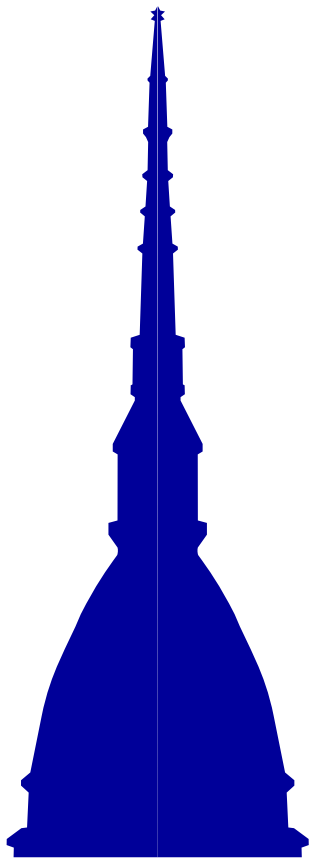


7th Conference on Field Cycling  
NMR Relaxometry  
Villa Gualino - Turin - Italy  
June 2<sup>nd</sup> - 4<sup>th</sup> - 2011



torino  
italy  
June  
2<sup>nd</sup> - 4<sup>th</sup>  
2011

**PROGRAM  
AND  
ABSTRACTS**

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**7** conferences  
of Field Cycling NMR Relaxometry  
June 2<sup>nd</sup>-4<sup>th</sup> 2011

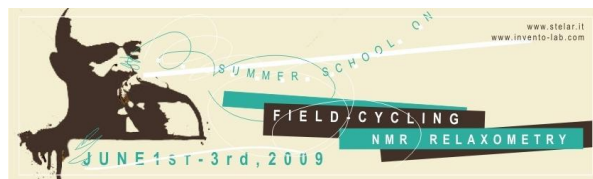


The [First symposium on Field Cycling NMR Relaxometry](http://www.ffcrelax.com/ffcrelax/mainpage.php?folder=history&page=index.php) was held in Berlin 1998, with the purpose of bringing together all the researchers practicing FC methods with those who do not yet but are interested in applying this technique in the future, forming a discussion forum promoting and cultivating the description of molecular motions in complex system by spectral densities in relation to recent condensed matter theories and dissemination of the information on the technique as well as the potential of its applications and it proved to be a big success. <http://www.ffcrelax.com/ffcrelax/mainpage.php?folder=history&page=index.php>

The following conferences, held in Torino in 2001, 2003, 2005, 2007 and 2009 were aimed with the intention of strengthening the interaction between FC users of different areas, stimulating the exchange of new ideas and technical features.

The 2009 6<sup>th</sup> symposium was particularly special in keeping with these objectives and the First Summer School On Field Cycling NMR Relaxometry was held in Mede (PV) - Italy on June 1-3, 2009 for the first time. The NMR School wanted to be a comprehensive introduction to the NMR Field Cycling and NMR Relaxometry on

the aim to enable researchers of any scientific discipline to profit in their work from the exceptional capacity of the field-cycling technology. <http://www.ffcrelax.com/schoolNMR/home.php>



As in the past, this 7<sup>th</sup> workshop is gathering people with active interests in nuclear and electron spin relaxation, fast magnetic field switching experiments, low field magnetic resonance, nuclear quadrupole resonance, and magnetic imaging. The discussion will focus on magnetic field cycling experimental techniques, data interpretation and theory, as well as applications performed by other low-frequency and low resolution NMR techniques to span a range of topics including experimental issues, interpretative foundations, liquids, solids, porous and heterogeneous materials, polymers, biological materials, and diagnostics.

This year's conference hosts for the first time two sessions devoted to field-cycling MRI and ultra-low-field MRI. The FC- MRI sessions are being held under the auspices of the project coordinated by Aberdeen University on Fast Field-Cycling MRI (2007-2011), funded by the UK's Engineering and Physical Sciences Research Council under the "Basic Technology" scheme.

While field-cycling MRI and ultra low-field MRI remain niche areas within worldwide MRI research, nevertheless the inclusion of ten oral presentations on these topics (comprising nearly a third of the oral presentations at the conference) indicates a steadily growing interest in these areas of MRI. Furthermore, not only do the presentations cover a very broad range of topics (from Earth's field imaging to sample-shuttled free radical imaging), it is also worth noting that the geographical spread of the researchers could hardly be wider, with presenters coming from Europe, North America and Japan.

We hope that all attendees of the 7<sup>th</sup> Conference on Fast Field-Cycling Relaxometry enjoy the sessions, and that much fruitful cross-relaxation will occur among the many disciplines represented at the meeting.

The committee

---

#### Scientific Committee:

- Silvio Aime
- David Lurie
- Gianni Ferrante
- Rainer Kimmich
- Jean Pierre Korb
- Esteban Anorado

#### Organizing Secretariat :

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**Language:** The official language of the Symposium will be English

**Conference web site:** <http://www.ffcrelax.com>

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# 7 conferences

## Field Cycling NMR Relaxometry

### June 2nd-4th 2011

## Program

### Thursday June 2, 2011

- 11:00-13:30 Registration and lunch  
 13:30-13:40 Welcome to the participants

<b>Chair: David Lurie</b>		<b>Oral Presentation - Session 1</b>
13:40-14:05	<b>J.P. Korb</b> - Ecole Polytechnique, Palaiseau, France Extreme-values statistic and dynamics of water at protein interfaces	01
14:05-14:30	<b>E.A. Rössler</b> - Universität Bayreuth, Germany Translational and rotational dynamics of viscous liquids revealed by field cycling <sup>1</sup> H NMR	02
14:30-14:55	<b>P. H. Fries</b> - CEA, INAC, SCIB, Grenoble, France Extracting reliable molecular information in paramagnetic solutions from field-cycling NMR relaxometry	03
14:55-15:20	<b>P. Levitz</b> - PMC- CNRS- Ecole Polytechnique, France Probing by field cycling relaxometry the dynamics of a magnetic nanoparticle in various environments	04
15:20-15:45	<b>G. Martini</b> - Università di Pavia, Italy Compensation of noise bias error in NMR by accumulation of signal modulus and power	05
15:45-16:05	<b>Coffee break</b>	
<b>Chair: Esteban Anoardo</b>		<b>Oral Presentation - Session 2</b>
16:05-16:30	<b>D.Kruk</b> - Jagiellonian University, Krakow, Poland Electrons and quadrupolar nuclei – line of analogy in NMR relaxometry	06
16:30-16:55	<b>T. Apih</b> - EN-FIST Centre of Excellence, Ljubljana, Slovenia Magnetic Field Cycling and Quadrupole Resonance Detection	07
16:55-17:20	<b>J. Seliger</b> - University of Ljubljana, Slovenia Field-cycling double-resonance spectroscopy of quadrupole nuclei in hydrogen bonded organic ferroelectrics and antiferroelectrics	08
17:20-17:45	<b>A. Gradišek</b> - Jožef Stefan Institute, Ljubljana, Slovenia Fast field-cycling NMR relaxometric study of molecular dynamics in chiral liquid crystalline systems	09
17:45-18:10	<b>V. Domenici</b> - Università di Pisa, Italy Dynamics of Bent-core Liquid Crystals: <sup>2</sup> H NMR Relaxation and Line-width analyses, <sup>1</sup> H NMR Relaxometry and Diffusometry	10
18:30	<b>Opening of Poster Session</b>	
19:30	<b>Dinner</b>	
From 21:00	<b>Cake &amp; wine party in the poster hall</b>	

## Friday, June 3, 2011

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8:55-9:20	<b>J. Tritt-Goc</b> - <i>Polish Academy of Sciences, Poznań, Poland</i> Evidence of Solvent-Gelator Interaction in Sugar-Based Organogels Studied by Field-Cycling NMR Relaxometry	12
9:20-9:45	<b>M. Geppi</b> - <i>Università di Pisa, Italy</i> Detailed characterization of the dynamics of organic molecules in the solid state: a multi-technique NMR approach	13
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18:00	<p><i>Departure to discover the "first" capital city of Italy from the <b>Roman Gates</b> to its splendid <b>Baroque Palaces</b>. Visit, in exclusive, of the splendid <b>Palazzo Cavour</b> that hosts the exhibition "Cavour genius gourmet seducer".</i></p> <p><i>Conference dinner at <b>'RistoranteAll'opera'</b></i></p>	

## Saturday, June 4, 2011

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10:35-11:00	<b>L. Vander Elst</b> - University of Mons, Belgium NMRD Profiles of Particulate Reporters for Magnetic Resonance Molecular Imaging. Does the coating matters?	32
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*Tracing the “Corset-Effect” : Polybutadiene in nanoscopic confinement*

**POSTER 2**

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*Localization and Quantification of Contrast Agents using FFC MRI at 1.5T*

**POSTER 3**

L. M. Broche, K. Carbis, J. Carr, H. Wackerhage, D. J. Lurie

*Clinical applications of FFC MRI: detection of muscle damage*

**POSTER 4**

A. Roque, D. Sousa, P. Sebastião

*Fast Field Cycling NMR Relaxometer: Featuring Wines*

**POSTER 5**

M. S. M. Preto, M. I. B. Tavares, P. J. Sebastião, R. B. V. Azeredo

*T<sub>1</sub> H studies of maytenus ilicifolia extracts by field-cycling nmr relaxometry, infrared and thermogravimetric analysis*

**POSTER 6**

E. Carignani, S. Borsacchi, A. Marini, B. Mennucci, M. Geppi

*Vibrational motions in the solid state investigated by NMR and ab initio methods: effects on 13C chemical shift tensors of Ibuprofen*

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*Fast Field Cycling NMR relaxometry for the assessment of biochar quality*

**POSTER 8**

G. Butera, P. Conte, C. De Pasquale, G. Alonzo

*Thermal degradation of microcrystalline cellulose in concentrated phosphoric acid*

**POSTER 9**

C. De Pasquale, P. Conte, V. Mineo, G. Alonzo

*Dynamics of different types of milk by Fast Field Cycling NMR relaxometry*

**POSTER 10**

R. Scotti, P. Conte, G. Alonzo, M. A. Rao

*Assessing soil organic matter evolution in sustainable agriculture by Fast Field Cycling NMR relaxometry*

**POSTER 11**

U. P. Sudhakaran , S. Borsacchi , M. Geppi , M. Messori , F. Bignotti

*Novel silica-reinforced rubbers obtained by sol-gel processes: Structure and dynamic properties as studied by Solid-State NMR***POSTER 12**

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*Relaxation in Bulk Polymer Melts at very low frequencies***POSTER 13**

R. Meier, D. Kruk, E. A. Rößler

*Intermolecular relaxation in glycerol -<sup>1</sup>H FFC NMR for isotopically diluted systems***POSTER 14**

L. Calucci, S. Bubici, Gianni Ferrante, M. Geppi

*<sup>19</sup>F Fast Field-Cycling NMR relaxometry of a nematic liquid crystal***POSTER 15**

A. Průšová, P. Conte, J. Kučerík, G. Alonzo

*Dynamics of hyaluronan aqueous solutions as affected by molecular size and ionic strength***POSTER 16**

A.N. Pravdivtsev, K. L. Ivanov, N. N. Saprygina, A. V. Yurkovskaya, T. Köchling, H.-M. Vieth

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*Synthesis of magnetic nanoparticles with narrow size distribution***POSTER 18**

A. Herrmann, B. Kresse, D. Kruk, A.F. Privalov, F. Fujara, E.A. Rössler

*Relaxation in Bulk Polymer Melts at very low frequencies***POSTER 19**

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*Kinetic <sup>19</sup>F Fast Field Cycling NMR study of a liquid crystal***POSTER 20**

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*A complete platform for PHIP method***POSTER 21**

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**POSTER 22**

V. Bortolotti, S. Bubici, P. Fantazzini, M. Polello, G. Ferrante

*Characterization of wide size rock cores by means of Field Cycling NMR Relaxometry*



---

## ORAL PRESENTATIONS

## Extreme-values statistic and dynamics of water at protein interfaces

J.-P. Korb<sup>1</sup>, Galina Diakova<sup>2</sup>, Jason Pajski<sup>2</sup>, Yanina Goddard<sup>2</sup>, R.G. Bryant<sup>2</sup>

<sup>1</sup>*Physique de la Matière Condensée, Ecole Polytechnique, CNRS, 91128 Palaiseau, France*

<sup>2</sup>*Chemistry Department, University of Virginia, Charlottesville, VA, USA 22904*

Immobilized proteins present a unique interface with water. The translational diffusive motions affect the high frequency dynamics and the nuclear spin-lattice relaxation as in all surfaces, however, rare binding sites for water make a profound difference in the low frequency dynamics. Binding sites in protein systems are not identical, thus, a distribution of energies and consequent dynamics are expected. We show that the statistics of rare events, *i.e.*, water sampling rare binding sites, implies an exponential distribution of activation energies for the strongest binding events. In turn, the exponential energy distribution leads to a Pareto distribution for the correlation times, and a power law in the Larmor frequency for the spin-lattice relaxation rate constants at low field strengths with a plateau at very low field strengths. We examine the consequences of these dynamics in two cases: a single well protein-bound environment for water, and a double well bound environment for water where the potentials for the local motions of the bound-state water are of different depths. This analysis is applied to  $D_2O$  on albumin and lysozyme, which is dominated by the intramolecular relaxation driven by the dynamical modulation of the nuclear electric quadrupole coupling. We also separate the intramolecular from the intermolecular contribution to water proton spin-lattice relaxation by isotope dilution, and show that the intramolecular proton data map onto the deuterium relaxation by a scale factor implied by the relative strength of the quadrupole and dipolar couplings. The temperature and  $pH$  dependence of the magnetic relaxation dispersion are complex, and accounted for by changing only the weighting factors in a superposition of contributions from single-well and double-well contributions.

## Translational and rotational dynamics of viscous liquids revealed by field cycling $^1\text{H}$ NMR

R. Meier, D. Kruk<sup>+</sup>, E.A. Rössler

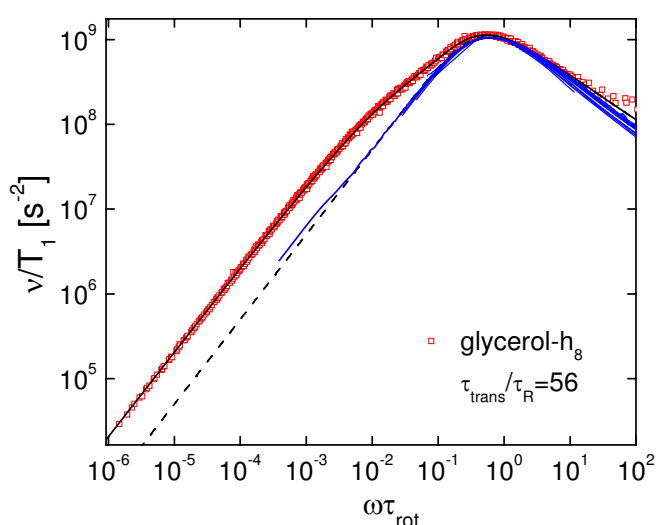
Experimentalphysik II, Universität Bayreuth, 95440 Bayreuth, Germany

<sup>+</sup> also Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Krakow, Poland

We compare the results of  $^1\text{H}$  NMR relaxometry and dielectric spectroscopy (DS) for several viscous liquids [1,2]. The DS spectra can be interpolated by Cole-Davidson spectral density providing correlation times which characterize the reorientational dynamics ( $\alpha$ -process) and which is determined by the glass transition phenomenon. In contrast, the  $^1\text{H}$  NMR  $\omega/T_1(\omega)$  susceptibility spectra show in addition to the  $\alpha$ -relaxation peak a low-frequency excess contribution. We attribute this distinct low-frequency process to contributions from translational motion while the relaxation peak itself originates from reorientational dynamics alone.

