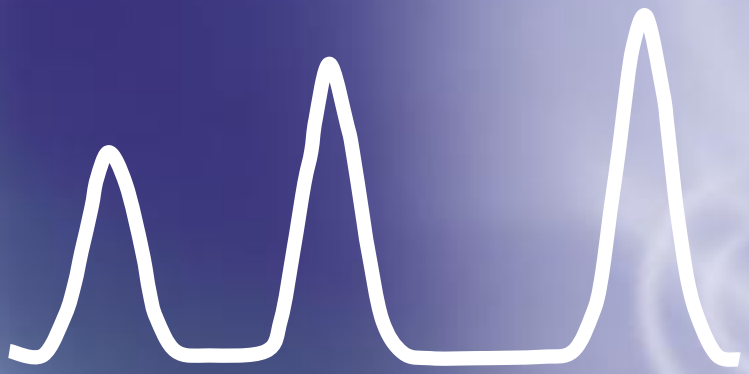

AMPERE NMR School

19 – 28 June 2008
Poznań, Wierzba
Poland

ABSTRACTS

Edited by S. Jurga

UNDER THE AUSPICES OF THE AMPERE GROUP
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Poznań, Wierzba (The Great Mazurian Lakes)
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BASIC OF NMR
&
TUTORIAL

STRUCTURE DETERMINATION ON BIOMOLECULES (AND FIBRILS IN PARTICULAR) BY SOLID-STATE NMR

Adam Lange, Hélčne van Melkebeke, Christian Wasmer, Theofanis Manolikas and Beat H. Meier

Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland

1) Recently several high-resolution protein structures have determined by solid-state NMR, with a precision approaching that of liquid-state NMR. This is the basis that establishes solid-state NMR as a technique to tackle problems in protein structure which may not easily solved with more established techniques such as x-ray crystallography and NMR in solution. The state of the field is reviewed and the basic principles are presented.

2) As an example for a system which can be solved by solid-state NMR more easily than by other methods, the 3D structure of the **HET-s(218-289)** prion-forming domain in its infectious form and the requirement to obtain the structure from solid-state NMR data will be discussed. Following the prion hypothesis, prion and non-prion forms of a protein are believed to differ solely in the 3D structure of the protein. The structure presented and solved by solid-state NMR allone allows us to explain the high level of structural order and the stability of HET-s(218-289) prion fibrils. Similarities and differences with the full-length protein will be mentioned.

ANALYSIS OF DIFFUSION AND FLOW BY SPIN ECHO

J. Stepišnik[1,1]

[1]University of Ljubljana, FMF, Physics Dept., [2]Institute J. Stefan, Ljubljana Slovenia

Lecture “Analysis of diffusion and flow by spin echo” will be an introduction into:

Labeling of spin by the magnetic field gradient, Spin position and motion encoding in the spin echo signal Self-diffusion and flow by NMR:

- Torrey’s method
- Averaged propagator method and diffusion diffractions
- Particle velocity autocorrelation measurement by spin echo
- Two-Dimensional distribution of diffusion and relaxation Applications of spin echo for the measurement of molecular motion in fluids in porous media and motions in the fluidized granular systems.

MULTIPLE QUANTUM NMR WITH EXAMPLES FROM LIQUID CRYSTALS

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Directly observed (single-quantum) NMR spectra consist of lines that arise from the flip of a single spin. Such spectra can be quite complicated and difficult to analyse, especially for orientationally ordered systems. Great simplification would be achieved if it were possible to observe directly transitions that involve the simultaneous flip of many spins. The direct observation of such multiple-quantum (MQ) transitions is not practical, and in fact such transitions are forbidden in the "normal" single-pulse NMR experiment.

The idea of 2-dimensional NMR provides an excellent technique for the indirect observation of such MQ spectra. In the generalized experiment a first pulse turns equilibrium Zeeman magnetization into transverse X and Y magnetizations which evolve under the spin Hamiltonian into additional single-quantum (1Q) coherences. A second pulse converts some of these 1Q coherences into MQ coherences that than evolve for a time t1 under the spin Hamiltonian. A third pulse converts the evolved MQ coherences back into transverse 1Q coherences that evolve back into observable X and Y magnetizations, and an echo is observed. The Fourier transform of the echo amplitude as a function of t1 gives the MQ spectrum corresponding to the MQ coherences that were evolving between the second and third pulses.

I shall first discuss the density-matrix approach to this problem using spin 1 as an example (see Chapter 2 of ref [1]). I shall then demonstrate using an energy-level diagram the MQ orders of a simple 3-spin example, 1,1,2-trichloroethane dissolved in a liquid crystal. I shall also use this example to show that additional simplification is achieved with the selective excitation (involving the first two pulses) of only some of the spins of the spin system [2].

I shall discuss other examples of MQ NMR experiments. In the simple experiment described above, all MQ orders contribute to and are included in the spectrum. The use of either phase cycling or field-gradient pulses allows the destructive interference of all but selected orders and thus permits the observation of one order at a time. A 3-dimensional experiment [3], involving collection of 2-D spectra as a function of the phase of the first two pulses gives MQ spectra of all orders as projections in the separate planes associated with the FT of the phase dimension.

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MAGNETIC RESONANCE IMAGING

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MRI (magnetic resonance imaging) the most innovative technique in diagnostic imaging since discovery of X-rays is presently applied in many fields outside medicine; in physics, chemistry, biology, materials sciences giving information on spatial properties of structured objects of all kinds in a non destructive manner.

The objective of the lecture is to provide an introduction to the subject, particularly to those participants who are less familiar with it.

Starting from the very beginning we shall present the basic principles of nuclear magnetic resonance and its applications to studying structure of molecules.

Contrary to classic experiments, in which the object is placed in a uniform Zeeman field, in MRI non-uniform magnetic field is applied. The purpose of this is to label different parts of the object with different NMR frequencies. It was Lauterbur, who first recognized that the profile of NMR signal, recorded in the presence of the magnetic field gradient, represents one dimensional projection of spin density along the gradient direction. He also showed that by subjecting the profiles, obtained with gradient applied in several different directions, to a back-projection algorithm a two-dimensional NMR image of the object's spin density can be obtained. We shall also discuss the Fourier relationship between the spin density and the NMR signal, which constitutes the foundation of contemporary Fourier imaging techniques. Some examples of the use of MRI will be given.

Finally, we shall mention the recent use of the technique to get localized NMR spectra in vivo and to monitor organism's functions.

ADVANCED SIGNAL PROCESSING FOR NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY: APPLICATION OF MAXIMUM ENTROPY METHODS

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The aim of the lecture is to introduce in the treatment of pulse NMR measurements where the data treatment is not related to Fourier-transform techniques. The Fourier transform methods were first introduced by the famous mathematician Leonhard Euler who has presented the complete formulae for the evaluation of the coefficients and amplitudes of this expansion. Later this method was reinvented by Charles Fourier. The first application to NMR was realized in 1958 in the Physics Department of the St. Petersburg (Leningrad) State University. But only after the systematic foundation of this methods by Ernst and Anderson Ray this techniques became the base of modern NMR spectroscopy. From the point of view of mathematics, the Fourier analysis of the time-dependent signals is a procedure where the configurational entropy is constant. In this contribution it will be shown that the spectral data (such as intensities, phases, frequencies, damping constants or line widths) may be also directly derived from the time domain data using maximum entropy methods. In the lecture the basic conception of these methods will be introduced. The principles of mathematical techniques based on maximum entropy principle were first applied in Astronomy and Astrophysics. It is based on the maximum entropy interpretation of thermodynamics and the foundations of probability and statistical inference, initiated in 1957 by Edwin Thompson Jaynes, Washington University in St. Louis [1]. Later these methods were used transient magnetic resonance methods (EPR, NMR). The pioneering contributions in these fields are related to the work of Kumaresan and Dufts, Van Ormondt, et al., and Tang and Norris. Basic principles and recent developments will be explained. This gives also the possibility to outline the achievements obtained in an European Project entitled "Advanced Signal Processing for Medical Magnetic Resonance Imaging and Spectroscopy" and to mention program package "jMRUI software package" which has been developed in this framework and which is freely available and worldwide used. Finally, the new European project "Signal-Processing for Ultra-Fast Magnetic Imaging – FAST" will be mentioned which is coordinated by the Creatis-LRMN Lab in Lyon.

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BASICS OF NMR OF MOLECULES IN UNIAXIAL ANISOTROPIC ENVIRONMENTS

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When molecules are partially oriented in an anisotropic liquid phase, they diplay NMR spectra that may be very different from the 'normal' isotropic ones. Partial orientation can be achieved by dissolving molecules in liquid-crystal solvents, or by employing strong electric or magnetic fields. Especially in the case of solutes in uniaxial nematic phases the anisotropic interactions tend to dominate, and extremely complicated NMR spectra may result [1,2]. The analysis of oriented NMR-spectra of most but the smallest molecules in an anisotropic environment is usually no trivial matter.

In this lecture the theory underlying the NMR of molecules partially oriented in uniaxial anisotropic environments will be discussed in detail. This theory is a very reliable predictor of NMR spectra of partially oriented species in the liquid phase, provides the basis for a detailed interpretation of such NMR spectra, and is essential for a good understanding of what can be learned from such NMR studies.

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NUCLEAR SPIN-LATTICE RELAXATION: BACKGROUND, EXAMPLES, INSTRUMENTATION

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My lecture (two hours) is addressed to students. It is meant to be a didactic introduction to the broad field of nuclear spin-lattice relaxation from the perspective of an experimentalist. I plan to proceed in a threefold way: In the first part I will introduce some basic notions of relaxation theory such as rate equations, the dipolar Hamiltonian, dipolar coupled spin systems, transition probabilities leading to a formulation of the relaxation rate, spin diffusion, spin temperature, quadrupole relaxation, the notion of ergodic and nonergodic systems. In the second part I will discuss some instructive examples of traditional (fixed frequency) relaxometry experiments taken from literature including my own work. The third part is devoted to field-cycling techniques, both electronic and mechanical. I will present some experimental examples from more recent work which demonstrate that field cycling relaxometry may be considered as a dynamic susceptibility method and can most favourably be applied in concert with other susceptibility methods like dielectric relaxation or dynamic scattering methods.

ANALYSIS OF POLYMER MORPHOLOGY BY HIGH- AND LOW-FIELD NMR

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NMR is one of the most important analytical methods in polymer science. Constitution and conformation of macromolecules is analyzed by different forms of NMR spectroscopy at high field as sensitivity and spectral dispersion are valued. Yet many investigations, in particular those concerning the morphology of solid polymers can be conducted by ^{1}H NMR at low spectral resolution. The morphology of most technical polymer materials does not correspond to the thermodynamic equilibrium state of the macromolecular chains. It is established by the mechanical and thermal history during processing. Moreover, it changes during use of the material under the influence of light, temperature, mechanical forces, and time. These processes are summarily referred to as aging, where physical aging is referred to as fatigue and chemical aging as corrosion. Laboratory aging strategies are devised to mimic representative real life aging processes to predict the life time of polymer products such as pipes. To understand the morphology and its changes in detail, NMR investigations of transverse relaxation and spin diffusion can be conducted at high and low field.

As both, physical and chemical aging lead to changes in molecular mobility, the time scale of aging processes can be followed by relaxation studies. Depending on the type of aging, the mobility may decrease or increase and the volume of the material may change homogeneously or develop a layer structure. The life times of technical products are predicted in accordance with procedures established in national and international committees which define standardized tests at extreme conditions for accelerated aging accepted to be representative for average real-life aging. Thanks to the outstanding sensitivity of NMR relaxometry, accelerated laboratory aging and real-life aging can be distinguished in many cases. Moreover, with mobile instruments like the NMR-MOUSE, objects can be investigated non-destructively at their regular location, and the stratigraphy developing from the surface into the bulk of the material by a one-sided aging attack can be resolved with high resolution. Results on aging studies of polymer pipes under mechanical and thermal load, of polymer sheets exposed to different aggressive fluids and gases, of rubber sheets under mechanical chemical and UV load will be presented and analyzed. Real-life aging over several centuries can be followed by analyzing the binder in the paint of old master paintings. It turns out, that naturally aged binders a few decades old can be distinguished by NMR relaxometry from those a few centuries old as well as from artificially aged binders.

LECTURES

FROM THE BASIC EQUATION OF MOTION OF MOLECULES TO NMR MEASURANDS: THE HARMONIC RADIAL POTENTIAL THEORY OF POLYMERS

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Under normal conditions (no tunnelling etc.), molecular dynamics can be described in classical terms. That is, Newton's equation of motion applies in principle. However, from this basic law to measurands that can be probed in NMR experiments it is still a far way. NMR methods of particular interest in this context are NMR diffusometry and relaxometry. This lecture undertakes the attempt to outline how NMR measurands can be considered as descendants of Newton's law.The most popular model of the dynamics of entangled polymers is the tube/reptation model suggested by Doi and Edwards [1]. A fact is that this treatment is not of a closed form. It is rather a 'limit-by-limit' approach leading to a combination of the well-known four cases 'free Rouse dynamics', 'longitudinal Rouse dynamics', 'reptation', and 'center-of-mass dynamics' arising subsequently on increasing time and length scales. It will be shown that a treatment in closed analytical form is possible if a harmonic radial tube potential is assumed [2]. The theory nicely reveals the confining effect imposed by the tube, and demonstrates the crossover between free Rouse and confined chain dynamics upon variation of the tube diameter.Free and confined chain dynamics can also be studied with the aid of Monte Carlo simulations. For this purpose the polymer must be modelled in respect to motional degrees of freedom in a suitable form [2,3]. The results corroborate the analytical treatment and detail the crossover from short-range to long-range chain modes.Experimentally chain dynamics has been studied in artificial 'tubes' of varying diameter formed by a solid methacrylate matrix. Both diffusion [4] and field-cycling NMR relaxometry [5] experiments have been carried out. The predictions by the theory and the simulations are reproduced.

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PROBING NUCLEAR SPIN-SPIN COUPLING TENSORS IN SOLIDS

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Consider a molecule containing two nuclear spins, *M* and *N*. The nuclear spin Hamiltonian will contain two terms bilinear in I_M and I_N, corresponding to the two fundamental interactions that describe how two spins interact with one another [1]. These interactions are known as the direct dipolar interaction and the indirect nuclear spin-nuclear spin interaction. The magnitude of the direct dipolar interaction is directly proportional to the inverse cube of the separation between the two spins. On the other hand, the indirect spin-spin coupling interaction does not depend on distance (i.e., internuclear separation) in any simple way since it is a two-step process mediated by the intervening electrons [2, 3].

Much experimental effort has been devoted to devising techniques to measure direct dipolar coupling constants, *R*, because of the potential structural information that they provide [4, 5]. Some of the basic techniques used to measure *R*-values will be reviewed. Examples illustrating the characterization of indirect spin-spin coupling tensors, *J*, will also be presented [1-3, 6]. Finally, the importance of using indirect spin-spin coupling interactions in spectral assignment and in determining molecular structure will be discussed [7, 8].

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ROTATIONAL MAGNETIC RESONANCE AND POSSIBILITIES OF A DETECTION

Jerzy S. Blicharski and Barbara Blicharska

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The aim of this paper is to present theoretical bases of Rotational Magnetic Resonance (RMR) and possibilities of a detection. It is well known that a molecule in a rotational state J (J = 0, 1, 2,..) has molecular angular momentum $\boldsymbol{K} = \boldsymbol{J}\hbar$ and molecular magnetic moment $\boldsymbol{\mu}_J = \gamma_J \hbar \boldsymbol{J}$, which interacts with nuclear spins $\boldsymbol{I}$ and nuclear magnetic moments $\boldsymbol{\mu}_I = \gamma_I \hbar \boldsymbol{I}$ by a spin-rotational interaction and dipole-dipole interaction, respectively [1- 6]. As a special case we consider solid hydrogen H_2 at low temperatures, containing approximately 75 molar percent of *ortho-*H_2 (with I=J=1) and 25 percent of *para-*H_2 (with I=J=0), in a presence of a strong magnetic field $\boldsymbol{B}_0$, where resonance frequency for RMR in *ortho-*H_2 is $\nu_J = (\gamma_J/2\pi)\boldsymbol{B}_0$. Taking into account a spin-rotational constant c and dipole-dipole constant d (Table I) one can calculate the following six frequencies ν (sextet) of the RMR spectrum, which should be observed in *ortho-*H_2: $\nu = [\nu_J \pm (c - 3d/2)]$, $(\nu_J \pm 3d)$, $[\nu_J \pm (c + 3d/2)]$.

The RMR signals may be enhanced by a magnetization transfer from protons to molecular rotors of *ortho-*H_2. Possibilities of a detection of the RMR in solid HD, D_2 and CH_4 will be also discussed.

$\gamma_1/2\pi = \gamma_H/2\pi$	42.575 MHz/T
$\gamma_J/2\pi$	6.717 MHz/T
$\gamma_J\eta = \mu_J/J \quad (J=1)$	$0.882910 \pm 0.000080\ \mu_N$
$\gamma_J\eta = \mu_J/J \quad (J=2)$	$0.882865 \pm 0.000035\ \mu_N$
γ_2/γ_1	0.99927 ± 0.00009
$c = C_R/2p$	113.904 ± 0.030 kHz
$d = C_D/10p$	57.671 ± 0.024 kHz
ν_J for $B_0 = 7$ T	47.019 MHz

Table I. Selected data for hydrogen molecule H_2 [5]

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SPATIALLY RESOLVED MONITORING OF CATALYTICALLY ACTIVATED HYDROGEN PEROXIDE DECOMPOSITION – A TEST CASE FOR REACTION MONITORING BY NMR

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Many reactions of technical and industrial significance include gas as one of several involved phases, either as a reactant or as a product. Even in reactions taking place entirely in the liquid state, localized temperature increases may lead to partial evaporation and therefore formation of steam at certain stages of the reaction process. Decomposition reactions can produce gas that may remain dissolved in the liquid phase, but also may accumulate to concentrations above the dissolution limit, thus forming bubbles within a reactor. The generation of gas and steam bubbles depends on the local geometry inside the reactor: frequently, such a device consists of a loose packing of individual pellets which, in turn, are microporous in order to accommodate the catalytically active metal at a sufficiently large accessible internal surface. Bubble formation occurs in dependence of the relative interfacial tension and is suppressed in nm-size pores, but does exist in the mesoporous network that is often found in commercial catalyst pellets. The reason for this choice of geometry is the observation that the presence of a well-connected macroporous network not only facilitates reactant and product transport to and from the internal surface, but also leads to bubble formation that can favourably influence the reactor performance: the continuous generation and release of bubbles generates an oscillatory behaviour that can greatly enhance fluid transport. Understanding the performance of a reactor, in order to achieve an optimized design strategy, thus requires a quantitative description of fluid transport in the presence of bubble formation in porous media.

The reaction H_2O_2 (liquid) → H_2O (liquid) + ½ O_2 (gas) was investigated in this study; the experiments were performed on one single, metal-containing catalyst pellet immersed in an aqueous solution of H_2O_2, and different types of commercial catalyst pellet containing Pd, Ni or Cu were compared. During the reaction, which typically lasts several hours until no significant bubble formation is observed any longer, proton relaxation times and average diffusion coefficients were monitored for a defined volume containing the pellet and the solution. A typical result for the effective diffusion coefficient averaged over this volume is shown in the figure. While the value of the diffusion coefficient is influenced by the bubble formation and thus provides a measure of the integrated reaction rate, the relaxation times provide evidence for the change of H_2O_2 concentration in the solution.

Furthermore, imaging experiments were performed in the interior of the pellet with and without the reaction taking place, and the obtained weighted spin density maps were analyzed in terms of the three relevant NMR properties, i.e. signal intensity, relaxation, and diffusion, in order to provide a measure of the local reaction efficiency within the pellet.

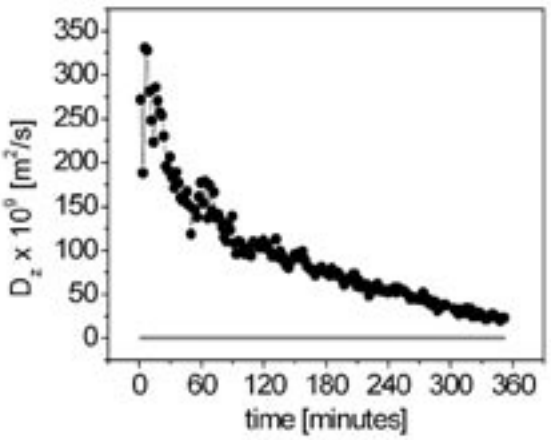

Fig.1. Effective diffusion coefficient of an aqueous solution of H_2O_2 in a volume containing one Cu-doped catalyst pellet during the decomposition reaction; the horizontal line denotes the bulk diffusion coefficient in the absence of reaction.

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VARIOUS WAYS TO ENHANCE NMR SIGNALS: RECENT THEORETICAL PROGRESS

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Limitations of numerous applications of Nuclear Magnetic Resonance are caused by a non- sufficient response of investigated systems under available experimental conditions. Then the problem of an appropriate enhancement of NMR signals attracts considerable attention, especially recently because of very fast development of experimental NMR techniques. My lecture will concern the following methods leading to an enhancement of NMR signals:

- Polarization transfer
- Paramagnetic relaxation enhancement
- Overhauser effect
- Dynamic nuclear polarization

Polarization transfer can occur in systems of dipolar and quadrupolar spins mutually coupled by dipole – dipole time independent interactions. If the magnetic field is set to a value which leads to the Zeeman splitting of the dipolar spin matching the energy splitting of the quadrupolar spin (determined by the quadrupolar and Zeeman interactions), the dipole-dipole coupling causes polarization transfer processes. Under these conditions the dipolar spin magnetization is taken over by the quadrupolar spins; this is detected as local dips of the dipolar spin magnetization curve detected versus the magnetic field. The mutual dipole-dipole coupling links transitions of the dipolar spin to some transitions of the quadrupolar spin, so they cannot occur independently. However, the entire system conserves the total energy. The transitions of the dipolar spin between the Zeeman states can occur only if the quadrupolar part of the system is ready to use the released energy for its transitions [1-3].

Paramagnetic relaxation enhancement is caused by random variations of electron spin – nuclear spin interactions, which open new pathways for longitudinal as well as transverse relaxation [2,4].

Overhauser effect leads to an enhancement of nuclear spin magnetization when a microwave saturating field is applied to equilibrate populations of the energy levels of an electron spin mutually coupled to the nuclear one.

Dynamic nuclear polarization is the most complex process. Typically, it takes place in solid state systems doped with paramagnetic centers In fact several different processes and potentially even multiple different mechanisms are involved in the dynamic nuclear polarization. Solid-state dynamic nuclear polarization experiments are commonly performed by irradiating a sample containing a dilute paramagnetic species with a saturating microwave field resonant or near-resonant with the electron Larmor frequency. Thereby the polarization of the nuclear spins in the sample is enhanced above the equilibrium value, in the ideal case by a factor given by the ratio between the electron and the nuclear gyromagnetic ratios. To achieve the enhancement of the nuclear polarization an effective coupling between the nuclear and the electron spins is needed, like in the case of mutually coupled dipolar and quadrupolar nuclear spins. This mutual interaction leads to eigenfunctions of the electron spin – nuclear spin system being a mixture of the 'ordinary' Zeeman states. Populations of the individual energy levels evolve in time following a set of relaxation equations. The relaxation coefficients, connecting the energy levels depend on the alternating microwave field and the absorption spectrum (ESR spectrum) of the electron spin involved. The ESR lineshape function, is crucial for the dynamic nuclear polarization process. The amplitude of an ESR spectrum at a given frequency tells one what is the fraction of electron spins which transition frequency is equal to this frequency. Therefore the ESR lineshape function gives 'weigh factors' for the transition probabilities (relaxation coefficients). The ESR spectrum is determined by many parameters and has to be calculated independently starting from an electron spin Hamiltonian appropriate for the considered case. During the evolution process there is a time point at which the momentarily populations of the energy levels are particularly favorable for the nuclear spin leading to an enhanced nuclear polarization. The enhancement does not last for ever, after some time all populations are equilibrated. This short time period of enhanced nuclear polarization is very profitable in NMR investigations of biological systems. Therefore the subject attracts recently so much attention and is also the main topic of my lecture.

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MECHANISMS FOR ION TRANSPORT IN SOLID-STATE ELECTROLYTES: INSIGHTS FROM NMR MULTI-TIME CORRELATION FUNCTIONS

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In recent years, there has been rapidly growing interest in materials with high ionic conductivities due to their potential applications in new electrochemical devices such as solid-state batteries, fuel cells and chemical sensors. Despite the enormous interest, many aspects of the ion transport in solid-state electrolytes are poorly understood at the atomistic level. It is well known that the macroscopic charge transport results from elementary jumps of mobile ions in an essentially frozen matrix. However, the mechanisms for this ionic hopping motion are very complex in nature. We demonstrate that ^{6}Li, ^{7}Li and ^{109}Ag NMR stimulated-echo experiments allow us to record multi-time correlation functions that yield detailed microscopic insights into ionic jump dynamics in crystalline and glassy ion conductors [1-4].

NMR two-time correlation functions measure the probability that an ion still occupies the initial site at a later time and, hence, they provide straightforward access to the repopulation of the ionic sites [1,4]. For lithium and silver ion conductors, the non-exponential correlation functions are well described by stretched exponentials, $\exp[-(t/\tau)\beta]$. Typical of complex molecular dynamics, small stretching parameters $\beta = 0.2–0.5$ indicate substantial deviations from simple exponential relaxation. The temperature dependent mean correlation times follow Arrhenius laws for all studied crystalline and glassy materials [1-4]. The activation energies are in agreement with that found for the dc conductivities, indicating that NMR two-time correlation functions probe the elementary steps of the long range charge transport.

The origin of the pronounced non-exponential ionic relaxation can be quantified when we analyze NMR three-time correlation functions, which correlate the resonance frequencies at three consecutive times [2]. Our ^{109}Ag NMR data for crystalline and glassy silver ion conductors indicate that the non-exponentiality is due to a very broad distribution of jump rates, i.e., dynamic heterogeneities, rather than to intrinsically non-exponential relaxation, which would result as a consequence of correlated back-and-forth jumps of the ions. Thus, NMR three-time correlation functions give no evidence for the latter type of motion, which has been assumed in several theoretical models of ion transport in solids.

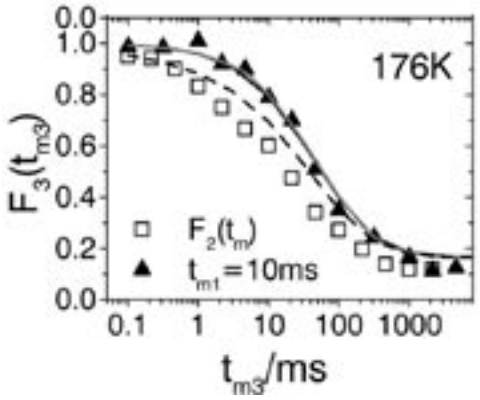

Fig. 1. ^{109}Ag NMR two-time (open squares) and three-time (solid triangles) correlation functions of polycrystalline $Ag_7P_3S_{11}$ at 176K. The solid and dashed lines are the predictions for the three-time correlation function calculated for the cases that the non-exponentiality of the two-time correlation function exclusively results from dynamical heterogeneities and intrinsic non-exponentiality, respectively.

Finally, recording NMR four-time correlation functions, it is possible to measure the lifetime of the dynamical heterogeneities in solid ion conductors, i.e., to determine the time scale of exchange processes within the broad rate distribution governing the ionic jumps. For crystalline and glassy silver ion conductors, we observed that the dynamical heterogeneities are short-lived and, hence, fast and slow jumps alternate during the diffusion process of a silver ion [2,3].

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SOPHISTICATED NANOSTRUCTURES AND THEIR APPLICATIONS

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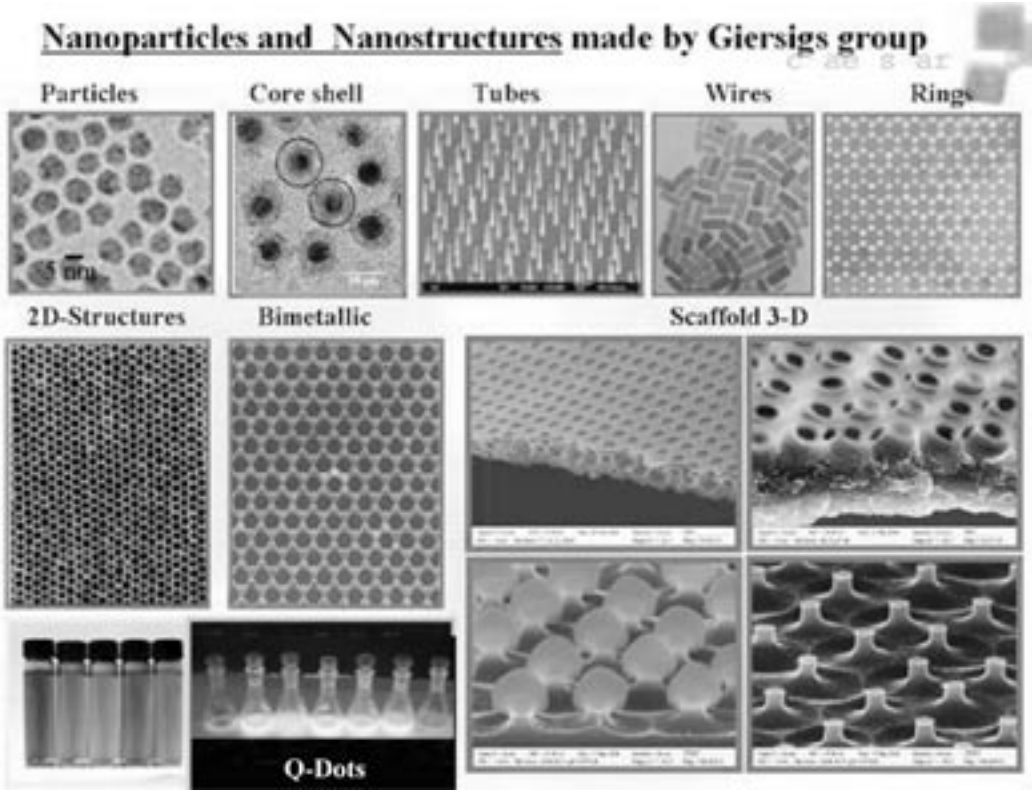
Nanomaterials exhibit unusual properties and are considered to represent a new physico-chemical dimension between the molecules and the bulk materials. All the properties depend on the particles' size, morphology, and crystal structures. A number of synthesis and characterization methods as well as the application of such nanostructures will be demonstrated and discussed.

Examples of various nanostructures are given in the gallery.



Gallery of selected images of nanoparticles and nanostructures created by the Giersig Group

NMR OF PHYSISORBED ^{129}XE USED AS A PROBE TO INVESTIGATE POROUS SOLIDS

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The fundamental idea was to find a chemically inert molecule, detectable by NMR and particularly sensitive to physical interactions with other species, which could be used as a probe to determine the properties of its environment. The 129 xenon isotope is this ideal probe.

Chemical shifts and relaxation times of xenon are solely affected by intermolecular interactions and are exquisitely sensitive to the atom's surrounding. This sensitivity to its environment means that the Xe nucleus can report on a wide variety of attributes of the physical systems in which it finds itself: gas, liquids, cages in a zeolite, nanochannels in a molecular solid, clathrates, proteins in solution, amorphous polymers, etc. It can be used also for imaging and gas diffusion measurements. By using optical polarization techniques the sensitivity of detection can be increased by several orders of magnitude and is particularly useful for several studies (porous materials, microimaging, polymers and elastomers, etc.). We present some examples of the applications of the Xe-NMR technique to the characterization of microporous and mesoporous solids.

NMR STUDY OF PHASE TRANSITIONS IN CONFINED GEOMETRY

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The aim of the contribution is to present examples of our recent research work on nano-structered materials. The influence of size effects on the ferroelectric properties of oxide perovskites. Investigations on these materials have obtained a great interest in recent years because Curie temperature, electrical polarization, coercive field, switching time and other properties potentially depend on the particle size. It will be shown that the NMR methods (completed by EPR measurements) sensitively probe changes of the structure and the local symmetry in the nanocrystalline material.

