase is referred to as the “H-cluster” and consists of a “classical” [4Fe4S] cluster connected via a protein cysteine side group to a unique $[2Fe]_H$ sub-cluster containing CN^- and CO ligands as well as a dithiol bridging ligand. It was recently shown that various biomimetic complexes of the diiron sub-cluster can be inserted into “apo” [FeFe] hydrogenase which contains only the [4Fe-4S] part of the H-cluster [1,2]. The mimic complex with a aza-dithiol bridging ligand activated the enzyme to full activity proving that the amine function is essential as proton accepting base. In a more recent study we discovered that oxidized [FeFe] hydrogenase from *C.reinhardtii* maturated with non-natural mimic complex $[Fe_2(CO)_4(CN)_2(pdt)]^{2-}$ in which the bridging amine is replaced by CH_2 strongly resembles active oxidized (H_{ox}) state of the native protein[3]. The H_{ox} state is EPR active and the signal originates from the mixed valence Fe^IFe^{II} state of the diiron subcluster [4]. Taking advantage of the readily available isotope labeled mimic complex as well as possibility to obtain a pure redox state we performed HYSCORE and ENDOR studies of the ^{13}C and ^{15}N labeled non-natural H-cluster. The ^{13}C hyperfine couplings of both CN^- ligands were observed for the first time. The $^{15}N/^{14}N$ coupling of the distal CN was detected and compared to those of the native enzyme [4].

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LINKED CLUSTER EXPANSION OF AN ELECTRON SPIN SPECTRAL DIFFUSION IN A NUCLEAR SPIN BATH

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Transverse dynamics of electron spins is very sensitive to fluctuations in their local environment. For instance, these fluctuations lead to incomplete refocusing of spin echoes, which can be described in terms of spectral diffusion.[1] Various theoretical approaches using stochastic noise were applied for modeling of electron spin spectral diffusion.[2]

Recently, interest to this problem has been renewed in the context of quantum information processing, where electron spins are used to store information, and any environmental fluctuations can be harmful. Specifically, sufficient attention has been paid to the noise due to nuclear spin environment, which is a main source of local magnetic field fluctuations at low temperatures. Several dynamical models that describe spectral diffusion as an entanglement of the electron spin state with the nuclear spin bath have been proposed.[3-6]

In this talk I will focus on a dynamical approach which is based on a linked cluster expansion formalism from many-body physics.[7] Within this approach evolution of an electron spin coupled to a nuclear spin bath is systematically decomposed in terms of spin clusters and can be described using a simple spin diagrammatic representation. The procedure provides analytical expressions for different processes contributing to the electron spin dynamics beyond pair correlations and can be applied for characterization of non-exponential decay in spin echo experiments.

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SPIN RELAXATION IN OLIGONUCLEAR TRANSITION METAL CLUSTERS

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Single Molecule Magnets (SMM's) are transition metal or lanthanide clusters exhibiting slow relaxation of magnetization, typically at liquid helium temperatures. This behavior stems from the combination of a large spin in the ground state of the cluster with a uniaxial magnetic anisotropy resulting from a negative value of the zero field splitting term D. These conditions generate an energy barrier for spin reversal and the relaxation time follows a thermaly activated, Arrhenius type, behavior. The conditions for SMM behavior are governed by the magnitude of the thermal barrier for spin reversal. Because this barrier strongly depends on the value of the spin of the ground state research has been focused on systems exhibiting such property, and more specifically on polynuclear transition metal clusters (PTMC's). The spin relaxation behavior of such systems is often assessed by Alternating Current (AC) magnetic susceptibility measurements. Electron Paramagnetic Resonance spectroscopy (EPR) is applied in order to determine critical parameters related with the spin dynamics of the system including the spin of the ground state, the zero field splitting terms, D etc.

During the last years, slow relaxation of magnetization has been observed in transition metal complexes that do not belong in the class of high spin PTMC's. The present talk will be devoted in such systems.

The trinuclear clusters $[Cu_3(\mu_3\text{-}X)_2(\mu\text{-}pz)_3X_3]^{2-}$ (pz = pyrazolato anion, X = Cl, Br) exhibit ferromagnetic interactions leading to an $S = 3/2$ ground state. Interestingly, slow relaxation of magnetization, monitored by AC magnetic susceptibility measurements, is observed for X = Cl but not for X = Br. On the basis of EPR spectroscopy the difference in the spin dynamics in these two, otherwise similar, clusters relates to both the magitude of the zero field splitting parameter of the $S = 3/2$ ground state and the strength of the ferromagnetic interaction. In the trinuclear cluster $[Fe_3(O_2CPh)_6(H_2O)_3]ClO_4{\cdot}py$ the magnetic interactions are antiferromagnetic resulting in an $S = 1/2$ ground state. Albeit this small spin value, slow relaxation of magnetization is observed. EPR spectroscopy indicates the presence of the antisymmetric exchange $[\mathbf{d_{ij}} \bullet (\mathbf{S_i} \times \mathbf{S_j})]$ term which results in a highly anitotropic $S = 1/2$ system that might relate to the spin dynamics.