For  $^1\text{H}$  NMR one has to distinguish between protons on the same molecule (intramolecular) and on different molecules (intermolecular), and the overall relaxation rate  $R_1 = 1/T_1$  can be split:  $R_1 = R_{1,\text{intra}} + R_{1,\text{inter}}$ . It is the intermolecular rate  $R_{1,\text{inter}}$  which is expected to be dominated by translational motion of spins located on different molecules. Assuming CD susceptibility for the intramolecular part reflecting reorientational dynamics and for the intermolecular part a spectral density derived from the force-free-hard-sphere model [3] (Fick diffusion), we are able to fit  $T_1(\omega)$  for differently deuterated glycerol [2]. Thereby, we extract the diffusion coefficient  $D(T)$  which is in good agreement with results from gradient NMR. For the hydrodynamic model of a sphere rotating and translating in a medium Abragam derived the relationship  $\tau_{\text{trans}}/\tau_{\text{rot}} = 9$  where  $\tau_{\text{trans}}$  is the time constant of translational diffusion and  $\tau_{\text{rot}}$  of rotation. Experimentally, we find  $\tau_{\text{trans}}/\tau_{\text{rot}} = 20 - 60$  being essentially temperature independent indicating translational-rotational coupling in liquids.

In order to prove our approach we apply the isotope dilution technique. Substituting protonated molecules of a liquid by their deuterated counterpart allows suppressing the intermolecular DD interaction. Extrapolating for infinite dilution one can isolate the intramolecular relaxation, thereby obtaining the intermolecular part via  $R_{1,\text{inter}}(T, \omega) = R_1 - R_{1,\text{intra}}$ . In the case of glycerol we can show that there exists also an intermolecular relaxation contribution originating from molecular rotation. Any rotation will also modulate the intermolecular distance between the spin pairs. This non-centrality effect has to be taken into account.



**Figure 1.** Master curves of the NMR susceptibility representation  $\omega/T_1(\omega)$  (red) in comparison with the dielectric spectrum (blue). Low-frequency shoulder originates from intermolecular relaxation.

- [1] Meier R.; Kahlau R.; Kruk D.; Rössler E.A. *J. Phys. Chem. A*, **2010**, *114*, 7847
- [2] Kruk, D.; Meier, R.; Rössler, E.A. *J. Phys. Chem. B*, **2011**, *115*, 951.
- [3] L.P. Hwang, J.H. Freed, *J. Chem. Phys.* **1975**, *63*, 4017.

## Extracting reliable molecular information in paramagnetic solutions from field-cycling NMR relaxometry

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Laboratoire de Reconnaissance Ionique et Chimie de Coordination,  
38054, Grenoble, France*

The paramagnetic relaxation rate enhancements (PREs) of nuclear spins  $I$  on diamagnetic solvent or solute molecules  $M_I$ , *i.e.*, the increase of the relaxation rates of these spins due to the electronic magnetic moments  $\mathbf{m}_e$  of paramagnetic solutes  $M_{\text{para}}$ , depend on both the random relative spatial motion of  $\mathbf{m}_e$  with respect to  $I$  and the time fluctuations of  $\mathbf{m}_e$ . The PREs should be an invaluable source of information on the relative distribution and motion of  $M_{\text{para}}$  with respect to  $M_I$  because they can be measured with great accuracy to the extent that they dominate the relaxation of nuclear spins  $I = 1/2$  as is often the case even at concentrations of paramagnetic solutes lower than 10 mM. However, this information can be hidden by the complicated time fluctuations of  $\mathbf{m}_e$  with electronic relaxation time  $\tau_e$ . In solutions of reasonable viscosity, the paramagnetic species  $M_{\text{para}}$  can be classified into three groups according to the value of  $\tau_e$  with respect to the characteristic time  $\tau$  of their relative translational diffusion with respect to  $M_I$ . The first group defined by the condition  $\tau \ll \tau_e$  of slow electronic relaxation includes the nitroxide radicals, the second group specified by  $\tau_e \cong \tau$  contains the complexes of paramagnetic ions in orbital  $S$  electronic ground states such as  $\text{Mn}^{2+}$  and  $\text{Gd}^{3+}$ , and the third group determined by the criterion  $\tau_e \ll \tau$  of fast electronic relaxation incorporates the complexes of paramagnetic lanthanide  $\text{Ln}^{3+}$  ions different from  $\text{Gd}^{3+}$  such as  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Er}^{3+}$ . The maximal information on the relative distribution and motion of  $M_{\text{para}}$  with respect to  $M_I$ , which can be derived from PRE measurements, is readily obtained for the first group of paramagnetic species of slow electronic relaxation with the help of a fast field-cycling Stellar relaxometer equipped with a 1 T polarization field. By contrast, this low- and medium-field information is blurred by the fluctuations of  $\mathbf{m}_e$  for the second group of paramagnetic species and additional high-field measurements have to be carried out to disentangle the effects on the PRE caused by the  $M_{\text{para}}/M_I$  relative motion from those due to electronic relaxation. Finally, the paramagnetic solutes of the third group can be employed to explore the  $M_{\text{para}}/M_I$  relative distribution at equilibrium.

**PROBING BY FIELD CYCLING RELAXOMETRY THE DYNAMICS OF A MAGNETIC NANOPARTICLE IN VARIOUS ENVIRONMENTS.**

**M. Levy (1), M. Devaud (1), Claire Wilhelm (1), Françoise Gazeau (1) and P. Levitz (2)**

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Superparamagnetic particles play a growing role in different fields of application especially in medicine as contrast agents or therapeutic nanoparticles for hyperthermia. The inner magnetic dynamics of these colloids coupled with the solvent diffusion around the particle can be probed by field cycling relaxometry. In this context, these nanoparticles can also be used as “nano spies” providing valuable information on the local confinement where they are localized.

In this presentation, we present a series of NMRD experiments involving either maghemite colloids, with a low magnetic anisotropy constant  $K$ , or cobalt ferrite particles, with a large magnetic anisotropy constant  $K$ , in various environments such as pure suspensions of various viscosity or diverse biological systems. Depending of the crystal anisotropy energy, the  $R1$  dispersion curves exhibit interesting differences that are analyzed. Potentiality for these “nano spies” to provide information on their localization is discussed.

# Compensation of noise bias error in NMR by accumulation of signal modulus and power

*Giuseppe Martini*<sup>a)</sup> and *Gianni Ferrante*<sup>b)</sup>

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When NMR signal is acquired in unstable magnetic field  $B$  and low Signal-to-Noise Ratio (SNR) condition, improved SNR is obtained by accumulation of many acquisitions taken in the same conditions. Since  $B$  field is unstable, carrier frequency fluctuates, and inphase and quadrature components (I&Q) can not be accumulated. Carrier frequency dependence is removed if modulus  $S$  is calculated instead, allowing  $S$  accumulation. The resulting averaged  $S$  has SNR improved by a factor  $\sqrt{k}$ , but it suffers from a non linear noise error related to both noise and signal, sometimes called “noise bias”, arising from Rice statistics of noisy  $S$  when noise is white, gaussian and additive to I&Q components of signal [1].

We propose a technique to compensate such an error from knowledge of the original SNR of each acquisition of I&Q components. Usually SNR is estimated from acquisition in absence of any NMR signal, e.g. by switching off RF generator or, in NMR Imaging (MRI), from background pixels. In the described error compensation technique we calculate the variance  $V$  of signal modulus from accumulated  $S$  and  $S^2$  instead, guessing a modulus estimate from  $S$  and  $V$  by exploitation of rician statistics of noisy NMR signal modulus [2]. The proposed technique is local, in the sense that each time sample of the signal is compensated by using its own averages of  $S$  and  $S^2$  on repeated measurements. The compensation of such a noise error is performed by inverting two suitably chosen functions of the original (true) signal and additive noise power. Look-up tables are used to improve calculation speed.

The underlying mathematics is briefly presented. Simulation results as well as some examples of real world results are reported, confirming robustness of the proposed local, non linear, noise error compensation method.

The proposed procedure for noise error compensation is fast enough to be applied on-line during signal acquisition. Noise bias error compensation allows NMR signal extraction from very noisy measurements, even those acquired in unstable  $B$  field condition, thus opening to previously unseen results.

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## Electrons and quadrupolar nuclei – line of analogy in NMR relaxometry

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Performing <sup>1</sup>H relaxation dispersion studies for systems containing unpaired electrons (like transition metal complexes or radicals) one observes several features – one of them is the presence of local relaxation maxima when the molecular motion and the electron spin dynamics is relatively slow. Similar, at the first sight, effects one also sees in <sup>1</sup>H (<sup>19</sup>F) relaxation dispersion of systems containing quadrupolar nuclei (like <sup>14</sup>N, <sup>35</sup>Cl, <sup>139</sup>La, etc), often referred to as quadrupole peaks. The aim of this lecture is to discuss similarities and differences in the mechanisms causing such effects for paramagnetic and quadrupolar systems and report on the recent progress in their theoretical treatment.

Quadrupolar peaks are often observed for solid state where residual dipole-dipole (DD) interactions provide a pathway for polarization transfer effects [1,2]. This phenomenon effectively leads to a faster magnetization decay, however it should not be mistaken with the relaxation process (especially it should not be called ‘cross-relaxation’), because it is of a ‘static’ origin. Polarization transfer can be hardly seen in paramagnetic systems.

Relaxation is caused by time-dependent parts of the DD interactions. Here one can see deep analogies between paramagnetic – (characterized by the spin quantum number  $S \geq 1$ ) and quadrupolar systems. The analogy is based on the similar formalisms of zero field splitting and quadrupolar interactions. There is a well established treatment of paramagnetic relaxation enhancement that is valid for arbitrary motional conditions and interaction strengths [3,4] (it is referred to as ‘Swedish slow motion theory’). This approach has been adapted to quadrupolar systems of  $S=1$  [5,6] and recently to an arbitrary spin quantum number of the quadrupole nuclei [7] and applied to some imidazolium-based crystals [7]. In analogy to paramagnetic systems the quadrupolar effects on the dipolar spin relaxation have been referred to as quadrupolar relaxation enhancement [7]. Several examples of quadrupolar effects and their interpretation will be shown. Their origin will be discussed in comparison to paramagnetic systems.

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## Magnetic Field Cycling and Quadrupole Resonance Detection

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The last decade has seen a renewed interest in the field of Nuclear Quadrupole Resonance of <sup>14</sup>N nuclei. The two most important reasons for this are:

- the assumed potential of the method to offer remote and non-invasive detection or identification of nitrogen-bearing illicit substances, e.g. explosives, illegal drugs, or counterfeit pharmaceuticals
- the immense sensitivity of the NQR frequencies to the variation of crystalline structure make possible the distinction between polymorphic structures, which can be difficult to distinguish even by high resolution solid state NMR

Unfortunately, <sup>14</sup>N NQR lines lie in a very low frequency range, typically 0.5 to 3.5 MHz. Combination of low resonance frequencies and typically long relaxation times which prohibit rapid accumulation of the signals, often results in a very low sensitivity of such experiments and makes them less attractive.

To improve the sensitivity, methods of nuclear quadrupole double resonance with magnetic field cycling have been developed, which rely on the <sup>14</sup>N - <sup>1</sup>H coupling. Here, the <sup>14</sup>N NQR resonances are detected indirectly by measuring <sup>1</sup>H nuclear magnetic resonance signals. In addition to this, we are using field cycling and <sup>14</sup>N - <sup>1</sup>H coupling to transfer magnetization from proton to nitrogen system, thereby increasing the <sup>14</sup>N NQR signal. Best results have been obtained when these techniques are combined with multipulse excitation and spin-lock effect.

## Field-cycling double-resonance spectroscopy of quadrupole nuclei in hydrogen bonded organic ferroelectrics and antiferroelectrics

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Ferroelectrics are polar substances, in which spontaneously generated electric polarization can be reversed by inverting the external electric field. Ferroelectrics have numerous practical applications. They are used to store and switch their polarity, sense temperature changes, interchange electric and mechanical functions and manipulate light. The ferroelectric phase persists up to the Curie temperature  $T_C$ , where the phase transition to the paraelectric phase occurs.

Antiferroelectrics are closely related to ferroelectrics. They consist of sublattices, which are polarized in the opposite direction, so the net macroscopic polarization is zero.

Hydrogen bonded inorganic ferroelectrics, as for example  $\text{KH}_2\text{PO}_4$ , are known for a number of years. Here the ferroelectric phase transition is associated with the ordering of protons in the O-H...O hydrogen bonds. In the paraelectric phase a proton exchanges between two equilibrium positions in a hydrogen bond: O-H...O  $\leftrightarrow$  O...H-O. Below  $T_C$  the exchange freezes and the spontaneous polarization occurs.

Hydrogen bonded organic ferroelectrics and antiferroelectrics have mostly been studied recently. They are either single-component compounds (thiourea, squaric acid, croconic acid...) or two-component co-crystals (phenazine - chloranilic acid, 2,3,5,6-tetra (2'-pyridyl) pyrazine - chloranilic acid...).

NQR frequencies of the nuclei of atoms, which participate in the hydrogen bonds ( $^{17}\text{O}$ ,  $^{14}\text{N}$ ,  $^2\text{H}$ ), are a sensitive test of the proton position and motion in the hydrogen bond. NQR can be used to investigate local properties of ferroelectrics and antiferroelectrics.

The  $^{14}\text{N}$  and  $^{17}\text{O}$  NQR frequencies are typically lower than 5 MHz, whereas the  $^2\text{H}$  NQR frequencies are of the order of 100 kHz. These frequency can be measured by double resonance based on magnetic field cycling between a high and a low magnetic field. Protons are polarized and the proton NMR signal is measured in the high magnetic field. The proton magnetization is manipulated via the quadrupole nuclei in the low magnetic field.

Here we discuss the results of the  $^{17}\text{O}$  NQR study of squaric acid and croconic acid and the  $^{14}\text{N}$  NQR study of phenazine - chloranilic acid, 2,3,5,6-tetra (2'-pyridyl) pyrazine - chloranilic acid, 5,5'-dimethyl-2,2'-bipyridine - chloranilic acid and 1,5-naphthyridine - chloranilic acid.