Particles of $BaTiO_3$ of small sizes were investigated in order to observe size effects on them in comparison to bulk material. These ultrafine $BaTiO_3$ powders were prepared from a monomeric metallo-organic precursor through combined-solid state polymerization and pyrolysis (CPP method) [1]. The particle diameter was varied in the range between 15 nm and 155 nm (powders were carefully characterized by FT-Raman, XRD and other methods).

^{137}Ba static NMR spectra were obtained in different magnetic fields at various temperatures in order to observe the paraelectric - ferroelectric phase transition. NMR powder spectra of the central line transitions were simulated using the second order perturbation theory of the quadrupole interaction to estimate the quadrupole coupling constant $|e^2qQ/h|$. Taking into account a structural model [2] for fine particles of barium titanate we fitted obtained spectra by two lines. On this basis a structural model for a nanograin is derived in which a only weakly distorted tetragonal core is surrounded by a highly distorted shell. The temperature dependence of the various components in the spectra was studied over the whole range of the tetragonal phase and around the phase transition into the cubic phase. The determination of the respective coupling constants in the ferroelectric phase was possible. This allows the study of subtle details of the size driven phase transition [3].

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DIFFUSION- EXCHANGE STUDIES BY PFG- NMR: ANALYZING DISTRIBUTION AND DYNAMICS OF GUEST MOLECULES IN COLLOIDAL CARRIER SYSTEMS

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The distribution and exchange dynamics of guest molecules in colloidal particles designed as materials for controlled release and delivery applications is of large interest. An example of a colloidal carrier is given by Polyelectrolyte Multilayer (PEM) capsules formed by layer-by-layer assembly. The time scale of permeation of active molecules through the nanoporous wall, or their incorporation into it is crucial for applications.

In this contribution the application on Pulsed Field Gradient (PFG)-NMR diffusion experiments combined with relaxation data to this type of problem is reviewed. Different regimes concerning the exchange dynamics can be observed and analyzed for different particles and different types of guest molecules.

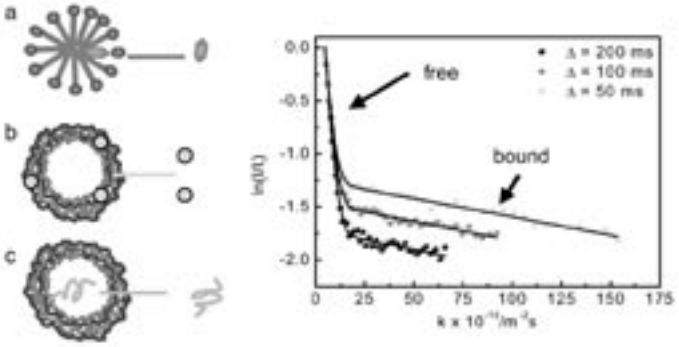

Fig. 1. Left: Examples of colloidal systems analyzed, a:. Fragrances in surfactant micelles; b: small alcohols in PEM capsules, and c: poly(ethylene oxide) in PEM capsule dispersions. Right: PFG-NMR echo decays for different diffusion times for poly(ethylene oxide) in PEM capsule dispersion (example c). The lines are fits by the 2-site exchange model.

Small guest molecules in surfactant micelles are in fast exchange and PFG experiments yield information about their partitioning between an incorporated and a free site, see Fig. 1a [1].

Polymeric chains in PEM capsule dispersions show two diffusing components [2,3], and are either in intermediate exchange, see Fig. 1, or in slow exchange. PFG experiments in dependence on the observation time, Δ, are analyzed in a two-site model [4]. For the permeation rate of polymers, a scaling law of the molecular weight dependence could be extracted.

Small hydrophobic molecules such as phenol show an interesting regime with monoexponential echo decays, but Δ-dependent diffusion coefficients, which is identified as a regime with $T_{2bound} << \tau_{exch}$ [5]. Here, adsorption of the probe molecules into the capsule wall leads to an effective magnetization sink. However, via their indirect influence on the apparent diffusion coefficient of the free site, a quantitative analysis of the partitioning and the exchange dynamics becomes feasible[5].

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DEUTERON NMR STUDIES OF THE DYNAMICS IN CLATHRATE HYDRATES

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Clathrate hydrates provide nanoscopic pores suitable for encapsulation of a variety of small molecules. The cages, formed by a water network, at sufficiently high temperatures are in turn stabilized by the reorientational motion of the embedded molecules. These host-guest systems are ideally suited to study how the dynamics of the encaged species are affected by the local crystal field stemming from the hydrogen-bonded environment and by their potential interaction with other small molecules in adjacent cages.

Using ^{2}H-NMR we investigated deuterated tetrahydrofuran (THF) in a protonated host, see Fig. 1, a system which was studied by NMR early on [1,2]. We find unstructured, but significantly broadened solid-echo line shapes for temperatures already much above that corresponding to the T_1 minimum. The pronounced temperature dependence of the line width is discussed in terms of various models for the motion of the guest molecules. For temperatures below the T_1 minimum the longitudinal magnetization recovery becomes bimodal with the two contributions exhibiting an interesting temperature dependence.

Fig. 1. Sketch of a THF molecule enclathrated in a cage formed by water molecules.

In the slow-motion regime the THF dynamics is investigated with two-time and four-time stimulated echo techniques. Using the former the strongly stretched reorientational motion of the guests is probed directly on the time scale of milliseconds to seconds. The four-time measurements reveal the existence of static heterogeneities in our samples.

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DIFFUSION AND STRUCTURE IN SELF-ASSEMBLING AND CONSTRAINED FLUIDS STUDIED BY NMR

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Recent explosion of interest to self-assembling systems was caused by their fascinating properties of molecular ordering and spontaneous structure formation on the mesoscopic length scale [1-3]. In particular, successes in molecular engineering permitted one to successfully exploit self-organization processes in production of novel mesoporous materials with tailored functionalities [4]. These materials are optimised for various industrial applications from sorption and catalysis to separation. When fluid systems are subjected to constraints produced by internal microstructures or pore wall confinements, their dynamical and transport properties tend to exhibit strong changes [5, 6].

In this work we study the influence of such constraints on complex molecular dynamics and diffusion in several systems. One group of systems is represented by self-assembling molecules exhibiting supramolecular structure formation and reach phase diagrams. They include a) thermoreversible core and core-shell microgels based on the cross-linked acrylamides b) "small surfactants" c) amphiphilic triblock copolymers consisting of PEO and PPO blocks ("Pluronics") with various affinity to water. Structure and dynamical changes associated with phase transitions are monitored using MAS NMR spectroscopy, NMR relaxometry and PFG NMR diffusometry. In particular, molecules of PEO-PPO-PEO in mixtures with water form four super-molecular structures: micellar, cubic, hexagonal, and lamellar. The diffusivities in all these formations could be measured with the same block copolymer and at the same temperature. Diffusion in the hexagonal and lamellar mesophases was shown to be anisotropic. Crucial effects on molecular dynamic properties and anisotropy of diffusion were observed. The potential use of NMR spectroscopy and diffusion studies as complimentary means of construction of phase diagrams was considered.

Second group of systems includes complex fluid systems confined in mesoporous materials. The examples are given by liquid mixtures in porous glasses and colloid solutions of block copolymers in the mesoporous material SBA-15. First (unique) diffusion study was performed with the PEO-PPO-PEO+water system confined in SBA-15. Diffusion attenuation curves at ambient temperatures exhibited strong deviations from the exponential behaviour and could be well described by the model of anisotropic diffusion. The results obtained were discussed in terms of the constraints imposed by specific molecular ordering and pore walls on the diffusion mechanisms. Dramatic influence of mesopores on the phase state and structure formation of block copolymers is elucidated. Effects of confinements on diffusion properties of liquid mixtures are discussed as well.

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CORRELATION OF PRIMARY RELAXATION AND HIGH-FREQUENCY MODES IN SUPERCOOLED LIQUIDS. A DEUTERON NMR STUDY.

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The question regarding a possible correlation of the time scales of primary and secondary relaxation in supercooled liquids is formulated quantitatively [1]. It is shown how this question can be answered using spin-lattice relaxation weighted stimulated-echo experiments. General expressions relevant for the description of such experiments in the presence of correlation effects are derived and analysed by Monte Carlo integration for various correlation scenarios.

Experiments are performed using deuteron nuclear magnetic resonance above the calorimetric glass transition of ortho-terphenyl, D-sorbitol, and cresolphthalein-dimethylether [2]. The data analysis provides direct experimental evidence for a correlation between both time scales. Limitations of the present experimental method will be discussed in my talk.

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NEW ASPECTS OF PROTON DECOUPLING IN SOLID STATE NMR

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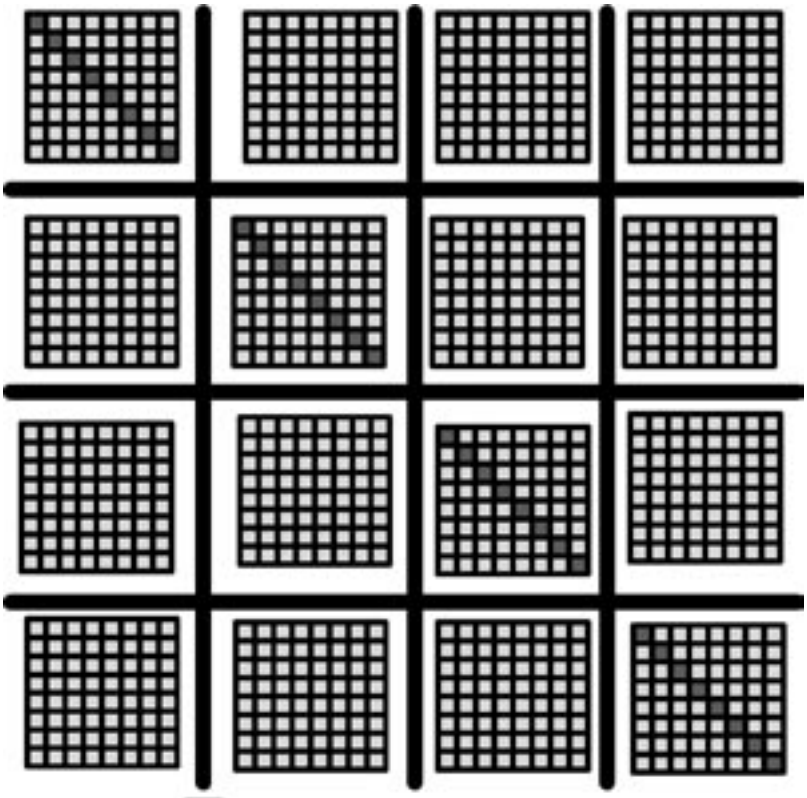
At first we will introduce some of the basic mathematical tools that enable us to describe NMR experiments on samples rotating at the magic angle. Starting with the Bloch equations and Chemical Exchange and mentioning Cross-Polarization, we will describe the unique features of MAS NMR on spins equal to and larger than one half.

Using Bimodal Floquet Theory it will be shown that the spin-density operator and the spin-Hamiltonians can be represented in (infinite) matrix form. This matrix representation provides an excellent tool to understand many of the MAS NMR recoupling and decoupling methodologies introduced in recent years.

After this introduction we will describe our latest decoupling experiments on dipolar coupled proton spin system.



$$H_F = \sum_{n,k} H_{n,k} F_n^r F_k^c + \omega_r N^r + \omega_c N^c$$

$$H_{n,k} = \sum_{i<j} G_n^{i,j} d_{m,k}^{(l)} T_{m,i,j}^{(l)}$$

APPLICATION OF SOLID-STATE NMR SPECTROSCOPY TO LOW GAMMA QUADRUPOLAR NUCLEI

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Two decades ago, the inherently low NMR sensitivity nuclei – mainly those with small magnetic moments, e.g. ^{25}Mg, ^{33}S, ^{43}Ca and ^{67}Zn – were considered to be difficult to characterize by solid-state NMR spectroscopy. These nuclei were termed 'low gamma'. The combination of low frequency, low natural abundance, and with the added complication in many cases of quadrupolar broadening hindered the application of low gamma solid-state NMR spectroscopy. However, it is becoming clear that low gamma nuclei have became more accessible in recent years to study by solid-state NMR[1]. This is mainly due to the availability of high magnetic field spectrometers (up to 900 MHz), where both an increase in signal sensitivity and a decrease in quadrupolar broadening can be achieved. In addition, the success of NMR methodology developments for signal enhancement (e.g. QCPMG, RAPT, HS)[2] has also greatly contributed to the increasing number of low gamma NMR studies. These enhancement techniques can be routinely performed using a low gamma NMR probe and at an immediate magnetic field, making it a valuable application to low gamma NMR studies. The different signal enhancement schemes will be discussed. In addition, improvements of computing resources and quantum chemical (QC) methods have also played a vital role in advancing low gamma NMR studies. Recent examples of low gamma NMR studies complementary with QC calculations will be given: (1) ^{33}S NMR to examine sulphur dissolution mechanisms in aluminosilicate glasses; (2) ^{43}Ca NMR to characterize the Ca-O bond environments in bio/organic model compounds[3,4], in different type of Ca-containing model glasses and in geomaterials; (3) ^{25}Mg NMR to probe the Mg sites in biomaterials; and lastly (4) the signal sensitivity of double rotation (DOR) is compared to conventional multiple-quantum (MQ) MAS for characterising insensitive nuclei with a large quadrupole contribution.

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SPIN DIFFUSION IN MAS SOLID-STATE NMR

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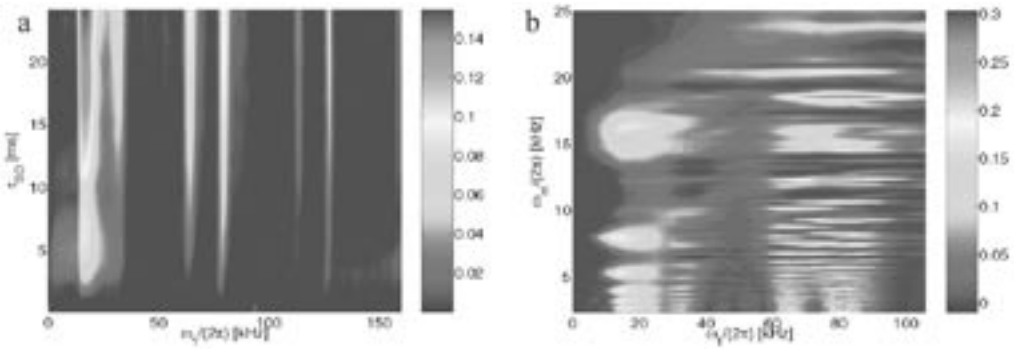
Proton-driven spin diffusion (PDSD) under magic-angle spinning (MAS) is one of the most important techniques in solid-state NMR to obtain distance constraints in uniformly or specifically labelled biomolecules. Advantages of PDSD over other pulse sequences are ease of implementation, low rf-field requirements, and reduced sensitivity to dipolar-truncation effects [1]. The latter is the reason that PDSD can also be used to obtain long-range distance constraints in uniformly labelled samples. At slower MAS frequencies, the residual line broadening by the heteronuclear dipolar couplings provides compensation for chemical-shift differences. At higher spinning frequencies, active recoupling of the heteronuclear dipolar couplings by cw irradiation of the protons at the n=1 rotary-resonance condition (DARR experiment [2], [3]) is used to broaden the lines and speed up the spin-diffusion process.

We have experimentally and theoretically investigated the spin-diffusion process under cw irradiation of the protons in more detail. Our experiments show that under cw irradiation there are distinct resonance conditions and strong polarization transfer is achieved if the rf-field amplitude equals an integer multiple of the spinning frequency plus or minus the isotropic chemical-shift difference of the two spins, i.e., $\omega_1 = n\omega_r \pm \Delta\omega_{iso}$. The strongest transfer is found for n=0, i.e., for $\omega_1 = \Delta\omega_{iso}$, while for larger values of n the polarization transfer is slower. These resonance conditions can be explained using triple-mode Floquet theory [4] as second-order resonance conditions between the homonuclear and a heteronuclear dipolar coupling. In order to see these resonance conditions, one has to transform the Hamiltonian into an interaction frame with the rf-field amplitude and the isotropic chemical shifts. Similar resonance conditions appear also if we apply phase-alternating rf irradiation on the protons. The relevant frequency is then the modulation frequency of the rf irradiation instead of the rf-field amplitude. Figure a) shows the experimental polarization transfer from



the C' resonance to the C^{α} resonance in 1,2-^{13}C-glycine ethylester as a function of the mixing time (τ_m) and the rf-field amplitude (ν_1) at a spinning frequency of ν_r = 45 kHz. One can clearly see that the best polarization transfer occurs around $\nu_1 = \Delta\nu_{iso} =$ 15.9 kHz. Additional areas of good polarization transfer occur for $\nu_1 = n\nu_r \pm \Delta\nu_{iso}$. Figure b) shows the polarization-transfer in the same sample for a mixing time of τ_m = 25 ms under phase-alternating irradiation. One can clearly see that we obtain the highest polarization transfer for $n\nu_m = \Delta\nu_{iso}$ and $n\nu_m = n\nu_r \pm \Delta\nu_{iso}$ Such recoupling experiments can be used to implement a band-selective version of the PDSD experiment. The width of the recoupled spectral region can be increased by replacing the constant rf-field amplitude by a rf-field ramp. We will show examples of such band-selective PDSD experiments on model systems and proteins.

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SPATIALLY RESOLVED NMR IN HEAVY ION IRRADIATED IONIC CRYSTALS

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My talk will deal with the development of a one-dimensional microimaging technique using a constant magnetic field gradient ("stray field imaging") and its current application to the study of radiation damages induced by heavy ion (^{12}C, ^{130}Xe, ^{238}U) irradiation of LiF single crystals. The irradiations take place at the UNILAC linear accelerator of the GSI Darmstadt. Some experimental details: The projectile energies have been, depending on the ion, in the 1 to 3 GeV range. This leads to typical penetration depths of about 100 µm. The NMR measurements are done in a specially designed superconducting gradient magnet at a magnetic field of 3.73 T and a field gradient of 74.3 T/m. The resonant nuclei have been ^{7}Li and ^{19}F. A saturation recovery/FID type experiment has been applied to measure the spin-lattice relaxation times T1 at room temperature. In our experiments the thickness of the excited slice, defining the spatial resolution, has been 7.5 µm according to a pulse length of 45 µs [1].

Fig. 1 exemplifies some spatially resolved ^{19}F signal intensity of a LiF sample after Xe irradiation. The figure indicates that only after sufficiently long evolution times the true rectangular crystal profile is found. For shorter evolution times the relaxation weighted image gradually changes such that eventually it represents the irradiated part of the crystal. From these data position dependent relaxation rates can been deduced (Fig. 2). Within the ion range the fluence dependence of the

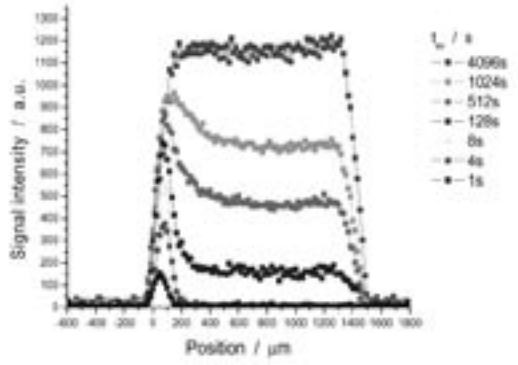

Fig. 1. Signal intensity profiles for a set of different evolution times as indicated. The fluence was 10^{11} Xe ions/cm^2, the excited slice thickness 7.5 µm. The left edge (about 100 µm) of the crystal (thickness 1500 µm) has been irradiated.

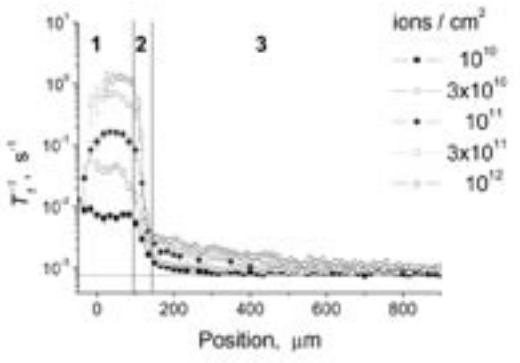

Fig. 2. Position dependent spin-lattice relaxation rates for the ^{130}Xe irradiated LiF crystals for several fluences. "1" to "3" denote the irradiated, transition and non-irradiated zones, respectively.

relaxation rate is clearly visible, and even beyond 100 µm depth (the ion penetration depth) a relaxation gradient persists. The physics of these phenomena and some more recent experimental results (on other systems) will be discussed.

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Acknowledgements

I like to thank the participating GSI scientists Reinhard Neumann, Kurt Schwartz and Christina Trautmann as well as my TUD coworkers Achim Gädke, Annika Hamburger, Beatrice Schuster and Holger Stork. I am also grateful to Peter Dinse and Peter Jakes (TUD, chemistry) who have carried out some accompanying EPR experiments. The project, which is also presented at this school as a poster prepared by Beatrice Schuster, will constitute a part of the Ph.D. thesis of Holger Stork.

MOLECULAR DYNAMICS IN SOFT AND HARD CONFINEMENT – A PLAYGROUND FOR ^{31}P NMR

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Low molecular glass formers dissolved in polymer matrices (soft confinement) as well as in porous silica materials like MCM, SBA and CPG (hard confinement) exhibit pronounced dynamic heterogeneities which are investigated by ^{31}P NMR methods, such as spin-lattice relaxation (T_1), 1D and 2D exchange NMR. Reorientational correlation functions are accessed by the stimulated echo technique. In comparison with ^{2}H NMR, traditionally often employed for addressing molecular dynamics, ^{31}P NMR offers several advantages. For example, due to a T_1 of up to 100 s the accessible 2D time window can be expanded to cover up to 8 decades (1 μs – 100 s) [1]. Only having this possibility at hand, the extremely stretched correlation functions typical of the dynamic heterogeneities in confined systems can be studied on a quantitative base. It is the purpose of the talk to elucidate the characteristics of the dynamics in both types of confinement.

Figure 1 displays the Hahn echo spectra of TCP in 7 nm pores (middle column). It is compared to the behavior of bulk TCP (left column) and to TCP dissolved in the polymer PMMA (right column). Whereas in the case of bulk TCP, within a narrow temperature interval a continuous collapse of a solid-state powder spectrum to a Lorentzian liquid line is observed upon heating, the spectra of TCP in the matrices exhibit a superposition of a powder spectrum and a Lorentzian line with a weighting factor changing continuously over a broad temperature range. Such spectra are explained by assuming a broad distribution of correlation times, i.e., pronounced dynamic heterogeneities are found which are not observed in the bulk system.

Inspecting the T_1(T) data for TCP in the silica matrices with different pore sizes (cf. Fig. 2) the minimum shifts to higher temperatures and becomes flatter with reducing the pore size. Hence, the glassy dynamics slow down, and again the extent of dynamic heterogeneities increases systematically. First confinement effects are observed around 50 nm and get very strong at 4 nm.

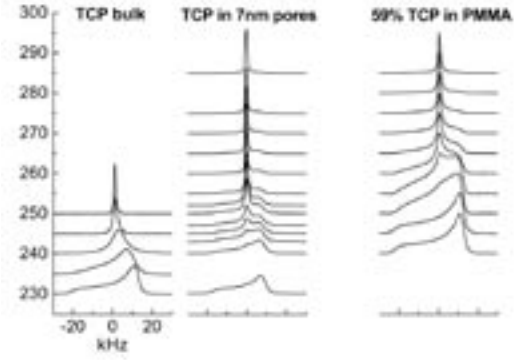

Fig. 1. ^{31}P Hahn-echo spectra for the bulk glass former tricresyl phosphate (TCP; left), for TCP in 7 nm SBA pores (middle), and TCP dissolved in the polymer PMMA; baseline of spectra indicates temperature in K.

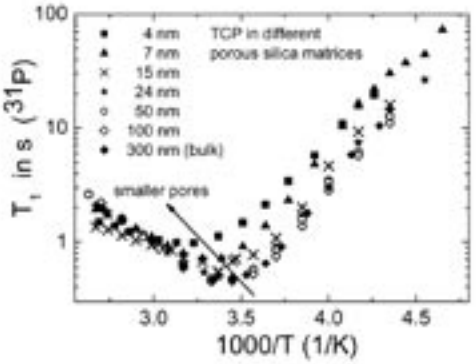

Fig. 2. Spin-lattice relaxation time T_1 of the glass former TCP for different porous silica confinement as a function of reciprocal temperature.

Studying the stimulated echo decay curves together with the 2D spectra, a crossover from a Kohlrausch decay in bulk TCP to an extremely stretched correlation function for the smallest pores is found which is quite similar to the results observed for TCP in PMMA. Moreover, in both cases the heterogeneous dynamics are transient in nature as demonstrated by characteristic exchange intensity in the corresponding 2D spectra (cf. Fig. 3). In other words, slow and fast molecules within the broad distribution exchange their correlation times.

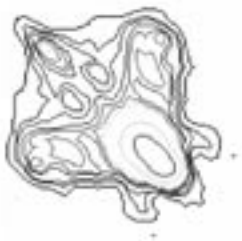

Fig. 3. ^{31}P 2D spectrum for TCP in 7 nm pores of a SBA matrix showing cross like exchange pattern proofing exchange among fast and slow molecules, i.e., the transient nature of the dynamic heterogeneities.

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ORDER AND DYNAMICS IN DISORDERED SOLIDS AS EVALUATED BY SOLID-STATE NMR SPECTROSCOPY

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Solid-state NMR spectroscopy is used to examine different types of surface-modified inorganic oxides. The materials, which play an important role in chromatography or catalysis, consist of an inorganic solid support - typically silica, zirconia or titania - whose surface properties are altered by the attachment of hydrocarbon, functionalized hydrocarbon and fluoroalkyl chains as well as mixed alkyl and fluoro-alkyl chains. Here, also mesoporous materials are considered which possess a well defined porosity and high surface area. ^{13}C, ^{29}Si, ^{1}H, ^{19}F NMR double and triple resonance experiments as well as relaxation studies provide information about the dynamic features, conformational behaviour, molecular interactions and packing properties of the attached organic components. It is shown that these molecular properties depend on various parameters, including type and character of the inorganic support, surface coverage, character and size of the attached organic component, etc.

In the second part of the contribution, solid-state NMR investigations of inclusion compounds and molecular crystals will be presented. For instance, ^{19}F, ^{1}H and ^{13}C CP/MAS NMR studies will be reported which address the structural composition of inclusion compounds made from phenylsubstituted triazines and decamethylferrocene. $^{1}H\{^{19}F\}$ and $^{19}F\ \{^{1}H\}$ cross polarisation dynamics, ^{1}H-^{19}F REDOR as well as ^{1}H-^{19}F and ^{13}C-^{1}H HETCOR experiments are used to provide information about the spatial arrangement of the guest species within the host channels. Dynamic NMR studies on inclusion compounds (host systems: urea, cyclophosphazene, perhydrotriphenylene) and on inorganic molecular crystals address the motional and ordering characteristics of these materials. In general, it is possible to distinguish between various motional contributions, including conformational as well as rotational and reorientational motions, the latter of which strongly depend on the symmetry of the examined molecular species. Moreover, it is found that molecular fluctuations may also play an important role for the relaxation behavior of the guest molecules in guest-host materials.

SCOPE AND LIMITATIONS OF ACCURATE STRUCTURE DETERMINATION USING LIQUID-CRYSTAL NMR

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When dissolved in liquid-crystal solvents the resulting partial orientation of the solute leads to anisotropic dipolar (and quadrupolar) couplings that usually dominate the high-resolution NMR spectrum [1,2]. The observed dipolar couplings depend on $1/r^3$ (with r the distance between nuclear spins), and hence relative solute structures can be derived from them. Since dipolar couplings can be measured often to appreciably better than 1 Hz, derived structural parameters may be expected to be quite accurate. However, to translate the accurate dipolar couplings provided by NMR to solute structures of similar precision is an area notorious for its pitfalls.

First, let us consider a solute with only one conformation. Since every molecule undergoes zero-point vibrational motions with amplitudes of typically 0.1 Å, it is clear that structures accurate to 0.01 Å or better can only be obtained if the process of vibrational averaging is well understood and accounted for. For small-amplitude vibrational motions the dipolar couplings $D_{\mu\nu}$ between magnetic nuclei μ and ν can be expressed as [3]:

$$D_{\mu\nu} = D_{\mu\nu}^{\ e} + D_{\mu\nu}^{\ a} + D_{\mu\nu}^{\ h} + D_{\mu\nu}^{\text{non-rigid}}$$

The various contributions to the dipolar coupling involve $D_{\mu\nu}^{\ e}$ (the dipolar coupling associated with the molecule in its rigid equilibrium configuration), $D_{\mu\nu}^{\ a}$ (the contribution to the dipolar coupling arising from the anharmonicity of the vibrational potential), and $D_{\mu\nu}^{\ h}$ (the contribution arising from averaging over the harmonic part of the vibrational potential). $D_{\mu\nu}^{\ e}$ can be obtained from the equilibrium structure of the molecule. For $D_{\mu\nu}^{\ a}$ knowledge about the anharmonic force field in the form of the $\Phi_{mll'}$ the semi-diagonal cubic anharmonic force constants, is required. For the determination of $D_{\mu\nu}^{\ h}$ knowledge of the harmonic force field F_{ij} is essential. The relatively unknown contribution $D_{\mu\nu}^{\text{non-rigid}}$ arises from the interaction between reorientational and vibrational motions [3-6]. In the case of large-amplitude vibrational motions the approach described here breaks down.

Additional complications arise for solutes that undergo conformational change. Unfortunately, a description in terms of an 'average' molecule that requires a single set of orientation parameters is not valid [8]. Instead, we must consider a situation where every conformation has its own set of orientation parameters. In additon, only products of orientation parameters and conformational probabilities can be derived from NMR spectra. In order to proceed, models that either predict orientation parameters, or conformational probabilities, must be introduced.

With the advent of novel methods of automated spectral analysis that rely on sophisticated genetic algorithms, NMR spectra of solutes in liquid crystals that were deemed to be 'insoluble' can now be analysed routinely [7]. This allows the detailed study of molecules such as butane and pentane that are benchmark examples of solutes undergoing conformational change.

The determination of accurate solute structures by means of liquid-crystal NMR cannot be considered to be a routine method. Available evidence of studies on simple solutes in which the various contributions to the dipolar couplings were accounted for carefully indicate that these solutes dissolved in a variety of liquid-crystals possess structures that cannot be distinguished from those in the gas phase. In the case of larger solutes, for which all the contributions to the dipolar couplings cannot be obtained easily, great care should be exercised in ascribing apparent 'discrepancies' to elusive effects such as specific chemical interactions, or exchange between several sites in the liquid-crystal environment.

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WHAT NMR OF SOLUTES IN LIQUID-CRYSTALLINE SOLVENTS CAN TELL ABOUT THE ORDERING POTENTIAL

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The NMR of orientationally ordered solutes in liquid crystalline solvents gives accurate values of order parameters, and these in turn can be interpreted in terms of the anisotropic intermolecular potential that causes the orientational ordering [1,2]. A wealth of experimental evidence leads to the conclusion that a single mechanism is incapable of describing solute orientational order in different liquid crystals. We shall demonstrate that experimental results can be rationalized in terms of two independent second-rank mechanisms whose relative importance varies with liquid-crystal solvent [3]. There is strong indication that the dominant mechanism involves short-range interactions that depend on solute size and shape. The second mechanism is less certain, and various possibilities will be discussed with the favourite involving the molecular quadrupole.