A recent advance in the field of the spin dynamics of molecular compounds is the observation of slow relaxation in *mono* - nuclear transition metal complexes. The majority of the mononuclear complexes studied so far are based on iron and cobalt ions. In the present talk, the relaxation properties of a mononuclear Mn(III)($S = 2$) complex will be presented. EPR spectroscopy gives invaluable information about the zero field splitting parameters that critically influence the relaxation properties.

LOW-TEMPERATURE EPR STUDY OF SOLID TREHALOSE

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Trehalose is a disaccharide found in nature which can form crystalline and glassy state. It is well known for its unusual bioprotective properties like ahydrobiosis or cryoprotection[1]. These phenomena are still not fully understood and have prompted the investigation of molecular dynamics in the wide range of trehalose preparations in the solid state[2]. Due to the fact that trehalose exhibits the highest glass transition temperature, T_g, and the most compact hydrogen-bonded network of saccharides, it is interesting to be studied in the context of low-temperature anomalies observed in glasses[3]. The advantage of applying electron paramagnetic resonance (EPR) spectroscopy is in the sensitivity of the electron-spin coupling with the disordered modes in the observed system. Here, electron spin-lattice relaxation times (T_1) measured by X-band EPR spectroscopy in irradiated trehalose glass and anhydrous polycrystalline state are presented in the large temperature interval, from 0.012 T_g to 0.7 T_g [4]. The largest difference in T_1 is detected below ca. 80 K indicating more efficient energy exchange between the spin system and the lattice for paramagnetic centers in the glassy than anhydrous trehalose polycrystalline state. The involvement of the disordered modes (glassy/soft/boson peak modes), which enhance the energy exchange between the spin system and the lattice in the glassy as compared to the crystalline state, is evaluated in the framework of soft potential model[5]. The results corroborate the idea of boson peak being a universal property of disordered solids.

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LOCAL MOLECULAR DYNAMICS INRUBBER NANOCOMPOSITES

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Nanocomposite rubber films were prepared from natural rubber (NR) crosslinked with sulfur. Samples were doped withnanosilica andorganically modified clays (Cloisite 10A, Cloisite 15A and Cloisite 20A).An effect of the addition of coupling agent was investigated on NR containing nanosilica particles. Nitroxyl radicals 4-oxo-2, 2, 6, 6-tetrametilpiperidin-1-oxyl (TEMPONE) and 4-hydroxy-2, 2, 6, 6-tetrametil-piperidin-1-oxyl (TEMPOL) were used as spin probes.

The main objective of this study was to characterize the dynamic behavior of polyisoprene chain segments in the presence of nanofiller. ESR spectra were recorded in tha wide range of temperatures, from −100 °C to 130 °C. Spectra of TEMPONE and TEMPOL measured in the temperature region around 0 °C consist of broad and narrow components being attributed to the slow and fast rotational motions, respectively. An effect of composition (the type and amount of nanofiller) and the presence of coupling agent on the probe dynamicswasobservedby changesin the spectral shapesandcorrelational times of broad and narrow components. Spectra were calculated using NLSL program. ESR results are compared with those obtained by DSC, X-ray scattering, TEM and swelling experiments.

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HF-ESR STUDY OF Cr(III) POLYMERIC OXALATE COMPLEXES

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Commercial electron spin resonance ESR spectrometers (X-band) are not appropriate for investigation of the transition metal complexes with spin $S > 1/2$. In order to obtain the spin Hamiltonian parameters in these systems: *g*-tensor, *D*-tensor (zero-field splitting) and *A*-tensor (hyperfine splitting), it is necessary to have spectrometers that operate in high magnetic fields and at high frequencies (High Field-High Frequency ESR, HF-ESR).

Among a large number of new compounds, oxalate complexes of transition metals are interesting because of high efficiency of oxalate bridge ($C_2O_4^{2-}$) in transmission of exchange interaction between metal ions. Two new polymeric oxalate complexes: $\{[CaCr_2(phen)_2(C_2O_4)_4]\cdot 0.33H_2O\}_n$ (CrPhen) and $\{[CaCr_2(bpy)_2(C_2O_4)_4]\cdot 0.83H_2O\}_n$ (CrBpy) are presented. [1,2] Mononuclear $[Cr(N\text{-ligand})(C_2O_4)_2]^-$ anions are bridged by calcium ions, and altogether form infinite, neutral heterobimetallic (chromium and calcium) double zigzag chains. Magnetic susceptibility study showed that both polymeric complexes are paramagnetic i.e. no exchange interaction between chromium spins $S = 3/2$ were detected. At low temperatures ($T < 20$ K) the susceptibility deviates from the Curie law, due to existence of the small magnetic anisotropy of Cr(III) ion. Here, detailed HF-ESR investigation ($\nu = 83$–332 GHz, $B = 0$ –16 T) of the anisotropy and determination of spin-Hamiltonian parameters of CrPhen and CrBpy complexes are presented.[3] Despite very similar crystallographic structures, HF-ESR spectroscopy resolved remarkably different magnetic anisotropies of Cr(III) ions in the investigated complexes.[3]

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