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## Fast field-cycling NMR relaxometric study of molecular dynamics in chiral liquid crystalline systems

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*Fast field-cycling NMR relaxometry enables us to measure the proton spin-lattice relaxation time  $T_1$  over a wide range of Larmor frequencies. In liquid crystalline (LC) systems, this method is appropriate to study molecular dynamics, as the collective motions contribute to the proton relaxation in the kilohertz region. The collective dynamic processes we can detect in various phases are the order director fluctuations, layer undulations and rotations mediated by translational displacements along the helical axis. Additionally, proton relaxation is sensitive to effects of both overall and internal molecular rotations and translational self diffusion.*

*We present a detailed dynamics study of two liquid crystalline systems. The rod-like lactate derivative HZL 7/\* exhibits several chiral phases upon cooling from the isotropic phase. This system is of special interest because of wide temperature range of stability for these phases, enabling us to study the evolution of dynamic processes with temperature [1]. Additionally, it has been observed that due to the molecular structure, different parts of the molecule have different relaxation times in the isotropic and the chiral nematic phases.*

*The second system studied was a model liquid crystal 5CB, mixed with small quantities of a chiral LC\*. Studying the  $T_1$  dispersion in the mixture and in each of the components separately, we were able to analyze how the introduction of chiral molecules changes the dynamics of the mixture [2].*

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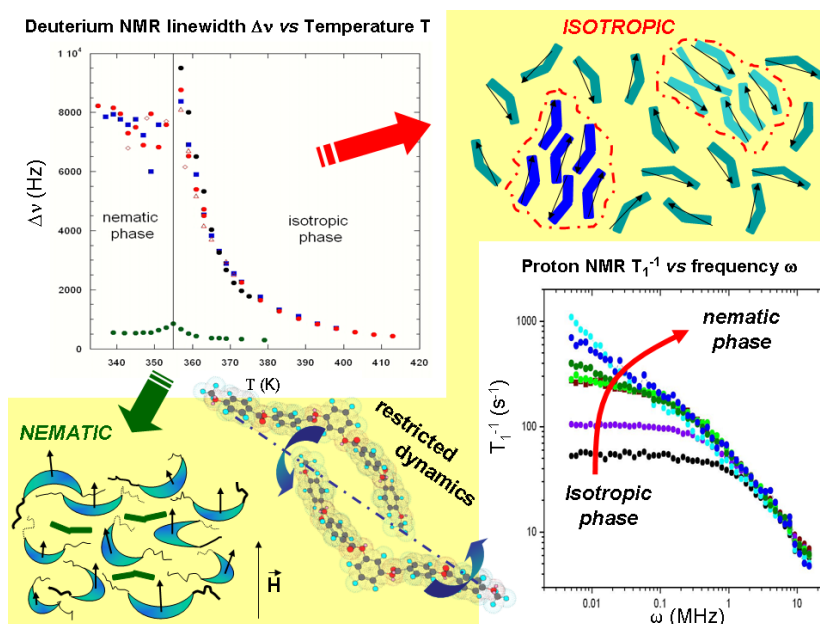
## Dynamics of Bent-core Liquid Crystals: $^2\text{H}$ NMR Relaxation and Line-width analyses, $^1\text{H}$ NMR Relaxometry and Diffusometry

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Dynamic properties of low-molecular-weight bent-core liquid crystals<sup>1</sup> revealed to be unusual with respect to the analogous rod-like mesogens.<sup>2</sup> First pioneering investigations based on Dynamic Light Scattering measurements were followed by intense and deep studies based on Nuclear Magnetic Resonance (NMR) spectroscopy, mainly  $^2\text{H}$  NMR relaxation and line-width analyses,<sup>3</sup>  $^1\text{H}$  NMR relaxometry<sup>4</sup> and diffusometry<sup>5</sup>. These studies were of help in identifying the molecular motions (single molecular, internal and collective ones) responsible of the observed slow relaxation and large  $^2\text{H}$  NMR spectral line-width.<sup>6</sup> Viscosity and rheology measurements provided further elements confirming the slow dynamics of bent-core liquid crystals at a macroscopic level. All these experimental techniques indicate the presence of restricted dynamic motions as a distinctive feature of bent-core liquid crystals both in the isotropic and nematic phases.<sup>7</sup> The case of bent-core mesogens discussed here is an example of comparative study in which different dynamic processes can be identified and characterized by using various experimental methods.<sup>8</sup>



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## EFFECT OF KINEMATIC VISCOSITY OVER THE DYNAMIC PROPERTIES OF AN EXTRA-VIRGIN OLIVE OIL

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Previous studies<sup>1,2</sup> have shown that kinematic viscosity values of food oils depend on the presence of added solvents and on the nature of the oil under investigation (e.g., geographical origin and treatments prior to oil production). However, to the best of our knowledge, only one paper<sup>3</sup> dealt up to now with the correlation between viscosity values and relaxation times of simple pure alkyl compounds. Up to now, no papers have been found in literature dealing with viscosity of complex mixtures and their relaxometric properties. In this study, we intended to investigate the effect of kinematic viscosity over the dynamic properties of an extra-virgin olive oil which is known as a very complex mixture of lipophilic triglycerides (more than 98%) and waxes, and hydrophilic secondary metabolites (around 2%) such as chlorophyll, salts and sterols. The relaxometric model<sup>2,4</sup> applied to the NMRD profiles of the oil added with increasing amounts of *n*-hexane, split the correlation time in two contributions. The first one, modulated by an amplitude indicated as  $A_D$ , was assigned to translational motions ( $\tau_D$ ). The second component of the correlation time, also modulated by an amplitude indicated as  $A_R$ , was due to the rotational motions ( $\tau_R$ ). Results revealed that all the relaxometric parameters had a diametric trend. A possible explanation for such a behavior was found in the aggregative properties of the inverse micelle-like<sup>1</sup> components of the food oil. In fact, in the absence of *n*-hexane, all the inverse micelle-like systems (in which triglycerides are shrink together) aggregate, thereby forming large sized units which are subjected to very slow rotations but fast translations. Conversely, as the amount of *n*-hexane was increased, kinematic viscosity decreased and rotations became preponderant over translations. In fact, *n*-hexane has the effect to separate the inverse micelle-like systems and to increase rotational freedom degrees over the translational ones. This study confirmed the inverse micelle-like nature of food oils reported in a previous paper<sup>1</sup>.

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## Evidence of Solvent-Gelator Interaction in Sugar-Based Organogels Studied by Field-Cycling NMR Relaxometry

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The solvent-gelator interaction in the gels composed of the low molecular mass gelator methyl-4,6-*O*-benzylidene- $\alpha$ -D-glucopyranoside and 1,2-*O*-(1-ethylpropylidene)- $\alpha$ -D-glucofuranose with chlorobenzene and toluene was the subject of the studies.<sup>1,2</sup> The interaction causes a significant slowing down of the motion of solvent molecules at the gelator surfaces when compared to bulk solvent. The motion manifests itself through the low frequency dispersion of the proton spin-lattice relaxation time of solvents in gels observed below  $10^5$  Hz as seen in Fig.1. The relaxation time was measured with the Fast Field Cycling relaxometry method in the function of magnetic field strength and temperature. The data were interpreted in terms of two-fraction fast-exchange model.<sup>3</sup>

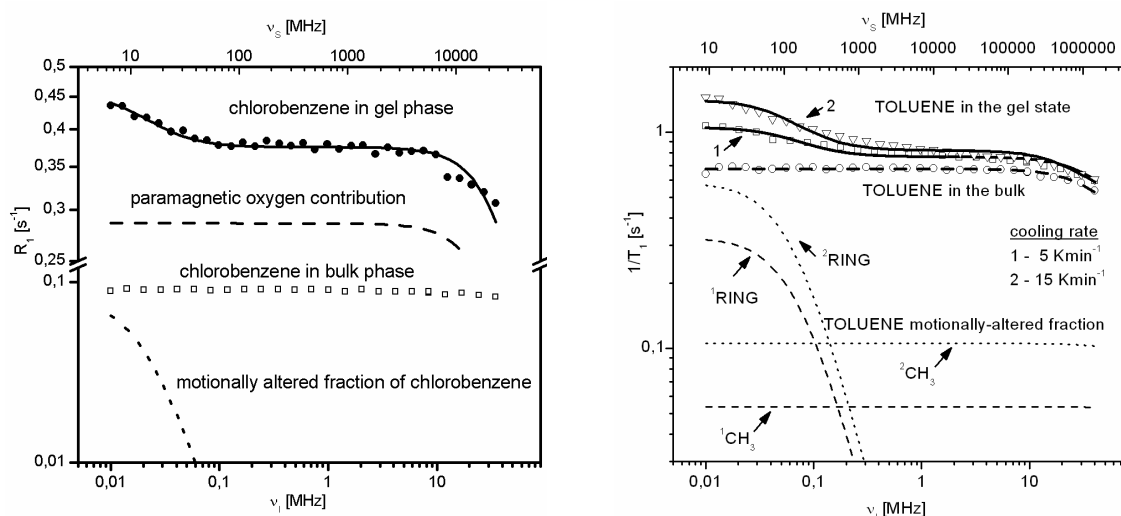


Fig.1. Proton-spin lattice relaxation rates of chlorobenzene in methyl-4,6-*O*-(*p*-nitrobenzylidene)- $\alpha$ -D-glucopyranoside gel and toluene in 1,2-*O*-(1-ethylpropylidene)- $\alpha$ -D-glucofuranose gel measured as a function of the magnetic field strength reported as the proton Larmor frequency (bottom) and electron Larmor frequency (top).

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## Detailed characterization of the dynamics of organic molecules in the solid state: a multi-technique NMR approach

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Solid State Nuclear Magnetic Resonance (SSNMR) is certainly one of the most powerful techniques to investigate molecular dynamics of organic molecules in solid phases, since it offers several approaches to study molecular motions over a wide range of frequencies [1]. In order to exploit the widest possible range of frequencies and to get the most detailed information about individual motional processes, a variety of techniques, involving several types of nuclei, must be applied and simultaneously analyzed. In our approach we combined:  $^{13}\text{C}$  and  $^1\text{H}$  longitudinal relaxation times ( $T_1$ ) to investigate fast motional processes, with characteristic frequencies of the order of MHz;  $^{13}\text{C}$  and  $^1\text{H}$  longitudinal relaxation times in rotating frame ( $T_{1\rho}$ ) and  $^{13}\text{C}$  line shape analysis (both arising from chemical shift anisotropy and MAS spectra) to investigate the intermediate motional region (frequencies of the order of kHz), while insights about the slow motional regime (frequencies of the order of 1 kHz or less) could be obtained by looking at exchange processes occurring in the  $^{13}\text{C}$  high-resolution spectra.

In particular, this approach was applied to the characterization of the dynamic properties of two forms of ibuprofen, acid (IBU-A) and sodium salt (IBU-S), which, from a previous preliminary work [2], were found to exhibit different dynamic behaviour, in spite of their very similar chemical structure. The combined analysis of all the data allowed the identification and the detailed characterization, in terms of correlation times and activation energies, of all the reorientational and interconformational motions taking place in these molecules, such as the  $\pi$ -flip of the phenyl rings, the reorientation of methyl groups and aliphatic chains, as well as the  $\pi$ -flip of the dimeric structure formed by the acidic groups in IBU-A [3].

Following the detailed characterization of internal reorientational motions, the comparison between experimental and DFT-calculated  $^{13}\text{C}$  chemical shift principal values could give precious information about the effect of vibrational motions on the  $^{13}\text{C}$  CSA of aromatic carbons. The use of suitable theoretical models allowed quantitative parameters to be obtained for a few vibrational motions involving the aromatic ring.

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## Field-cycling NMR Relaxometry Studies of Magnetic Order in the Colloidal State

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The physicochemical properties of nanostructures in the fully hydrated form in suspension are critical to their performance in biomedical applications. Over the last few years we have applied field-cycling NMR relaxometry, in the  $10^3$  -  $10^8$  Hz range, to study aqueous and non-aqueous magnetic nanoparticle suspensions. This has been facilitated by the development of a workable theory for solvent relaxation due to superparamagnetic nanoparticles, by Robert Muller and his colleagues at Mons-Hainault.<sup>1</sup> Our research demonstrates that for magnetic nanoparticle and nanocomposite suspensions, <sup>1</sup>H NMR relaxation time measurements of the solvent provide insight into the extent of solvation, the surface and bulk magnetisation, and the magnetic order.<sup>2-7</sup> This arises because the diffusing solvent molecules interact dynamically with the nanocomposite surface. The information obtained on the structures *in situ* is complementary to that available from dynamic light scattering, magnetometry and electron microscopy. The implications of the findings for the assembly of nanocomposites and for developing applications will be discussed.

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## Field-Cycling Singlet NMR

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Singlet states are exchange-antisymmetric, non-magnetic, states of coupled spin-1/2 pairs. In many circumstances, singlet-triplet transitions are much slower than the relaxation of magnetization. The long-lived nature of nuclear singlet states suggests many useful applications, including the long-term transport of hyperpolarized spin order, generated by dynamic nuclear polarization (DNP) and by parahydrogen-induced polarization (PASADENA/PHIP). In most cases, nuclear singlet states are either difficult to access (for example in symmetrical molecules such as water), or are destabilised by chemical shielding differences in magnetically inequivalent systems. Our group has demonstrated that nuclear singlet states may be accessed and utilized in magnetically inequivalent systems by switching the symmetry of the nuclear spin Hamiltonian. There are several ways to do this: (1) reducing chemical shielding effects by reducing the magnetic field to a low value; (2) suppressing chemical shift differences by a resonant radiofrequency field; (3) manipulating heteronuclear spin-spin couplings; (4) using symmetry-breaking chemical reactions.

In this talk I will concentrate on field-cycling singlet NMR (method 1), which involves shuttling the sample out of the NMR magnet into a low magnetic field, and back again for observation. A variety of manipulations may be performed on the coupled nuclear spin system in low field. For example, audiofrequency pulses may be applied at the low-field Larmor frequency, to induce triplet-triplet transitions. More surprisingly, extremely low-frequency pulses (in our case, ~8Hz) may be applied at the singlet-triplet energy difference to induce extremely slow “forbidden” singlet-triplet transitions (in our case, the 90 degree pulse length is ~ 2.5 seconds). One application of these manipulations is to transform nuclear magnetization into singlet order, outside the NMR magnet. This is an important component of hyperpolarized nuclear singlet experiments.

Singlet NMR may also be performed in systems that are almost, but not quite, symmetric. In these cases, nuclear singlet states are stable in a wide range of magnetic fields, without radiofrequency spin-locking. This allows nuclear singlet relaxation to be studied over the full range of magnetic fields, from zero to tens of Tesla.

## Controlling the SABRE effect using magnetic field cycling.

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The phenomenon of magnetic resonance is employed in the fields of chemistry and medicine in the form of NMR spectroscopy and MRI. In medicine MRI plays a key role in non-invasive diagnosis, while it also plays a significant role in clinical research.<sup>1</sup> However, NMR spectroscopy and MRI suffer inherently from the underlying physical basis of the method which limits sensitivity.<sup>2</sup>

Hyperpolarization deals with the generation of non-equilibrium populations of nuclear spins, and has been successful in providing enhanced sensitivity to both NMR and MRI experiments.<sup>3-6</sup> One variant of the hyperpolarization method is dynamic nuclear polarization (DNP) which has been used to increase the sensitivity of <sup>13</sup>C detection by over 10,000 fold such that 65% of the material present has been measured.<sup>7</sup>

An alternative approach to achieve substrate hyperpolarization involves the use of *parahydrogen*, a molecule that exists in a pure magnetic state.<sup>4-5</sup> However, it is not *parahydrogen* itself that is detected in these experiments, but rather reaction products that are formed by a metal catalyzed hydrogenation.<sup>4-5</sup> The newly formed molecules now contain non-equilibrium spin state populations for nuclei that are spin coupled to protons that were originally located in *parahydrogen*. Consequently they yield MR signals that are substantially larger than normal. Indeed 100% polarization has been generated for a pair of metal hydride protons using this method.<sup>8</sup> A newer route to substrate hyperpolarization with *parahydrogen* has been termed signal amplification by reversible exchange (SABRE).<sup>9-10</sup> This approach yields substantial polarization without the need for chemical modification. It is achieved instead through the temporary binding of a substrate and *parahydrogen* in a suitable transition metal complex. This process of bringing together two materials, pyridine, for example, and *parahydrogen*, into temporary contact enables the sharing of their magnetization and hence the spontaneous enhancement of the MR signals of what correspond to ultimately the free substrate and has been illustrated extensively for pyridine.<sup>10-11</sup> This talk will illustrate how this approach is developing, discuss the type of magnetisation that is created, and consider its relaxation.