Nematic liquid crystals exhibit orientational order while smectic liquid crystals exhibit, in addition, positional order. Obtaining information from NMR experiments about the positional order is challenging. We have applied the ideas of Kobayashi / McMillan theory for smectic ordering to the results obtained from a collection of solutes in several liquid-crystal solvents that exhibit both a smectic A phase and a higher-temperature nematic phase [4]. The main problem in the analysis involves extrapolating the nematic potential into the smectic A phase. We use the idea (above) that the nematic potential can be described in terms of a maximum of two second-rank interactions in order to obtain estimates for the positional order parameter and for the strength of the coupling between positional and orientational ordering.

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CONSTRAINED MOLECULAR SELF-DIFFUSION IN THE BULK WATER MEASURED BY NMR

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Intermolecular hydrogen (H) bonds leads to the associative structure in the most abundant substance on earth, the water. The ordered associates of water molecules-the clusters[1], strongly affects water properties compare to other hydrides. It evinces interest of scientists because they are formed in the region of a temperature interval of the existence of live nature and thus determines, on the global scale, the Earth's climate, the origins and maintenance of life. Much work has been invested in developing models for individual water molecules for use in molecular dynamics simulations. These models are very useful, particularly for investigating short-range order, but have difficulty addressing the totality of the unusual nature of water including the long-range ordering. According to the current thinking, on a very short pico-second time scale, water is more like a "gel" consisting of a single, huge hydrogen-bonded cluster. Rotations and other thermal motions cause individual hydrogen bonds to break and re-form in new configurations. Investigations of molecular self-diffusion provide important information on molecular organization and interactions with the environment in many systems as well in water. Recent NMR measurement of molecular motion in water by treating the effect of the magnetic field gradient via the time dependence of the accumulated spin phase[2] (MGSE method) provides the spectrum of velocity auto-correlation in water.

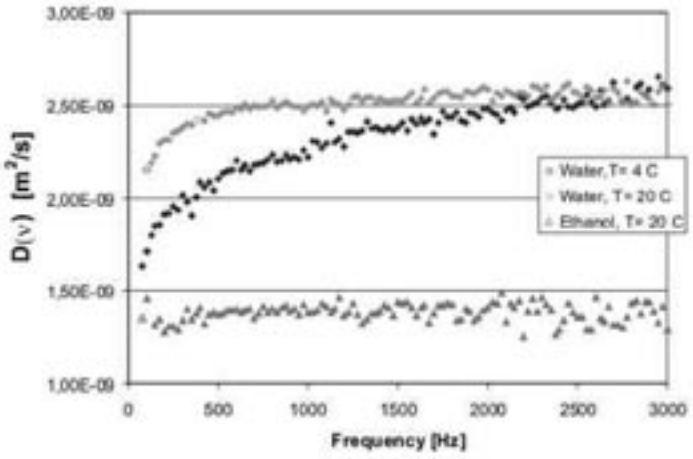

Fig. 1. Molecular velocity autocorrelation spectra of pure water at different temperatures measured by MGSE method. The constant spectrum value of non polar ethanol emphasizes the role of hydrogen bonding at the diffusion of water molecules

The spectrum decrease in the low frequency range came as surprise giving the frequency dependence of the water velocity autocorrelation spectrum with almost linear dependence on $D_{(\nu)}$ versus $1/\sqrt{\nu}$ resembles the restricted molecular motion. Constant spectrum value of nonpolar ethanol in the low frequency range gives an indication about the water diffusion constrained by the hydrogen bond interaction. Low frequency lowering of water spectrum can be fitted by the solution of Langevine equation where stochastic motion is impeded by attractive centers.

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ORAL PRESENTATIONS

PHYSICAL BACKGROUND TO NUCLEAR MAGNETIC RESONANCE

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NUCLEUS-MAGNETIC RESONANCE (NMR) AND ITS APPLICATIONS TO SCIENCE AND TECHNIQUES

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Discovering NMR phenomenon takes its origin from the very moment when Ampere's hypothesis concerning atomic magnetic moments has been proposed. Contemporary theory of atom magnetism and substance determines the nature of magnetism phenomenon by orbit movement of electrons, their spin and, besides, by atomic nucleus spin [1].

Shtern and Herlah's experiment (1922) confirmed that atoms have magnetic moment. Later, it was confirmed that atom's nucleus could be stimulated or be under conditions that corresponded to a certain (quantum) data of energy.

NMR is a phenomenon of resonance energy absorption of changeable magnetic field of fixed frequency by a substance which is located in a strong stable magnetic field $\vec{H}_0$ which in its turn is under a slight radio frequency ($10^6 \div 10^7$ Гц) magnetic field $\vec{H}$. (besides, ($\vec{H} \perp \vec{H}_0$). That's why NMR phenomenon is considered to be one of electroscopic methods [2].

Order of magnitude of resonance absorption is determined by balanced nucleus magnetizing of a substance (nucleus paramagnetism)): $\boldsymbol{\mu}_0 = \boldsymbol{\chi}_0 \vec{H}_0$ where $\boldsymbol{\chi}_0$ - is a static nucleus susceptibility.

Under real conditions nucleus spins interact between themselves and their environment, for example, with a crystal grating. It results in establishing heat balance in a certain period of time (time of relaxation) Processes of relaxation depend on a change of longitudinal and cross components of nucleus magnetization. They are called spin-grating and spin-spin relaxation correspondently.

Investigation of NMR spectrums is performed by a slow change of field $\vec{H}$ frequency $\boldsymbol{\omega}$ or field intensity $\vec{H}_0$. Often modulation$\vec{H}_0$ by a field of sound frequency is applied.

Under researching crystal structure methods of „quick modulation" result in higher sensibility. It happens when a field $\vec{H}_0$ is modulated by a sound frequency in such way that processes of relaxation can't be finished in a period of modulation and spins system isn't stationary. Impulse methods like „spin echo" are also used.

Resonance frequency for every nucleus has its definite value. If frequency of external field $\vec{H}_0$ differs a little from its critical meaning than the transitions between energy levels of a nucleus aren't stimulated. In other words the width of a line of resonance absorption is little. If we know critical frequency and other characteristics of frequent dependence of transitions we can obtain the following information about solid bodies' properties [3]:

- we can precisely define the value of nucleus magnetic moment;
- we can appoint the influence of paramagnetism electrons conductivity on resonance characteristics;
- we can appoint that the width of resonance line mostly depends on degree of violation of resonance conditions by stimulated influences of neighbor nucleus. Researching these stimulations we can obtain certain information about atomic diffusion;
- in fusions and also in transformed materials internal local fields change resonance conditions;
- the measurement of resonance absorption of these materials can be used in the field researching;

Interaction of electrical quadrofields nucleus' moment with a local electrical field in a substance mostly influence the time of relaxation< width and the shape of NMR lines. Thus, for example, in liquids that have nucleuses with a large quadrofields moment NMR could be obvious only in a substance with a symmetrical structure of molecules.

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APPLICATION OF NUCLEAR MAGNETIC RESONANCE

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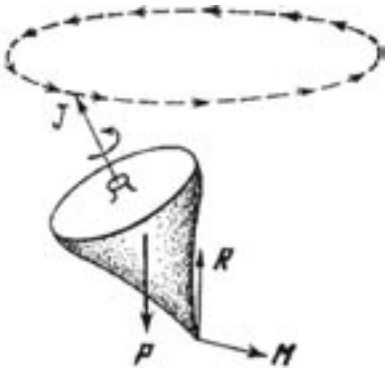
To look what is inside of the man virtually, has always been the doctor's dream. Now it can be done by tomographs with using the effect of nuclear magnetic resonance (MR-tomography). Such examinations are widely used all over the world, moreover, the images of organ's layers and tissues have high separating ability and contrasting. In fact it is possible to get images which are similar to the pictures of anatomic cuts in quality.

In computer's tomographs on the base of effect of nuclear magnetic resonance (NMR) there isn't ionizing radiation, and that is why diagnostic examinations on MR-tomographs are practically completely safe. The effect of NMR was discovered by scientific groups in Standford and in Harvard universities in 1946. Fist, who discovered it were F. Bloch and E. M. Purcell. They won Nobel prize in physics in 1952. They established that nuclei of some atoms at their disposition in the magnetic field absorb the energy of electromagnetic impulse, and after completion of impulse radiate it as a radio signal. For the appearing of such nuclear resonance, induction of the magnetic field and frequency of electromagnetic impulse must correspond each other in some way.

Nuclear magnetic resonance (NMR) is resonance absorption of electromagnetic energy by a substance, caused by extraorientation of magnetic moments of atomic nuclei. Is is one of methods of radiospectroscopy. It is observed in the strong permanent magnetic field of H_0, which with the weak radio frequency magnetic field of H is imposed on H ($H \perp H_0$). Resonance character of the phenomenon is determined by properties of nuclei which have a moment of quantity of motion and magnetic moment.

NMR, as well as other types of magnetic resonance, can be described as the classic model of gyroscope. In the permanent magnetic field of H_0 some forces, caused by magnetic moment, cause precession of magnetic and mechanical moments (figure 1). A magnetic moment makes a precession round the direction of H_0 with frequency $\omega_0=gH_0$, the angle to precession here remains unchanging (g is gidromagnetic ratio). As a result of radio-frequency field H influence with resonance frequency ω_0; the precession angle changes, which causes considerable changes in the projections of magnetic moment in the direction of the field of H_0 even in the weak field of H. It is accompanied by resonance absorption of electromagnetic energy and becomes apparent after the appearance of induction in the coil, which surrounds the model, which is investigated.



NMR spectrums are observed by slow changing frequency of the field H or tension of the field H_0. Modulation of the field H_0 is often accompanied by the field of audio frequency. That is why experiments are carried out in strong magnetic field.

For medical purposes the effect of NMR has been applied since the beginning of 80th of the last century. First MR-tomograph was shown on congress of radiologists in Paris in 1982. Principle of magnetic resonance of nuclei of hydrogen is the base of MR-tomograph. Much water is contained in organs and tissues of man, that's why hydrogen is most widespread element in man's organism. Diagnostic examinations are executed in such way: a patient is placed in the strong static magnetic field of MP-tomograph, where nuclei of atoms of hydrogen in the man's body which are a little magnetic, are oriented in the direction of the field. The explored area is chosen by adding the weak variable magnetic field with the help of gradient coils. Then tomograph sends an electromagnetic signal (radio wave); it is done by the radiofrequency impulses generator. The atoms of hydrogen are stimulated and generate the proper signal which is caught the receiving coils-detectors of tomograph. Different types of tissues (bone, muscle,, etc.) contain different number of atoms of hydrogen, that is why they generate signals with different descriptions. After decoding signals the rendering of appropriate layer is erected(by special methods).

The phenomenon of magnetic resonance is used for the discovering and measurement of electric and magnetic co-operations of electrons and nuclei in the macroscopic quantities of tissues.

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NMR INVESTIGATIONS OF THE AGING OF COLLOIDAL LAPONITE AQUEOUS SUSPENSION

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Introduction: In recent years, dynamical arrest in colloidal, aggregation and gelation, are topics of fundamental interest in soft condensed-matter physics [1]. Laponite suspension is a colloidal aqueous suspension which undergoes a dynamical arrest following different routes [2,3], depending on the clay concentration. In laponite suspensions, nanometric size form a charged colloidal dispersion with a rich phase diagram. Moreover, it is characterized by an anisotropic charge distribution and by the competition between attractive and repulsive interactions. It is known that also in isotropic liquid phase and for very low clay concentrations, laponite experiences aging phenomena [4].

NMR advanced techniques are powerful tools to investigate colloidal systems. Triple-quantum ^{23}Na NMR provides important knowledge about counterions dynamic (rotational correlation time τ_C and quadrupolar couplng constant QCC=e^2qQ/h) and static properties (counterion concentration p_b) within the multi-exponential quadrupolar relaxation theory. The selection of triple-quantum intramolecular coherences ensures that the signal detected arises exclusively from sodium nuclei which are involved in coulombian screening shells of colloidal particles or clusters, allowing the monitoring of system dynamics. The Diffusion Tensor contains information describing the anisotropy of the diffusive phenomena assuming Gaussian diffusion of particles and a mono-exponential behaviour of the signal decay. Specifically the log of the diffusion-weighted signal attenuation is linearly dependent on the b value, which derives from diffusion gradient strength G and on diffusion time Δ. The Apparent Diffusion Coefficient (ADC) along different directions allowing water dynamics to be characterized.

Aim of our work was to monitor the aging process by means of triple-quantum filter NMR and to investigate water dynamics of the arrested state by means of diffusion techniques in Laponite suspensions at different clay concentrations, all belonging to the isotropic phase range.

Methods and Materials: Six Laponite aqueous suspensions, at the weight concentration of 1.2, 1.4, 2.0, 2.4 and 2.8 wt % were prepared in a glove box under N_2 flux. The powder was dispersed in deionized water and D_2O, stirred vigorously until the suspensions were cleared, filtered through 0.45 μm pore size Millipore filters and then sealed in quartz NMR tube. The route towards the arrested state was monitored by triple-quantum ^{23}Na NMR on a 9.4 T Bruker Avance NMR system; we performed both spin-echo and inversion recovery triple quantum filtered measurements to extract p_b, τ_C and QCC. After the arrested state has been reached, we investigated the diffusion water properties with a Pulse Gradient Stimulated Echo (PGSTE) sequence. We chose two different b-value range to investigate slow and fast diffusion components.

Results: From the triple-quantum experimental data we extracted the variation of p_b, τ_C and QCC for increasing aging time and we were able to differentiate two different routes towards gelation. In fact the samples can be divided into two groups on the basis of their concentration; at low concentrations (<2%) pb has a decreasing trend, QCC increases while τ_C decreases down to the asymptotic value of 21ns. At higher concentrations instead, a jump to a lower screening length is exhibited, QCC values are higher and have a decreasing trend, while τ_C increases up to 19ns. Since p_b gives the weakly bound counterions ratio, τ_C establishes the time scale the system retains memory of the electric field gradient fluctuations and QCC provides the magnitude of the fluctuating interaction, our results agree with a model in which at low concentration the arrested state is reached though the formation of clusters of Laponite disks while at higher concentrations single disks are the basic units of the arrested phase. From the diffusion experimental data we recognize the existence of a fast and a slow-diffusing component; the first one has an ADC value slightly smaller than that exhibited by pure water, while the second one has a diffusion constant of the order of 10^{-11} m²/s. Both ADC values show a decreasing trend as concentration increases. Moreover, in the arrested state the isotropic phase does not correspond to isotropic diffusion since the ADC value is higher along the gradient direction parallel to the applied magnetic field respect to the orthogonal directions.

Conclusion: We studied Laponite colloidal suspensions at different clay concentration during the aging process by means of Triple-quantum ^{23}Na NMR, and we found evidence for two different routes to gelation: at low concentrations the gel is reached with clusters formation while at high concentrations single Laponite platelets are the basic units towards the arrested phase. We also investigated the arrested phase by means of ADC measurements. We outlined that in the arrested state the isotropic phase does not correspond to isotropic diffusion since the ADC value is higher along the gradient directions parallel to the magnetic field. This feature is common both to the slow diffusing component and to the fast diffusing one. Our results prove NMR advanced techniques to be an original tool to investigate the aging phenomenon in aqueous colloidal dispersions.

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RELAXATION PROCESSSES IN BIOPOLYMERS

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To interpret the temperature, frequency and hydration dependences of NMR relaxation times of protons of water molecules in biopolymer matrices one has to assume a model for the interactions the protons are involved in and for the dynamics of the water molecules [1-4]. Assuming that pure dipole-dipole interaction are present, and that we have at least two different motions of absorbed water, we are able to simulate the relaxation time dependences and, in the next step, to estimate the values of molecular dynamics parameters (e.g., correlation times and activation energies) [5].

To verify the theoretical models the spin-lattice relaxation time, T_1, spin-spin relaxation time, T_2, and spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, have been measured over the temperature range 5 to 70 °C for potato starch and pure cellulose powders for three states of hydration. The hydrations were attained by i) letting the samples hydrate under ambient humidity conditions, ii) drying them over silica gel and iii) fully saturating them with liquid water. In addition, the dispersion of $T_{1\rho}$ has been analysed for slow molecular motions of absorbed water molecules. Indirectly, information about the structure of biopolymers has been deduced.

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THE STRUCTURAL DYNAMICS IN A PROTON CONDUCTING IMIDAZOLIUM OXALATE

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The imidazole salts of dicarboxylic acids constitute alternatives to polymer membrane electrolyte fuel cells relying on water solvated protons as their conduction media. The proton conductivity of imidazole salts do not depend on the relative humidity and they can be used at the temperature above 100 °C. We studied the structure, proton conductivity and molecular dynamics of different imidazole salts of dicarboxylic acids: imidazolium oxalate, imidazolium adipate monohydrate and diimidazolium suberate [1,2]. In this work we will present only the results of the study of imidazolium oxalate ($C_5H_6N_2O_4$). The studied compound was obtained by the method described in [1]. Our crystallographic data of imidazolium oxalate confirmed the previous results obtained by [3]. The crystal structure belongs to the monoclinic system with $P2_1/n$ space group, Z=4. Imidazolium cations and carboxylate anions self-assembled via N-H...O hydrogen bonds to form chains composed of alternating imidazolium cations and carboxylate anions (motif A). The anions formed O-H…O hydrogen bonds in head-to-tail arrangements (motif B). Intersections of motifs A and B formed layers of molecules in the studied structure as shown in Fig.1

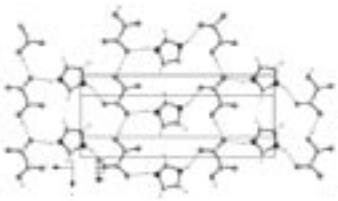

Fig. 1. Molecule arrangement in a single layer of imidazolium oxalate showing the hydrogen bonds network

The function of the materials as well as the proton conductivity depends not only on the static structure of the material, but also on the structural dynamics. In imidazole based proton conducting materials the proton transport is a Grotthus mechanism. This cooperative process assumes that the fast proton hopping between hydrogen bonded molecules has to be followed by thermally activated molecular rearrangements, which involves the imidazolium ring reorientation. Our ^1H spin-lattice relaxation and ^1H - ^{13}C CP/MAS NMR measurements (Fig. 2) evidence the imidazolium ring reorientation in the imidazolium oxalate.

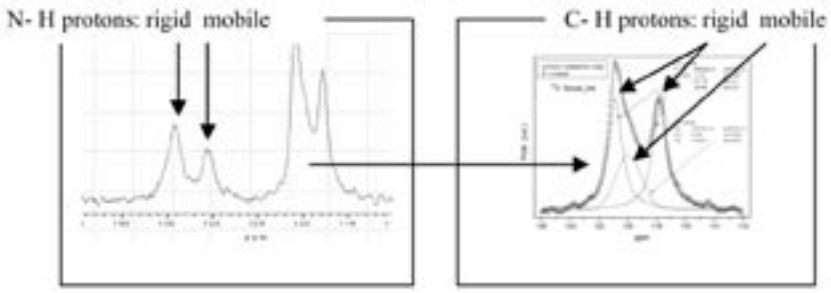

Fig. 2. ^1H - ^{13}C CP/MAS NMR spectra of imidazolium oxalate (only the part characteristic for imidazilium ring is shown)

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THE NMR SPECTRUMS

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The NMR spectrums in liquids for nucleus with a spin *I = 1/2* (not having a quadrupole moment) differ in features. Because of small width of lines this field is determined as NMR of high permission. The spectrums of high permission turn out for the protons F^{19} ,C^{13}, P^{31}, and some other nuclei in mobile liquids. Single lines in this case are found only in compounds, where the NMR nucleus occupies chemically equivalent positions (water, benzene, cyclohexane). More complex compounds give many line spectrums (figure). Spectrums structure is defined by two effects. First, so-called chemical shift appears as a result of co-operating field H_0 electrons surrounding *nucleus*. Electrons excitation causes the shift of permanent constituent of the field influencing the nucleus. This shift is in proportion with tension of the field and is measured in relative numbers (in millionths for protons). Chemical shift scale depends on the structure of electronic shells and the character of chemical ties which allows to judge about the structure of molecules on a spectrum. Chemical shift is characteristic of wide lines, but it presents basic and visible effects in the spectrums of high permission. Besides chemical shift, the structure of spectrums of high permission is determined by indirect spin-spin co-operation [1]. Direct magnetic diploes co-operation of nucleus in mobile liquids is ineffective, as a result of Broun motion of molecules (this effect was indicated as the reason for narrowing lines). Indirect spin-spin co-operation is the secondary effect caused by polarization of electronic shells by the field of nuclear moments. This effect reminds direct co-operation of spins in quality, but the size

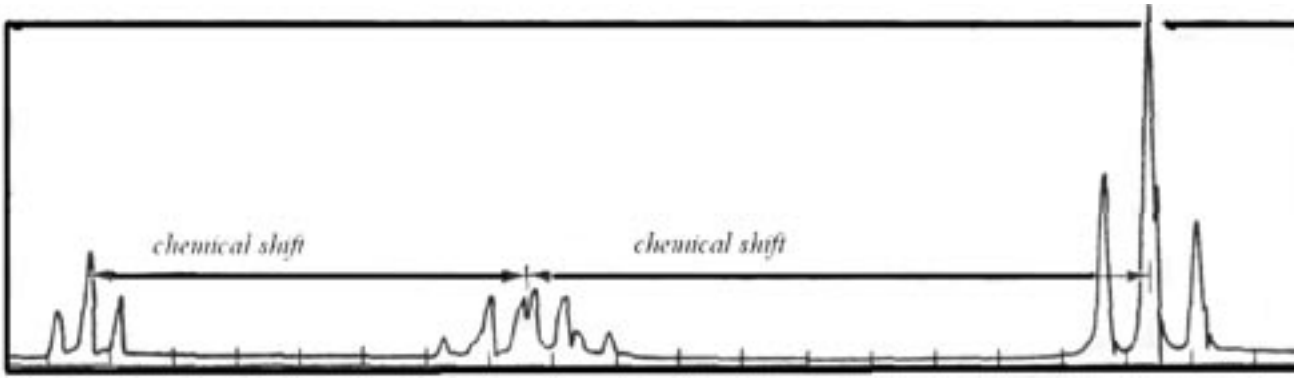

Figure 1. The proton's NMR in pure ethil spirit. Resonanse line spliting of OH, CH_2 and CH_3 which depend on spin-spin interactions

of splitting is much less. Splitting does not depend on H_9 and is measured in *Hertz*. The size of splitting often turns out close in size of with chemical shift those results in spectrums complication. The most easily interpreted spectrums appear in applying the strong field H_0, where the spin-spin splitting is less dependent from chemical shifts [2].

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MOBILITY OF CD4 MOLECULES IN CAGES OF ZEOLITES AS STUDIED BY DEUTERON NMR RELAXATION

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Deuteron spin–lattice relaxation was applied to study translational and rotational mobilityof CD_4 molecules trapped in the cages of zeolite NaMord. When going from high temperatures down, we observed a change in the slope of the relaxation rate at T_{TR} (Fig.1), similar to that found in the case of other molecules in zeolite cages [1]. This change is related to a transition of molecular mobility from predominantly translational (molecules fly across the cage) to reorientational (molecules roll over the cage walls). Free CD_4 rotators fly across cages and undergo collisions with cage walls and each other. There is no relaxation between collisions, but each collision introduces a change of orientation, however by a small angle only. Therefore many collisions are necessary to provide effective relaxation and the correlation time is long. That explains the slope characteristic for low temperature side of the relaxation rate maximum above T_{TR}.

Tetrahedral methane molecules are treated as quantum rotators. Relaxation rates related to the intra quadrupole interaction are derived for the T and A+E symmetry species in the presence of large tunnelling splitting, consistently with the assumption that the A and E species molecules relax at the same rate. An exchange model is presented, which describes the effect on relaxation of CD_4 jumping between two positions characterized by different potentials. While staying at either position the molecule has some freedom to move in the vicinity of Na^+ ions. This causes a time–dependent external electric field gradient, which contributes to the deuteron relaxation rate via the electric quadrupole interaction. Spin conversion transitions couple the relaxation of magnetizations of T, A and E spin species, which is taken into account by reapplying the presented model under somewhat different conditions. Such two step procedure leads to successful fits with the experimental results obtained in the range of temperatures roughly 20–200K for zeolites HY, NaA and NaMordenite [2].

Fig. 1 and 2 show fitting theoretical results for NaMord zeolite in the range 100 – 16K. Upper continuous line shows a fit for T species and begins at the temperature where its weight deviates significantly from zero. At higher temperatures CD_4 molecules fly freely across zeolite cages and relaxation changes accordingly, while incoherent tunneling dominates for immobile molecules below 16K.

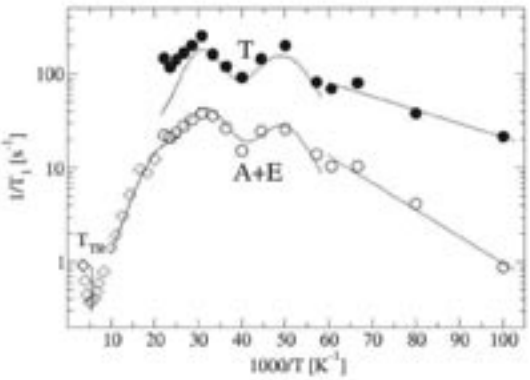

Fig. 1. Deuteron spin-lattice relaxation rates for CD_4 in NaMord.

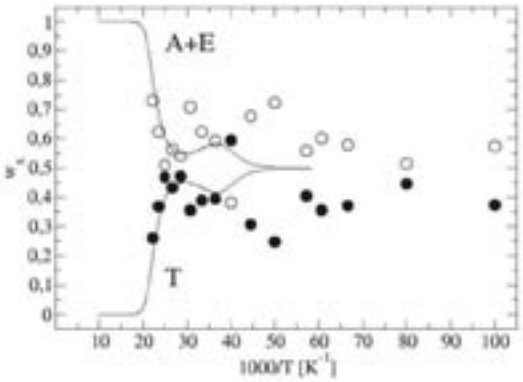

Fig. 2. Weights of the relaxation rates.

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THEN TUNNELING DISSOLVES IN THE AIR

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The paper concerns the dynamics of methyl bearing and hydrogen bonded solids in a wide temperature regime. The title of the paper is a quotation from the referee's report on one of our paper rejected in 2000. The referee wrote - everything that is "new" is also basically wrong. He also advised us - in that case the rate constants k_{ov} and k_{tu} of the two processes, assumed to be independent, simply add and lead to one single inverse correlation time $1/\tau = k_{ov} + k_{tu}$. Such an expression for the total rate constant approximated by the biexponential dependence whose first term is the Arrhenius-like dependence and second one describes the deviations from the Arrhenius law inserted into expression for the spectral density representing the uniform, single motional process has been accepted in literature since many years. The authors of ref. [1] wrote "In this letter, we present experimental data which finally and categorically confirm that the transition between quantum and classical regimes is smooth and continuous and characterized by a single correlation time".

Our theoretical approach [2-11] to the to the NMR relaxation of solids containing tunnelling molecular groups (O-H…..O $\leftrightarrow$ O….H-O, CX_3 undergoing hindered rotation) is based on the Woessner method of total spectral density determination [12] and solution of Schrödinger equation which gives an explicit tunnelling rate constant. Woessner wrote: "Although the two types of motion are independent, their contributions to relaxation are not". In the space of the potential barrier, the particles with kinetic energy lower than the height of the potential barrier undergo tunnelling jumps or are reflected from the potential barrier (Schrödinger). The sum of the tunnelling and reflection probabilities is one. The probability of particle jumps above potential barrier is governed by the Arrhenius law. The Maxwell distribution of thermal energy implies that the probabilities of tunnelling and stochastic jumps over the barrier can exist simultaneously at any temperature. However, above the temperature at which the average thermal energy equals the activation energy, the probability of tunnelling jumps practically becomes zero.

The methyl group relaxation differs from the hydrogen bonded proton relaxation by the third source of stochastic motion which modulates the interaction Hamiltonian. This motion does not refer to the mass transportation, but the tunnel splitting frequency fluctuations.

The performed by us the spin-lattice relaxation measurements are discuss in terms of the new theoretical approach.

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^{2}H SOLID STATE NMR INVESTIGATIONS OF NAPHTHALENE INSIDE THE MESOPOROUS SILICA OF TYPE MCM-41. LINESHAPE ANALYSIS SHOWS MELTING POINT DEPRESSION AND THE PROCESS OF MELTING OF NAPHTHALENE BTW 190K-210K

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The melting point of pure Naphthalene is 354K (81°C). After sublimation into the pores of MCM-41 (pore diameter 3.3nm) the melting point is no longer well defined. This observation was first done by H. Günther [1]. Via ^{1}H-NMR we show that there is no hydrogen bond btw. the surface silanol groups and the aromat at room temperature. Because of the huge surface of the host material (1040m^2 per Gramm) the host-guest interaction is important and lead to a frozen sample at 190K (-83°C). From 180K to 190K in steps of 2K only a rotation about the C_2-axes of the molecule is observed while the melting starts very slowly. From 190K to 210K in steps of 2K the melting process is observed. The solid echo sequence is used with an echodelay τ of 35µs and a puls lenght of 3.5µs.

Via lineshape analysis using a laboratory written MatLab program the kinetic parameter of the processes , the jump rate k, and the thermodynamic parameter, the enthalpie ΔH, is determined. For the lineshape analysis the Liouville formalismen is used which will be intruduced. The melting is simulated as an isotropic rotation of one C—D. The quadrupol tensor is transformed using the symmetry of an octahedron. For the simulation of the rotation about the C_2-axes the quadrupol tensor is transformed according to the structure of the molecule.

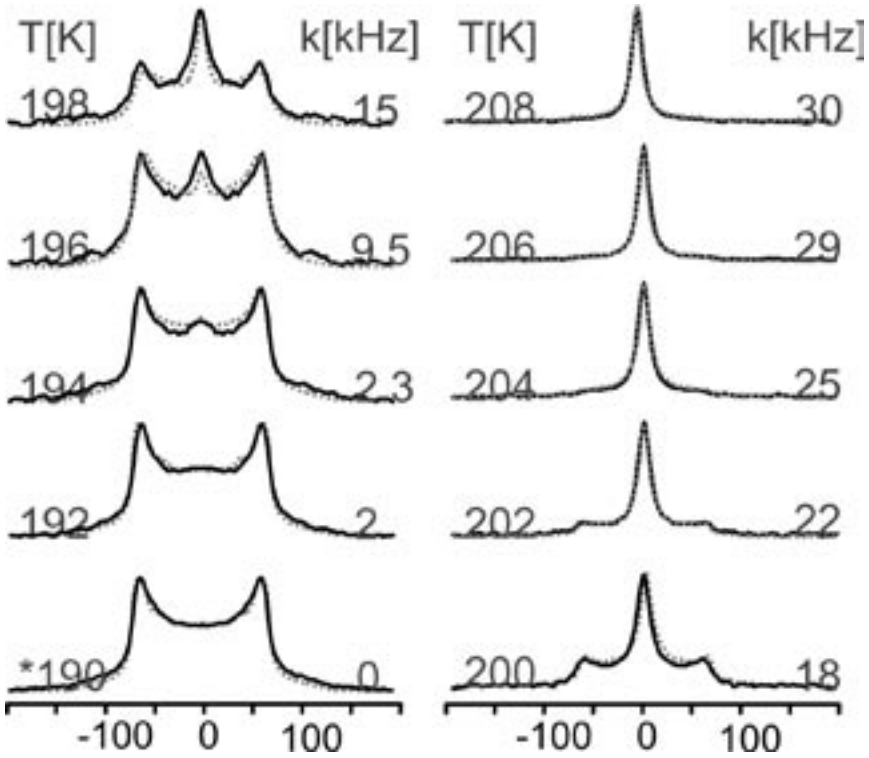

Fig.1. Experimental spectra (black line) and simulated spectra (dotted line) of naphthalene in MCM-41.