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## <sup>15</sup>N hyperpolarization using PHIP (ParaHydrogen Induced Polarization) and magnetic field cycle

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The application of Hyperpolarization techniques is gathering increasing attention as this affords several order of magnitude enhancement on NMR signals. This is particularly interesting for low sensitivity nuclei (e.g. <sup>13</sup>C, <sup>15</sup>N) whose signal could then be used for the acquisition of fast MR images<sup>[1]</sup>.

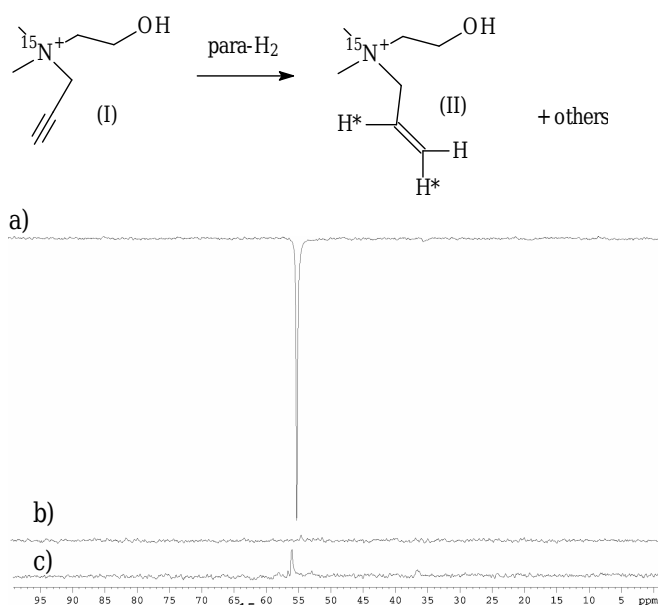
Hyperpolarization using parahydrogen can be applied on molecules that contain an unsaturated group, furthermore the *in vivo* application requires bio-compatibility of the hydrogenation product. Then slowly relaxing nuclei are preferred for *in vivo* MRI application of polarized molecules.

In order to attain a substrate that met those features, a choline derivative (<sup>15</sup>N-propargyl choline) has been synthesized (**I**). Hydrogenation using parahydrogen has been carried out using first at earth magnetic field (ALTADENA experiment) and, while hyperpolarization is obtained on <sup>1</sup>H signals, nothing is observed in the <sup>15</sup>N spectrum. On the contrary, when hydrogenation using parahydrogen is followed by field cycling<sup>[2]</sup>, a polarized signal is obtained in the <sup>15</sup>N spectrum (T<sub>1</sub> ≈ 140s). In this case the magnetic field is suddenly (non-adiabatically) lowered from 50 μT (earth field) to zero and then slowly (adiabatically) raised back to earth field.

In order to explain these experimental results it must be considered that, when the ALTADENA experiment is carried out, hyperpolarized antiphase signals ( $I_z^X I_z^H$ ) can be observed on heteronuclei, whose intensity is a function of scalar coupling values with parahydrogen protons. After magnetic field cycle longitudinal magnetization ( $I_z^X$ ) is formed during the adiabatic passage from zero field to earth magnetic field. The amount of longitudinal magnetization on <sup>15</sup>N is a function of the speed at which transport is carried out. This has been demonstrated using a density matrix treatment of the spin system formed by the parahydrogen protons and <sup>15</sup>N at variable field. Furthermore the amount of longitudinal magnetization achieved on the heteronucleus can be higher than spin order derived from the ALTADENA experiment.

In this case field cycling demonstrated to be necessary to achieve heteronuclear polarization.

Using inverse-INEPT it has also been possible to identify that, among other reaction side-products, hyperpolarized <sup>15</sup>N signal is related to (**II**) which is quite similar to choline. This is particularly important for *in vivo* studies with this hyperpolarized molecule.



a) Hyperpolarized <sup>15</sup>N spectrum acquired at 14.1T of parahydrogenated II; b) equilibrium 1 scan spectrum; c) 16 scans <sup>15</sup>N spectrum.

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## Manipulation of relaxation in hyperpolarized spin systems

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Any deviation of spin polarization from its thermal equilibrium is subject to spin lattice relaxation; therefore the optimization of relaxation processes is an important factor for both producing high levels of polarization and keeping the spins polarized for a time period long enough to perform the desired experiments. One way taken for achieving this goal is to polarize spin isotopes with low gyromagnetic ratio such as <sup>13</sup>C or <sup>15</sup>N that have long intrinsic relaxation times. Another strategy for reducing relaxation is to work at variable levels of the external magnetic field since relaxation is known to be field dependent. This approach is discussed here. The dispersion of longitudinal relaxation with the magnetic field, the NMRD, will be analyzed and the main factors responsible for the field dependence will be discussed in detail. Of particular importance in this respect are so-called long lived states that do not relax under the influence of dipolar interactions. They are of singlet character formed by scalar spin-spin interaction at conditions of strong coupling and thus are dependent on the external magnetic field. Examples of such long-lived states will be shown and their manipulation by field cycling will be demonstrated. Both, maximizing the level of polarization formation and the preservation of hyperpolarization will be shown and compared with the states relaxing in the standard way.

## Fast Field-Cycling Magnetic Resonance Imaging

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While relaxometry of small samples using FFC has been used for several decades, the combination of FFC with magnetic resonance imaging (MRI) remains relatively uncommon, but has been increasing in recent years [1].

One application is in imaging free radicals using Field-Cycled Proton-Electron Double-Resonance Imaging (FC-PEDRI). This uses the Overhauser effect: irradiation of the free radical's ESR causes a transfer of polarisation from electron spins to coupled nuclear spins, resulting in a change in image intensity. Field-cycling allows the ESR irradiation to be applied at low field (hence relatively low frequency, and low non-resonant absorption), while NMR signal detection and imaging is carried out at higher field, to preserve SNR. We have constructed two FC-PEDRI scanners, both of which can also be used for FFC-MRI [2,3].

Relaxometric MRI is the imaging equivalent of field-cycling relaxometry. The aim is to obtain spatially-resolved  $T_1$ -dispersion data, by collecting images at a variety of evolution field strengths [1,4,5,6]. We have recently demonstrated methods for implementing relaxometry on localised regions defined from a pilot image [7]. We have also shown that FFC relaxometry can detect the formation of cross-linked fibrin protein from fibrinogen *in vitro*, in a model of the blood clotting process [1,8,9]. This relies on  $^{14}\text{N}$ - $^1\text{H}$  cross-relaxation phenomena, also known as "quadrupole dips" in the  $T_1$ -dispersion plot [10]. These reductions in  $T_1$ , occurring at Larmor frequencies equal to the  $^{14}\text{N}$  nuclear quadrupole resonances, reveal information about the concentration and conformation of immobilised protein molecules. In other recent work we have demonstrated that FFC-MRI can be used with tailored contrast agents which exhibit significantly different relaxivity over the range of field strengths accessible to an FFC-MRI scanner; in this way, the sensitivity of the experiment can be enhanced [11]. Another application of FFC is to study the phenomenon of magnetisation transfer contrast (MTC) as a function of magnetic field at low field [12,13].

In summary, developments in FFC-MRI have demonstrated this technique's ability to extract extra information that is not obtainable from conventional, fixed-field techniques. In addition to biomedical applications, field-cycling magnetic resonance may have applications in the characterisation and monitoring of industrial processes, for example in the preparation of foodstuffs.

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## SQUID-Based NMR and MRI in Microtesla Fields

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Nuclear magnetic resonance (NMR) systems operate at magnetic fields up to 23 T and clinical magnetic resonance imaging (MRI) machines operate typically at 1.5 T. There is increasing interest, however, in NMR and MRI systems that operate in microtesla fields, using a Superconducting Quantum Interference Device (SQUID) to detect the NMR signal. Such systems are lower in weight and cost than conventional high-field machines, require only modest homogeneity in the imaging field, are insensitive to variations in the magnetic susceptibility of the specimen being imaged, and have an enhanced contrast in the longitudinal relaxation time  $T_1$  for different tissue types. The decrease in the polarization of the nuclear spins and hence in the NMR signal amplitude due to the low field is compensated partly by the frequency-independent sensitivity of SQUID-detection and partly by prepolarization of the spins in a field much higher than the imaging field.

Early NMR experiments confirmed that 1-Hz linewidths in liquids were readily achievable, even with relatively inhomogeneous magnetic fields. Linewidths of 0.034 Hz in the spectrum of benzene obtained in the Earth's field and of 0.34 Hz in the spectrum of J-coupled nuclei in 2,2,2-trifluoroethanol phosphate have been demonstrated.

Our current MRI machine operates at 132  $\mu\text{T}$ , corresponding to a proton frequency of 5.2 kHz. The system is constructed from wood and copper-wire coils. The SQUID-based gradiometer has a noise level of 0.5 fTHz<sup>-1/2</sup>. Images show an in-plane spatial resolution of about 1 mm for phantoms and 2 mm for *in vivo* images of the arm. Measurements of  $T_1$  in phantoms containing different concentrations of agarose gel in water show a much higher contrast at microtesla fields than at fields even as low as a few millitesla. Measurements on surgically removed prostate tissue show that the value of  $T_1$  in healthy tissue is typically 50% higher than in cancerous tissue. Provided similar values are found for *in vivo* tissue, microtesla MRI has the potential to image prostate cancer and possibly other kinds of cancer using  $T_1$ -weighted contrast imaging. Challenges and future prospects are discussed.

This research was in collaboration with Sarah Busch, Erwin Hahn, Michael Hatridge, Nathan Kelso, SeungKyun Lee, Robert McDermott, Michael Mössle, Michael Mück, Whit Myers, Alex Pines, Paul SanGiorgio, Dan Slichter, Bennie ten Haken and Andreas Trabesinger, and supported by the Department of Energy, Basic Energy Sciences and the National Institutes of Health.

**Magnetic Resonance Relaxometry at low and ultra low fields**

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Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) are ubiquitous tools in science and medicine. NMR provides powerful probes of local and macromolecular chemical structure and dynamics. Recently it has become possible and practical to perform MR at very low fields (from  $\mu\text{T}$  to mT), the so-called ultra-low field (ULF) regime. Pulsed pre-polarizing fields greatly enhance the signal strength and allow unprecedented flexibility in signal acquisition sequences. Improvements in SQUID sensor technology allow ultra-sensitive detection in a pulsed field environment.

In this regime the proton Larmor frequencies (1 Hz – 100 kHz) of ULF MR overlap (on a time scale of 10  $\mu\text{s}$  to 100 ms) with “slow” molecular dynamic processes such as diffusion, intramolecular motion, chemical reactions, and biological processes such as protein folding, catalysis and ligand binding. The frequency dependence of relaxation at ultra-low fields may provide a probe for biomolecular dynamics on the millisecond timescale (protein folding and aggregation, conformational motions of enzymes, binding and structural fluctuations of coupled domains in allosteric mechanisms) relevant to host-pathogen interactions, biofuels, and biomediation. Also this resonance-enhanced coupling at ULF can greatly enhance contrast in medical applications of ULF-MRI resulting in better diagnostic techniques.

We have developed a number of instruments and techniques to study relaxation vs. frequency at ULF regime. Details of the techniques and results are presented.

Ultra-low field methods are already being applied at LANL in brain imaging, and detection of liquid explosives at airports. However, the potential power of ultra-low field MR remains to be fully exploited.

## Portable Earth Field Imager and field-cycling activities

Steffen Lothar, Uvo Hölscher, Peter M. Jakob and Florian Fidler

An overview will be given about current development of portable NMR instrumentation, earth field and field cycling activities at our research center.

We developed a portable broadband control unit based on state-of-the-art digital and analog circuitry working from DC up to 60 MHz. Due to its digital nature, this unit allows real-time interactions and therefore can perform earth-field NMR detection as well as field-cycling or high field experiments. It contains a broadband transmit and receive channel and 4 gradient channels for imaging, arbitrarily expandable.

Prepolarized Earth Field NMR (EFNMR) enhances the magnetization to measurable values, as shown by Packard and Varian [1], while conserving the advantage of the homogeneous magnetic field. In this talk a portable EFNMR Imager developed by Steffen Lothar is presented. Prepolarization with a field strength of 80 mT is ramped with a novel field cycling control circuit to minimize ramp time for both adiabatic and non-adiabatic field ramps [2,3]. First results of this setup will be presented.

A detailed presentation of combining fast field-cycling and magnetic resonance imaging will be given in a separate talk by Uvo Hölscher.

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## Development of field-cycling Overhauser enhanced MRI with sample-transport device

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Modification of In vivo redox status are involved in mechanisms of oxidative diseases. The redox imaging technique is important to diagnose redox-induced diseases and to access cure effects of pharmaceutical drugs. Redox contrast reagents widely used are aminoxyl radicals which can be measured using magnetic resonance technique.

Overhauser enhanced MRI (OMRI) is a new technique for imaging free radicals in animals based on the Overhauser effect [1,2]. The large magnetic moment of electron is utilized to enhance proton NMR signal. The detection process is the same as that in MRI and the high resolution of MRI can be utilized in free radical imaging. ESR excitation field is restricted at 5 to 40 mT for biological applications due to the large gyromagnetic ratio of electron spin. Previous studies reported that Field-cycling technique is useful in OMRI or MRI detection process [1,3].

To further enhance MR detection sensitivities, we have developed prototypes of Field-cycling OMRI scanner with sample-transport device, in which the sample object was transported between ESR to MR magnets, to achieve field cycling. The OMRI scanner consisted of two resistive magnets, which were operated at 1.5 T and 20 mT for MR detection and ESR excitation, respectively. The physical resolution of the OMRI image for the phantom object was less than 0.2 mm, indicating that the OMRI with transport-system would be useful for imaging redox reaction at high MR detection field. The developed OMRI system would have a significant advantage for imaging in vivo redox status.

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## **Delta Relaxation Enhanced MRI: Overview and Current Challenges**

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Molecular imaging is the visualization of specific biological, cellular or molecular processes for treatment planning and monitoring of therapeutic efficacy. A common molecular imaging modality is positron emission tomography (PET), which achieves sufficient sensitivity to detect minute signals, but is hampered by poor spatial resolution. Magnetic Resonance Imaging (MRI) generates excellent spatial resolution and tissue contrast; however, MRI suffers from poor sensitivity to targeted contrast agents, and is limited by poor detectability of these molecules or cells because of inherent interference from high physiological background signals. The development of MRI technologies that enable true MR molecular imaging becomes pertinent, with one goal being to more closely mimic the PET imaging paradigm (high sensitivity, low background) without sacrificing the spatial resolution advantages of MRI. Delta relaxation enhanced MRI (dreMR) aims to produce a major breakthrough in MR molecular imaging.

MR image intensities are typically enhanced by the local concentration of contrast agents, and the longitudinal relaxivity ( $r_1$ ) is common measure of an agent's ability to provide contrast enhancement. A subset of contrast agents is capable of reporting the presence of a target molecule. An example is the MS-325 (Bayer Schering Pharma AG; Tradename: Vasovist or Ablavar) which binds to plasma albumin non-covalently. Not only does the  $r_1$  of albumin-bound MS-325 increase approximately fourfold at 1.5T, it becomes a strong function of the imaging field, exhibiting a peak at  $\sim 0.7T$  and rolling off steeply up to  $\sim 2T$ . Therefore, the imaging field becomes an additional dimension to probe the presence of the agents. The decreased tumbling rate of the macromolecule is largely responsible for the dispersion behavior, given that fast tumbling small molecular agents have virtually field-independent  $r_1$ . dreMR exploits this understanding about  $r_1$  dispersion of contrast agents and involves the implementation of a form of field-cycled MRI, in combination with the use of either "conventional"  $r_1$  dispersive contrast agents such as MS325, or newer "smart" contrast agents that become dispersive upon recognition of a specific molecular or cellular target. By cycling the magnetic field along the steep dispersion slope and collecting data that have been sensitized to  $r_1$  relaxation at two or more field strengths, this method generates images that are proportional to the  $r_1$  dispersion, or the change in relaxation rate with magnetic field, hence the term "delta relaxation enhanced MRI" or dreMR.

dreMR can be implemented with a  $B_0$ -cycling magnet that must provide both sufficient imaging volume and homogeneity. The insertion of a field cycling magnet into a MRI system is a cost-effective alternative that leverages the homogeneous main field, gradient coils and standard interface of conventional scanners. This method faces unique challenges. The imaging bore of typically 60cm places an upper limit on the size of the insertable magnet. The dreMR magnet typically comprises a solenoidal coil which defines an imaging volume, must be cooled by liquid coolant, and must be mechanically housed and stabilized. Active-shielding windings can be optionally used to suppress stray field and coupling to the main magnet of the MRI system. Possible strong torques due to inhomogeneous main field requires sturdy construction, while low resistance placing a lower limit on wire cross section, and power dissipation of up to tens of kW are design parameters to be addressed. A few magnet designs have recently emerged (Alford et al. 2011; Hoelscher et al. 2011), differing in imaging volume and electrical characteristics.

An important design decision is whether to include active shielding as part of the magnet design. The shield serves to reduce fringe fields that couple onto conductive structures within the superconducting main magnet. The coupled field introduces eddy currents that cause a transient shift in the  $B_0$  field of

the scanner that decays with time constants of typically tens of milliseconds. Constant frequency shifts result in translation of images in the frequency encoding direction, and transient shifts produces 'smearing'. We have recently begun to study whether active shielding sufficiently reduces eddy current effects to justify the real estate taken by reverse windings. An alternative to active shielding is to design a much smaller primary magnet, which reduces coupling to the MRI magnet, and to further compensate for eddy current effects by using waveform pre-emphasis or receiver modulation, similar to what is typically used in MRI gradient driver systems (Jehenson et al. 1990; Crozier et al. 1992). We have made initial steps toward the design, construction and initial characterization of such a small, unshielded, high-efficiency dreMR magnet.

Eddy current induced image artifacts are likely to remain a key hurdle to overcome for the dreMR method. In this paper, we present an update on dreMR theory and technology, with a focus on challenges for the effective implementation of dreMR.

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## Combining Fast Field-Cycling and Magnetic Resonance Imaging

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**Introduction:** Conventional magnetic resonance imaging (MRI) gives access to the parameters  $T_1$ ,  $T_2$ ,  $T_2^*$  and spin density. Combining MRI with fast field-cycling (FFC) expands the group of accessible parameters by relaxivity dispersion ( $dR_1/dB$ ) and therefore can serve as new source of image contrast. It gives insight into local molecular behavior in the sample. Relaxivity dispersion can be used for solving new imaging challenges. Among them are localization and quantification of contrast agents and better image contrast for certain diseases [1,2]. In general FFC MRI provides a whole new field for MR applications of which only few have been investigated so far. Both hardware and methods are still in development.

**Methods:** FFC MRI requires solving some important technical design issues. Many problems arise from the coupling between imaging scanner and FFC coil. The coupling can cause a quench of the superconducting magnet and induces eddy currents in the scanner cold bore. Therefore precise active shielding needs to confine the magnetic flux of the FFC coil to the space within the scanner bore. Usually an additional method is necessary to compensate for remaining  $B_0$  eddy current fields. This can be achieved by either current waveform preemphasis or by dynamic adjustment of the scanner radio frequency (RF) minimizing frequency offsets between scanner hardware and spin system.

A second very important consideration are imaging sequences and data processing. Relaxivity dispersion effects usually occur as small changes on top of comparably large signals. Therefore FFC MRI requires stable sequences and an elaborate reconstruction algorithm. Furthermore interleaved image acquisition from various FFC fields is important to reduce systematic errors due to long term drifts.

**Results:** A FFC MRI setup has been realized with a 60cm bore clinical 1.5T scanner (compare Fig. 1) and a homebuilt 90mT FFC coil (compare Fig. 2). Its imaging region is large enough for mouse imaging. The coil is actively shielded by a set of counter windings which reduce fringe fields by a factor of  $>35$  at the scanner bore in comparison to an unshielded coil. Remaining eddy current fields are compensated within 5Hz by dynamic adjustment of the scanner RF frequency. This method proves to be easier and more precise than waveform preemphasis.

A reconstruction algorithm has been implemented to separate relaxivity dispersion contributions from other signals. Spin echo and multi-spin echo sequences have been developed for image acquisition and prove to be robust. The sequences allow acquiring images with a relaxivity dispersion weighted contrast. From multiple measurements relaxivity dispersion maps can be calculated.

**Conclusion:** It is possible to set up a FFC MRI experiment with reasonable imaging region size inside a clinical 1.5T scanner. Relaxivity dispersion weighted images or relaxivity dispersion maps can be calculated from the images. Artifacts in the images arising from eddy currents and sequence design can be kept small enough to not degrade resulting image quality.

**Acknowledgements:** This work was performed with support from the BMBF under Award No 01EZ0816 and support from the BayStMWIVT and SIEMENS, Healthcare Sector, Erlangen, Germany.

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Fig. 1: Image of the FFC coil inside the 1.5T clinical scanner.



Fig. 2: Image of the 90mT FFC coil with cooling pipes. The outermost windings are the active shielding coil, the actual field coil is not visible.

## FFC Relaxometric Investigations of paramagnetic liposomes

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The limited sensitivity of MRI probes prompts the use of nanosized systems containing a high number of paramagnetic complexes [1,2]. Among several possibilities, liposomes are under intense scrutiny because of the easiness of their preparation and because they have already entered the clinical applications as drug delivery carriers.

Paramagnetic metal complexes can be loaded into liposomes either through their inclusion in the inner aqueous cavity or through the incorporation in the lipidic bilayer. The use of amphiphilic metal complexes that are incorporated into the liposome's membrane endows the nanosystem with field dependent relaxation enhancement properties. This property has been exploited for the design of FFC-MRI agents. According to the formulation of the phospholipid composition and the incorporation extent of the amphiphilic paramagnetic complex, the water permeability of the liposome's membrane can be properly modulated in order to tackle specific application.

One important task deals with the possibility of exploiting the field dependence relaxivity of a novel class of FFC-MRI contrast agents.

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## Use of an insert coil and surface RF coil for *in vivo* whole-body relaxometry

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In conventional biomedical MR applications, the relaxation behaviour of tissue is of central importance in determining a diagnosis. Field-cycling, with its ability to manipulate the main magnetic field strength during an examination, allows the study of  $T_1$  dispersion in the body and will expose new sources of endogenous information. However, the availability of instruments capable of field-cycling on a human-sized scale is limited to a handful of home-built systems world-wide [1, 2]. A new approach is that of the ‘insert coil’ [3]: a removable electromagnetic field offset coil that can be installed in a conventional imager. In this work, we present the integration and use of such a coil, capable of *in vivo* relaxometry.

The coil was designed to suit an existing imager: a whole-body sized 59 mT ferrite permanent magnet with vertical field orientation. Built by Tesla Engineering Ltd (West Sussex, UK), our insert coil is portable and easily installed in the imager by one person in around 15 minutes. The disc shaped coil generates a projected homogeneous region (56 mT +/- 5% over a 50 mm DSV) located 50 mm from its front face, which offsets the main magnetic field of the imager. In this way, a small volume under investigation can be exposed to magnetic field strengths between 3 and 115 mT. Ramp times are less than 10 ms (0-100%) and the current is provided by a gradient amplifier and high-voltage DC power supplies [4].

After initial experiments with a solenoidal RF coil, it was decided that a surface RF coil placed in the same plane as the insert coil would allow more flexible geometry. A butterfly RF coil was built ( $N=10$ ,  $Q=116$ ) and used with an interleaved saturation-recovery / inversion-recovery pulse sequence (described in [4]) to measure the  $T_1$  of a localised volume marked on a pilot image. With a volunteer’s forearm placed over the homogenous region, a dispersion curve of  $T_1$  versus magnetic field strength was measured. Quadrupole dips were observed where the  $^{14}\text{N}$  and  $^1\text{H}$  NMR frequencies are coincident – attributed to the presence of immobilised protein.

In summary, a compact and portable insert coil was used to vary the field over a localised region inside a whole-body sized imager. Together with a surface RF coil and localised  $T_1$  relaxometry pulse sequence, it is possible to study  $T_1$  dispersion *in vivo*. One concern is the noise coupled into the signal path via the current supply, which we intend to address in future work.

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## Clinical applications of FFC MRI

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Field-cycling NMR allows the detection of  $^{14}\text{N}$  quadrupolar cross-relaxation effect in biological tissues [1]. This allows detecting variations in protein contents, with applications in various fields of medicine. This presentation will focus on three projects established in collaboration with clinicians and medical research groups at the University of Aberdeen that aimed to use quadrupolar detection by FFC MRI for the detection of variations of protein contents.

A preliminary validation was conducted using FFC-NMR relaxometry on the fibrinogen/fibrin (blood clotting) system *in vitro*. We have measured the amplitude of the quadrupolar peaks at different fibrin concentrations and have shown that the peak amplitude increases linearly with fibrin concentration, as expected. It was also shown that soluble and thus mobile fibrinogen did not exhibit a quadrupolar signal.

FFC-MRI experiments have been conducted using a modified PRESS sequence [2] on two groups of volunteers to detect the quadrupolar relaxation *in vivo* following two types of exercises aimed to create oedema or Delayed Onset Muscle Soreness (DOMS). The results show differences in the evolution of the quadrupolar peaks between the two groups, suggesting the possibility to detect muscle damage independently from the formation of oedema.

FFC NMR experiments on osteoarthritic cartilages have also revealed large diminutions of the quadrupolar peaks amplitude between healthy and diseased samples, which correlate with the values of GAG protein contents taken from the literature. This may be a quantitative measurement of GAG content, which could lead to early and quantitative detection of OA.

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## RHEO-FFC AS A TOOL TO INVESTIGATE SLOW MOLECULAR DYNAMICS UNDER SHEAR

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Shear of polymer melts is one of several possibilities to affect equilibrium conformation and dynamics of the macromolecules. While a partial alignment relative to the shear forces is straightforward to predict, the precise extent of this alignment, and its influence on the dynamics on a molecular length and time scale, has been discussed only for very few selected systems [1]. High shear rates may lead to order which can be detected with appropriate multipulse techniques; at the same time, dipolar interactions between nuclei will also be affected by a change of the immediate environment. This must lead to a variation of relaxation rates, either by affecting the distribution function of reorientation modes from their equilibrium shape, or by changing the relative weight of intra- and intermolecular contributions with their respective frequency dependencies. Dynamic deformation can be considered as an extension of static deformation where the abovementioned phenomena have already been observed [2,3], but its application is limited to crosslinked elastomers. Most deformation experiments demonstrate that the influence on relaxation times at high magnetic fields is minor [4], but it can be expected that low-field relaxation parameters, probing much slower ranges of molecular dynamics, are more susceptible to macroscopic deformation of polymer melts.

The design of a shear cell to be introduced into a commercial field cycling relaxometer faces a number of limitations considering space and signal quality. In this contribution we present the design of a prototype rheo-FFC unit, suggest possible applications of the technique which can be combined by other low-field and high-field rheo-NMR cells, and show first results of relaxation investigations which demonstrate that molecular dynamics of high molecular weight polymers are indeed affected by relatively small and experimentally accessible shear rates.

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## Dynamics in Solid Polyethylene Studied by NMR Spin Lattice 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].

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

The frequency dependence of  $T_1$  was observed in the range between 5 kHz and 30 MHz with the aid of a field-cycling NMR relaxometer [2] from Stelar S.R.L. (Italy).

The temperature dependence of the  $T_1$  dispersions for the different samples is examined. These dispersions have stronger temperature dependence in the low density sample due to the presence of short side chains (branchings) in the amorphous phase than in the case of the more crystalline PE. 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].

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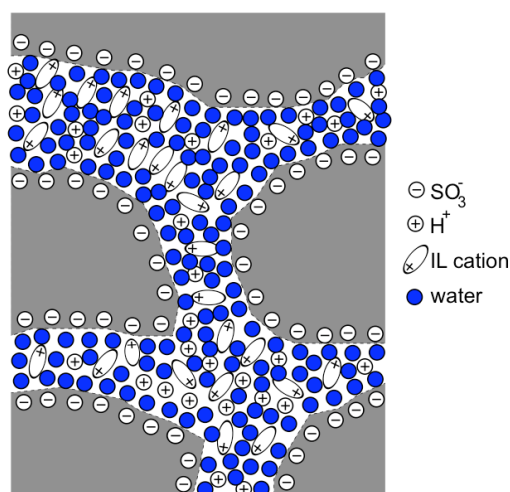
## Proton NMR Relaxometry Study of Nafion Membranes Modified with Ionic Liquid Cations

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Proton nuclear magnetic resonance (NMR) relaxometry was used to study the ionic mobility and levels of confinement within Nafion membranes modified by incorporation of selected ionic liquid (IL) cations.<sup>1-2</sup> These studies were performed aiming at understanding the effect of using different types of ionic liquid cations, and their degree of incorporation, in the values of the spin-lattice relaxation times ( $T_1$ ) obtained at different values of frequency and thus detect the influence of confinement level on the ions mobility. The frequency dependence of the proton spin-lattice relaxation rate,  $R_1 = 1/T_1$ , for the modified Nafion/IL cation membranes was compared with those obtained for an unmodified Nafion membrane and for a pure IL, allowing for distinguishing different contributions of the motions of the molecules depending on the frequency tested. The experimental  $R_1$  results were analysed in terms of models that consider the sum of the most effective relaxation contributions,<sup>3-5</sup> in order to estimate the translational self-diffusion coefficient of the moving molecular species in the modified membranes. The stability of these membranes with temperature in terms of the spin-lattice relaxation was compared with results obtained by thermogravimetric analysis.<sup>6</sup>



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## **NMRD Profiles of Particulate Reporters for Magnetic Resonance Molecular Imaging. Does the coating matters ?**

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In the early days of the MRI technique, paramagnetic ions have been proposed as contrast agents to enhance the diagnostic quality of the images.

Since then, academic and industrial efforts have been devoted to the development of new and more efficient molecular, supramolecular and nanoparticulate systems.

Old concepts and theories, like paramagnetic relaxation, were revisited and exploited, leading to new scientific tracks.

With their high relaxivity payload, the nanoparticles are very appealing in the context of molecular imaging but challenges and questions are still numerous: structure/relaxivity relationship, absence of toxicity, specificity, ability to cross the biological barriers...