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PHASE TRANSITIONS UNDER CONFINEMENT: FURTHER INSIGHT USING PFG NMR

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Understanding of the details of phase transitions under confinement is very important for their application in industrial and environmental applications such as catalysis or mass separation. This is also related to structural characterization of porous materials. Indeed, one of the widely accepted approaches for characterization of novel nanoporous materials is the measurement of gas adsorption, where the amount adsorbed is measured as a function of external conditions (pressure, chemical potential) [1,2]. The adsorption isotherms provide information about the pore structure, surface, volume, and the adsorbate-wall interaction [1], however their behaviour is still not understood in all details. One of such examples is the adsorption hysteresis phenomenon where in mesoporous materials with pore sizes from 2 to 50 nm the amount adsorbed depends on the direction how the external conditions are changed.

Being a non-equilibrium phenomenon, adsorption hysteresis behaviour is governed by the phase transition dynamics of the adsorbate molecules in the pores [3]. To study the phase transitions under spatial confinement, pulsed field gradient (PFG) NMR provides additionally to the macroscopic information (amount adsorbed) the microscopic information (self-diffusivity) about the system. In parallel to the adsorption hysteresis, the hysteresis behaviour of the self-diffusivity has been observed (Fig. 1).

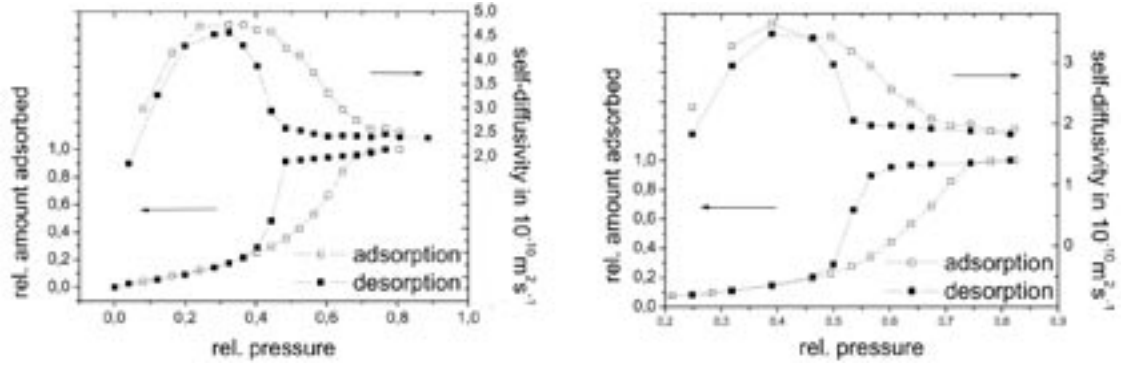

Fig.1. Hysteresis behaviour of adsorption and self-diffusivity isotherms for cyclohexane in Vycor (left), and in porous silicon (right) at 297K, respectively.

On the left-hand side, the hysteresis behaviour for amount adsorbed and the corresponding self-diffusivities of cyclohexane in Vycor 9730 porous glass with random disordered pores are presented as function of external pressure and adsorption history. In line with Vycor, the hysteresis loops for electrochemically etched porous silicon with set of straight parallel pores are shown on the right-hand side. Both experiments provide alike isotherms for completely different materials leading to failure of established characterizing methods.

This example should give an impression of the importance of further understanding of phase transitions in nanoporous materials. This may be gained experimentally assessing microscopic information about the self-diffusion provided by the PFG NMR and correlating the computer based calculations (Monte Carlo and Mean Field Theory) with the experimental results [4, 5].

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MULTINUCLEAR AND DOUBLE RESONANCE SOLID-STATE NMR STUDIES OF PRECURSOR-DERIVED CERAMICS

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Polymer-Derived Ceramics (PDCs), such as SiCO, SiCN and SiBCN systems, possess very unusual thermal, electrical, mechanical and chemical properties and are of great interest for various areas of application [1]. Some of these properties, i.e. the oxidation and creep resistance to high temperatures, are related to the formation of free carbon domains. As was recently proved in the case of SiCO materials, these properties can be further enhanced when a high excess of free carbon is incorporated in the microstructure [2]. Another way to improve further the thermal stability of PDCs is the inclusion of boron in the ceramic composition [3].

Among the techniques routinely used for the characterization of PDCs materials, multinuclear solid-state NMR has proved to be particularly powerful to investigate the polymer-to-ceramic thermal conversion process. In the present contribution, solid-state NMR has been applied to study the thermal evolution of several SiCO, SiCN as well as SiBCN ceramics derived by different polymer precursors. ^{29}Si, ^{13}C, ^{1}H and ^{11}B MAS NMR spectra of the starting polymers as well as the thermolysis intermediates were recorded. These results provide information about the microstructure and composition of the amorphous phases formed during the ceramization process.

Double resonance and double quantum NMR experiments (^{13}C-^{1}H HETCOR, DQ ^{1}H MAS NMR), were applied to investigate the backbone structure and the supramolecular arrangement of some carbodiimides polymers.

Moreover, in the particular case of the SiCBN ceramics, ^{11}B{^{15}N} REDOR and ^{11}B{^{14}N} REAPDOR double resonance NMR experiments were also used to investigate structural details of the B-C-N phase in the quarternary Si-B-C-N ceramics.

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THE EFFECT OF MAGNETIC FIELD AND SAFETY OF MAGNETIC RESONANCE OBSERVATIONS

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Scientists differentiate between primary (physical and chemical), cybernetic and general mechanisms of the biological effect of magnetic field. The main physical and chemical mechanisms are the change of charge trajectory (it moves in the magnetic field), winding anizothropical parts which have different magnetic perception; chemical polarization of electrons and nucleuses which changes the kinetics of chemical reactions.

Cybernetic mechanisms are distinguished by the registration of biosystem under the effect of magnetic field. It is known that the ranges of magnetic field providing biological effects to make the parts or units of the ampere for 1m of magnetic field while using different tests are heterogeneous.

Magnetic field causes great changes under equal circumstances. Intermittent effect of magnetic field leads to more effective reaction of biosystem. Direction, quantity and expression of such biosystem reactions depends more on its primary state (period of disease development, psychological state and so on) than on the magnetic field index. But the magnetic field of high voltage doesn't destroy biosystem.

General biological mechanisms don't have electromagnetic specific character. They should be studied from the point of view of general physiological positions. In the process of evolution living beings have been adjusted to the effect of magnetic field of some range. If the voltage of magnetic field exceeds the voltage of geomagnetic field of the Earth some separate physiological and biochemical processes quicken the movement. That's why it's necessary to point out biological intensiveness of the new industrial factor. It was indicated that under the effect of magnetic field of high voltage the chemical elements of blood change. Also under a long effect of magnetic field there are some phase changes in morphological state of blood and marrow; activation of the anticlotting system of blood; lessening of blood clotting; immunological reactivity according to phagocyte index. Well-known effect of magnetic field on the functional correlation of the process of excitement and inhibition in the brain structures is the process of excitement in the cerebral cortex. As a result of magnetic field effect the number of adrenaline and noradreneline increases in blood. In its turn, the change of hormone level leads to the breach in the function of cardiac system.

Consequently, magnetic field is widely used for observations in medicine. In the world medical practice the use of magnetic resonance tomography has been very popular for the last years. The possibility to investigate morphological changes and get important information on the functional and metabolical breach in organs and tissue show the advantage of magnetic resonance tomography [4, 1330].

The introduction of magnetic-resonance tomography into the clinical practice helped to increase the effectiveness of the research of cerebral cortex and marrow, bone system, stomach and pelvis.

The absence of X-ray radiation and physiology of the method give a possibility to conduct safe investigations for pregnant women, children, patients with pathology of immune system and blood disease.

The use of magnetic-resonance tomography helped to improve the diagnostics of oncological illnesses, anomalies of development, inflammation processes and the degenerative and dystrophic changes in organs and systems.

Magnetic field is used in medicine to conduct magnetic-resonance observations such as magnetic-resonance tomography. It can be of such types:

- magnetic-resonance observation of cerebrum;
- uncontrusted magnetic-resonance observation of cerebrum vessels (arterial and vein angiography);
- cerebrum observation with the use of magnetic-resonance spectroscopy in vivo on 1H cores;
- magnetic-resonance observation of neck, including angiographic observation of neck vessels;
- magnetic-resonance observation of thorax organs;
- magnetic-resonance observation of the organs of stomach emptiness;
- uncontrusted magnetic-resonance observation of pelvis organs in women and men;
- magnetic-resonance observation of soft tissues [1, 4].

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OPTIMISATION OF RF MICROCOIL PARAMETERS FOR MR IMAGING AND SPECTROSCOPY

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Microcoils are necessary for MR imaging and spectroscopy of volume limited biological and chemical samples. Due to small coil size, skin effect, proximity effect and susceptibility are important factors in microcoil design. Since there are no exact analytical direct methods for solving of those effects, computer simulation is used. General method of RF microcoils design and parameter optimisation is presented.

Finite Element Method software (Comsol Multiphysics, Comsol AB, Sweden) is used for solving Maxwell's equations. For initial coil geometry spatial distribution of magnetic and electric fields generated by alternating current flowing in a coil is calculated. Characteristic electric parameters: R, L, C of microcoil are extracted from the model. Coil SNR is approximated. Various model parameters are optimised to get the best SNR.

To calibrate the method electrical parameters (RLC) from FEM simulation were compared with analytical results for simple geometries like single wire loop and solenoid. Good accuracy was found. Test of result accuracy dependence on mesh size was performed. Then three geometries were analyzed: solenoid, planar helix and microstrip. Planar mutliarray of microcoils was optimised as well (Fig 1).

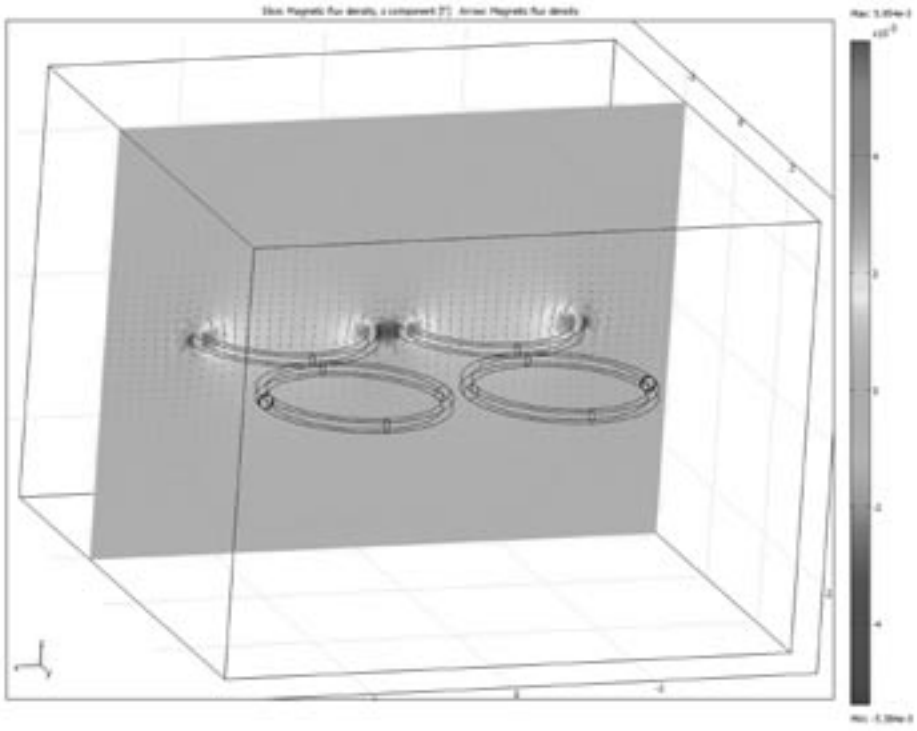

Fig.1 Magnetic field generated by planar array of 4 microcoils.

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UNIPLANAR GRADIENT COILS DESIGN WITH STREAM FUNCTION APPROACH

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The are number of analytical and numerical methods for MRI gradient coils design [4]. The aim of this work was to implement a method sensitive to layer shaped subjects, (i.e. human body surface). The stream function method, based on a cost function and combining advantages of numerical and analytical methods was used [3]. Uniplanar geometry is of special interest due to region of interest (ROI) accessibility and variety of potential applications.

This model takes into account a number of arbitrary coil surfaces in 3D, target field over ROI as well as the influence of mechanical torque and/or inductance. Every target point originated from ROI has its own weighing. The model is mapped to linear matrix equations system using stream function approach [2]. This procedure has been implemented using scripting language of the Comsol Multiphysics package (Comsol AB, Sweden). The solution yields discrete current elements. Contour plot procedure based on IDL (ITT VIS, USA) is used to transform it into current paths. Magnetic field generated by current patterns were analyzed using Comsol AC/DC module to verify numerical predictions. An example of the uniplanar gradient coil set was designed. Coil surface was tangential to B_0 field and limited to a flat board 100x100 mm parallel to XZ plane. ROI was 50x9x50 mm cuboid cantered 7.5 mm above coil surface. Gradient in x-, y-, and z-directions was set to 1 T/m.

Simulations limited to 18 wires were executed with and with out feeding wires. The resulting field of view (FOV) within 5% gradient deviation contour was 2.38 x 0.14 x 2.72 cm , 3.14x0.44x1.54 cm and 3.13x0.13x1.98 cm corresponding to x-, y-, and z-gradient coil. The gradient 1T/m was achieved with total current of 53, 55, 42 A in in x-, y- and z-direction respectively. Current paths covered ca. 10 cm square on a gradient board. Then different feed wires systems were tested. Pattern with the lowest field disturbances caused by feed system were chosen. FOV discrepancy were below 20%. Currently the gradient coil patterns are ready for the final assembly.

Gradient homogeneity in direction perpendicular to coil can be achieved only in the thin layer, so it is necessary to correct data in postprocessing or limit ROI to a shallow layer [1]. The alternative approach is to try to use different coil geometries. A few tests of other geometries like hemisphere or multiplane-one-sided were also done. The preliminary results shown usefulness and flexibility of the proposed method and its implementation. The future improvement of the software will be focused on implementation of graphical user interface which enable designer to define model in an easy, user friendly way.

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MICROWAVE RESPONSE OF HG1201 SAMPLES

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Measurements of surface impedance on optimally doped $HgBa_2CuO_4$ single crystal (T_c=95 K) were performed using a resonant microwave method. By changing the configurations of the microwave electric and magnetic fields we observed various absorption signals - signatures of anisotropic normal state conductivity σ_{ab} and σ_c. An external DC magnetic field was applied in two orientations: H_a || c and H_a || ab, and the estimate of the upper critical field in them reveals anisotropy of the GL coherence length $\xi_{ab} \approx 10\ \xi_c$. Temperature dependence was measured up to 300 K, and a characteristic temperature T^* was observed around 180 K indicating a pseudogap opening temperature. Temperature measurements in magnetic field H_a || c reveal interesting feature of superconducting fluctuations up to 105 K.

INVESTIGATION OF BINDING OF NOVEL MURD LIGANDS USING THE LIGAND OBSERVED NMR METHODS

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UDP-*N*-acetylmuramoyl-L-alanine:D-glutamate ligase (MurD) is a 47 kDa cytoplasmic enzyme involved in synthesis of bacterial peptidoglycan. It catalyses the addition of D-glutamic acid to the cytoplasmic intermediate UDP-*N*-acetylmuramoyl-L-alanine (UMA). MurD represents attractive target for the design of novel antibiotics. It is suggested that D-glutamic acid is an essenial fragment of a potent inhibitor. Recently, a series of novel MurD inhibitors based on sulfonamide derivatives of D-glutamic acid were synthesized [1]. These inhibitors mimic the transition state of the reaction.

In our studies we are using high-resolution NMR methods to determine interactions of novel MurD inhibitors with the enzyme active site. At the first stage of research we are focused on NMR methods, which do not require isotope enrichment of the protein. These methods are based on observation of ligand signals. We are using differential line broadening [2], longitudinal relaxation time T_1 [2] and STD experiments [2,3] to determine ligand dissociation constants (K_D). In these experiments the protein solution is titrated with the ligand. With a large excess of the ligand, the dissociation constant can be determined from the NMR parameters as a function of the ligand concentration [2,3]. Nonlinear regression analysis is applied to extract the K_D values from the experimental data. Our results indicate that the most accurate K_D values are obtained by STD titration experiments.

We perform STD group epitope mapping experiments to determine binding interaction of individual protons with the protein [4]. Protons which show the highest degree of STD effect are in tightest contact with the protein. Conformational properties of the bound ligands are studied by transferred NOESY experiments.

NMR results are presented for two of the novel D-glutamic and L-glutamic acid derivatives (Fig. 1). Their X-ray structures in the complex with MurD enzyme have already been published [1]. Our results are compared with the data from X-ray studies.

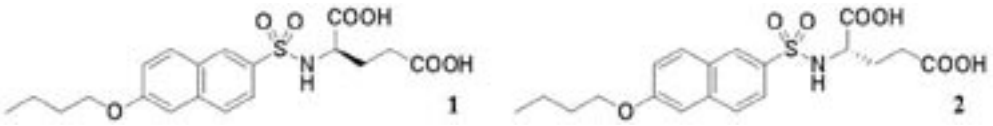

Fig. 1 MurD inhibitors [1]: N-(6-butoxy-naphthalene-2-sulfonyl)-D-glutamic acid (compound 1); and N-(6-butoxy-naphthalene-2-sulfonyl)-L-glutamic acid (compound 2)

We can conclude that compound 1 (D-glutamic acid derivative) exhibits better binding properties than compound 2 (L-glutamic acid derivative). This is in accordance with reports that MurD is highly stereospecific for its substrate, D-glutamic acid. Estimated K_D values for compounds 1 and 2 are in good agreement with previously reported IC_{50} values [1].

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MRI OF ANISOTROPIC WATER DIFFUSION IN NERVOUS TISSUE – FROM BASIC PHYSICS TO CLINICAL APPLICATIONS

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Diffusion of water molecules in biological tissue is sensitive to its structure. Diffusion Weighted Magnetic Resonance Imaging (DW MRI) methods which are used to measure anisotropic diffusion of water in nervous tissue of a spinal cord and brain, allow to characterize their structure, visualize and quantify tissue pathology, follow damage recovery and assess effects of neuroprotective drugs at *in vivo* conditions.

Present understanding of water diffusion in nervous tissue is based on assumption of three water compartments: intra-cellular, myelin and extra-cellular, with different diffusion and relaxation properties. Limited size of compartments causes diffusion restrictions, especially in direction perpendicular to nervous tissue axis, which property is effectively utilized for fiber tracking.

Traumatic injuries which influence spinal cord structure, result in alteration of parameters of the anisotropic diffusion. This allow for application of the Diffusion Weighted MRI for assessment of the primary and secondary mechanisms of the injury.

Application of neuroprotective drugs may limits secondary effects of the injury.

During lecture the different aspects of DW MRI methodology and its applications to assessment of the structure and state of nervous tissue will be presented.

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FIRST POSTER SESSION

SYNTHESIS AND APPLICATION OF HOMOGENOUS CATALYSTS IMMOBILIZED ON THE MESOPOROUS SILICA MATERIAL: ^{29}SI AND ^{31}P SOLID STATE NMR STUDIES

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The favorable properties of heterogeneous catalysis, as for example the easy separation and recovery of the catalyst from the reaction mixture, are the motivation for attempts to immobilize homogenous catalysts on a solid support.

Well ordered silica mesoporous materials like MCM-41 and SBA-15, or their derivates are promising inorganic supports. Owing to the presence of reactive silanol groups on the surface, they are easily covered with functional groups, which can serve as anchoring points for the immobilization of the catalyst (grafting). Moreover, because of their narrow and adjustable pore size distribution, they may provide a size selectivity which is not available by technical silica materials as for example xero- or pyrogels or silica nano-particles with their large, irregular shaped surfaces.

We present the synthesis of ruthenium and rhodium catalysts and the process of their immobilization on the surface of SBA-3 material as a promising approach to combine advantages of heterogenous and homogenous catalysis. We also present first applications of immobilized complexes as successful catalysts in the reactions of hydrogenation.

The structure of the functionalized mesoporous material and the immobilized catalysts is investigated by employing ^{29}Si CP-MAS and ^{31}P CP-MAS Solid State NMR. Using these techniques we can observe the changes of the silica surface in the course of the grafting process, like also the structure of immobilized catalysts.

Fig.1. ^{29}Si CP-MAS NMR of SBA-3

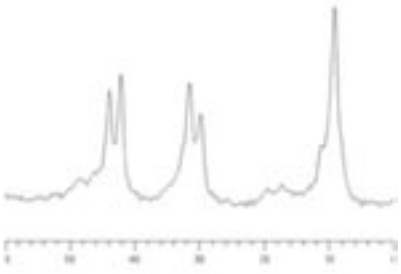

Fig.3. ^{31}P CP-MAS NMR of $RuCl_2(PPh_3)_3$

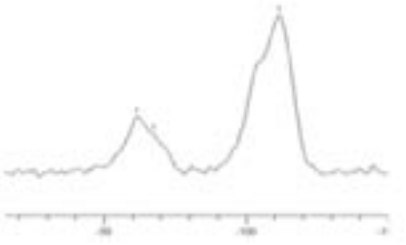

Fig.2. ^{29}Si CP-MAS NMR of SBA-3 with $RuCl_2(PPh_3)_3$ on the surface

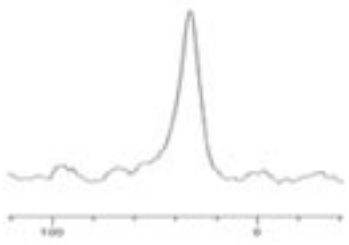

Fig.4. ^{31}P CP-MAS NMR of $RuCl_2(PPh_3)_3$ on the silica surface

THE MOLECULAR MECHANISM OF DEHYDRATION RESISTANCE IN ANTARCTIC LICHENS FROM THE GENUS UMBILICARIACEAE OBSERVED BY PROTON NMR, DSC AND SORPTION ISOTHERM

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Many of Antarctic lichen species may dehydrate to extremely low hydration level and rehydrate from gaseous phase to the hydration level sufficient to initiate photosynthesis [3,4,5]. The Antarctic lichen *Umbilicaria aprina* reveals the lowest detected photosynthetical activity in field, and in laboratory conditions [1]. The spontaneous dehydration of thallus is a way to resist very low temperature experienced by lichens in their habitat, therefore both drought and cold resistance may have similar molecular mechanism. The formation of molecular glass may by the way for cell to survive deep dehydration [8].

The understanding of the molecular mechanism of the metabolic activity recovery during rehydration of thallus requires the knowledge on a number and distribution of water binding sites, sequence and kinetics of their saturation, and the formation of tightly and loosely bound water fractions at different steps of hydration process.

The thalli of *Umbilicaria decussata* were collected from nunatak, and the U. aprina from glacial stream at Schirmacher Oasis, Queen Maud Land, Continental Antarctics.

The hydration courses performed from the gaseous phase, show: (i) a very tightly bound water not removed by incubation over silica gel, and (ii) bound water fraction. At relative humidity higher than p/p_0=76%. *U. aprina* reveals the presence of loosely bound water fraction. The sigmoidal in form sorption isotherm yields the relative mass of water bound to primary binding sites equal $\Delta M/m_0 = 0.059$ for *U. decussata*, and $\Delta M/m_0 = 0.054$ for *U. aprina*.

DSC (differential scanning calorimetry) shows the reversible freezing of water bound in the thallus of investigated species. The freezing temperature was not significantly altered with the freeze-thawing cycles.

Proton FID is a superposition of the solid signal and two liquid signal components coming from tightly bound ($T_2^* \approx 100$ μs) and loosely bound water fraction ($T_2^* \approx 1000$ μs). Although Gaussian function yields satisfactory approximation of solid signal, much better fits supplies Abragam function (with the line halfwiths equal to 32 kHz) and/or superposition of Abragam and Gaussian function (with the line halfwiths equal to 38 kHz) for *U. aprina* [9].

Non-linear form of liquid signal, L/S, hydration dependency suggests the presence of water soluble solid fraction in the thallus. The NMR data showed the absence of water 'sealed' in pores of [7].

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DIVERSE MOBILITY OF D_2O MOLECULES IN ZEOLITES: DEUTERON NMR AND IR STUDY

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Synthetic faujasite-type zeolites NaY with Si/Al = 2.4, 1.8 and NaX (Si/Al = 1.3) were used. Prior to NMR experiments the zeolites were activated under vacuum at 650 K for 1 hour, cooled to 100 K and subsequently D_2O was adsorbed. Amounts of D_2O were 100 %, 200 %, and 300 % respective to the number of Na^+ cations in the unit cell. The NMR experimental set up was described in detail elsewhere [1].

There are two components of different width observed in the spectra for all cases considered. Their weights change with temperature (Fig.1). We can define a parameter T_{50} as the temperature when contributions of both are equal (Fig.1). T_{50} decreases with increasing filling factor and Si/Al ratio. Relaxation rates were measured and activation energies derived. Exponential relaxation was observed in spite of an evidence for two subsystems in the spectra (Fig.2). In general we expect in such case $1/T_1 = w_1/T_1^1 + w_2/T_1^2$. However, the exponential relaxation could be observed under condition of fast exchange between subsystems. Observation of the two components in the spectra excludes such possibility here. Therefore we consider another case.

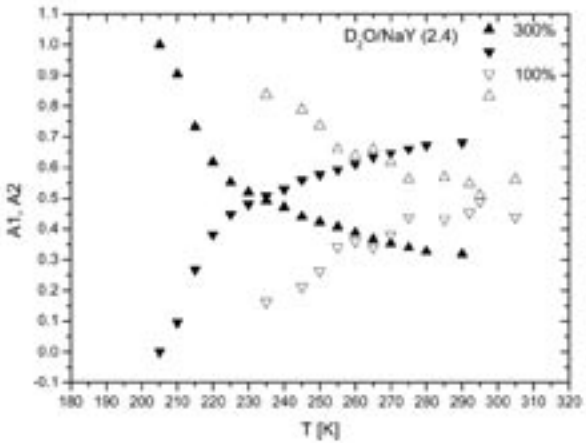

Fig.1

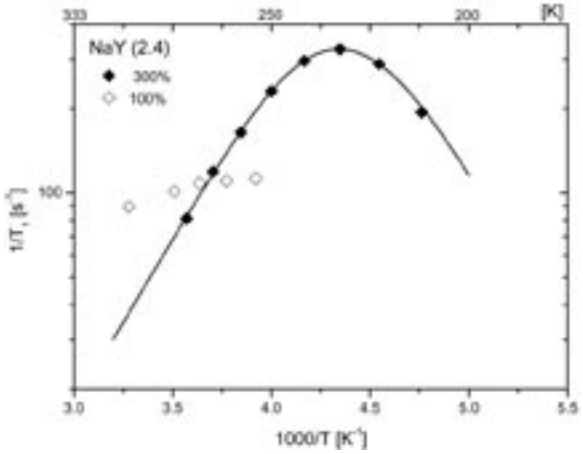

Fig.2

The narrow line (▼) can be attributed to tetrahedral jumps of O-D bonds, which by virtue of symmetry are averaging the quadrupole interaction most effectively. Roughly 60% D_2O molecules perform the tetrahedral jumps at room temperature irrespective of the Si/Al ratio. This observation can be related to recent evidence for water hexamers at 12-ring windows of NaX zeolite obtained by neutron diffraction [2]. Molecules in excess have a tendency to solidify on the ordered ones when temperature goes down and thus destroy step-wisely the local tetrahedral symmetry. Interactions of H_2O in NaY (Si/Al=2.4, 1.8) and NaX (Si/Al=1.3) were studied also by IR. Adsorption of water results in the appearance of the OH stretching band at 3693 cm^{-1} of H_2O molecules interacting directly with Na^+, the broad bands around 3100 and 3600 cm^{-1} from OH groups engaged into hydrogen bonding (water to water or water to framework oxygen) as well as the band at 1635-1655 cm^{-1} related to deformation vibrations of H_2O (δ_{H2O}). The δ_{H2O} band at 1640 cm^{-1} and 1644 cm^{-1} were observed for NaY with Si/Al ratios 2.4 and 1.8, respectively. Two δ_{H2O} bands are present for NaX at 1660 and 1645 cm^{-1} and at low water content intensities of these bands increase in parallel. At higher loading, but still below 100%, only the band at lower frequency grows. It suggests that in zeolites NaY there is only one kind of Na^+ (one δ_{H2O} band) whereas in zeolite NaX two different δ_{H2O} frequencies of water bonded to Na^+ are present. The Na^+ sites of higher δ_{H2O} interact with water only at higher water loading.

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IMPLEMENTATION OF MAGNETISATION TRANSFER MRI AT LOW FIELD

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Magnetisation transfer contrast (MTC) has been widely used for over a decade as one of the most important MRI contrast-generating mechanisms. Most MTC research to date has been performed at medium or high magnetic field strengths, typically at 0.5 T or above. Nevertheless, there is value in implementing MTC at low field, although this presents technical challenges not encountered at higher magnetic fields. In this work, we have implemented MTC at very low magnetic field, 0.059 T, corresponding to 2.5 MHz proton resonant frequency.

The key technical aspect of MTC is the ability to apply off-resonance irradiation, in order to saturate protons in the bound pool, without directly affecting protons in the free pool; the basic method employs continuous-wave (CW) off-resonance irradiation [1]. In order to study MT effects a range of offset frequencies is needed, from 0.01 kHz to around 50 kHz resonance offset. This presents the main technical difficulty of MTC at low field, because the larger offset frequencies are likely to be outside the bandwidth of the RF transmit system (amplifier and RF coil), causing the applied B_1 RF magnetic field to vary with the frequency offset. With increasing frequency offset, a higher CW amplitude is required to maintain a desired constant B_1 field strength. To counter this effect, B_1 calibration curves were measured (Fig. 1) and the results incorporated into the pulse program via a look-up table. In this study, seven B_1 values (5, 7.5, 10, 15, 20, 30, and 40 μT) were used and 32 frequency offsets were chosen from 0.01 kHz to 49 kHz. The frequency offsets were distributed on a logarithmic scale in order to cover a wide range of offsets, with high frequency-resolution close to resonance (zero to 1 kHz offset range). A home-built MRI scanner operating at 59 mT was used in this work [2].

Experiments were carried out using samples composed of Agarose gels (1 %, 2 % or 4 %) doped with $MnCl_2$ (0 mM, 0.03 mM or 0.3 mM). T_1 and T_2 can be controlled by altering the concentration of the gel and of $MnCl_2$, respectively [3]. Two phantoms, each containing 7 samples, were also prepared for imaging experiments, combining Agarose gels with either $MnCl_2$ solutions or distilled water. In addition, samples containing aqueous solutions of $MnCl_2$ (without agarose) were used as a control. In order to estimate the extent of the direct effect, T_1 and T_2 values were measured using Inversion Recovery and Spin Echo pulse sequences.

The MT effect was studied as a function of CW duration, with the optimum being around 2 seconds. The MT effect was also measured as a function of frequency offset at a range of B_1 values. From these data, conditions for the maximum MT effect with each sample were determined: these were typically B_1 = 20 μT and approximately 10 kHz offset frequency. Finally, the phantoms were imaged using an interleaved (CW-off and CW-on) MTC Gradient Echo imaging pulse sequence, and the magnetisation transfer ratio (MTR) was determined [4].

Fig. 2 shows the MT effect observed in a control sample and in 1, 2, and 4 % Agarose gels under the conditions of 10 kHz frequency offset, 20μT B_1, and 2s CW duration. Due to the absence of macromolecules in the control sample, the MT effect was zero while MT effects increased with increasing concentration of macromolecules, as expected.

In conclusion, MTC has been implemented on a 59 mT home-built MRI scanner. Initial results from Agarose gel test objects compare well with those in the literature, obtained at higher fields. We intend to use the scanner to measure MT effects as a function of magnetic field, using magnetic field-cycling.