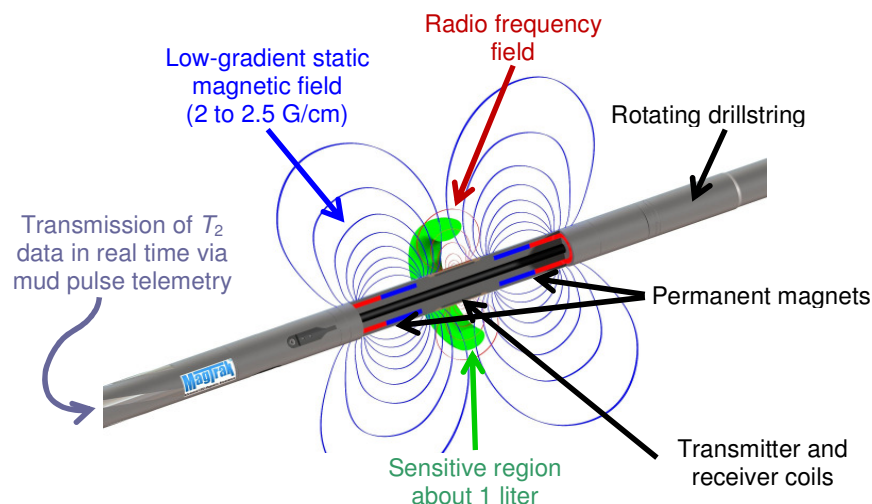
In this talk we will tackle the issue of the influence of the coating of the magnetic crystals on their relaxivity, a point of major importance for the applications of magnetic particles in the context of magnetic resonance molecular imaging.

## From the early days of FFC to NMR while drilling oil and gas wells

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When I started my diploma thesis in 1980 at the “Sektion Kernresonanzspektroskopie” of Prof. Rainer Kimmich at the University of Ulm, Germany, fast field cycling (FFC) was still quite exotic and stayed so for many years. Exotic, because whoever wanted to perform field cycling experiments in those early days had to construct the experimental setup by himself. Actually, this was exactly the reason I started to work with Prof. Kimmich’s group; I was more interested in the challenges of FFC than in the NMR results. The switching of high-power magnets fascinated me and consequentially I continued by constructing a more powerful, faster-switching FFC machine at the Max Planck Institute (MPI) for Metals Research in Stuttgart, Germany, as part of obtaining my PhD. The original object of my research at the MPI was the migration of diluted hydrogen atoms in Niobium metal at low temperature, detected by FFC and nuclear quadrupole double resonance (NQDR). I was not able to accomplish this. This was not the fault of my FFC machine, which I proved by successfully detecting low-concentration impurities of palladium in copper foils by NQDR. After that experience I joined for my post-doctoral fellowship the NQR laboratory of Prof. J.A.S. Smith at King’s College London and constructed yet another, again more powerful, FFC machine, switching a 1 T magnet with a 35 mm usable bore and a magnetic field inhomogeneity of 6 parts in  $10^5$  within 0.7 ms (M. Blanz, T.J. Rayner and J.A.S. Smith, Meas. Sci. Technol. 4 (1993) 48-59).

Eleven years ago I turned to a new, exciting and challenging application of NMR: oil and gas well logging while drilling. In my presentation I will show how to record high-quality NMR data while drilling, which has now become a routine measurement for the oil industry. Perhaps surprising for many people, NMR while drilling can often gather higher-quality data than those obtained by wireline NMR, despite many obstacles like lack of space for the NMR apparatus, vibrations and high temperatures (up to 150°C). I will explain how some of these obstacles have been overcome and show example NMR logs (i.e., NMR measurements versus depth) and their interpretation.



## Characterizing the $\alpha$ -relaxation with relaxometry and mixed echo decays

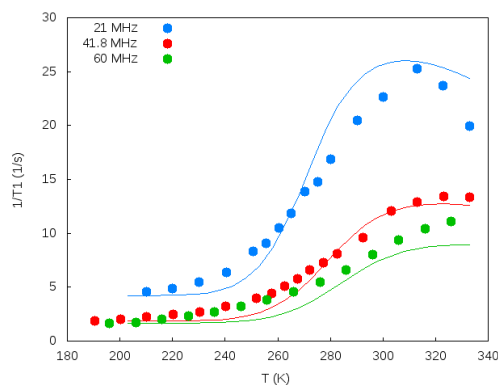
Simone Sturniolo - Università degli Studi di Pavia  
 Kay Saalwächter - Martin Luther Universität Halle-Wittenberg

A series of simple  $^1\text{H}$  NMR relaxation measurements, without use of Magic Angle Spinning, have been performed at fields ranging from 0.5 to 1.5 T on a sample of industrial Nitrile Butadiene Rubber (NBR) in a temperature range going from 203 K to 333 K, covering the whole glass transition of the material (whose  $T_g$  is around 253 K). The various evidences of the transition are classified, assessed and discussed.

Free Induction Decay (FID) shape and parameters, such as characteristic relaxation times and stretching exponentials, are studied, as well as spin-lattice relaxation times. Each parameter shows evidence of the  $\alpha$ -relaxation process crossing its characteristic timescale of sensitivity. A special attention is dedicated to the use of a mixed Magic Sandwich-Hahn Echo sequence, which is employed both as a mean of reconstructing the FID at short times, avoiding the loss of data due to instrumental dead times, and as a probe for the dynamics.

It is well known how the reconstruction of this kind of echo partially fails in presence of molecular motions on time scales comparable to the inverse of the duration of the pulses which compose the sequence itself. This effect here is systematically assessed and combined with both computer simulations performed with the software SPINEVOLUTION (M. Veshtort and R. G. Griffin, 2006) and a theoretical model following the trails of the Anderson-Weiss treatment in order to get a consistent estimate of a VFT law controlling the temperature dependence of the central relaxation time of the  $\alpha$ -relaxation process. The dynamic heterogeneity of the process (approximated with an Havriliak-Negami distribution, in analogy with the fittings used in other techniques such as broadband dielectric spectroscopy) has been assessed as well through simulation of spin-lattice relaxation times and their comparison with experimental values - respectively, the curves and the dots in fig.1.

It must be stressed how all the measurements in this work have been performed with use of basic NMR equipment, and how the results can be addressed as 'software-intensive' ones, since they mostly depend on an apt use of pulse sequences, fittings and simulations. If perfected, this kind of approach is believed to be the best one to get meaningful results in the field of polymer science and glass transition characterization with relatively low-end hardware such as the one which many chemical or material science labs can have at their disposition.



**Fig.1** - Simulated vs. experimental T1 data

## Field cycling NMR at low frequency bands

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Among others, prepolarization and field-cycling solutions were used to tackle the well known limitations related to signal to noise ratio at low fields. We can distinguish between three different situations: experiments at a low fixed field, experiments at “supposed” zero field and field-dependent experiments. Optimal hardware solutions for each case strongly depend on the involved relaxation times and the purpose of the experiment. The time dependence of the magnetic field during the switching, the damping time & peak values of transients and the NMR conditions for signal detection are also critical parameters. But, how critical are these parameters for field-cycling experiments? Which parameters are critical for relaxometry experiments within the ULF (ultra low frequency) band? What means doing NMR relaxometry within the ULF or lower frequency bands? Do local fields represent any limitation? How can local fields be quantified? Is this really a must? When is needed a magnetic field compensation? If field-cycling turns too complex, why not ULF experiments in the rotating frame or by multipulse sequences? The aim of the talk is to revise and trigger the discussion about these topics. Some advances will be commented on technical developments in progress related to the discussion.

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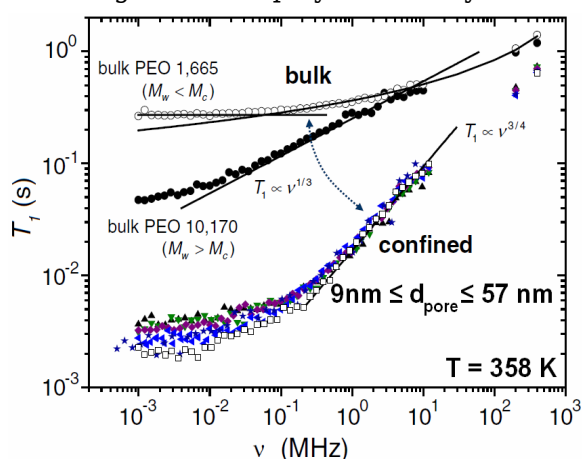
## POSTERS

## Tracing the “Corset-Effect” : Polybutadiene in nanoscopic confinement

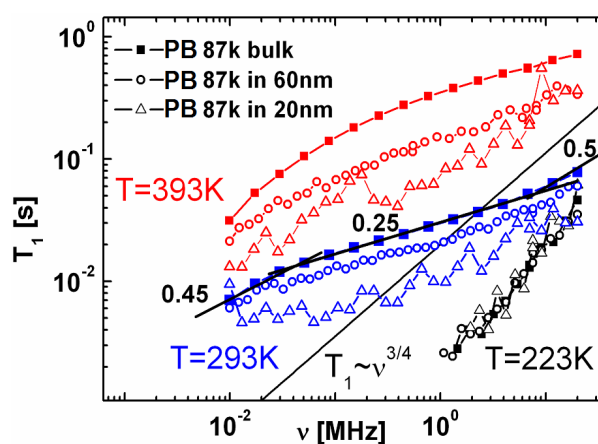
M. Hofmann, D. Kruk, E. A. Rössler

Experimentalphysik II - Universität Bayreuth, D-95440 Bayreuth, Germany

Relying on FFC-NMR relaxometry studies, Kimmich et al. characterized a phenomenon concerning polymer dynamics in nanoscopic confinement termed “corset effect” in 2004 [1]. Accordingly, the spin-lattice relaxation dispersion of bulk polymer melts, which they describe in the frame of the widely accepted Rouse formalism (for  $M < M_e$ ) and re-normalized Rouse formalisms ( $M > M_e$ ), which are competed by the tube/reptation theory, respectively, significantly changes inserted into nanoscopic confinement. Thereafter a transition to reptation dynamics in the sense of de Gennes and Doi/Edwards tube/reptation model (more precisely regime (II)<sub>DE</sub>) occurs (cf. Fig.1) independently of the confinement size and above as well as below the entanglement molecular weight  $M_e$ , even for confinement sizes being much larger than the polymers’ Flory radius.



**Fig. 1 :**  $T_1(\nu)$  of bulk polyethylene oxide PEO and infiltrated in porous methacrylate matrices. The prediction for regime (II)<sub>DE</sub> ( $T_1 \propto \nu^{0.75}$ ) is indicated by the black line. From [1].



**Fig. 2 :**  $T_1(\nu)$  of bulk PB 87kDa and infiltrated porous  $Al_2O_3$  with 20 nm and 60 nm pore diameter. The regime (II)<sub>DE</sub> prediction is again indicated. From [3].

We applied  $^1H$  FFC-NMR relaxometry to polybutadiene (PB,  $M=87$  kg/mol) confined in porous anodic alumina oxide AAO with 20nm and 60nm pore diameter. In contrast to the Kimmich results a transition to (II)<sub>DE</sub> doesn’t occur and the confined samples exhibit essentially the bulk behavior (cf. Fig. 2) besides a systematic decrease in amplitude, which we impute to a decrease in the coupling constant representing the sum over all interspin distances. In bulk, regime (II)<sub>DE</sub> is only expected for highest molecular weights ( $M/M_e \geq 50$ ) as the transition to fully established reptation dynamics is highly protracted [2]. As we can falsify the corset effect in its origin form, we nevertheless found another result which gives rise to a reinterpretation: As the segmental dynamics remains unchanged, the intrinsic friction coefficient increases in confinement [3], so we find confinement effects for  $d_{pore} \gg R_{Flory}$ .

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## Localization and Quantification of Contrast Agents using FFC MRI at 1.5T

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<sup>a</sup>Research Center for Magnetic-Resonance-Bavaria (MRB), Würzburg, Germany

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**Introduction:** Localization and concentration measurements of MR contrast agents are highly desired in clinical MRI. Conventional imaging methods use  $T_1$  or  $T_2$  weighted sequences to acquire images with a high contrast ratio between tissue with and without contrast agent. However this information usually is not unambiguous and can suffer from imaging errors. FFC MRI offers to measure relaxivity dispersion ( $dR_1/dB$ ) weighted images or even relaxivity dispersion maps. For tissue with intrinsic low and contrast agents with high relaxivity dispersion FFC MRI therefore can improve the contrast ratio between tissue and contrast agent significantly.

**Methods:** We employed a contrast agent with high relaxivity dispersion at 1.5T: Gadofluorine M. The FFC MRI setup was realized by an offset coil inserted into a 1.5T clinical scanner to cycle its  $B_0$  field by  $\pm 90$ mT. The sequence comprises a saturation pulse followed by the field-cycling with duration  $T_{evol}$  and finally an imaging module. Specially processed subtraction of two images [1] (one with in- and one with decreased  $B_0$  field) yields an image with  $dR_1/dB$ -contrast. Tissue without contrast agent does not change its relaxivity significantly, hence signal vanishes after subtraction. Tissue with contrast agent changes its relaxivity and shows signal in the processed image.

FFC MRI images were acquired from a raspberry in which Gadofluorine M was injected into some compartments of the berry. The spot is marked in a conventional  $T_1$  weighted image in Fig. 1 (A); the FFC MRI image is shown in Fig. 1 (B).

Additionally quantitative concentration measurements were carried out with a phantom containing three different concentrations of Gadofluorine M. Plotting the FFC MRI signal as function of cycling time  $T_{evol}$  shows a linear fit (displayed in Fig. 2). The slopes of the lines are proportional to the contrast agent concentration.

**Results:** The FFC MRI image of the raspberry shows a contrast between tissue with and without contrast agent which is about one order of magnitude higher than in the conventional image. It serves as mask for regions with contrast agent and can - contrary to the conventional image - be regarded to be unambiguous. From the slopes of the second measurement sample concentrations can be derived in good agreement with known concentrations from sample preparation.

**Conclusion:** We have demonstrated localization and concentration measurements of a contrast agent with FFC MRI. Its signal can be used as mask for regions with contrast agent and can be processed to determine the concentrations of the contrast agent. After having shown a proof of principle we plan to adopt this method to small animal applications.

**Acknowledgements:** This work was performed with support from the BMBF under Award No 01EZ0816 and support from the Bavarian Ministry of Economic Affairs, Infrastructure, Transport and Technology. We thank Philipp Kagerbauer for sample preparation.

**References:** [1] Hoelscher et al., ISMRM Poster #4939, 2010

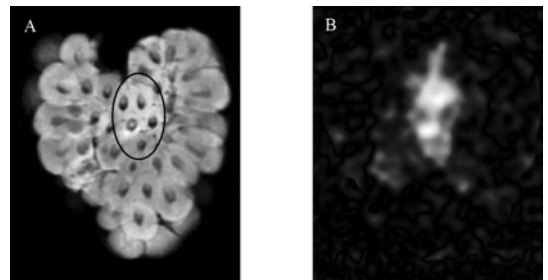


Fig. 1: (A) Conventional,  $T_1$  weighted image of raspberry, region with injection of Gadofluorine M is marked; (B) FFC MRI image showing the location of the contrast agent.

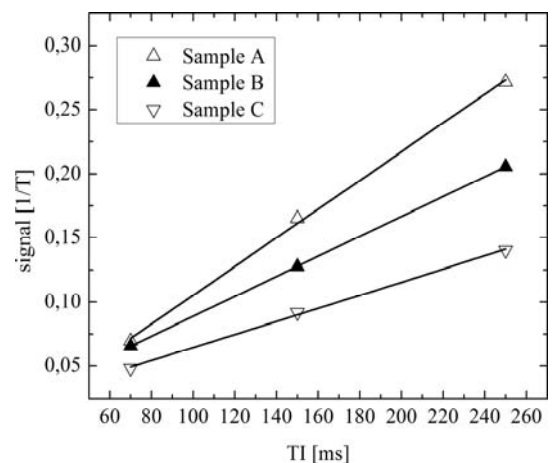


Fig. 2: Intensity from three FFC MRI images with FFC cycling times  $T_{evol}$ =70ms, 150ms and 250ms for three Gadofluorine M samples. The slopes of the lines are proportional to the concentration of the contrast agent.