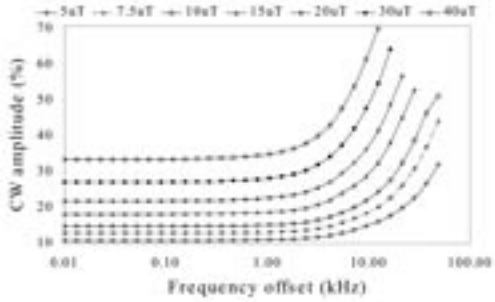

Fig.1. B1 calibration curve

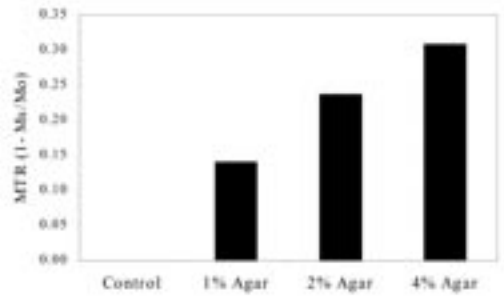

Fig.2. Magnetisation Transfer Ratio of Agarose gels

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ARYLDIKETO ACIDS COMPLEXATION ABILITY AND KETO-ENOL TAUTOMERS RATIO IN PRESENCE OF MG^{2+}. UV/VIS AND NMR SPECTROSCOPY STUDY IN NONAQUEOUS MEDIA

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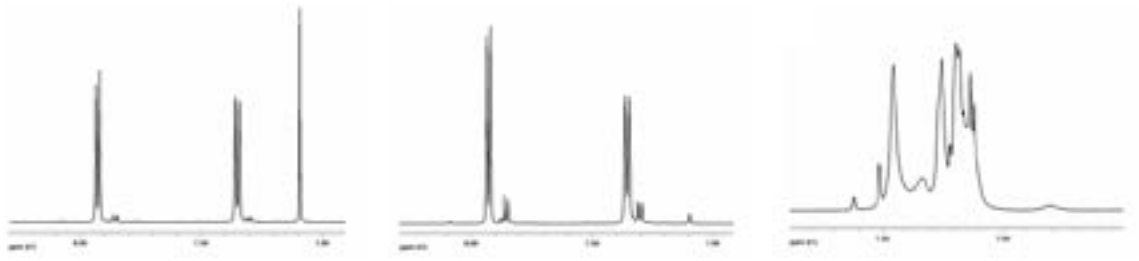
4-Aryl/heteroaryl-2,4-dioxobutanoic acid (ADK) derivatives exert widespread biological activities. Targeting HIV-1 integrase, the enzyme responsible for integration of viral DNA in host genome, is among the most important ones [1]. ADK–Mg^{2+} complex formation in the active site is postulated as an important factor that determinates degree of enzyme inhibition [2]. Congeneric set of 4-; 3,4- and 2,5-phenyl substituted ADK was synthesized. During routine characterization, mass spectra obtained by liquid chromatography-electrospray ionization (LC-ESI MS) showed presence of 2M–1 and 2(M–1)+Na ions for all compounds. It was observed that 2(M–1)+Na are more intensive than 2M–1 peaks in spectra of compounds with 3-alkyl substituents, despite substitution in other positions on the phenyl ring. In turn, in MS spectra of all other studied compounds 2M–1 peaks are more intensive. This could indicate significantly better complexation ability of 3-alkyl substituted derivatives and might have pharmacological implications.

We have found that there is no significant complexation ability between ADK and Mg^{2+} in aqueous solutions (pH range 1-8). To check potential differences in complexation ability between 3- and 4- phenyl substituted ADK, ^{1}H and ^{13}C NMR spectra were recorded in CD_3OD with and without Mg^{2+} ion. ^{1}H NMR spectra of 4-(4-Methylphenyl)-2,4-dioxobutanoic acid and 4-(2,5-Dimethylphenyl)-2,4-dioxobutanoic acid in presence of Mg^{2+}, are shown on Figure 1 a) and b).



a) b) c)

Fig.1. Regions of ^{1}H NMR spectra of 4-(4-Methylphenyl)-2,4-dioxobutanoic acid alone (a), 4-(4-Methylphenyl)-2,4-dioxobutanoic acid (b) and 4-(2,5-Dimethylphenyl)-2,4-dioxobutanoic acid (c) forty minutes after Mg^{2+} was added to ADK in 1 : 2 (M : L) molar ratio; recorded in CD_3OD.

As can be seen on selected spectra regions, there is no significant complexing ability of 4-Me- comparing to 2,5-di-Me- substituted derivative. Another interesting observation, considering spectra of 4-Me- derivative, is that keto-enol ratio is significantly changed when Mg^{2+} ion is present in solution. This was not observed in DMSO-d_6.

Job's spectrophotometric method [3, 4] was used to confirm the complex stoichiometry (M:L = 1:2) and to compare abilities of 4-; 3,4-; 2,5-phenyl and β-naphthyl substituted derivatives to complex with Mg^{2+}.

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QUANTITATIVE NMR DETERMINATION OF LAMBDA CYHALOTHRIN IN ULV FORMULATIONS

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Synthetic pyrethroids are an important group of active ingredients of insecticide formulations widely used in plant protection products and public health commodities. The advantages of pyrethroids in comparison with organochlorine and organophosphorus insecticides are their photostability, enhanced insecticidal activity and relatively low toxicity.

A pyrethroid lambda-cyhlothrin formulation used against adult mosquitoes by aerial application, named ULV (ultra low volume), is basically a solution of lambda-cyhlothrin in a mixture of aromatic hydrocarbons, Solvesso 200D™ (heavy aromatics) and vegetable oil.

It is known that the presence of vegetable oil in such formulations creates considerable problem to an analytical chemist in the sample preparation for GC analysis. The chromatographic analysis of such formulations usually requires tedious clean-up procedures, evaluation of suitable elution conditions, preparation of calibration curves for quantitations and removal compounds that interfere with the detection of the analyte.

Quantitative ^{1}H NMR (QNMR) measurement of the active component in ULV preparations, described in this report, was developed in order to overcome the above problems regarding the GC analysis. The decisive advantage of the NMR spectroscopy for quantitative analysis over chromatographic methods is due to the fact that preparation of the sample is much more simple. Nowdays, due to the enhanced sensitivity and introduction of the new pulse sequences, the NMR spectroscopy (especially ^{1}H NMR) is becoming a routine quantitative method for such complex mixtures. The QNMR analysis requires an internal standard, whose signal doesn't interfere with those of the analyte. In this case, 2,6-*bis*(1,1-dimethylethyl)-4-methylphenol, widely used as antioxidant additive under the commercial name BHT, was the compound of choice. BHT is rather soluble in $CDCl_3$ and its one-proton NMR signal (O<u>H</u>) (δ 4.92) is not overlapped with the remaining signals of the analysed preparation (Fig. 1).

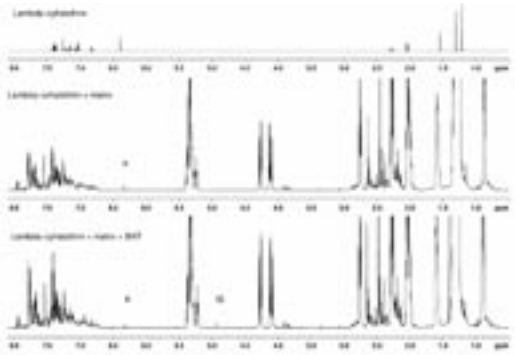

Fig. 1. ^{1}H NMR spectra of analyte, and mixture of analyte with the ULV formulation of lambda-cyhalothrin and internal standard

The analyte, lambda-cyhalothrin, the matrix, a mixture of vegetable oil and Solvesso 200D, and internal standard were accurately weighed (± 0.0001 g., total volume ca. 2 ml), and dissolved in CCl_4, 1 ml. The NMR measurements were performed on a Bruker Avance 500 instrument equipped with broad-band direct probe (^{1}H at 500.26 MHz). All spectra were measured in $CDCl_3$ solvent at 298 K.

The delay time between two scans (d1) was determined by measuring longitudinal relaxation time (T1) of the analyte and internal standard, and set to be 8.5 s. The influence of various factors, such as concentrations of components, receiver gain (RG), number of scans (NS) on precision and accuracy of the quantitative method were determined.

The limit of detection (LOD) of lambda-cychalotrin was determined by adjusting the experimental conditions to achieve a S/N 3:1 [1]. For NS = 128, LOD was 0.003 mM. The limit of quantification, with precision and accuracy better than 1%, for NS = 128 was determined to be 0.5 mM. In order to shim the sample correctly it is important that the concentration of the matrix in the NMR cuvette does not exceed 500 mg/ml, otherwise the precission and accuracy would exceed 1%.

Satisfactory precision and accuracy (lower than 1%) was achieved in the concentration range 0.5 – 10 mM of the analyte. For the 3.75 mM solution, RG was automatically determined to be 32. If RG was set manually and if it exceeding the range 4 - 64 would be affected the precission and accuracy.

It was demonstrated that using an appropriate choice of experimental conditions, the QNMR spectroscopy is a suitable tool for the quantitative determination of lambda-cyhalotrin in ULV preparations. The results obtained by this method were found to be sufficiently precise and accurate with a relative standard deviation < 1 %. The application of ^{1}H NMR method enabled the quantitation of lambda-cyhalotrin in much shorter time than required by the conventional GC methods.

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DNA REHYDRATION BY NMR AND SORPTION ISOTHERM

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Deoxyribonucleic acid (DNA) is a linear biopolymer composed of nucleotide units (purine and pyrimidine bases, deoxyribose, diesterified phosphate groups). It is responsible for storage, transmission, and realization of genetic information in cells. Watson and Crick proposed the successful model of the native structure of the DNA molecule placed in vacuum. They ignored presence of water, although, it was already known that the native form of DNA requires up to 40 wt% of water [1]. Although the hydration properties of DNA molecule were investigated using various methods (IR [2], DSC [3], etc.), the question arises what is the effect of water on DNA native structure formation at the initial stages of rehydration of dry DNA molecule.

Some subcellular structures (eg. photosynthetic membranes) may resist the drastic dehydration (at lyophilization) [4]. Moreover there are some living organisms, which may survive extremely low hydration level (even below two-dimensional percolation of water bound on the surface), namely Antarctic lichens [5-8]. The cytoplasmic vitrification may be possible way used by anhydrobiotic organism to survive extreme desiccation [9].

These focused our attention on initial phases of salmon sperm DNA molecule rehydration from the anhydrous state. To understand the molecular mechanism of the structural changes during rehydration one needs the knowledge on a number and distribution of water binding sites, sequence and kinetics of their saturation, and the formation of tightly and loosely bound water fractions at different steps of hydration process.

The hydration kinetics reveals (i) a very tightly bound water not removed by incubation over silica gel ($\Delta m/m_0 = 0.052$), (ii) tigtly bound water, and (iii) loosely bound water fraction. For the atmosphere at $p/p_0 = 100\%$ after 200 h of incubation the swelling process begins. Sorption isotherm is sigmoidal in form and well fitted by Dent model [10] with the mass of water saturating primary binding sites $\Delta M/m_0 = 0.11$. Proton FID is a superposition of the solid signal (Gaussian in form) and two liquid signal components coming from tightly bound ($T_2^* \approx 70$ μs, with the mass saturating at $\Delta m/m_0 = 0.09$) and loosely bound water fraction (with the amplitude proportional to the mass of water added, and $T_2^* \approx 3000$ μs).

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DYNAMICS OF POLYMER MELTS STUDIED BY FAST FIELD CYCLING NMR

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We use fast field cycling NMR to investigate the crossover from simple liquid dynamics through Rouse to reptation dynamics in a series of polymers covering a broad range of molecular weights M and temperatures. The dispersion data of spin-lattice relaxation time $T_1(\omega)$ are transformed to the susceptibility representation $\chi''(\omega)=\omega/T_1(\omega)$ and by applying frequency temperature superposition master curves are constructed as a function of $\omega\tau_\alpha$, in which τ_α denotes the time constant of the glass-process (segmental motion). The susceptibility representation facilitates comparisons with spectra obtained by, e.g., dielectric spectroscopy and allows to separate spectral contributions from glassy and polymer specific dynamics.

Eleven samples of Polydimethylsiloxane (PDMS) with $M=M_w$ (in g/mol) in the range of 162 and 232000 have been systematically measured between 163 K and 363 K. Their susceptibility master curves are displayed in Figure 1. Our analyses provide an estimation of the longest relaxation times $\tau_{max}(M)$ and after Fourier transform of the master curves segmental correlation functions covering six decades. In order to extract the spectral contributions attributed to polymer dynamics for each sample we subtract the glassy spectrum, which is identified with that of the lowest M systems. Thereupon the relaxation strength $f(M)$ of polymer dynamics is obtained, which is the relative correlation loss due to polymer dynamics on time scales $t>\tau_\alpha$. Moreover, the normalized polymer spectra are compared to spectra calculated from discrete Rouse theory. The study on PDMS yields results similar to our previous study [1] on polybutadiene (PB): The M dependence of both τ_{max} and f as well as the glass-transition temperature T_g, measured by dielectric spectroscopy, reflect a crossover between the regimes of simple liquid, Rouse and reptation dynamics.

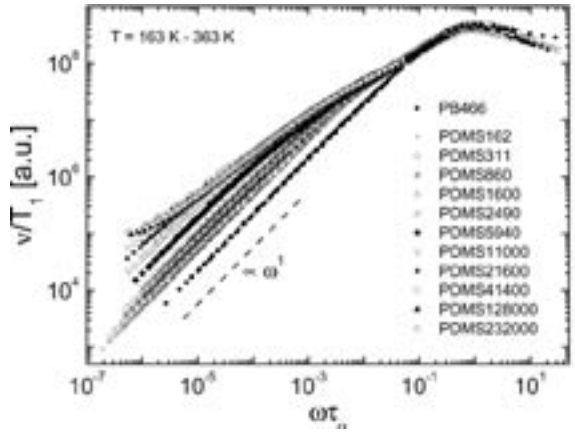

Fig.1. Susceptibility master curves of polydimethylsiloxane (PDMS) with molecular weight M as indicated and polybutadiene (PB) with M=466, which is taken as a reference for simple liquid dynamics: Excess spectral contributions on the low frequency side ($\omega\tau_\alpha<1$) are due to polymer dynamics.

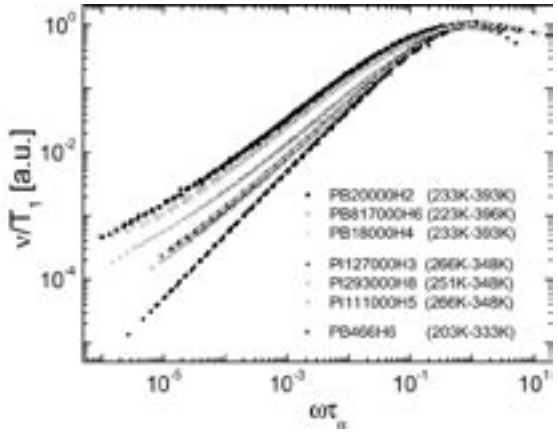

Fig.2. Master curves of fully protonated low and high M polybutadiene (PB) and high M polyisoprene (PI) (H6 and H8, respectively) as well as partially deuterated PB and PI [2] (H2, H4 and H3, H5, respectively) within temperature range as indicated: Different relaxation strength f of polymer dynamics.

Our approach of separating the polymer specific contribution from the total spectra is checked with differently deuterated PB and polyisoprene (PI) [2]. Their susceptibility master curves (Figure 2) are different in the high M limit, which can be explained by different values of the relaxation strength f that depend on the orientation of the proton spin pairs with repect to the local chain contour. Taking glassy dynamics explicitly into account yields spectra revealing universal features of polymer dynamics and therefore consequently demonstrates the importance of this approach when interpreting NMR relaxation data of polymers.

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THE STRUCTURE AND MOLECULAR MOTIONS IN POLY(STYRENE-B-ISOPRENE) DIBLOCK COPOLYMER

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Block copolymers can be made to exhibit highly useful combinations of thermoplastic and elastomeric properties. A typical example is the copolymer poly(styrene-b-isoprene) (SI). Morphologically, such polymers form a system in which the polystyrene (PS) component is in the form of domains of regular size and geometry in polyisoprene (PI) elastomeric matrix [1]. The investigated diblock copolymer was nearly symmetric in composition, comprising of polystyrene and polyisoprene chain blocks of molecular weight of 11500 and 10500 g/mol respectively.

The nuclear magnetic resonance (NMR) and broadband dielectric spectroscopy (BDS) studies were applied to characterize molecular motions in copolymer and its neat components. It was found that the all motions observe in pure components exist also in copolymer, showing two phase character, visible especially in $T_{1\rho}$ experiment in which the particular components of copolymer relax separately (Fig. 1). However there are some differences : i) the move of glass transition to higher temperature for PI block and to lower temperature for PS block. ii) broadening of distribution of correlation times connected with these processess. It is assumed that these changes result from an effect of linked chains mutual interactions, in which PS blocks make spatial confinement effect on the dynamics of PI chains, whereas the moving PI chains act as plasticizer for PS blocks. Additionally normal mode motion of polyisoprene chain as well as rotation of methyl group were reveald.

Based on the SAXS data typical for symmetrical block copolymers the lamellar architecture was stated. The estimated PS lamella thickness is consistent with the results obtained from NMR spin diffusion measurements.

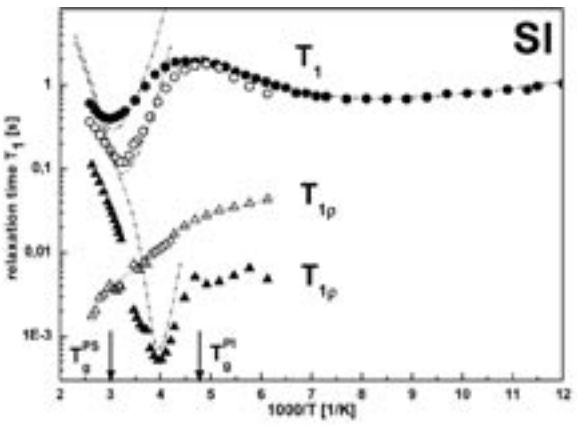

Fig. 2. BDS relaxation map for neat polymers and copolymer.

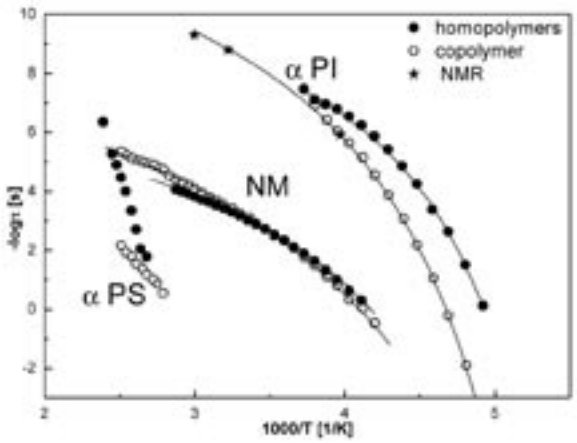

Fig. 1. T_1 and $T_{1\rho}$ relaxation times versus 1000/T for poly(styrene-b-isoprene).

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Acknowledgements

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THE INVESTIGATION OF THERMAL AND PHYSICAL PROPERTIES OF LOW MOLECULAR WEIGHT GELATORS, METHYL-4,6-*O*-*p*-NITROBENZYLIDENE-α-D-GALACTOPYRANOSIDE

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Methyl-4,6-*O*-p-nitrobenzylidene-α-D-galactopyranoside, a derivative of monosaccharides, is a new member among the family of the low molecular weight gelators (LMG), particularly interesting because it has ability to gel various organic solvents and water in a wide range of gelator concentration. The gelation process involves the self-assembly of low molecular weight gelators to fiber-like structures, which entangle to form a 3D network and immobilize organic fluids or water. A self-assembly occurs under non-equilibrium conditions such as the cooling of the solution which is used as the typical preparation method. LMG form a physical gel because only non-covalent interactions between the gelator molecules are involved.

The hydrogel samples were prepared by mixing different amount of gelator powder (Methyl-4,6-*O*-*p*-nitrobenzylidene-α-D-galactopyranoside) with distillated water. The mixture was heated until the solid dissolved and then a few further seconds to obtain a homogeneous liquid. Then the solution was cooled to room temperature and left for few minutes. As a result the partially transparent hydrogels were obtained for different gelator concentrations.

In this work, we present the study of the gel-to-sol phase transition and ^{1}H NMR relaxation investigations of water in the hydrogel. The phase transition measurements were performed as a function of gelator concentration. The energy related to the gel-sol phase transition was determined and compared to values obtained for other saccharide-based gels. The state of water in the gel was examined by the proton spin-lattice relaxation performed as a function of temperature.

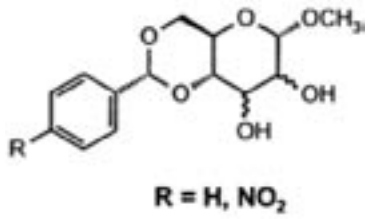

Fig. 1. A schematic structure of Methyl-4,6-*O*-*p*-nitrobenzylidene-α-D-galactopyranoside.

DO SIMPLE SYSTEMS EXHIBIT SIMPLE DYNAMICS? NMR INVESTIGATION OF FLUORINE DYNAMICS IN BAF_2-TYPE SUPERIONIC CONDUCTORS

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Superionic conductors have been the subject of extensive research because of their interesting dynamic properties as well as their potential application [1]. Materials with fluorite structure (CaF_2, BaF_2, SrF_2) are known for their fast ionic conductivity at high temperatures. It is known that ionic disordering plays an important role for fast ionic mobility [2]. Superionic conductors with fluorite structure can be disordered either by thermal activation or by doping with heterovalent admixtures. These systems are therefore, good candidates for studies of the mechanism of ionic transport in crystalline superionic materials [3, 4].

Fluorine dynamics in pure and doped single crystals of BaF_2 and CaF_2 has been studied by NMR-line shape technique and field cycling NMR relaxometry. The measurements of frequency dependent spin-lattice relaxation times have been performed from 20 kHz to 40 MHz in the temperature range from 300K to 1300K. The fluorine relaxation processes are caused by dipole-dipole interactions modulated by ion jumps, but also affected by quadrupole relaxation of the lanthanum spins. They are analyzed in terms of single exponential correlation functions as well as correlation functions including explicitly translational degrees of freedom. The most difficult problem of the studies is to develop an appropriate model of fluorine dynamics, and formulate a suitable expression for the time correlation function of the fluorine ions. The relaxation method is sensitive to dynamic processes on the time scale from 10^{-4}s to 10^{-9}s. To extend the time scale of the investigated fluorine dynamics to 10^{-3} s a line-shape analysis is performed.

The line-shape interpretation is based on structural and dynamic properties of the crystals. In this case the character of the fluorine ions motion does not matter; the only important factor is that due to the motion the 'spin configuration' of the ion environment changes. Therefore, a comparison of the correlation times obtained by the spectral analysis with the relaxation results, based on a certain motional model, is particularly valuable.

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NUCLEAR MAGNETIC RESONANCE AND ELECTRON SPIN RESONANCE IN APPLICATION TO BIOLOGY AND MATERIAL SCIENCE SOFTWARE DEVELOPMENT

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Paramagnetic systems are materials with positive magnetic susceptibility, associated with unpaired electrons. The paramagnetic solutions of interest for Magnetic Resonance Imaging contain transition metal complexes. The presence of unpaired electron spins has a profound influence on Magnetic Resonance Spectra of such solutions. The origin of the effects is found in the large value of the electronic magnetic moment about 650 times that of the proton. The paramagnetic species enhance the nuclear spin relaxation rates. The paramagnetic relaxation enhancement [1-4] is caused by random variations of the electron spin – nuclear spin dipole-dipole interactions, which open a pathway for the nuclear spin relaxation. A very active field of applications of the paramagnetic relaxation enhancement effects is the development and use of paramagnetic materials as contract agents in Magnetic Resonance Imaging. In this context it is of primary importance to formulate a theoretical description of the nuclear spin relaxation which can be use to predict the efficiency of a given paramagnetic compound.

In this contribution a general treatment of Electron Spin Resonance spectra and nuclear spin relaxation in paramagnetic systems valid for arbitrary motional conditions and interaction strength is presented. This theory is known in the literature as the 'slow motion theory' or the 'general theory'[1,2,5]. The name 'slow motion' indicates that the motion modulating the relevant interaction is too slow, compared to the timescale of the spin dynamics, for the perturbation theory to be valid. This approach is based on a full solution of the Liouville von-Neumann equation by the multipole representation of tensor operators and the Wigner-Eckart theorem, and has been developed and modified depending on applied motional models. Nevertheless, so far the theory has been applied only to the problem of inner-sphere paramagnetic relaxation enhancement (PRE).

This treatment has been extended to ESR spectra and nuclear spin relaxation caused by relative translational diffusion of the nuclear and electron spins (the outer-sphere part of PRE). In this way, a very general tool appropriate for a variety of molecular systems is provided.

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RELAXATION PROCESSES IN $GU_3SB_2B_{R9}$ GUANIDINE COMPOUND

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$Gu_3Sb_2Br_9$ ($Gu=(NH_2)_3$) crystal is a very interesting example of systems of mutually coupled dipolar and quadrupolar spins. The system contains two types of dynamically non-equivalent guanidine rings. Protons belonging to both rings are coupled to nitrogen, antimony and bromine quadrupolar nuclei. As a consequence of the different dynamics of the two types of protons one observes experimentally proton relaxation as well as polarization transfer effects. Polarization transfer can take place only if there is an efficient (not averaged out) coupling between the dipolar and quadrupolar spins. If the magnetic field is set to a value which leads to the Zeeman splitting of the dipolar spin matching the energy splitting of the quadrupolar spin (determined by the quadrupolar and Zeeman interactions), the dipole-dipole coupling causes the polarization transfer. The mutual dipole-dipole coupling links transitions of the dipolar spin to some transitions of the quadrupolar spin, so they cannot occur independently. The polarization of the dipolar spins is transferred to the quadrupolar subsystem with an efficiency directly related to the probability of the joint transitions. The fact that one can clearly see the polarization transfer effects (as dips of the magnetization curve recorded versus the magnetic field) allows us to state that one of the rings is quite rigid and therefore there are efficient proton – quadrupolar nuclei dipole – dipole couplings. At the some time proton relaxation is observed. We attribute this process to a fast movement (rotation) of protons belonging to the second type rings. The relaxation processes are considerably affected by dipole-dipole couplings to the quadrupolar nuclei, mainly bromine. In this case these dipole-dipole interactions fluctuate stochastically in time (are averaged out) due to the proton motion and therefore they contribute to the proton relaxation. In addition there is a mutual dipole-dipole coupling between the two types of protons and therefore one cannot treat them as separated subsystems.

A proper description of such systems is demanding but profitable. We shall demonstrate that one can obtain in this way quite unique information on the dynamic processes in complex molecular systems.

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DEUTERON NMR STUDIES ON ICE II

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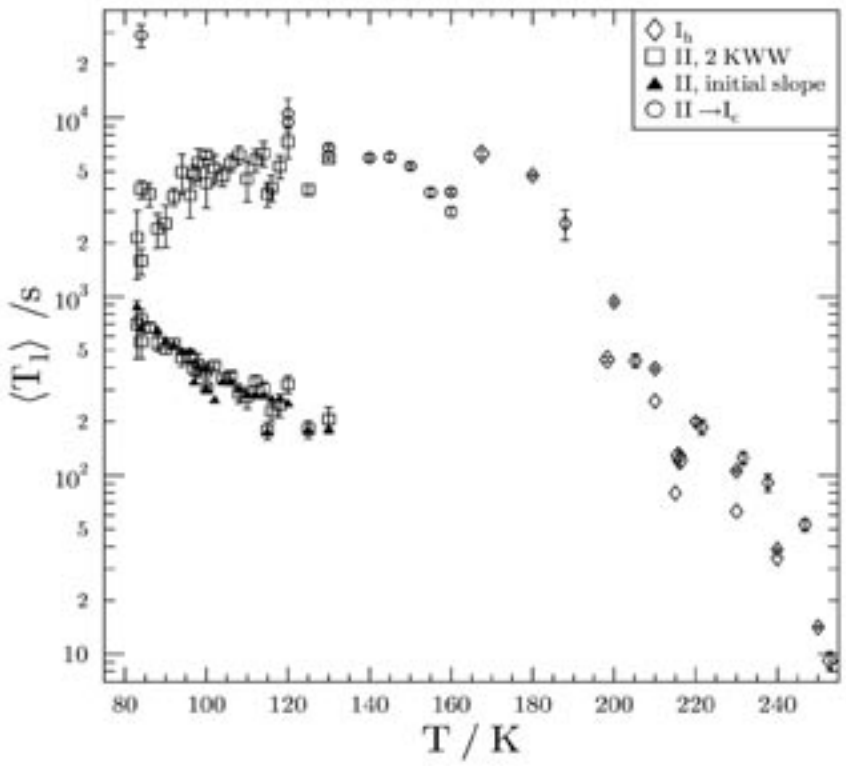
Deuteron spin-lattice relaxation in high pressure ice II has been investigated at different temperatures.

Ice II, one of the high pressure polymorphs of ice, is a completely proton-ordered structure in which two crystallographically distinguishable types of water molecules form a tetrahedrally linked network of hydrogen bonds.

Deuteron spin-lattice relaxation is sensitive to dynamics in the domain of the Larmor frequency at *46.7* MHz. Measurements at different temperatures of the deuteron spin-lattice relaxation time T_1 show that the magnetization recovery is unequivocally non-exponential which indicates a distribution of correlation times.



The samples (D_2O) have been prepared at appropriate pressures and temperatures. They can be recovered to ambient pressure at liquid nitrogen temperature where they remain metastable and can be studied. The sample quality is verified by x-ray diffraction. T_1 -measurements have been performed while increasing the temperature stepwise. At a temperature of *145* K a discontinuity in T_1 indicates a phase transition. The high pressure ice phase transforms to crystalline cubic ice I_c.

Acknowledgements

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APPLICATION OF NMR-SPECTROSCOPY FOR INVESTIGATION OF STRUCTURE OF HYBRID NANOCOMPOSITES BASED ON POLYMER AND CHALCOGENIDE GLASSES

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Nanocomposites are defined as materials made from significantly different constituents, that are mixed in nanometer scale. Such materials have properties that are superior to the conventional microscale composites. So far the greatest attention has been given to inorganic/organic nanocomposites. Especially to polymer nanocomposites with semiconductor materials. Recently a new possibility to obtain composite materials based on chalcogenide glasses and polymer have been appeared and great attention is given to this hybrid composite materials combining the advanced properties of initial materials. The composites based on chalcogenide glasses (ChG) and polymer material represent an important class of hybrid materials with promising physical and optical characteristics. For application in optoelectronics it is very important that both chalcogenides and polymer materials exhibit high photoinduced changes [1,2]. It was shown that organic polymers manifest high photoinduced changes and low stability and on the contrary the chalcogenides glasses – comparatively low photoinduced changes and good stability.

Composite and nanocomposite materials based on the amorphous arsenic sulphide and polymer polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) received by chemical dissolution of As_2S_3 and polymer separately, mixing and deposited on various substrates (optical glass, polyethyleneterephthalate and monocrystalline silicon, etc.) have been investigated [3-5]. Research of morphology of layers has revealed that composites represent a polymeric material as matrix in which As_2S_3 spheroids with submicron sizes (500-1000 nm) are regularly distributed. The as synthesized composite materials were characterized by UV-VIS-IR spectroscopy, scanning electron microscopy/energy dispersed spectroscopy (SEM/EDS). The decreasing of the As_2S_3 component in the composite leads to absorption edge shift to higher energies and spheroid dimensions decreasing. The chemical analyses of composites As_2S_3-polymer showed that stochiometric ratio of As_2S_3 in coated composite film remained the same as in evaporated As_2S_3 film and in As_2S_3 bulk glass matrix. Optical properties of the composites are changed due to ultraviolet (UV) light irradiation. This allows these structures to be used for optical recording of information in particular holographic recording of diffraction gratings.

Previously it have been studying the structure of the synthesized polymers by means of the NMR-spectroscopy [6]. We have focused on the conformational peculiarities and statistical structure of macromolecules. Therefore the present work would be a natural continuation of our previous studies. We would like to combine the acquired knowledge to synthesize novel hybrid nanocomposite materials and study their structure with original NMR experiments.

The crystalline phase of the semiconductor materials can be studied with X-ray diffraction methods. NMR spectroscopy is the best method to study the local order of the materials and understand the microscopic mechanisms. Local order plays the most important role in the applications of the nanocomposites. The anticipated structure of the materials we are going to study – organic parts entwined with nonorganic parts – allows to presume, that the dynamics of the nuclear spin system in these parts of the material are different. This, on the otherhand, forms the basis for selective resolution of the NMR signals and selective NMR spectroscopy the composites of the nanocomposite materials. To our knowledge this has not been done before.

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MAGNETIC RESONANCE IMAGING OF PROLONGED RELEASE DOSAGE FORMS

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Because hydrophilic matrix requires water to activate the drug release mechanism it is important to study time dependence of water concentration in the matrix. Magnetic Resonance Imaging (MRI), which allows for dynamic measurements of various parameters of dissolution, is very well suited method for this purpose,

Dissolution studies of two prolonged release, polymer based drug delivery systems tablets supplied by two different manufactures are presented. MRI was used to observe hydration kinetics and gel layer formation during dissolution of the dosage forms. The tablets under studies had the same active substance, similar release profiles but different formulations.

The study was performed using digital console Maran DRX, 4.7T superconducting magnet and home made, dedicated, MR-compatible flow-through dissolution cell (USP apparatus 4) combined with MR probe [3]. Studies were performed under flow condition using pure water as dissolution medium. Temperature of the medium was maintained at 37 °C. Flow insensitive spin echo imaging sequence was applied to compensate for flow induced artifacts during MR imaging. Each tablet was investigated for 6 hours to cover the changes in dissolution process.

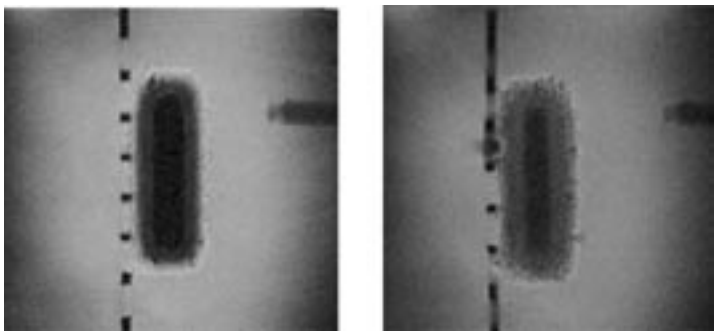

Fig. 1. Tablet cross-section at 2h of the study for two formulations.

MR imaging method was found useful for comparative studies of different dosage form formulations. The difference in dissolution mechanisms was clearly visible (see Fig. 1). Time evolution profiles of cross-sections areas of dosage forms were obtained. The areas of diffusion, hydrogel formation and ‘dry core’ regions were measured on consecutive MR images.

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INFLUENCE OF DISORDER ON VARIABLE-RAGE-HOPPING EXPONENTS IN HCL – DOPED POLYANILINE PELLETS

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Polyaniline is a conjugated polymer that exhibits a finite electrical conductivity when doped by a protonic acid. In our work, we have studied the influence of doping by HCl on the conducting properties of pressed polyaniline pallets.

Generally, polyaniline samples constitute a three-dimensional network (3D) of one-dimensional (intrachain) conductors. If the interchain coupling is sufficiently strong in comparison to the intrachain mean backscattering time, the system can be effectively regarded as a 3D one. Furthermore, if the Coulomb interaction between an excited electron and the corresponding hole is not completely screened, it should be taken into account in addressing the nature of the charge transport. Since polyaniline samples possess a high degree of structural disorder, the charge propagation occurs by variable-range-hopping mechanism.

In our own-made samples we have found that increase of the doping not only enhances the electrical conductivity but also weakens the structural disorder, which affects the variable-range hopping. This is revealed in the temperature dependence of conductivity $\sigma(T)=\sigma_0\exp[-(T_0/T)^{\alpha}]$, where α and T_0 contain information on the underlying physics. At low temperatures (below 200 K), α undergoes a significant change at the doping level Y=[Cl]/[N]~0.3, i.e., 60% of the full doping (Y=0.5): α=1/2 for lower doping, whereas more-doped samples exhibit α=2/5, see Fig.1.

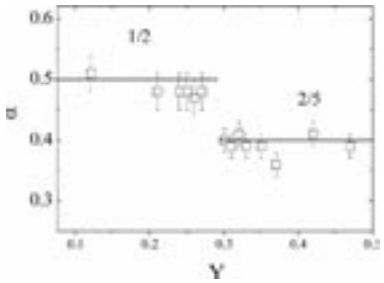

Fig.1. Low temperature exponent α versus doping level Y. Around Y=0.3 there is a well-defined change from α=1/2 to α=2/5, which are indicated by the solid lines. [1]

The obtained low temperature results can be well explained by the recent variable-range-hopping theory of Fogler, Teber and Shklovskii [2]. The same theory also applies above T~200 K where α=1/4 regardless of the doping level. Other relevant features, such as the charge localisation length (~2 nm) and the level of disorder, are inferred from magnetoconductivity and X-ray diffraction measurements, respectively.

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BINARY LIQUID MIXTURES AND LIQUID CRYSTALS CONFINED IN POROUSES GLASSES STUDIED BY MAS PFG NMR

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Porous materials are ubiquitous in nature and find important applications in many industrial fields like sorption, catalysis and separation. Modern nanoporous materials exhibit a large diversity with respect to pore architecture and surface chemistry. They open novel routes of exploring molecular diffusion under confinements and establishing the correlations between the properties of the host systems and diffusivities of guest molecules. Since many years, the pulsed-field gradient nuclear magnetic resonance (PFG NMR) is a well established technique for direct measurements of diffusion of liquids in bulk [1] and in confined geometries [2]. However, if dipole-dipole interactions are not completely averaged out by molecular motions, the NMR signals are very broad, and the free induction decays are very fast [3]. This limits the time available for the application of gradient pulses [4] and makes impossible measuring diffusion in liquid crystals without special line-narrowing techniques [5]. In the case of liquid mixtures confined in nanoporous materials [6], dipolar broadening deteriorates the resolution in the chemical shift scale necessary for selective diffusion measurements of the mixture components. This kind of problems can be overcome by combining magic-angle spinning (MAS) with pulsed field gradients. This relatively new technique is referred to as MAS PFG NMR, see e. g. [7]. MAS implies the orientation of the spinning axis with respect to the external magnetic field at the angle of $\theta_m \approx 54.7$. In comparison with other techniques [5], this type of measurements has considerable advantages. First, the increased resolution in the ppm scale permits one to observe separately each individual group with identical electronic surroundings. Second, the longer transverse relaxation time upon MAS allows for sufficient time for the application of pulsed magnetic field gradients.

Dynamic properties of the confined nematic liquid crystal 5CB has been studied by several techniques including the Dipolar Correlation Effect [8] and Field Cycling Relaxometry [9, 10]. However, no NMR diffusion measurements were performed so far. In this work we apply for the first time the MAS PFG NMR technique to liquid crystals. The nematic liquid crystal 5CB confined in 30-nm and 200-nm-Bioran glasses were studied. It was shown, that the diffusion coefficient of 5CB in the isotropic phase exhibits an Arrhenius-like temperature dependence $D_{iso} = D_0 \exp[-E_a / kT]$ with an activation energy of $E_a^{iso} = 26.7 \pm 2.7$ kJ mol^{-1}. The temperature dependence of the diffusion coefficient in the nematic phase can also be well approximated by an Arrhenius relationship with an activation energy of $E_a = 38.3 \pm 3.8$ kJ mol^{-1}, which is approximately the same for 30-nm and 200-nm-Bioran glasses. The measured diffusivities in the both phases did not differ significantly from the values in bulk 5CB [5].

Measurements of methanol / cyclohexane-mixtures in porous glass with 7.5 nm diameter (CPG7.5) yield the self-diffusion coefficients for both compounds. A comparison with the values obtained for single-component adsorption shows that the diffusivity of methanol is by factor of 2 smaller in the confined binary mixture than in the system methanol + CPG7.5. At the same time, cyclohexane has the same self-diffusion coefficient in the confined mixture and in the single component system cyclohexane + CPG7.5.

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SPATIALLY RESOLVED NMR ON HEAVY-ION IRRADIATED LiF CRYSTALS

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Interaction of swift heavy ions with solids lead to a wide variety of irreversible changes of the structural and chemical composition. When heavy ions, with energies higher than 1 MeV per nucleon, pass through a solid they deposit most of their energy by exciting and ionizing the target atoms along the ion trajectory, creating so-called latent tracks. In LiF, the most significant type of defects along tracks are paramagnetic F-centers (an electron on an anion vacancy) [1].

Due to the magnetic moments of ^{19}F and ^{7}Li, Nuclear Magnetic Resonance (NMR) has proven to be a valuable tool to study radiation induced damage in LiF. For relation between the spin-lattice relaxation time T_1 and defect density has beendemonstrated [3]. In this study, we apply spatially resolved NMR which opens new posibilities to investigate heavy ion tracks as a function of depth. The NMR measurements were accompanied by absorption spectroscopy (VIS and UV).

All LiF crystals were irradiated with ^{130}Xe ions at the Universal Linear Accelerator (UNILAC) at GSI with energies of 11.1 MeV per nucleon. The fluences varied from 10^{10} to 10^{12} ions/cm^2. At this energy the range of the ions in LiF is about 87 µm, which is considerably lower than the crystal thickness of 1 mm [2].

The spatially resolved ^{19}F-NMR measurements were performed at room temperature in a specially designed superconducting gradient magnet at a field of 3.73 T and a static field gradient of 74.3 T/m [4]. A saturation pulse sequence was used for the determination of the spin-lattice relaxation rates. Using a stepping motor the sample could be moved parallel to the magnetic field gradient with a repositioning precision better than 10 µm. For our experiments the thickness of the excited slice was between 6 and 8.5 µm (see Fig. 1)

We measured the relaxation rate profiles for several fluences (see Fig. 2). In the first region up to approximately 100 µm a clear increase of the relaxation rate can be observed. The signal also increases with ion fluence, which can be explained by the increased creation of paramagnetic F-centers. Since the ion penetration depth is defined within less than 3 µm only [2], we cannot exclude that the width of region 2 is caused by a not well defined crystal surface. Of great interest is region 3 where the relaxation rate is still increased compared to a non-irradiated sample although the ions, which have a well defined penetration depth, could not have reached this layer of the sample. It is assumed that beyond the range of the ion beam color centers are created by X-rays or neutrons induced from the fast delta electrons in the ion track.

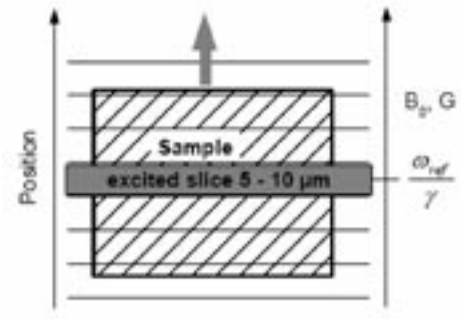

Fig.1. Sample moving in a magnetic field gradient G.

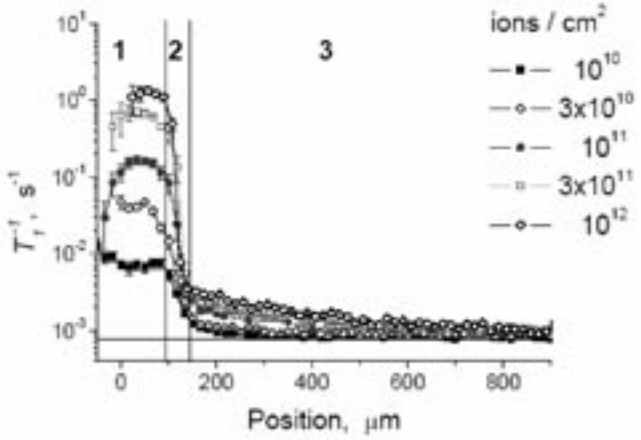

Fig. 2. Position dependent spin lattice relaxation rates for several fluences.

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Acknowledgements

I would like to thank for financial support by the Graduate Program for Hadron and Ion Research.

APPLICATION OF NMR SPECROSCOPY FOR INVESTIGATION OF STRUCTURE OF PHARMACEUTICAL SUBSTANCES AND NATURAL COMPOUNDS

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^{1}H and ^{13}C NMR spectra represent the extensive information on molecular structure of analyzed substance. Position of resonance signals in a spectrum, their fine structure and the areas allow to define number of atoms of hydrogen and carbon in the separate groups, the nearest chemical environment, presence of impurity etc [1, 2].

At the Institute of Chemistry of Moldova a number of derivatives of malonyl amides and p-aminobenzoic acids were synthesized. These compounds have biological activity with respect to some cardiovascular diseases [3]. ^{1}H NMR spectra of some compounds were recorded in DMSO solutions at the temperature 298 K by Bruker-400MHz spectrometer. Structure of the investigated compounds and chemical shifts in ^{1}H NMR-spectra are shown in Fig.1 and Table 1.

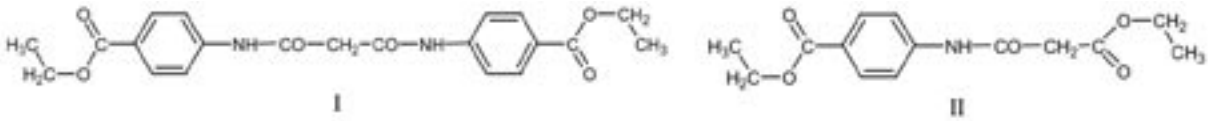

Fig. 1. Structure of compounds ethyl 4-(4-ethyloxycarbonylphenylcarbamoylmethylcarboxamido)benzoate (I) and ethyl 2-(4-ethyloxycarbonylphenylcarbamoyl)acetate (II)

Table 1. Chemical shifts in ^{1}H NMR spectra of compounds I and II

Number of compound	^{1}H NMR δ (ppm)
I	1.32 – 1.28 (t, 6H, $2CH_3$), 3.56 (s, 2H, - CO – CH_2 – CO -), 4.31 – 4.25 (q, 4H, $2CH_2$), 7.93 – 7.72 (m, 8H, arom.), 10.52 (s, 2H, 2NH).
II	1.21 – 1.18 (t, 3H, CH_3), 1.32 – 1.28 (t, 3H, CH_3), 3.49 (s, 2H, - CO – CH_2 – CO -), 4.14 – 4.09 (q, 2H, CH_2), 4.31 – 4.25 (q, 2H, CH_2), 7.93 – 7.69 (m, 4H, arom.), 10.50 (s, 1H, NH).

As these compounds are potential pharmaceutical substances it is of interest to me application of NMR spectroscopy for identification and quantitative determination in pharmacopoeial analysis.

It is well known that the variety of the structural information of NMR spectra practically excludes coincidence of spectra of different compounds. In this connection the method of spectroscopy of a nuclear magnetic resonance is applied to identification of pharmaceutical substances and natural compounds. For this purpose the fullest set of the spectral parameters characterizing structure of substance is used. If the full interpretation of NMR spectrum is difficult to realize in consequence of their complexity then some specific signals of spectrum of the analyzed substance will use for identification.

Other objects of the investigations can be different natural compounds. For example, in a clary sage (Salvia sclarea L.) a number of flavonoides with P-vitamin activity was revealed by TLC method [4]. In the future using NMR method allow to obtain exact information on structure of flovonoides and other compounds isolated from clary sage.

For solution of these purposes it is necessary to improve my knowledge in application of NMR spectroscopy for identification and quantitative determination of different pharmaceutical and natural substances.

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Acknowledgements

I would like to thank Dr. K.D. Gavrilov from Ryazan State University S. A. Esenin (Laboratory of Coordination Chemistry) and Dr. F.Z. Macaev from Laboratory of Organic Synthesis (Institute of Chemistry, Academy of Sciences of Moldova) for the support during my research in obtaining of NMR spectra (Bruker 400 MHz-spectometer).

THE SYNTHESIS OF 4-HYDROXY-3-METHOXY-4'-IZOTHIOCYANATOCHALCONE

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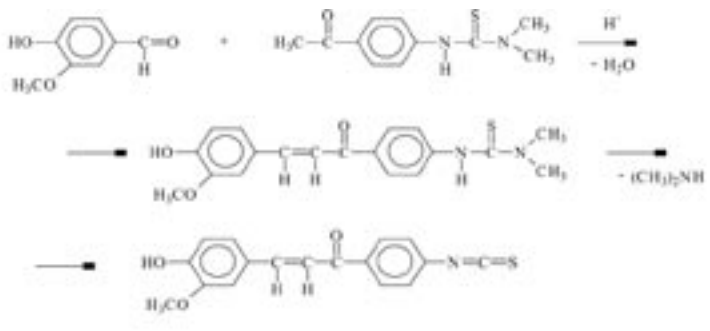
The object of the synthesis it's obtaining of a 4-hydroxy-3-methoxy-4'-izothiocyanatochalcone by the method of the condensation of a 4-hydroxy-3-methoxy-benzaldehyde (vanilla) with the 3-(4-Acetyl-phenyl)-1,1-dimethyl-thiourea and elimination of a dimethyl-amine, also the investigation of her useful properties (anticancer and anti ageing). The reaction was effectuated in the dioxan and $H_2SO_{4\ conc.}$(1 ml dioxan – 0,001 mol $H_2SO_{4\ conc}$) 2 hours at the 80 ºC. The ending of the reaction was verified by means of the chromatographic slate.



After neutralisation (by solution $NaHCO_3$), the sediment was filtered and the chalcone was obtained with 60 % efficiency. Other percents belong to unused vanilla, thiourea and impurities. After purification on silicagel (eluent hexane-benzene) and recrystallisation (hexane-benzene) the pure chalcone was obtained (m.p.=124-126 °C) which were analysed by NMR and IR spectroscopy.

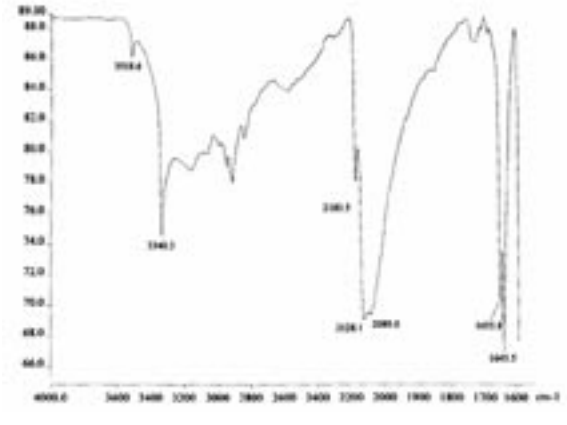


Fig.1. IR spectra of investigated substance.

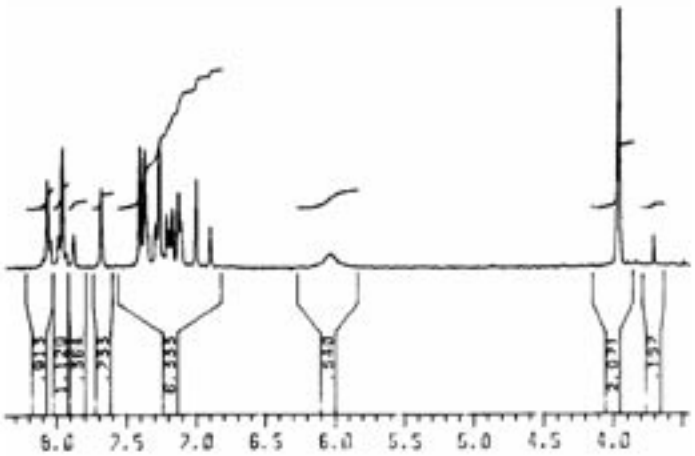


Fig.2. NMP spectra of investigated substance.

In the IR spectrum the bands of adsorption 1645 cm^{-1} (ν (C=O)), 3340 cm^{-1} (ν (OH, phenolic)), 2100 cm^{-1} (ν (NCS, izothiocyanato group)) were identified. In NMR spectrum there were found: a peak at 4 p.p.m. the metoxy group $–OCH_3$, the peaks at 6-9 p.p.m. which represent ~9 atoms of the hydrogen of 2 benzene and –CH=CH– groups. These data confirm the structure of title substance, and the realisation of the reaction.

NMR RELAXATION IN SOLUTIONS OF HYDROGEN PEROXIDE AND PARAMAGNETIC IONS

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Hydrogen peroxide (H_2O_2) at low concentration is widely used for bleaching and disinfection. A number of biological processes also produce and consume H_2O_2.

The chemical action of H_2O_2 is carried out by oxygen, which, from the NMR point of view, is paramagnetic. In this communication we will show the results of measurements of relaxation times: spin-lattice T_1, spin-spin T_2 and the relaxation time in the rotating frame $T_{1\rho}$ in aqueous hydrogen peroxide solutions as a function of H_2O_2 concentration, temperature and time of reaction. We also present the results of relaxation time measurements in blood serum after addition of H_2O_2. For comparison, similar measurements for solutions of paramagnetic ions like iron $Fe^{2+}$and copper Cu^{2+} were done. It is interesting that T_2 and $T_{1\rho}$ behaviour in aqueous H_2O_2 solutions is similar to that obtained for paramagnetic ions, however T_1 is independent at H_2O_2 concentration up to very high concentrations (see Fig.1).

Our preliminary measurements are an introduction to NMR relaxation investigations of these systems and the interpretation of our data may help us to understood oxygenation processes in biological systems like blood serum.

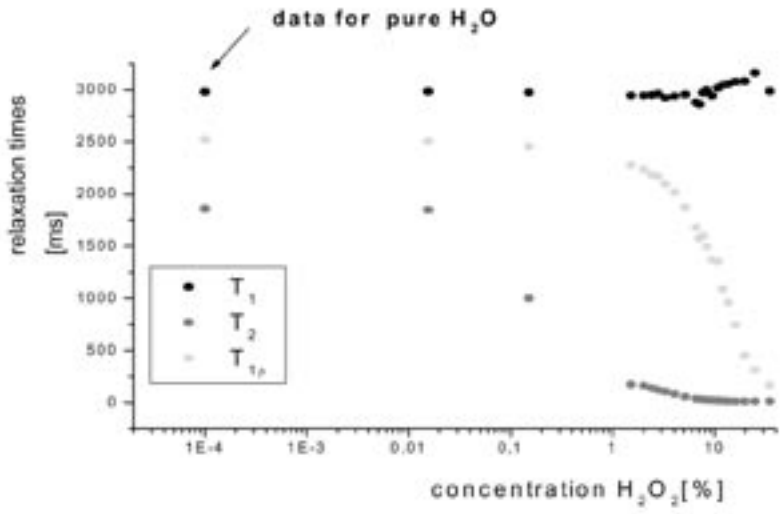

Fig. 1 Concentration dependence of proton relaxation time T_1,T_2 and $T_{1\rho}$ for aqueous solution of H_2O_2 at room temperature.

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NMR STUDY OF 4-PHENYL-2,4-DIOXOBUTANOIC ACID KETO-ENOL TAUTOMERISM IN AQUEOUS SOLUTIONS. CONTRIBUTION TO UNDERSTANDING OF ADME TOX PROPERTIES OF ARILDIKETO ACIDS

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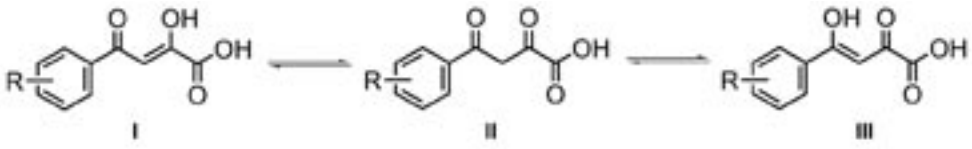
4-Aryl/heteroaryl-2,4-dioxobutanoic acid (ADK) derivatives exert widespread biological activities. Targeting HIV-1 integrase, the enzyme responsible for integration of viral DNA in host genome, is among the most important ones [1]. ADK simultaneously exist in two enolic forms (conformationally locked by the pseudo-ring) and one diketo form having two rotatable bonds responsible for the conformational flexibility [2, 3] (Scheme 1).



Scheme 1. The diketo (II) and two enolic (I and III) forms of 4-Phenyl-2,4-dioxobutanoic acid

It is proposed that *β*-diketo moiety functionally sequestrate divalent metal ions, critical cofactors at the enzyme catalytic core, while the enolic forms act by ligation of one metal ion and simultaneous H-bonding to catalytic core amino acid residues [4]. Study of pH dependence of ADK keto-enol tautomerism in aqueous solutions (pD range 0–10), important for their ADME Tox properties, exemplified on 4-phenyl-2,4-dioxobutanoic acid (parent derivative), was the main aim of this work. Acidity constants for parent derivative (pK_{a1} 2.06 ± 0.03, pK_{a2} 7.56 ± 0.02) were previously determined [3]. The relative ratio of tautomeric forms (molecular and anionic) was estimated from the area under ^{1}H NMR peaks, using spectra recorded in buffered D_2O solutions (I = 0.1 M ($NaNO_3$), t = 25 ± 1°C). The representative ^{1}H NMR spectra are given on Figure 1.

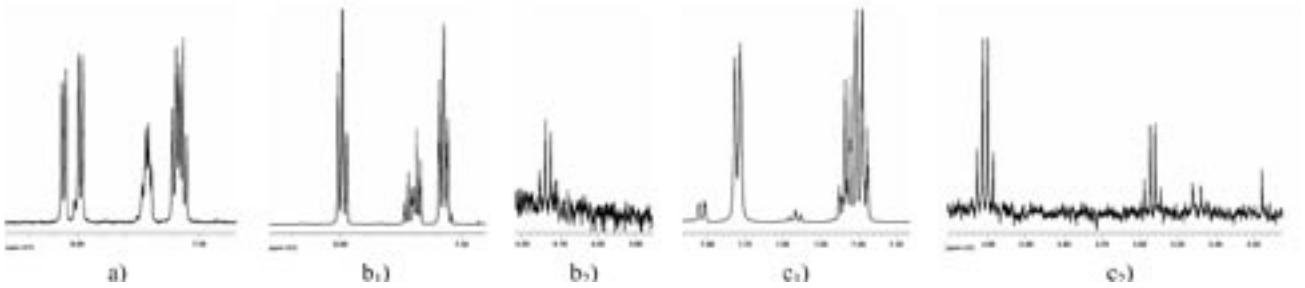


Fig. 1. Selected regions of ^{1}H NMR spectra of 4-Phenyl-2,4-dioxobutanoic acid in buffered aqueous solutions: a) pD<1 – molecular form (H_2A); b_1) and b_2) pD 5 – monoanionic form (HA^-); c_1) and c_2) pD 10 – dianionic form (A^{2-})

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Acknowledgements

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NMR OF SOLUTES PARTIALLY ORIENTED IN ORDERED FLUIDS TO PROBE THE LIQUID CRYSTAL NEMATIC AND SMECTIC-A POTENTIAL AS CONCEIVED IN A MEAN FIELD APPROXIMATION

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The NMR spectra of Furan, Thiophene, 2,2-Dichloropropane and 1,3,5-Trichlorobenzene were investigated in the Liquid Crystals 8CB and 8OCB. The orientational order of all solutes was obtained from the very accurate dipolar couplings yielded by the spectra in both liquid crystals. A change in temperature dependence of orientational ordering is observed at the nematic to smectic-A phase transition where the liquid crystal molecules are stacked into layers as well as having the orientational order of the nematic phase.

In a previous study of different solutes in the same liquid crystals we analyzed the results with Kobayashi-McMillan theory applied to solutes, i.e. by incorporating smectic-A layering and nematic-smectic-A coupling into a mean-field orientational Hamiltonian with reasonable success. However the fit required the linear extrapolation of the asymmetry in the solute molecular tensor from the nematic into the smectic region and one of the six solutes considered showed a degree of curvature which remained unexplained at the time. Since even more curvature is observed in the present study, we seemed to be at an impasse with inadequate theory to rationalize the results of these NMR measurements.

Fortunately a study of the nematic phase of solutes in other liquid crystals by Burnell and coworkers demonstrated the currency of a nematic potential with two Maier-Saupe terms which reproduced the correct values of liquid crystal properties that should be able to deal with the observed curvature. This amounts to saying that the two terms in the potential (one associated with size and shape while the nature of the second is still disputed) need not change in the same way with respect to temperature.

In light of these developments we propose a new Kobayashi-McMillan Hamiltonian with the two-term nematic potential and determine Hamiltonian prefactors. This study brings the range of our probes beyond the planar aromatic solutes of previous studies to broaden our knowledge of the liquid crystal environment and more rigorously test the theory.

INVESTIGATION OF WATER STATUS IN MATURING LUPIN SEED

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Water status of maturing lupin seeds (*Lupinus luteus* L.) was investigated by both MRI and NMR spectroscopy. The magnetic resonance imaging visualized local inhomogeneities of water distribution inside the seed. At the late seed-filling stage the most intensive signal was observed in the seed coat and the outer parts of cotyledons in the hilum area. During maturation drying MR images intensity declined faster in the outer part of cotyledons then in the central part. The NMR spectroscopy characterized the changes of water status in maturing lupin seeds. Analyses of T_2 relaxation times revealed a three-component water proton system in seeds (Fig. 1). The different magnetic environment of each proton system causes different relaxation time. These results correlate well with three fraction of water (structural, intracellular, and extracellural) that were observed during seed germination [1]. This study provides evidence that lupine seeds have similar states of the different water components with regard to seed moisture content at two distinct physiological stages, seed maturation and germination [2].

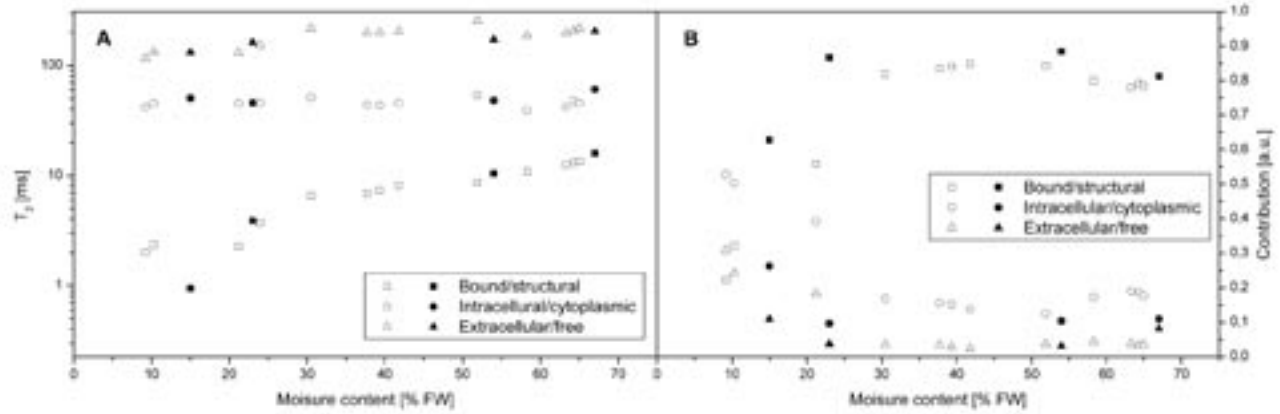

Fig. 1 (A) Components of spin–spin relaxation (T2) of maturing (closed symbols) and germinating (open symbols) lupin seeds. (B) Contribution of various T2 relaxation time components of water in maturing lupin seeds (closed symbols) and germinating seeds (open symbols) expressed in relation to moisture content. Mean values of five measurements. SEs do not exceed 5%.

References

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SECOND POSTER SESSION

LOW MOLECULAR WEIGHT ORGANOGELATOR, AS A NEW APPROACH TO CREATION OF PHYSICAL GELS: INFLUENCE OF ORGANIC SOLVENT

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Functional materials are distinctly different from structural materials, and their physical and chemical properties are sensitive to a change in the environment such as temperature, pressure, electric field, magnetic field, optical wavelength, adsorbed gas molecules and the pH value. The functional materials utilize the native properties and functions of their own to achieve an intelligent action.