## Clinical applications of FFC MRI: detection of muscle damage

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Fast Field Cycling (FFC) MRI is a technique that combines field-cycling with imaging, offering new possibilities of image contrast and contrast agents. In particular, it can make use of the  $^{14}\text{N}$  quadrupolar signal to measure changes in protein concentration/hydration *in vivo* [1]. This work reports our findings in using this quadrupolar signal to investigate the detection of oedema and damage in lower leg muscles by FFC MRI.

Two experiments were designed using venous occlusion and eccentric exercise separately in order to create oedema in the first case and muscle damage in the second. In total, 12 volunteers were scanned using a PRESS sequence especially modified for localised FFC relaxometry [2] focusing on the soleus and gastrocnemius regions of the left leg. The data obtained were processed using an adapted model [3] in order to obtain the amplitude of the quadrupolar signal.

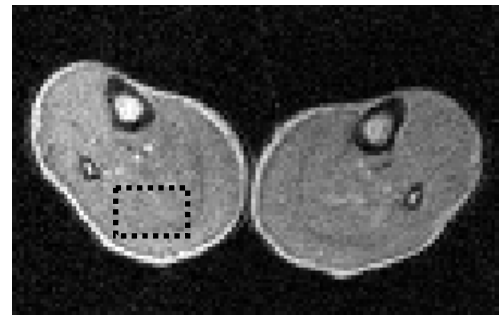


Figure 1: Localised relaxometry in the lower left leg, using field-cycled PRESS and gradient echo images.

The results showed significant changes in quadrupolar signal from oedematous and damaged tissue, but the physiological mechanisms that led to these changes still need to be investigated. This technique may provide a novel way to detect muscle damage non invasively.

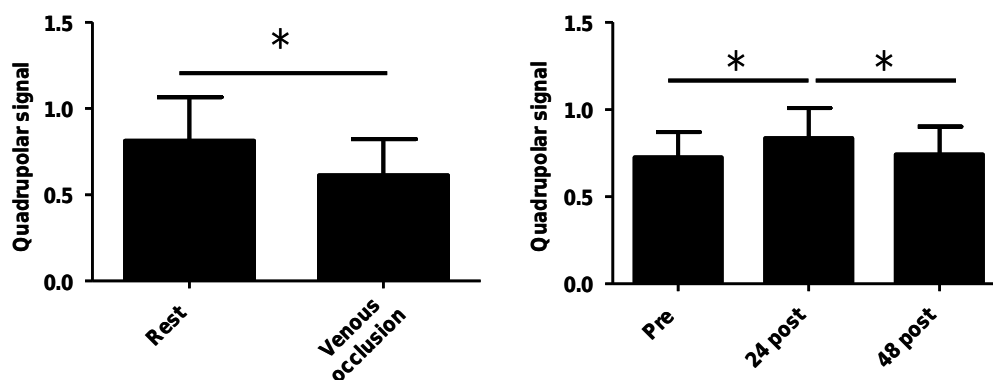


Figure 2: Left: Venous occlusion significantly decreased the quadrupolar signal (t-test,  $p=0.02$ ). Right: Eccentric exercise showed an increase of signal 24 h after exercise compared to pre and 48 h after exercise (ANOVA,  $p=0.01$ ). Quadrupolar signal units are in  $\text{s}^{-1}$ .

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## Fast Field Cycling NMR Relaxometer: Featuring Wines

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One important challenge related with the FFC Nuclear magnetic Resonance is the know-how transfer to the industry and unexplored economic sectors. From a strategic point of view, the wine sector in Portugal has a relevant economic importance. In last decades, the production of wine (from grape growing to bottling) have evolved technologically incorporating new and innovative techniques for analyzing and monitoring the quality of both wine and grapes.

Recent technological developments incorporated in the new FFC NMR relaxometer prototype [1]-[4] made possible to reduce its size, increase the versatility, and efficiency. The overall performance of the new equipment opens the possibility of using FFC NMR for wine characterization in routine analysis.

Preliminary FFC NMR studies of Porto wines, produced by the same vineyards, but with different stages of aging (years 1985, 1997 and 2009) were performed using the new equipment [4]. The results presented in Fig. 1 and Fig. 2 shown that it is possible to distinguish different wines. In fact, as it can be observed in the figures each sample presents distinct longitudinal relaxation times ( $T_1$ )

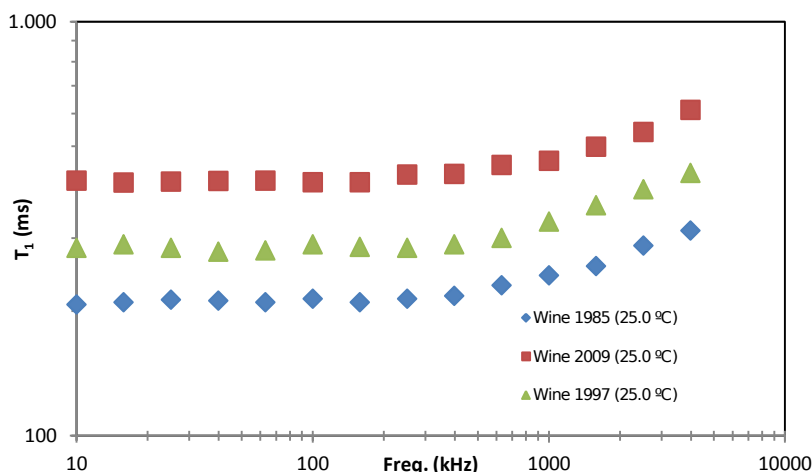


Figure 1 -  $T_1$  measurements at 25° C for wines of different aging.

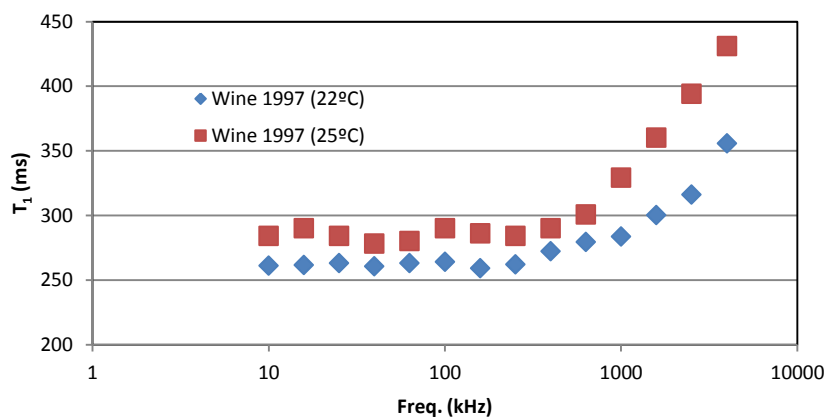


Figure 2 -  $T_1$  measurements at different temperatures (22° C and 25 °C) for the wine produced in the year 1997..

that depend on the frequency and temperature. The obtained results are very promising and clearly confirm the possibility to characterize and identify specific characteristics of different types of wines and eventually grapes by FFC relaxometry.

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[4] D. M. Sousa, G. D. Marques, J. M. Cascais and P. J. Sebastião, *Solid State Nuclear Magnetic Resonance*, Volume 38, Issue 1, Pages 36-43, July 2010

## **T<sub>1</sub>H STUDIES OF *Maytenus ilicifolia* EXTRACTS BY FIELD-CYCLING NMR RELAXOMETRY, INFRARED AND THERMOGRAVIMETRIC ANALYSIS**

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The safe use of herbal medicines requires an authentication process of the raw materials prior to their use. Is an important step, since their ingestion or the ingestion of their extracts can cause serious health problems. Among different analytical techniques, nuclear magnetic resonance (NMR) spectroscopy has the advantage of being non-invasive and therefore used with advantage on the characterization of natural products such as medicinal plants. This work presents a characterization study of the popular plant samples of *Maytenus ilicifolia*, from different commercial producers. This plant is used on the treatment gastrointestinal disorders, and referred to possess antitumorigenic, analgesic, anti-inflammatory, and antioxidant properties. Differences in functional groups detected by infrared (FTIR), Molecular organization investigated using <sup>1</sup>H by fast field cycling (FFC) NMR relaxometry and thermal behavior analyzed by thermogravimetric analysis (TGA) were evaluated in this study. All results confirmed the similarity between the control sample and only one of test plant samples. The differences detected between the samples could be related with the non-authenticity and/or contamination of some of the commercial samples of the plant *Maytenus ilicifolia* investigated.

## Vibrational motions in the solid state investigated by NMR and ab initio methods: effects on $^{13}\text{C}$ chemical shift tensors of Ibuprofen

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Solid State NMR (SSNMR) spectroscopy is one of the most powerful techniques for the study of molecular motions occurring in solid systems over a wide range of frequencies (from Hz to Gz). The so-called large-amplitude motions, such as interconformational jumps,  $\pi$ -flips and internal rotations, can be characterized in detail, determining their frequency and geometry. On the other hand, the effects on SSNMR observables of small-amplitude motions, such as vibrations and librations, due to their much higher frequency are usually quite difficult to be clearly detected and analysed and, indeed, only few studies have been reported in the literature [1]. Recently, by exploiting the measurement and the combined analysis of a variety of spectral and relaxation properties of  $^1\text{H}$  and  $^{13}\text{C}$  nuclei, we could obtain a detailed characterization of all the reorientational and interconformational motions taking place in the acid form of solid Ibuprofen [2]. Thanks to the very slow motion experienced by the phenyl ring ( $\pi$ -flip with characteristic frequency of about 100 Hz at room temperature), we could investigate the vibrational motions of this fragment by exploiting their effects on the  $^{13}\text{C}$  chemical shift tensors ( $\delta$ ).  $^{13}\text{C}$   $\delta$  were both measured through 2D-PASS experiment [3] and calculated, in the absence of motions, through DFT methods [4]. The observed discrepancies between experimental and calculated  $\delta$  could be successfully explained taking into account the out- and in-plane CH bending and a libration of the whole phenyl ring about its para axis. By fitting the experimental  $\delta$  with suitable motional models applied to the calculated tensors, the amplitudes of these motions could be quantified. The very good reproduction of the experimental data clearly showed that this approach represents a relatively simple but very effective method for the identification and characterization of the vibrational motions most affecting  $^{13}\text{C}$  chemical shift tensors. Moreover, given the absence of internal reorientational motions, this represents an ideal case which provides the extent of the contribution of vibrational motions to  $\delta$  which should be taken into account in dynamic studies based on chemical shift tensors.

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## **FAST FIELD CYCLING NMR RELAXOMETRY FOR THE ASSESSMENT OF BIOCHAR QUALITY**

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Biochar is a complex carbon-based mixture produced by heating biomasses in a low or zero oxygen environment. It can be added to soils to either improve soil fertility or reduce release of carbon dioxide to the atmosphere. Biochar properties and, therefore, its effects on soils depend on biomass nature, temperature and time of thermal treatment. For this reason, a full physico-chemical characterization is needed prior to biochar soil application.

The aim of this study was to emphasize the possibility to use FFC NMR relaxometry to characterize biochars obtained from an industrial thermo-chemical process.

FFC NMR offers several advantages over solid state NMR spectroscopy. In fact, as an example, cross polarization magic angle spinning (CPMAS) <sup>13</sup>C NMR is unable to reveal differences among chars due to the poor protonation degree of the char aromatic carbons. Conversely, FFC NMR relaxometry, although sensitive-less as compared to CPMA <sup>13</sup>C NMR, is capable to reveal dynamic of water molecules in porous media, thereby providing information on porous size and distribution of char systems. The present study presents a first evaluation of FFC NMR char properties. These latter are of paramount importance as they can be used to understand how and when biochars can be applied to improve soil quality.

## **THERMAL DEGRADATION OF MICROCRYSTALLINE CELLULOSE IN CONCENTRATED PHOSPHORIC ACID**

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Ethanol is nowadays considered as the most common renewable fuel. It is a liquid produced by fermentation of glucose which is very abundant in cellulose based materials. Bioethanol is achieved in a two-steps process: 1. hydrolysis of the cellulose included in the ligno-cellulosic materials to fermentable reducing sugars; 2. fermentation of such sugars to ethanol. While the second fermentation step, mediated by yeasts or bacteria, is very well established, the first one must be still assessed for process optimization. Many efforts have been made to identify solvents for cellulose in order to develop methods for the achievement of fermentable glucose. In the presence of mineral acid, cellulose undergoes hydrolysis whose extent depends on acid concentration, reaction temperature and duration of treatment. In the last years, dissolution in phosphoric acid (a weak mineral acid, non toxic and safer to use as compared to other inorganic acids) has been increasingly considered as a simple and economic method for cellulose pretreatment before its degradation to glucose. Up to now, it has not been reported yet cellulose conversion to glucose in  $H_3PO_4$  solutions. Aim of the present study was to evaluate kinetic of glucose formation during cellulose degradation by using 85% phosphoric acid. It was investigated the role of residence time on the efficiency of glucose release during the hydrolysis of microcrystalline- cellulose in  $H_3PO_4$  at the constant reaction temperature of 80°C. Moreover, High field NMR measurements showed that heating treatment is fundamental to have conversion of cellulose in glucose with formation of same degradation products, how supported by GC MS analysis results.

In addition, relaxometry measurements have been carried out to observe how thermal treatment may change the relaxation time distribution of cellulose acid solutions. In particular, relaxometry results showed that, the  $T_1$  distribution of the complex mixture obtained from cellulose degradation was similar to that of the pure phosphoric acid. This study suggests that simple relaxometry monitoring can be applied to check the degradation degree of cellulose in phosphoric acid.

## **DYNAMICS OF DIFFERENT TYPES OF MILK BY FAST FIELD CYCLING NMR RELAXOMETRY**

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Natural milk is a complex mixture of colloidal and dissolved proteins, dispersed fat aggregates, phospholipids, lactose, and inorganic salts. The presence of different molecules as well as their amounts determines the physico-chemical properties of the whole milk. The quality of milk is conventionally evaluated mainly considering its viscosity, density, surface tension, diffraction index and other analytical parameters.

Large amounts of milk, each day, leave the farms and reach the dairy factories. Because of the precisely controlled production conditions, there are no worries about the possible presence of residues of pesticides, antibiotics and other unwanted chemicals. Scarce is however the knowledge about dynamics of molecules and molecular aggregates inside milk. Such knowledge has a relevant value for the assessment of milk quality or, even, for possible damages resulting from routine industrial practices.

In the present study, a Stellar Fast Field Cycling NMR (FFC-NMR) equipment has been used for water molecular dynamics evaluation in milk. The technique allowed investigation and characterization of different commercial milks. The NMRD profiles were used to obtain a medium correlation time ( $\tau$ ) for each sample. Data from this preliminary study suggest the possible use of correlation times as new analytical parameters to investigate milk quality by largely reducing current sample preparation efforts which are time consuming and labor intensive.

## **ASSESSING SOIL ORGANIC MATTER EVOLUTION IN SUSTAINABLE AGRICULTURE BY FAST FIELD CYCLING NMR RELAXOMETRY**

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Intensive agricultural practices decrease soil fertility, due to crop systems based on monoculture, continuous tillage, and excessive use of pesticides and mineral fertilizers. One of the most worrying aspects of intensive agriculture is the gradual loss of organic matter (OM). In fact, decline of OM content in many agricultural soils is the major cause for soil degradation. Organic amendment is generally considered as a key factor for soil health and sustainable agriculture, particularly in terms of maintaining the amount and quality of soil OM.