Low Molecular Weight Organogelators are substances which can constitute a new approach in this mater. As smallest and most efficient gelators of different organic solvents which involves the self-assembly phenomena to create fiber-like structures, which entangle to form a 3D network and immobilize organic fluids [1].

The study of 1, 2–O (1-ethylpropylidene)-α-d-glucofuranose, which is a representative of recently designed and synthesized new saccharide-based gelators [2] are reported. An experimental approach based on a combined use of techniques – NMR, FT – IR, RAMAN, and phase transition measurements allows us to gain information about the physical properties of 1, 2–O (1-ethylpropylidene)-α-d-glucofuranose organogel and shedding light on the gel formation.

The FT-IR spectra revealed the existence of a hydrogen-bond network formed by gelator molecules in the crystalline and gel phase. The phase transition measurements performed as a function of gelator concentration allowed the calculation of the energy correlated with the transition from gel to solution phase [3].

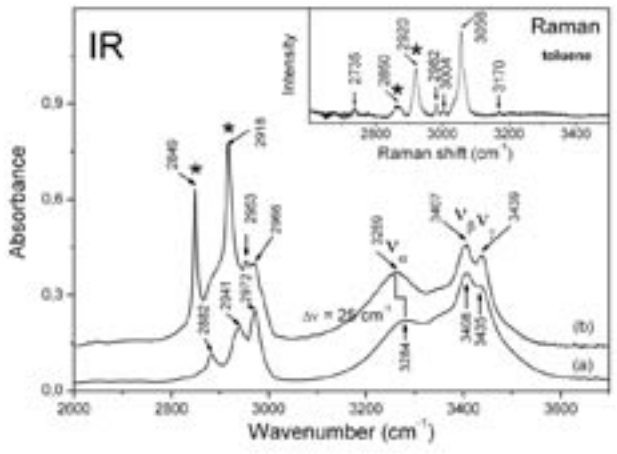

Fig. 1. Absorption spectra of 1,2–*O*-(1-ethylpropylidene)-α-D-glucofuranose in the crystalline state (a) and in the toluene gel-state (b). The inset shows a Raman spectrum of toluene.

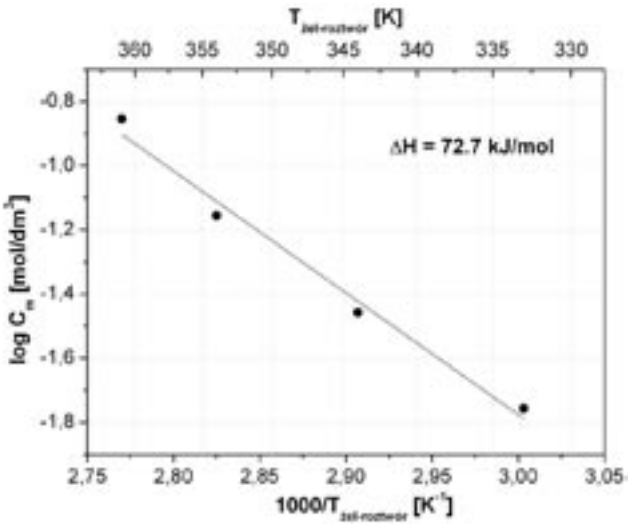

Fig. 2. Plot of the logarithm of gelator concentration vs the reciprocal absolute temperature of T_{GS}. The solid line is the best fit of Schreder relation to the experimental points.

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SECONDARY RELAXATIONS IN MOLECULAR GLASSES, POLYMERS AND PLASTIC CRYSTALS STUDIED BY 2D ^{2}H NMR

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[3]Institut für Festkörperphysik, Technische Universität Darmstadt, Darmstadt, Germany

When a liquid is supercooled, the structural relaxation (α-process) dominates the relaxation behaviour above the glass transition temperature T_g. In addition, for numerous systems there arises at low temperatures, e.g., in the dielectric spectrum a second peak at higher frequencies than that of the α-process. The nature of this secondary relaxation, the so-called β-process, has yet to be understood. Fig. 1 [2] shows dielectric time constants τ_β for several systems. While $\tau_\beta(T)$ coincides for four of them on the reduced temperature scale T_g/T, the relaxation strength can be quite different. We present a two-dimensional (2D) ^{2}H exchange NMR study, attempting to clarify the geometry of the molecular motion involved in the β-process of different glass formers, bailing the possibilities of 2D NMR with the aptitude of selective deuteration.

We study PMMA-d_3, polybutadiene-d_5 and a mixture of decaline-d_{18} and chlorobenzene. In comparison with data of o-terphenyl, which does not show a secondary relaxation, we are able to circumscribe the temperature range, in which the β-process is expected to dominate the spectra. Fig. 2 shows selected 2D spectra pointing up the manifestation of the β-process in 2D NMR: below T_g the spectra are dominated by signs of small angular reorientations, which are however spatially restricted. This pattern grows in amplitude for $T>T_g$ but remains its shape until only at temperatures well above T_g the α-process enters the time window of the experiment and gives rise to a qualitative change: the spectra strive towards full isotropic reorientation.

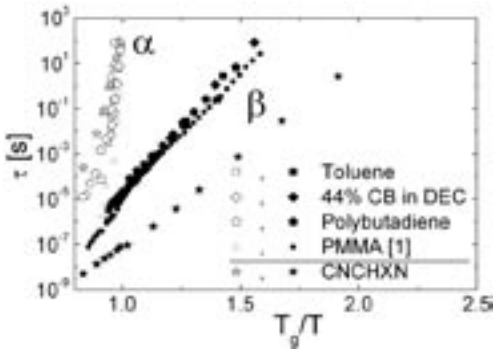

Fig. 1. Dielectric time constants for several glass forming systems plotted on a reduced temperature scale T_g/T. Note that in this representation $\tau_\beta(T)$ coincides for four systems.

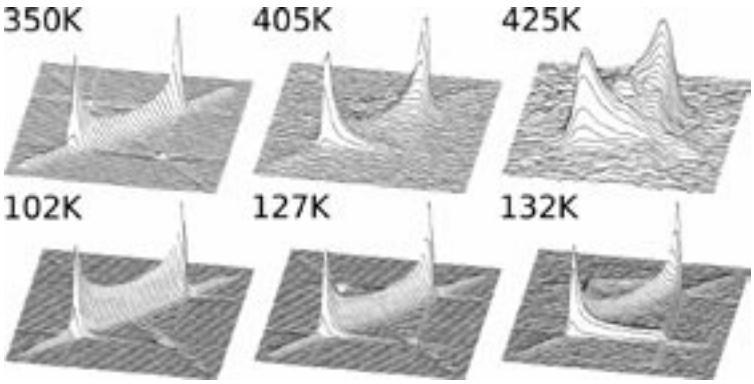

Fig. 2. 2D ^{2}H NMR spectra of PMMA-d_3 (top, T_g=400K, t_m=10ms, spectral width ~100kHz) and cis-decaline in chlorobenzene (bottom, T_g=127K, t_m=100ms, spectral width ~300kHz). One column represents roughly analogue T_g/T values, and the spectra exhibit similar features. At highest temperatures the onset of full isotropic reorientation due to the α-process is seen.

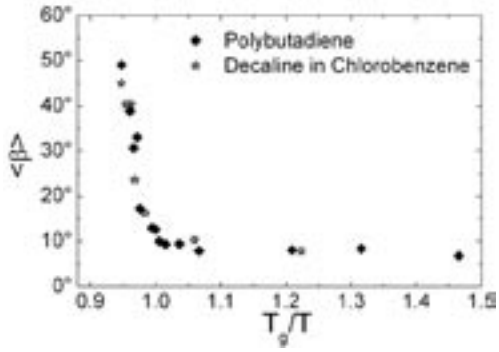

Fig. 3. Average reorientation angles extracted from the 2D spectra of two systems (t_m=100ms), clearly demonstrating the decrease of spatial restriction above T_g.

In contrast to the dielectric spectra with quite different relaxation strengths, the manifestation of the secondary relaxation in 2D NMR is very similar for the studied systems (cf. Fig. 2), which implies strong similarities in the geometry of motion. Average reorientation angles extracted in a first approach from the spectra not influenced by the α-process coincide nicely (cf. Fig. 3). To get further insight on the general underlying geometries of motion, simple motional models are compared against the spectra. Additionally data of cyano-cyclohexane (CNCHXN), a plastic crystal with reduced degrees of freedom which shows pronounced NMR effects concerning its secondary relaxation (although different in $\tau_\beta(T_g/T)$, cf. Fig. 1), is analyzed.

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MOLECULAR DYNAMICS OF THE HUMAN PROTEIN HC (α_1 – MICROGLOBULIN) IN WATER SOLUTION STUDIED BY FAST FIELD CYCLING NMR RELAXOMETRY

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The human protein HC (α_1 – microglobulin) is a low molecular weight heterogeneous glycoprotein widely distributed in the human body fluids and belonging to the lipocalin superfamily. This biomolecule is produced by the human liver and used in the clinical routine as a sensitive indicator of tubular dysfunction. The monomer of protein HC contains a single (183 amino acid residues long) glycosylated polypeptide chain with 3 cysteine residues (2 of which form a disulfide bridge). The molecular mass of the glycosylated protein is about 27 kDa. The monomer of protein HC is characterized by a radius of gyration R_G=2.16 nm and the dimer by R_G=2.93 nm [1].

Fast Field Cycling NMR Relaxometry is a powerful method to describe hydration, aggregation, and dynamic properties of proteins in water [2-4]. This technique was used to analysis of molecular motions of the human protein HC, especially it's rotational motions, in solution (the 50 mM $NaHCO_3$ buffer, pH 7.0). Relaxometric investigations were made for few aqueous solutions of human protein HC, prepared at different concentration of the protein (varying from 7.5 mg/ml to 30 mg/ml). For all samples the ^{1}H NMR dispersion of spin-lattice relaxation rates $R_1 = T_1^{-1}$ (^{1}H NMRD) were recorded at 298 K in the range of Larmor frequencies between 10 kHz and 12 MHz.

Because of deviations from Lorentzian behaviour, all experimental ^{1}H NMRD profiles, were analysed by Model-Free approach [2]. According to the rigid sphere model, the Stokes-Einstein equation provides for the monomer form of human protein HC a rotational correlation times of 10.3 ns and for dimer 25.6 ns. The values of correlation times provided by Model-Free analysis are closer to the Stokes-Einstein estimate expected for dimmer form. The tumbling motion of HC protein dimer in solution is probably the main source of dispersion in the system studied.

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SOLID-STATE NMR CHARACTERIZATION OF THE DISORDER OF AN ORGANIC INTERCALATED LAYERED SILICATE (DDABCO-HECTORITE)

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The intercalation of large organic molecules (pillars) in layered compounds provides new synthetic pathways to microporous materials. These are expected to show new properties, e.g for catalytical purposes since they allow to introduce functional or even chiral enviroments. To design new materials knowledge about structure and dynamics is essential. Solid-state NMR is an ideal analytical tool to investigate both the orientation and the dynamical behavior of an organic molecule in a confined enviroment.

A synthetic Cs-fluorohectorite ($Cs_{0.5}[Mg_{2.5}Li_{0.5}]Si_4O_{10}F_2$) was intercalated with a cationic pillar ($DDABCO^{2+}$) and a microporous material is obtained. This pillared clay was then characterized by X-Ray diffraction and solid-state NMR, involving ^{1}H, ^{2}H, ^{7}Li, ^{13}C, ^{19}F, and ^{29}Si NMR.

Investigation of the silicate layers by ^{29}Si NMR confirms a crystallographically unique position of Si atoms in agreement with single crystal data [1], whereras ^{19}F NMR exhibits two resonance, assigned to different Mg/Li enviroments. $^{19}F\{^{7}Li\}$-REDOR experiments show a clustering of Li atoms in the octahedral sites and therefore a distribution of the silicate layer charge.

To gain orientational and topological information about pillar position and interactions of the guest molecules in the interlayer space of the host lattice a pillared clay with doubly $^{13}CD_3$-labelled D*DBACO^{2+} was synthesized. ^{13}C-^{19}F distances between ^{13}C atoms of the guest molecule and ^{19}F atoms of the host lattice were measured by $^{13}C\{^{19}F\}$-REDOR NMR, applying ^{1}H decoupling simultaneously. Resulting REDOR curves show different distances between methyl group and silicate layer as function of humiditiy (see figure 1). This confirms powder X-ray diffraction measurements showing varying interlayer distances depending on relative humidity. By simulating the REDOR curves the tilt angle of the pillar molecule could be calculated to 30° relative to the silicate layer.

The molecular dynamic was investigated by wide-line ^{2}H NMR spectroscopy at varying temperatures. Line-shape analysis shows sigificant large angle jumps and T_1 measurements allow to estimate an activation energy of 20 kJ/mole. Additional MAS NMR measurements with natural abundance samples were made to check equivalent behavior of the enriched and the natural abundance samples.

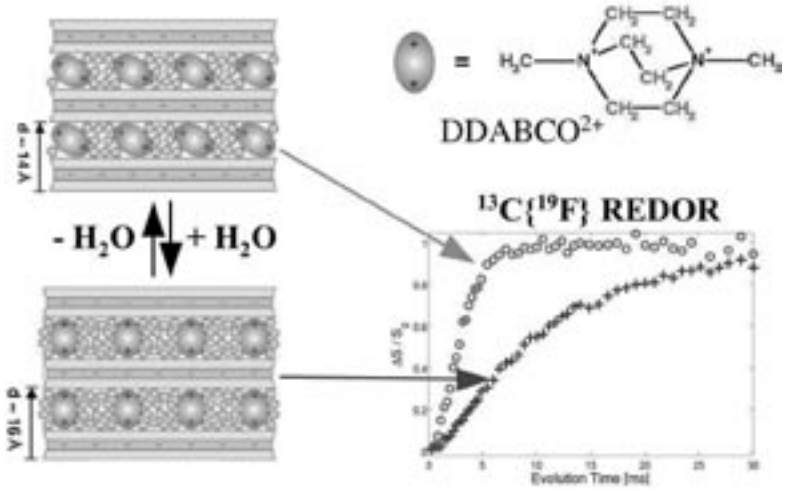

Fig. 1. Sketch of DDABCO-Hectorite with different possible orientations of the pillar molecules and according REDOR curves for 0% (circles) and 100% (crosses) relative humidity.

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MOLECULAR DYNAMICS IN MODIFIED POLYDIMETHYLSILOXANES STUDIED BY DSC, NMR AND RHEOLOGY

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Silicoorganic polymers (Polydimethylsiloxane - PDMS) belong to the family of water resistant molecular silicates of wide application in science and industry [1].

The aim of the study was to check the effect of random incorporation of alkyl side chains into the PDMS chain on its molecular motion. Molecular dynamics of linear and modified PDMS was studied using rheological and NMR techniques, whereas its thermal behaviour was determined by DSC.

It was found that modified polymers have amorphous structure while the linear polymer is partially crystalline. The increase in vitrification temperatures with increasing amount of the modifier fraction was observed. Results of NMR measurements made it possible to distinguish two relaxation processes: rotation of methyl groups around the Si-C bond (low temperature process) and segmental motions of the main chain (high temperature process). Temperature dependencies of NMR spin-lattice relaxation times correlate well with DSC measurements and indicate that an increase in the modifier amount in the polymer leads to the slowdown of the main chain segmental motion connected with the glass transition. This motion is observed also in the rheological studies as a high frequency process (α-relaxation) [2], additionally a slow motion due to normal mode processes is visible. The increase in the modifier fraction influences both the strength and frequency of the normal mode relaxation.

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MOLECULAR DYNAMICS IN FERROELECTRIC POYMER STUDIED BY NMR AND DIELECTRIC METHODS

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Ferroelectrics polyvinylidene fluoride – PVDF $[-CH_2-CH_2-]_n$ [1, 2] exhibiting also pyroelectric and piezoelectric properties are attractive for applications since both the sensing and actuating functions can be realized in the same element, polymer can be easily produced in variety of forms, properties can be tailored to various requirements. PVDF is a semicrystalline polymer, which forms with trifluoroethylene - TrFE random copolymers $[-CHF-CF_2-]$ [3, 4] at any VDF/TrFE ratio. The copolymers with VDF content between 40 and 82 mol% favours the ferroelectric all-*trans* conformation and undergo a ferroelectric-paraelectric transition below melting point. The phase transition is related to the change of the chain conformation from the al-*T* form to the *TGTG*' form.

In this work the proton nuclear magnetic resonance (NMR), dielectric spectroscopy and differential scanning calorimetry (DSC) have been used to study the structure and molecular dynamics of PVDF polymer and P(VDF/TrFE)(50/50) copolymer.

Dielectric dispersion and absorption of the radially-oriented by hot pressing thin films of PVDF and P(VDF/TrFE)(50/50) were measured in frequency range from 100 Hz to 1 MHz and temperature range from 100 K to 450 K [6]. Three anomalies in dielectric response, with increasing temperature, are observed: anomaly related to the segmental motion in the amorphous phase (glass transition, obey the Vogel-Fulcher relation), anomaly related to the local mode in the crystalline phase of the polymer (obey the Arrhenius law) and anomaly related to the ferroelectric-paraelectric phase transition observed at about 425 K and 341 K for PVDF and P(VDF/TrFE)(50/50), respectively.

The proton spin-lattice relaxation time T_1 of powder of PVDF polymer and P(VDF/TrFE)(50/50) copolymer were measured for two Larmor frequencies, over a temperature range from 100 K to 400K. The experimental data were analyzed in terms of segmental main-chain motion and described by Havriliak – Negami model [5]. Ferroelectric phase transition in P(VDF/TrFE)(50/50) reveals as a discontinuity in T_1 *vs* T curve at about 343 K. This temperature agree approximately with the corresponding temperatures obtained from the dielectric and DSC measurements.

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APPLICATION OF NMR-SPECTROSCOPY FOR INVESTIGATION OF STRUCTURE OF HYBRID NANOCOMPOSITES BASED ON POLYMER AND CHALCOGENIDE GLASSES

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Nanocomposites are defined as materials made from significantly different constituents, that are mixed in nanometer scale. Such materials have properties that are superior to the conventional microscale composites. So far the greatest attention has been given to inorganic/organic nanocomposites. Especially to polymer nanocomposites with semiconductor materials. Recently a new possibility to obtain composite materials based on chalcogenide glasses and polymer have been appeared and great attention is given to this hybrid composite materials combining the advanced properties of initial materials. The composites based on chalcogenide glasses (ChG) and polymer material represent an important class of hybrid materials with promising physical and optical characteristics. For application in optoelectronics it is very important that both chalcogenides and polymer materials exhibit high photoinduced changes [1,2]. It was shown that organic polymers manifest high photoinduced changes and low stability and on the contrary the chalcogenides glasses – comparatively low photoinduced changes and good stability.

Composite and nanocomposite materials based on the amorphous arsenic sulphide and polymer polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) received by chemical dissolution of As_2S_3 and polymer separately, mixing and deposited on various substrates (optical glass, polyethyleneterephthalate and monocrystalline silicon, etc.) have been investigated [3-5]. Research of morphology of layers has revealed that composites represent a polymeric material as matrix in which As_2S_3 spheroids with submicron sizes (500-1000 nm) are regularly distributed. The as synthesized composite materials were characterized by UV-VIS-IR spectroscopy, scanning electron microscopy/energy dispersed spectroscopy (SEM/EDS). The decreasing of the As_2S_3 component in the composite leads to absorption edge shift to higher energies and spheroid dimensions decreasing. The chemical analyses of composites As_2S_3-polymer showed that stochiometric ratio of As_2S_3 in coated composite film remained the same as in evaporated As_2S_3 film and in As_2S_3 bulk glass matrix. Optical properties of the composites are changed due to ultraviolet (UV) light irradiation. This allows these structures to be used for optical recording of information in particular holographic recording of diffraction gratings.

Previously it have been studying the structure of the synthesized polymers by means of the NMR-spectroscopy [6]. We have focused on the conformational peculiarities and statistical structure of macromolecules. Therefore the present work would be a natural continuation of our previous studies. We would like to combine the acquired knowledge to synthesize novel hybrid nanocomposite materials and study their structure with original NMR experiments.

The crystalline phase of the semiconductor materials can be studied with X-ray diffraction methods. NMR spectroscopy is the best method to study the local order of the materials and understand the microscopic mechanisms. Local order plays the most important role in the applications of the nanocomposites. The anticipated structure of the materials we are going to study – organic parts entwined with nonorganic parts – allows to presume, that the dynamics of the nuclear spin system in these parts of the material are different. This, on the otherhand, forms the basis for selective resolution of the NMR signals and selective NMR spectroscopy the composites of the nanocomposite materials. To our knowledge this has not been done before.

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BINARY MIXTURE OF HARD SPHERES AS A MODEL COLLOIDAL SYSTEM INVESTIGATED BY MOLECULAR COMPUTER SIMULATION AND NMR EXPERIMENTS

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Computer simulation is a very important tool in the investigating physical properties of colloidal suspensions, melts and other mixtures.

In this work, we use the standard Molecular Dynamics simulation for binary hard sphere mixtures. The model is a system consisting of many small spheres which surround few large spheres. There is only repulsive hard potential between any pair of spheres.

Hydrodynamic interactions between components (large sphere -> small sphere -> large sphere) originate from the microscopic structure. We do not use any approximation such as Onseen's tensor etc.. Static and dynamics properties of colloidal suspensions are similar to those of the simple fluids. Especially phase transitions in the simple fluid can be compared to the phase transitions in our binary mixtures (fluid -> glass -> crystal). However, diffusivity, and relaxation times for fluid molecules are about 10^9 larger than relaxation times of molecules in suspensions. Therefore, lifetime of the metastable phase of suspension observed before crystallization, can be long enough (from minute to hours) to allow experimental studies. This long time gives possibility to accurately measure physical properties in this state [1]. Colloidal suspension can be studied by many experimental methods such as: rheological experiments (viscosity and elastic properties), light scattering (structural properties and diffusion coefficients) and NMR (memory coefficients and structure relaxation). For example cores of polymethylmetacrylate (PMMA) stabilized by thin layers of poly-12-hydroxystearic acid and suspended in cis-decalin can be used [2]. In our simulation we calculated radial distribution function (RDF) and the compressibility factor (Z). The results are compared to Monte Carlo (MC) simulations [3],theoretical results [3] and NMR diffusion experiments.

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MOLECULAR DYNAMICS IN COPOLYMERS OF METHYL METHACRYLATE WITH BENZYL METHACRYLATE

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Molecular dynamics in random copolymers methyl methacrylate with benzyl methacrylate poly(MMA/BzMA) and theirs homopolymers have been studied by Dielectric Spectroscopy (DS) and high-resolution solid-state ^{13}C NMR. These copolymers has attracted our interest because of nanoscopic aggregation in their structure was detected by photochemical hole burning spectroscopy [1] and then confirmed by Low Frequency Raman Spectroscopy [2].

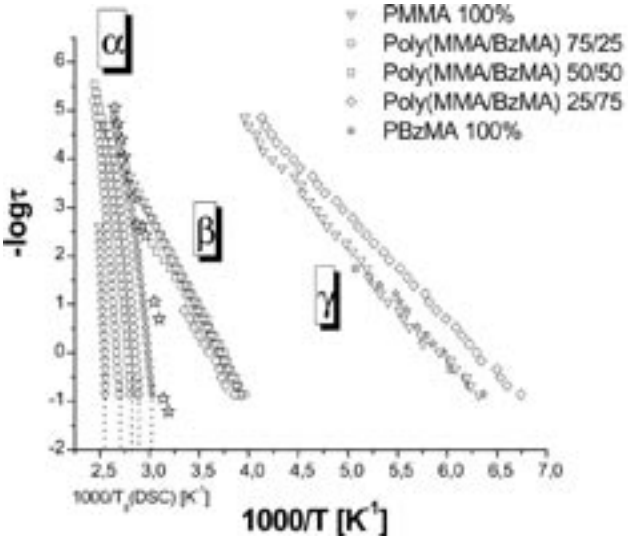

Fig.1. Relaxation map from DS

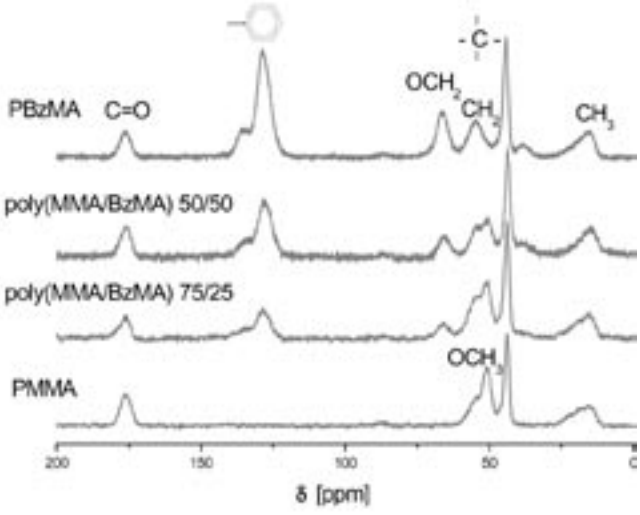

Fig.2. ^{13}C CPMAS NMR spectra at room temperature temperature

The calorimetric studies revealed that the copolymers exhibit single glass transition, which is located between the T_g values of the two homopolymers and decreases with decrease of the MMA content. DS allows to observe three relaxations i.e. main α-process (connected with glass transition) and at lower temperatures the secondary processes: β and γ (Fig. 1).

The NMR studies indicate that nanoagregation process doesn't influence either the ^{13}C CPMAS NMR line shape or the relaxation times $T_{1\rho}$. It was found that for all polymers $T_{1\rho}$ relaxation at room temperature is driven by methyl group rotation in limit of fast spin diffusion.

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CHAIN DYNAMICS IN SOLID POLYETHYLENE STUDIED BY NUCLEAR MAGNETIC RELAXATION DISPERSION

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The dynamical properties of chain segments in the amorphous phase of solid polymers depend on a variety of parameters including degree of crystallinity, chain length but also the density and distribution of side chains along the backbone [1].

In this contribution the proton spin-lattice relaxation times (T_1), measured in dependence of the Larmor frequency in different types of solid (semicrystalline) polyethylene (PE) are reported. The measurement were performed at different temperatures in a range from -60 °C to 85 °C for three different, well characterized samples: low branched, high density linear PE with a degree of crystallinity of 80% (HDPE); linear low density PE (LLDPE) with random distribution of side chains (methyl and ethyl groups) along the backbone, 47% degree of crystallinity; and low density with random distribution of short side chains (from two to four carbons atoms) along the backbone, 52% degree of crystallinity (LDPE).

The frequency dependence of T_1 was observed in the range between 3kHz and 30 MHz with the aid of a field-cycling NMR relaxometer [2] from Stelar S.R.L. (Italy).

Figure 1 shows the dependence of the spin-lattice relaxation time on the frequency at two different temperatures, for HDPE and LLDPE. The crossover at low frequencies reflects a stronger temperature dependence in the LLDPE sample due to the presence of short side chains (branchings) in the amorphous phase. The side chains in the LLDPE sample restrict the mobility of the chain segments. This can be identified in the dispersion curve due to the increase in the relaxation times at low frequencies.

A model is proposed to account for the T_1 dispersion at low frequencies, based on the correlation function [3] for the restricted translational diffusion of chain defects. The results are discussed in the frame of a previous model introduced by Kimmich et al.[4].

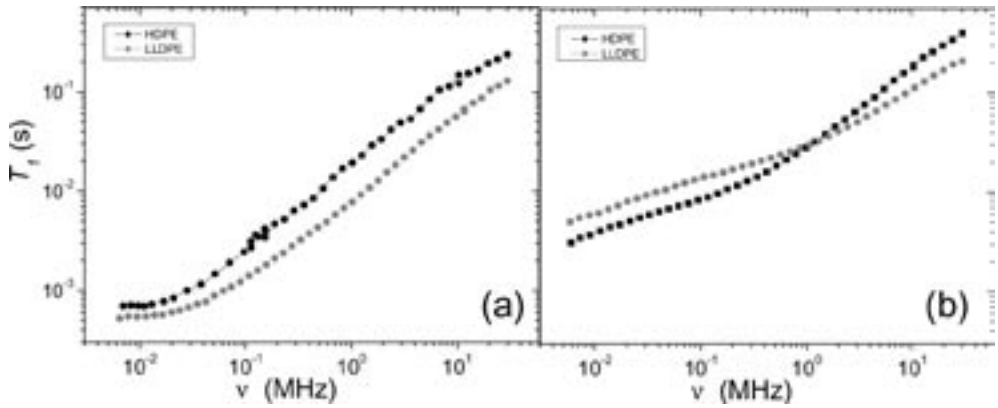

Fig.1. Frequency dependence of the T_1 relaxation time at (a) 22.4 °C and (b) 85 °C for solid PE. The melting point of the samples are 122.8 °C and 130.8 °C for LLDPE and HDPE, respectively, measured with differential scanning calorimetry (DSC).

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DETERMINATION OF HETERONUCLEAR COUPLING CONSTANTS FROM 3D NMR EXPERIMENTS

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A new 3D NMR experiment for measurement of heteronuclear coupling constants of organic compounds yielding complex spectra is proposed. Presented here 3D HSQC-TOCSY technique is based on random sampling of the evolution time space followed by Multidimensional Fourier Transform [1], [2]. Due to the application of this approach it is possible to acquire 3D NMR spectra in a reasonable time and preserve high resolution in indirectly detected dimensions [3].

In this communication we show that the interpretation of 3D HSQC-TOCSY spectra with E.COSY-type multiplets allows us to evaluate heteronuclear coupling constants of strychnine with high accuracy, which is impossible to determine using conventionally recorded 3D NMR spectra in the same experimental time. This method [4] enables one to measure the coupling constants smaller than the natural line-width of proton multiplets.

We have evaluated both heteronuclear single-bond and long-range coupling constants, the determination of these parameters is crucial to structural and stereochemical analysis of organic molecules.

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DEGRADATION AND CREATION OF HYDROGEL NETWORK IN POLY(ACRYLIC ACID)/NON-IONIC SURFACTANT SYSTEMS

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Poly(acrylic acid) (PAA) hydrogels are widely used in many pharmaceutical applications especially in so-called drug delivery systems. The control of drug delivery can be provided trough the physical and chemical modification of hydrogel matrices the drug is placed. The modifications of the hydrogel network structure are often intensified by addition of active substances like surfactants. In our studies we investigate the influence of the non-ionic surfactant Brij 58 on structure and permeability of hydrogel network of PAA. Analysis of structural changes were made by means of rheological and NMR diffusometry methods. The samples of PAA at several concentration of Brij 58 were prepared and studied over the temperature from 283 to 323 K. This rather narrow temperature range was chosen to detect the differences in hydrogel network properties over usable temperature.

Results of studies suggest that the addition of non-ionic surfactant to the polymeric hydrogel, despite induced weak interactions between poly(acrylic acid) chains and surfactant molecule, dramatically changes the structure of polymeric network and in consequence also diffusion processes and viscoelastic properties. Moreover, such system are much more thermosensitive what means higher precision in determination of diffusion coefficients D and activation energy for diffusion E_a. The phase transition at temperature about 300 K was detected for several samples with different surfactant concentration. Results indicate that the temperature is responsible for reversible creation/degradation process of three-dimensional network in a PAA/surfactant system.

Acknowledgements

I would like to thank SoftComp for the support during my research.

MOLECULAR DYNAMICS AND LOCAL ARRANGEMENT OF P-PODAND FAMILY SYSTEMS

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In the last decade the world chemical industry is highly focused on the new technologies featuring cost cutting and carbon dioxide emission reduction, mainly by lowering thresholds of energy reaction. Many classes of natural as well as artificial substances can be used at different points of chemical reaction paths. One of such group are "supramolecular ligands" systems, which are described by supramolecular chemistry. Many unique properties, e.g. complexation, conformational minimising steric hindrance, chelating metal ions of different size and key-and-lock matching mechanism make them very attractive for modern chemistry and physics. The recognition of molecular motions in the systems studied can provide insight into their structure-property relationship. Identification of different structural regions can be done on the basis of their characteristically different motions.

In our work we focused on P-Podand family (Phosphorous Podands) comprising compounds having different types of chains binded to central posphorous ion, which are specific for each of individual compound. Three types of P-Podand systems with following types of chains: alkyl (P-[O-$(CH_2)_{17}$-$CH_3]_3$), glycol (P-[O-$(CH_2CH_2O)_{15}$-$CH_3]_3$) and glycol-alkyl (P-[O-$(CH_2CH_2O)_{10}$-$(CH_2)_{15}$-$CH_3]_3$)) were investigated by Differential Scanning Calorymetry (DSC), Nuclear Magnetic Resonance (NMR) and Broadband Dielectric Spectroscopy (BDS) techniques.

The DSC studies show that the presence of alkyl groups causes stiffening of the system in comparison with P-Podand with glycol chains. Moreover, in P-Podand with glycol-alkyl chains, we observed two-stage crystallisation process interpreted as a result of independent crystallisations of the alkyl and glycol blocks. The glycol-alkyl P-Podand system shows self-assembling properties driven by amphiphilic interactions.

The spectroscopic methods (NMR and BDS) permitted us to distinguish three types of motions: a) methyl groups rotation around the C_3 symmetry axis; b) segmental motions of the alkyl groups and/or glycol groups in the disordered phase (depending on the substance) and c) the overall motion (both rotational and translational).

Acknowledgements

A partial support of the SoftComp grant No. 502235-1 within the 6th Framework Programme is gratefully acknowledged.

NMR PROTON AND CARBON MOBILITY IN SELECTED PROTON-CONDUCTING IMIDAZOLIUM SALTS

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The purpose of this work was to obtain information on molecular dynamics in selected imidazolium salts of dicarboxylic acids in the solid state, i.e., imidazolium oxalate (imi-oxa), imidazolium adipate monohydrate (imi-adi) and diimidazolium suberate [di(imi-sub)], from measurements of the temperature dependences of the ^{1}H spin-lattice relaxation times and ^{13}C CPMAS evidences.

The imidazole molecules in the imidazole-based materials are held together by a hydrogen-bond network. It is interesting that only small part of the material exists in the mobile state (of about 5 – 20 %). The ordered part is attributed to the rigid imidazole rings with strong hydrogen bond, whereas the disordered one is due to mobile rings and weak hydrogen bonds. The existence of the mobile parts in the imidazole-based materials plays the crucial role in terms of the protons transport. According to the Grotthuss-type mechanism, the fast proton hopping between hydrogen-bonded molecules has to be followed thermally activated molecular rearrangements as the fast 180°-flip reorientations of the imidazole rings mainly in the mobile parts of the crystals.

In this work we showed that the temperature dependencies of the proton spin-lattice relaxation times in imi-oxa, imi-adi and di(imi-sub) can be successfully used to evidence the reorientation of the mobile imidazole rings and to calculate their activation energy. We obtained a long T_1 values (of about 100 – 400 s) for rigid phase, whereas for mobile one – the shorter T_1 values (on the order of about few seconds) were measured. Moreover, we found the verification of the existence of the mobile parts in imi-oxa using ^{13}C CPMAS technique and we were able to assign the particular lines to the studied structure.

DEUTERON NMR MEASUREMENTS ON AOT-D_2O-DECANE MICROEMULSIONS

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The ternary mixture AOT [sodium bis(2-ethylhexyl)sulphosuccinate]-D_2O-decane forms a microemulsion (ME) of nearly spherical droplets with an aqueous core of water/Na+ solution. This system has been studied by deuteron NMR from room temperature down to 226 K. D_2O spin-lattice relaxation time measurements in a ME with a water/AOT molecular ratio of 40 and a droplet volume fraction of 0.2 are presented.

Studying a similar system, Quist and Halle [1] reported that below the water freezing temperature the system freezes out most of the water but residual water molecules still remain in aqueous form. In the present system fractioning was identified visually and via differential scanning calorimetry, occurying around 265 K. Above this temperature the ME is stable and the water is supercooled (melting temperature of bulk D_2O: T_m=277 K)[2]. Below this temperature we identified two dynamically differnent types of water. This can be concluded from the two-exponential form of the longitudinal relaxation, fit results are shown in Fig. 1. The slow (10 s scale) spin-lattice relaxation component is ascribed to precipitated ice and the fast one (1 ms scale) to an aqueous part. In Figure 1, it can be seen that by heating up the ME (tags 4-7) an ordinary phase transition does not occur.

The existence of a fast component after freezing (tag 5-7) raises interesting questions (surface effects?) and data will be shown on the poster for discussion.

Further evidence of residual liquid water can be seen in deuteron spectra showing a broad Pake spectrum and a narrow line in this temperature range.

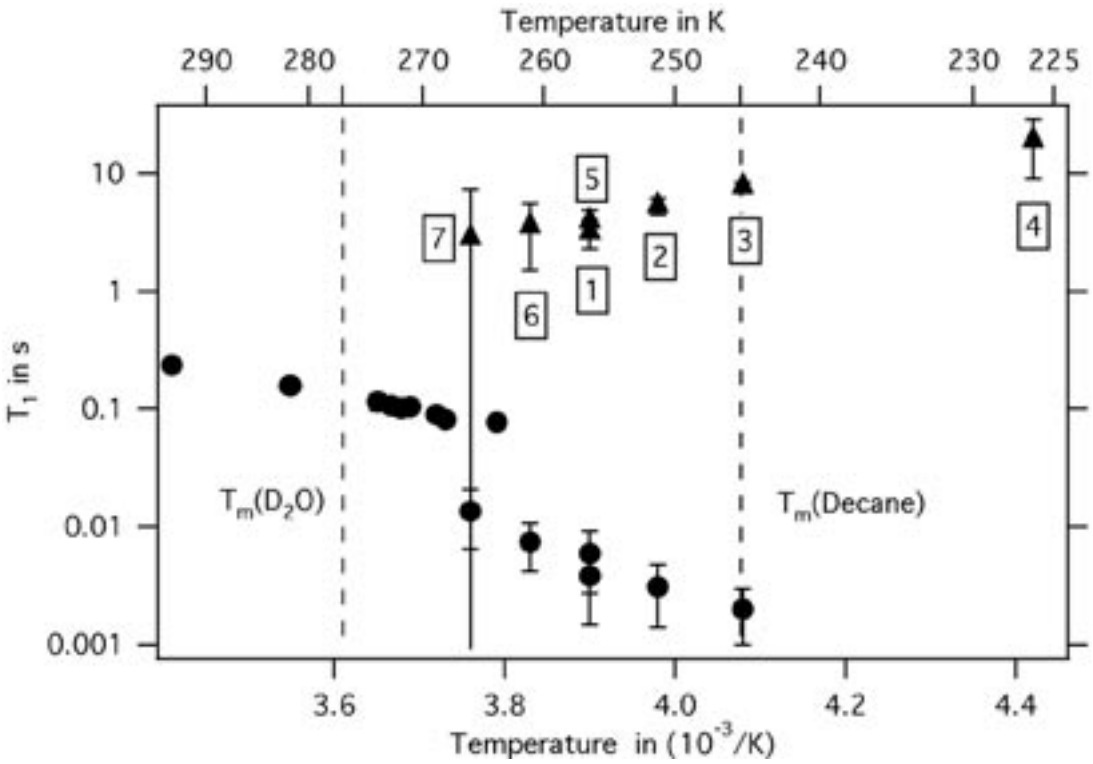

Fig. 1. Temperature dependent deuteron spin-lattice relaxation times of a D_2O/AOT/decane microemulsion. Dashed lines show the melting temperature of D_2O and decane. The first seven measurements are numbered chronologically, whereas the untagged data has been obtained from higher to lower temperatures.

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^{51}V MAS NMR INVESTIGATIONS OF MODEL COMPLEXES FOR VANADIUM HALOPEROXIDASES

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Vanadium haloperoxidases (VHPOs) are a class of enzymes, which are capable of catalyzing the two electron oxidation of a halide ion to hypohalous acid in the presence of hydrogen peroxide. The hypohalous acid can further react with an organic substrate, leading to halogenated substances.

Despite a large number of investigations concerning VHPOs, many aspects of their structure and their reaction mechanism are still not fully understood. In the last years it could be shown that ^{51}V solid-state NMR spectroscopy is an especially suitable tool to investigate these enzymes [1]. For the interpretation of such spectra, it is essential to have reference spectra and the respective NMR parameters from model systems with well established structure. Therefore we started to systematically investigate different model complexes (Fig. 1) for VHPOs by means of ^{51}V MAS NMR spectroscopy [2,3].

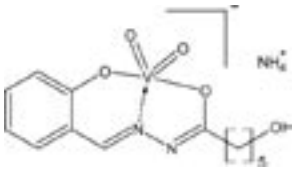

Fig.1. Chemical structure of model complex 8

The NMR parameters (isotropic chemical shift, anisotropy and asymmetry of the CSA tensor, quadrupolar coupling constant, asymmetry of the EFG tensor and the Euler angles) are obtained by least-squares fitting of the simulated to the experimental spectra (Fig. 2) by a program written in our laboratory combining genetic and simplex fitting routines.

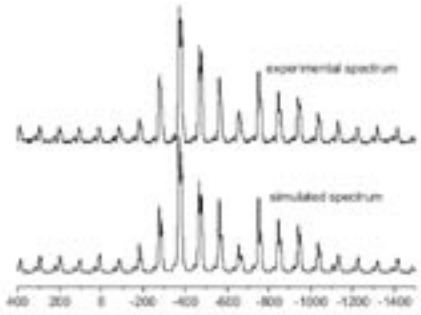

Fig.2. Experimental (top) and simulated (bottom) MAS-NMR spectrum of model complex 8

The NMR parameters of a large number of model complexes were correlated with structural features like coordination number, number of oxo-groups and specific bond lengths and –angles. Moreover, DFT calculations of the NMR parameters using different methods and basis sets were performed [2,4] and the results were compared to the experimental ones.

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Acknowledgements
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SAXS, NMR AND DSC STUDIES OF BICELLAR SYSTEMS

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Phosphatydylcholine derivatives represent the most abundant class of lipids in mammalian cells and the major membrane component in eukaryotic organisms. In aqueous solutions, the mixtures of phospholipids with long hydrophobic chains and phospholipids with short hydrophobic chains can form discotic nematic liquid-crystalline phase also known as bicelles. Their morphology is intermediate between that of lipid vesicles and classical mixed micelles, combining some of the attractive properties of both of these model membrane systems. The bicellar structures also are very useful in structural studies of integral membrane protein and peptides as models of biological membranes.

The aim of the study was to determine the structure of a well-defined model of a phospholipid bicellar system and the solvent diffusion in this system. The objects of the study ware the DMPC/DHPC (in the molar ratio of 2.8:1) and DMPC/surfactant systems characterised by the method of differential scanning calorimetry (DSC), small angle scattering of synchrotron radiation and measurements of self–diffusion coefficient.

PROTON DYNAMICS IN $K_3H(SO_4)_2$ – RELAXATION AND POLARIZATION TRANSFER STUDIES

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The transport of protons in the hydrogen-bonded insulator family $M_3H(XO_4)_2$ (M = K, Cs, Rb, NH_4, and X = S, Se) is a problem, which has not yet been satisfactorily explained. All of these systems show at least one phase transition and possess one (or more) proton conducting phases. Several models of proton diffusion in the conducting phases have been proposed in the literature [for example: 1,2]. It has been shown [3] that $M_3H(XO_4)_2$ –type systems crystallize in the monoclinic space group A2/a. This implies that the proton motion in the low-temperature phase (below the transition temperature to the superionic phase) is strongly anisotropic.

Our work is focused on the non-conducting phase of $K_3H(SO_4)_2$, the transition to the conducting phase occurs at about 450 K. The unit cell (a = 9.777 Å, b = 5.674 Å, c = 14.667 Å, and ß = 102.92°) has 56 atoms. It contains two crystallographically different potassium ions, while all protons are crystallographically equivalent. The proton-potassium distances are comparable for both potassium sublattices [4]. The samples were grown as indicated in [5, Chap. 2].

Field dependent proton spin-lattice relaxation times have been measured utilizing field cycling relaxometry in a field range corresponding to proton frequencies of 30 kHz to 30 MHz at temperatures ranging from 300 K to 420 K. The measurements suggest two distinct relaxation processes. The “slow” process can clearly be attributed to thermally activated proton dynamics on the ms or sub-ms timescale range and parametrized by an activation energy of 65(4) kJ/mol (0.67(4) eV), in agreement with stimulated echo measurements on $K_3D(SO_4)_2$ [1]. So far the origin of the “high frequency” process is not known.

At 360 K detailed polarization transfer experiments have been carried out to further investigate the coupling of protons and potassium. The polarization transfer experiments show well pronounced proton magnetization dips. The data is presently being analyzed using the Liouville density operator formalism. To understand the results one has to be aware that the proton magnetization can be taken over by the potassium nuclei only if there is an effective dipole-dipole coupling between the participating spins [6]. This condition can be fulfilled by one type of potassium ions. Generally, the potassium-proton dipole-dipole interaction is modulated by the proton motion and the relaxation of potassium caused by electric field gradient fluctuations due to crystal vibrations. Since the polarization transfer effects have been observed experimentally, one can conclude that at one of the crystallographic positions of potassium the electric field gradient fluctuations are less efficient as a relaxation mechanism, and in consequence the potassium-proton dipole-dipole coupling is not averaged out. In addition, the positions and structure of the proton magnetization dips provide information on the quadrupolar interaction parameters.

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MECHANISTIC INVESTIGATIONS ON NISOD BIOMIMETICS USING REDOR-NMR

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SODs are metalloenzyms which catalyze the disproportionation of the superoxide anion (O_2^{-}) to peroxide and molecular oxygen. SODs play an important role in the protection of cells from the toxic products of the aerobic metabolism.[1] During the last few decades two independent classes of SODs have been identified, containing either a dinuclear Cu, Zn or mononuclear Fe, Mn or Ni cofactors.[2] NiSOD, as a mononuclear Ni-containing metalloenzyme cycles between Ni^{II} and Ni^{III} oxidation states during catalysis.[3] In the oxidized state, the Ni^{III} centre is penta-coordinated with the histidine imidazole placed in axial position (Figure 1). Since the NiSOD is structurally not related to other SODs and the coordination sphere is provided by the so called Ni-hook the catalytic mechanism of O_2^{-} degradation by NiSOD is probably different to other SODs.

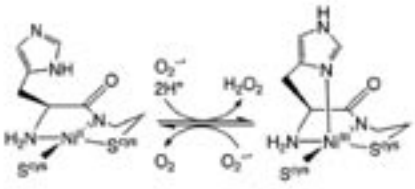

Fig.1. Coordination geometry and catalytic scheme[4]

Metallopeptide based NiSOD biomimetics perfectly match the spectroscopic and functional properties of the native enzyme.[4, 5] For our investigations we used metallopeptides which are based on the first 9 residues from the N-terminus of the active form of *S. coelicolor* NiSOD (Figure 2). Concerning the discussions about an inner- vs. outersphere mechanism REDOR NMR

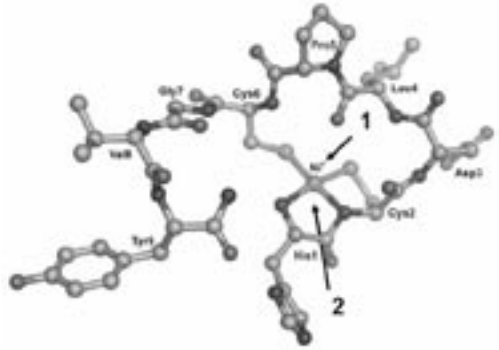

Fig.2. metallopeptide structure (based on liquid NMR data and computational structure optimising[5]) showing the possible cyanide positions 1 and/ or 2

is used to localize the position of cyanide, which we used as a substrate analogue in the NiSOD metallopeptide. For this we synthesized the cyanide adduct of the metallopeptide using different ^{15}N and ^{13}C labelled positions in the peptide backbone and ^{13}C or ^{15}N labelled CN.

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Acknowledgements

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SYNTHESYS OF SOME NATURALY DITERPENOID ACYLGLYCEROLS

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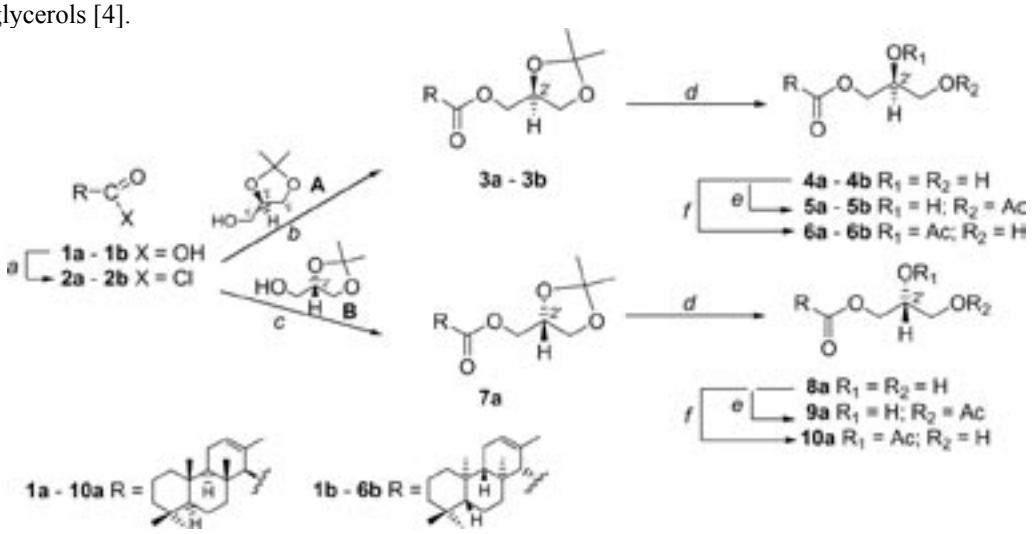
Terpenoid acylglycerols represent an interesting group of natural bioactive molecules, which could be considered the chemical marker of marine dorid nudibranchs belonging to the related genera *Anisodoris, Archidoris, Austrodoris, Doris* and *Sclerodoris* [1-2]. These compounds display very interesting pharmacological properties, such as the activation of protein kinase C *in vitro* and the induction of morphogenetic effects in the regenerative test *in vitro* with the fresh water hydroyoan *Hydra vulgaris* [3].

With few exceptions, the majority of natural terpenoid acylglycerols are structurally characterized by the presence of a terpenoid acid residue esterified at C-1' of glycerol, which is further linked to an acetyl group at C-2' or C-3'. Synthesis of natural bicyclic and tricyclic diterpenoid diacylglycerols has been performed by regioselective coupling of terpenoid acid with glycerol at 1'-*sn* position. This method may be considered a general approach to obtain optically active acylglycerols [4].



Reagents: (a) $(COCl)_2$, C6H6, r.t.; (b) glycerol **A**, NaH, CH_2Cl_2, (c) glycerol **B**, NaH, CH_2Cl_2; (d) H_2SO_4, MeOH; (e) N-acetylimidazole, DBU, C_6H_6; (f) 1) TBDMSCl, Py, r.t.; 2) Ac_2O, Py, r.t.; 3) $PdCl_2(MeCN)_2$, Me_2CO, r.t.

The structure and stereochemistry of the synthesized compounds were established on the basis of NMR spectral data. For example the ^1H NMR shape (fig.1) of the protons at C-2' are sufficiently diagnostic to distinguish between the two diastereomers **4a** (a) and **8a** (b).

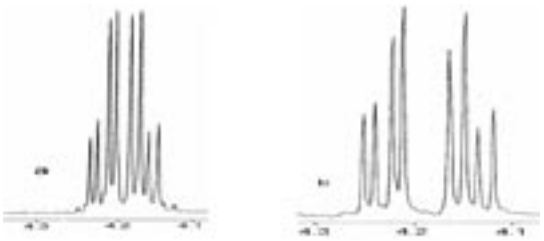


Fig. 1. Partial ^1H NMR spectrum ($CDCl_3$, 500 MHz) of glycerols **4a** (a) and **8a** (b).

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COMPLETE ASSIGNMENT OF ^{1}H AND ^{13}C NMR SPECTRA OF NEW FLAVANONOL FROM SESELI ANNUUM ROOTS

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The genus *Seseli* (family Apiaceae) comprises ca 55 species distributed mainly in Europe. Ten of them could be found in Serbia. Numerous species of the genus have been used in folk medicine since ancient times [1]. They are the well-known source of the linear or angular pyranocoumarins possessing antiproliferative, antiviral or antibacterial activities [2]. Continuing our investigation on *S. annuum* [3,4], we now report isolation and structure elucidation of new flavanonol from the roots of the plant.

The plant material was collected in Deliblatska Peščara (Deliblato Sand) in south Banat (Vojvodina, Serbia), in July 2006. The air-dried roots were powdered and extracted with $CHCl_3$ twice at room temperature. The crude extract was fractionated by dry column flash chromatography on silica gel using CH_2Cl_2 and MeOH with increasing polarity (0-20%). Similar fractions (TLC control) were combined and purified using CC and preparative TLC. Three known compounds - falcarinol, falcarindiol and phellopterin were isolated, together with new flavanonol type compound.

The new compound, named seselinonol, showed $[MH]^+$ ion in HR ESI MS at *m/z* 441.19078, corresponding to the molecular formula $C_{25}H_{28}O_7$. The signals in ^1H NMR spectrum at δ 5.38 (d, *J* = 12.0 Hz) and 4.73 (d, *J* = 12.0 Hz) indicated 2,3-*trans*-flavanonol derivative. ^1H NMR spectrum also showed signals due to hydrogen-bonded hydroxyl group (δ 11.67 s) and four aromatic potons. Their chemical shifts and signal patterns suggested that -OH groups are located at C-3, -5, -7, -2' and 4'. This led to the conclusion that new compound is C_{10} prenylated dehydromorin. The ^{13}C NMR spectrum of the new compound was fully in accordance with literature data for dehydromorin [5]. The DEPT-135 analysis of the remaining ^{13}C NMR signals (three CH_3 groups, four CH_2 groups, one aliphatic and two olefinic quaternary C-atoms) revealed the structure of C_{10} prenyl unit. Its position was determined to be at C-6 from the NOE correlation of 5-OH with CH_2-1" and CH_3-8". Positive optical rotation suggested (*2R,3R*) absolute configuration. Thus, new compound is identified as (*2R,3R*)-6-((2,4,4-trimethylcyclohex-1-enyl)methyl)-dehydromorin (Fig. 1). Similar compounds were isolated from the roots of *Sophora flavecens*, which is used for preparation of oriental crude drug "Kushen" in Chinese traditional medecine [6].

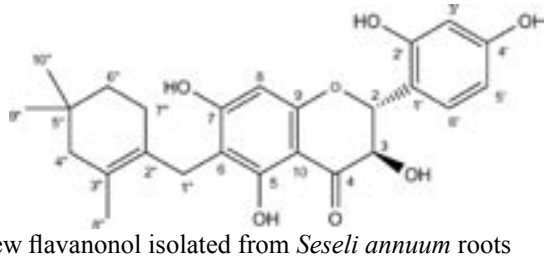

Fig. 1. Structure of seselinonol, new flavanonol isolated from *Seseli annuum* roots

(+)-*Seselinonol*: white powder; $[\alpha]_D^{20}$: +16.0° (c = 1.0, MeOH); UV (MeOH) λ_{max}: 232 sh, 295, 335 sh; IR film: ν_{max}: 3350 (br), 1624, 1461, 1270, 1155, 1109 cm^{-1}; HR ESI MS *m/z*: 441.19078 $[MH]^+$ (calcd for $C_{25}H_{29}O_7$ 441.19133), ^1H NMR ($CDCl_3$ + CD_3OD) δ 0.85 (6H, s, H-9″,10″), 1.27 (2H, t, J=6.5 Hz, H-6″) 1.76 (2H, s, H-4″), 1.79 (2H, s, H-8″), 1.86 (2H, br t, H-7″), 3.40 (2H, s, H-1′), 4.73 (1H, d, J=12 Hz, H-3), 5.38 (1H, d, J=12 Hz, H-2), 5.95 (1H, s, H-8), 6.35 (1H, d, J=2.5 Hz, H-3′), 6.43 (1H, dd, J=8.5; 2.5 Hz, H-5′), 7.26 (1H, d, J=8.5 Hz, H-6′), 11.67 (1H, s, 5-OH); ^{13}C NMR ($CDCl_3$ + CD_3OD) δ 196.2 (C-4), 165.3 (C-7), 161.2 (C-5), 161.0 (C-9), 158.2 (C-4′), 156.2 (C-2′), 129.2 (C-6′), 126.9 (C-3″), 126.4 (C-2″), 114.5 (C-1″), 107.8 (C-5′), 107.3 (C-6), 103.5 (C-3′), 100.3 (C-10), 95.2 (C-8), 78.4 (C-2), 71.9 (C-3), 46.3 (C-4″), 35.79 (C-6″), 29.0 (C-5″), 28.1 (C-9″), 28.05 (C-10″), 25.8 (C-7″), 25.0 (C-1″), 19.4 (C-8″).

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NMR RELAXATION IN SOLUTIONS OF HYDROGEN PEROXIDE AND PARAMAGNETIC IONS

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Hydrogen peroxide (H_2O_2) at low concentration is widely used for bleaching and disinfection. A number of biological processes also produce and consume H_2O_2.

The chemical action of H_2O_2 is carried out by oxygen, which, from the NMR point of view, is paramagnetic. In this communication we will show the results of measurements of relaxation times: spin-lattice T_1, spin-spin T_2 and the relaxation time in the rotating frame $T_{1\rho}$ in aqueous hydrogen peroxide solutions as a function of H_2O_2 concentration, temperature and time of reaction. We also present the results of relaxation time measurements in blood serum after addition of H_2O_2. For comparison, similar measurements for solutions of paramagnetic ions like iron $Fe^{2+}$and copper Cu^{2+} were done. It is interesting that T_2 and $T_{1\rho}$ behaviour in aqueous H_2O_2 solutions is similar to that obtained for paramagnetic ions, however T_1 is independent at H_2O_2 concentration up to very high concentrations (see Fig.1).

Our preliminary measurements are an introduction to NMR relaxation investigations of these systems and the interpretation of our data may help us to understood oxygenation processes in biological systems like blood serum.

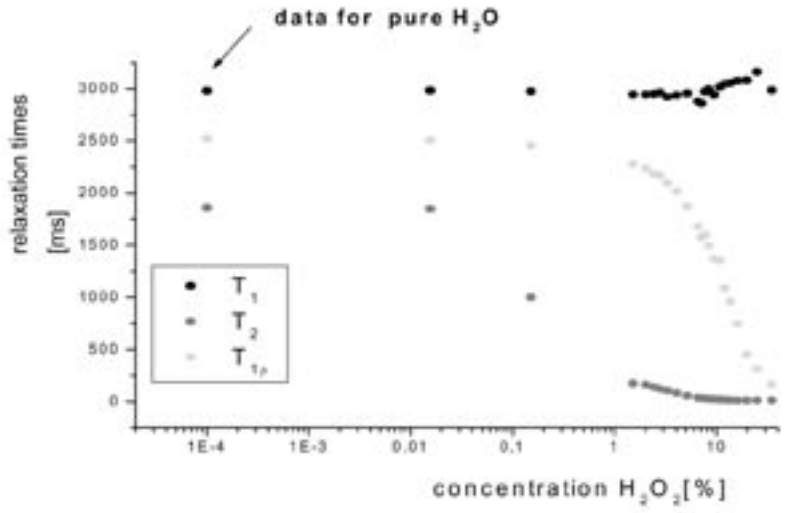

Fig. 1 Concentration dependence of proton relaxation time T_1,T_2 and $T_{1\rho}$ for aqueous solution of H_2O_2 at room temperature.

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PROGRAMME AMPERE NMR SCHOOL, WIERZBA 2008

	SUNDAY	MONDAY		TUESDAY		WEDNESDAY	THURSDAY	FRIDAY	SATURDAY
8.00-9.00	ARRIVAL AND REGISTRATION	BREAKFAST		BREAKFAST		BREAKFAST	BREAKFAST	BREAKFAST	BREAKFAST
9.00-9.45		***R. Kimmich*** From the basic equation of motion of molecules to NMR measurands: The harmonic radial potential theory of polymers		***J. Fraissard*** NMR of Physisorbed ^{129}Xe Used as a Probe to Investigate Porous Solids		***Sh. Vega*** New Aspects of Proton Decoupling in Solid State NMR	***F. Fujara*** Spacially resolved NMR in heavy ion irradiated ionic crystals	***C.A. de Lange*** Scope and limitations of accurate structure determination using liquid-crystal NMR	DEPARTURE
9.45-10.30		***R. Wasylishen*** Probing nuclear spin-spin coupling tensors in solids		***D. Michel*** NMR on ferroelectric materials with very small sizes and on particles confined in nanoporous matrices		***A. Wong*** Application of solid-state NMR spectroscopy to low gamma quadrupolar nuclei	***E. Rössler*** Molecular Dynamics in Soft and hard confinement – a playground for ^{31}P NMR	***E. Burnell*** What NMR of solutes in liquid-crystalline solvents can tell about the ordering potential	
10.30-11.00		COFFEE BREAK		COFFEE BREAK		COFFEE BREAK	COFFEE BREAK	COFFEE BREAK	
11.00-11.45		Parallel sessions		Parallel sessions		***M. Ernst*** Spin Diffusion in MAS Solid-State NMR	***K. Müller*** Order and dynamics in disordered solids as evaluated by solid state NMR spectroscopy	***J. Stepišnik*** Constrained molecular self-diffusion in the bulk water measured by NMR	
		J. Blicharski Rotational Magnetic Resonance and possibilities of a detection	***S. Stapf*** Spatially resolved monitoring of catalytically activated hydrogen peroxide decomposition – a test case for reaction monitoring by NMR	***M. Schönhoff*** Pulsed Field Gradient NMR studies of molecular exchange in colloidal systems	***R. Böhmer*** Deuteron NMR studies of the dynamics in clathrates				
11.45-12.30		***D. Kruk*** Various ways to enhance NMR signals: recent theoretical progress	***M. Vogel*** Mechanisms of Ion Transport in Solid-State Electrolytes: Insights from NMR Multi-Time Correlation Functions	***F. Grinberg*** Diffusion and Structure in Self-assembling Systems Studied by NMR	***B. Geil*** Correlation of primary relaxation and high-frequency modes in supercooled liquids. A Deuteron NMR study	Oral presentations ***B. Grünberg*** ***S. Naumov*** ***F. Poli***	Oral presentations ***Y.S. Postolenko*** ***K. Jasiński*** ***G. Woźniak***	Oral presentations ***M. Grbić*** ***M. Simčič*** ***W. Węglarz***	
12.30-15.00		LUNCH		LUNCH		LUNCH	LUNCH	LUNCH	
15.00-17.00		Oral presentations ***I. Rostykus*** ***S. Dekarchuk*** ***T. Mykhailova*** ***S. De Santis***		Oral presentations ***B. Blicharska*** ***J. Tritt-Goc*** ***S. Poberezhets*** ***L. Lalowicz*** ***L. Latanowicz***		Social event	Poster presentations (1-23)	Poster presentations (1-22)	
17.00-19.30		**Workshop** ***M. Giersig*** Nanomaterials and their Applications in Electronic and Biomedicine	**Workshop** ***F. Fujara, D. Kruk, E. Rössler*** Perfect recipe for dealing with strange relaxation data	**Workshop** ***R. Wasylishen, D. Michel*** NMR of Quadropolar Nuclei	**Workshop** ***E. Burnell, C.A. de Lange*** NMR of Ordered Liquids		Poster session I	Poster session II	
19.30-20.30	DINNER	"ALL TOGETHER PARTY"		DINNER		DINNER	DINNER	DINNER	