Structural and conformational OM characteristics can be analysed by high field (HF) nuclear magnetic resonance (NMR) spectroscopy either in the solid or in the liquid state. In both cases, information on the chemical nature of OM can be achieved. Conversely, Fast Field Cycling (FFC) NMR relaxometry allows a fast investigation of the conformational and dynamic properties of whole complex molecular systems through measurement of longitudinal or spin-lattice relaxation rates ( $R_1 = 1/T_1$ ). HF-NMR relaxometry limitations are related to the strength of the magnetic fields which limits the range of relaxation rates that can be investigated. In fact, high magnetic fields (e.g.  $\geq 10^8$  Hz) reduce the possibilities to observe molecular dynamics at very low frequencies such as those between  $10^6$  and  $10^3$  Hz. To this aim, nuclear magnetic resonance relaxometry at low fields and in the fast field cycling (FFC) setup is the most powerful way to retrieve information on the dynamics at low frequencies. In this work, FFC-NMR relaxometry was used to assess the effects of different organic amendments on agricultural soils.

Two farms, with different soil properties, in an important agricultural area of Campania Region, Italy, were selected in order to apply different organic amendments on soils cultivated under plastic cover. In order to understand their effects on soil OM, after one year, amended soils were sampled, dried, sieved, and, analysed by FFC-NMR relaxometry.

In this study, an innovative application of spectroscopic technique, as FFC-NMR relaxometry, to soil allowed to obtain interesting information on the effects of organic amendments on soil properties. In particular results suggest that amendments induced an increase of the soil pore size, by organo-mineral aggregates formation, which, in turn, can ameliorate soil structure and aggregation.

## Novel silica-reinforced rubbers obtained by sol-gel processes: Structure and dynamic properties as studied by Solid-State NMR

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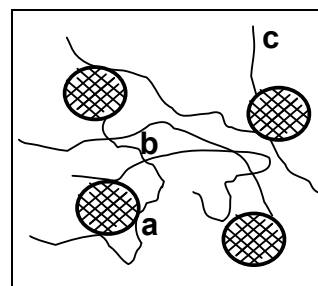
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Silica-reinforced rubbers are studied due to the specific properties exhibited by these composites, especially in the field of tyres. In this work, new composites obtained by in situ generating silica through sol-gel process in synthetic polyisoprene matrices have been investigated by means of Solid State NMR, in order to obtain a characterization of their structural and dynamic properties at a “molecular” level [1]. In particular, the molecular dynamic properties of the filled rubbers have been investigated mainly through the study of  $^1\text{H}$ - $^1\text{H}$  dipolar couplings. Here  $^1\text{H}$   $T_2$  relaxation has been investigated in low resolution [2], in order to characterize the dynamic properties of the polymer and the effect of the presence of sol-gel silica. The pure cis-1, 4 -polyisoprene rubber, composites containing variable amount of silica and obtained at different times of sol-gel reaction have been studied. Three regions with different chain mobility have been detected and related with sample composition and silica-polymer interactions. Additional dynamic and structural information were also obtained from  $^1\text{H}$   $T_1$  and  $T_{1\rho}$  low-resolution measurements and high-resolution  $^{29}\text{Si}$  and  $^{13}\text{C}$  spectra, respectively. In particular,  $^{29}\text{Si}$  spectra allowed a detailed characterization of the chemical structural properties of the in situ generated silica and of the added compatibilizers.



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## Relaxation in Bulk Polymer Melts at very low frequencies

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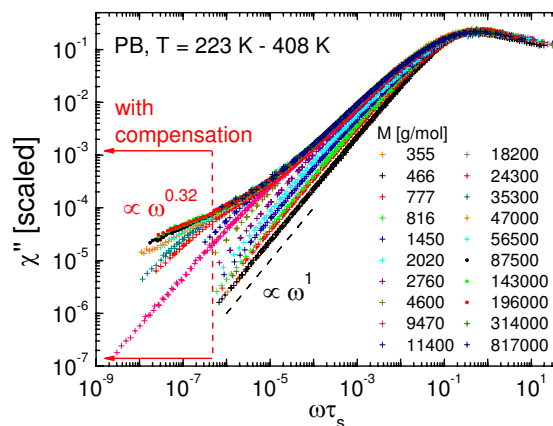
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Fast field cycling (FC)  $^1\text{H}$  NMR is applied to study segmental reorientation dynamics in melts of linear 1,4-polybutadiene (PB) with different molecular weights ( $M$  in g/mol). By applying frequency-temperature-superposition (FTS) for each  $M$  we create master curves  $\chi''(\omega\tau_s)$  ( $\tau_s$ : segmental correlation time) in the susceptibility representation  $\chi''(\omega) = \omega/T_1(\omega)$  and therefore extend the accessible frequency range to cover more than 8 decades. This enables us to observe the different dynamic regimes of the tube-reptation model for the high  $M$  limit ( $M \gg M_e$ ,  $M_e$ : entanglement  $M$ ) [1-4].

The susceptibility master curves reflect segmental ("local") as well as collective polymer dynamics. The scaling by  $\tau_s$  yields "isofrictional" spectra (see Fig. 1) and the common peak at  $\omega\tau_s \approx 1$  represents the primary relaxation governed by the glass transition. While a simple liquid (PB with  $M = 466$  in Fig. 1) only exhibits glassy dynamics represented by the  $\alpha$ -peak, for polymers with higher  $M$  an excess intensity is discernible on the low frequency side ( $\omega\tau_s < 1$ ) which is due to the slower,  $M$  dependent polymer dynamics. For low frequencies or long times where polymer dynamics contribute predominantly, the datasets can be supplemented with FC experiments compensating earth and stray fields (cf. Fig 1) or with  $^1\text{H}$  double quantum NMR data (cf. [5]), respectively.

As a result we find that the crossover from Rouse to fully established tube-reptation dynamics is highly protracted. Only for very large  $M$  ( $Z = M/M_e > 100$ ) the power law exponent approaches the predicted value from the model. Moreover, by investigating blends of protonated and deuterated PB we are able to separate intra- and intermolecular contributions to relaxation [6].



**Fig. 1.** Susceptibility master curves as a function of the reduced frequency for 1,4-polybutadiene (PB) with different  $M$  and in the temperature range as indicated.

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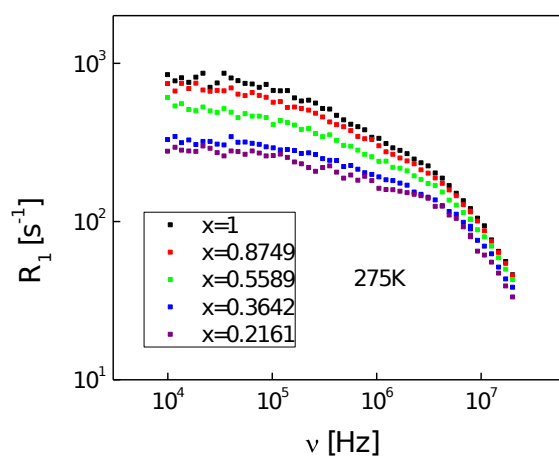
# Intermolecular relaxation in glycerol - $^1\text{H}$ FFC NMR for isotopically diluted systems

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$^1\text{H}$  FFC NMR has been applied to study dynamics in mixtures of glycerol- $h_5$  and glycerol- $h_0$ . The relaxation studies have been performed in a broad temperature range of 248K – 348K. Several concentrations,  $x$ , of glycerol- $h_5$  have been used. The overall relaxation consists of intramolecular and intermolecular contributions.

The intramolecular relaxation reflects rotational dynamics whereas the intermolecular one results from translational as well as rotational motion. By decreasing the molar ratio  $x$  of glycerol- $h_5$  in the mixtures the share of the intermolecular relaxation linearly diminishes:  $R_1 = R_1^{\text{intra}} + xR_1^{\text{inter}}$ . Extrapolating the relaxation results to the zero concentration limit the intra- and intermolecular contributions can be separated.



The extrapolation reveals a significant effect of the molecular tumbling on the intermolecular relaxation due to non-central positions of the interacting nuclei in the molecule. This effect can be quantitatively described by treating the intermolecular spectral density as a sum of translational-like and rotational-like contributions. The spectral density function for translational part can be modeled according to the force-free hard-sphere approach [1], while the rotational part is well described by Cole-Davidson function. NMR master curves as well as individual relaxation dispersion data have been analyzed within this approach. The results have been compared with those from a treatment assuming that the intermolecular interactions are entirely modulated by translational dynamics [2]. Translational diffusion coefficients extracted from  $^1\text{H}$  NMR relaxometry have been compared with the results of NMR diffusometry [3,4].

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## $^{19}\text{F}$ fast field-cycling NMR relaxometry of a nematic liquid crystal

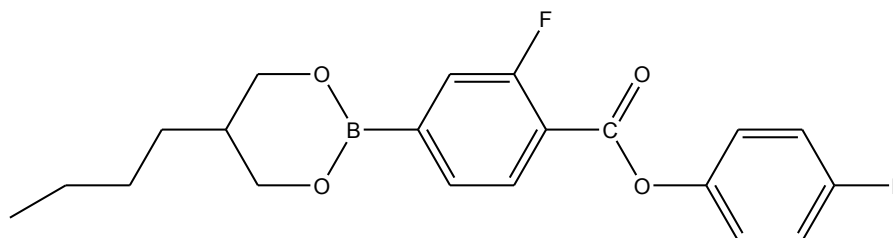
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Fast field-cycling NMR was applied to investigate the field dependence of the  $^{19}\text{F}$  longitudinal relaxation rate of the calamitic mesogen 4DBF2 fluorinated in two positions of the aromatic core (Figure 1) [1]. 4DBF2 shows a nematic phase between 67 and 86 °C, with a supercooling of the mesophase down to room temperature, and its orientational order has been extensively investigated by  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{11}\text{B}$  NMR spectroscopies, as well as by dielectric and optical techniques [2, 3].



**Figure 1.** Molecular structure of 4DBF2.

In the present work,  $^{19}\text{F}$  relaxation rates ( $R_1$ ) were measured at one temperature (90 °C) in the isotropic phase and at five temperatures (80, 75, 70, 65 and 60 °C) in the nematic phase of 4DBF2 using a Stelar SpinMaster FFC2000 relaxometer. The obtained dispersions, covering the Larmor frequency range between 10 kHz and 30 MHz, showed frequency dependences analogous to those previously observed in  $^1\text{H}$  field-cycling measurements on nematogens [4, 5] and in the  $^{19}\text{F}$  field-cycling measurements on  $\text{C}_6\text{F}_6$  dissolved in a nematic solvent [6]. In particular, in the nematic phase a  $\nu^{-1/2}$  dependence of  $R_1$  was detected over a broad range, starting from the lowest frequency and ending to a plateau in the MHz region, while a smaller dispersion was observed at higher frequencies. The low frequency  $\nu^{-1/2}$  dispersion disappeared in the isotropic phase, whereas comparatively small changes were found in the high frequency region. Moreover, in the nematic phase,  $R_1$  increased by decreasing the temperature at a fixed Larmor frequency, and dips due to the presence of the quadrupolar nucleus  $^{11}\text{B}$  were also detected.

The experimental dispersions were analyzed on the basis of theoretical models for individual and collective motions in nematic liquid crystals.

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## Dynamics of hyaluronan aqueous solutions as affected by molecular size and ionic strength

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Effect of different molecular sized hyaluronan systems on water structure was investigated by  $^1\text{H}$   $T_1$  fast field cycling (FFC) NMR relaxometry.

FFC-NMR relaxometry probes the molecular dynamics of complex systems by measurement of longitudinal ( $T_1$ ) relaxation times. In particular, the technique appears to be very sensitive to water molecules in aqueous systems, due to its ability in monitoring solute-solvent interactions. In fact, water mobility becomes slower as water is involved in H-bonds with solute molecules. For this reason homonuclear  $^1\text{H}$ - $^1\text{H}$  dipolar interactions become stronger and faster longitudinal relaxation rates (i.e. short  $T_1$  values) are achieved.

Hyaluronan (HYA) is an anionic, unbranched, non-sulfated glycosaminoglycan. It is ubiquitous as it occurs, for example, in the extracellular matrix of connective, epithelial, and neural tissues. In addition, it is also the main component of the synovial fluid which lubricates and maintains the cartilage. HYA has a unique water binding capacity. That is the reason why studies on the interactions between HYA and water are carried out in many laboratories around the world.

Previous results revealed that three different water-structural systems surround the molecule of hyaluronan in water solution. In addition, backbone fluctuations were identified which allowed to recognize that the structure of hyaluronan goes from intra-molecular hydrogen-bonded organization to inter-molecular hydrogen-bonded structure where water molecules can bridge carboxyl and amido groups of adjacent saccharide units of HYA chains.

In the present study, different molecular sized HYA molecules dissolved in MilliQ grade water and in a 3M NaCl solution (25mg/mL) were investigated. Results showed that mobility of water molecules become more restricted as HYA molecular size increases. Moreover, no bulk water was hypothesized to surround large molecular sized HYA systems. Further the extreme ionic strength in all investigated systems produced a reduction of the  $T_1$  relaxation times all over the range of the used frequencies.

The present study confirmed results from previous experiments obtained by rheological analyses dealing with reduction of viscosity of HYA water solution at very large ionic strengths. In addition, it confirmed the conclusions of other authors (based mostly on results from thermal analysis) about the existence of three hydration shells around HYA molecules depending, among others, on HYA molecular size. Namely, change in HYA molecular size influences the numbers and dimensions of respective hydration layers.

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## COHERENT TRANSFER OF HYPERPOLARIZATION IN FIELD-CYCLING NMR EXPERIMENTS

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Aim of this work is to show the importance of polarization transfer phenomena in field-cycling NMR experiments. For demonstration we studied coupled spin systems of protons, which were hyperpolarized by means of Chemically Induced Dynamic Nuclear Polarization formed in light induced reactions of short-lived radical pairs (photo-CIDNP). High-resolution NMR experiments were done by means of a fast field-cycling device in the following way: Spins are thermally polarized at 7 T, the observation field  $B_0$  of our NMR spectrometer; then the field is reduced to a variable value,  $B_{int}$ . After letting the spins evolve at  $B_{int}$  during a variable period  $\tau$  the field is switched back to  $B_0$  where the NMR spectrum is detected to observe the changes in polarization caused by the field-cycling. Signals of individual nuclei are measured as a function of the duration  $\tau$ .

Here we report the results obtained for the amino acid tryptophan (Trp) having four coupled aromatic protons in its 6-membered ring (with only two of them directly polarized by means of CIDNP) and, in addition, three coupled protons ( $\alpha$ -CH and  $\beta$ -CH<sub>2</sub>) in the peptide group. We observed that once  $B_{int}$  was sufficiently low so that the spins were strongly coupled at this field polarization was efficiently transferred among them; moreover, the transfer process was coherent as there were pronounced oscillations in the transfer kinetics, i.e., in the  $\tau$ -dependence of polarization. The condition of strong coupling implies that the difference in Larmor frequency for two spins becomes comparable to their scalar spin-spin interaction. In our experiments it was possible to rapidly transfer polarization, for instance, between the H4 and H7 ring protons, which have negligible direct coupling. The mechanism, which nonetheless enables the polarization transfer, is the strong coupling of all protons to their neighbors in the 6-membered ring, which couples the entire system. We also found pronounced features in the  $B_{int}$  dependence of the CIDNP transfer efficiency.

For explaining the experimental findings we modeled the transfer process by means of the Liouville-von Neumann equation for the spin density matrix with a time-dependent Hamiltonian. For modeling the actual time profile of switching the magnetic field was used. The coherent spin dynamics of the system was assumed to result from Zeeman and scalar spin-spin interactions; chemical shifts and coupling constants were determined from the NMR spectrum. The simulation was performed separately for the four coupled spins of the aromatic protons and for the three coupled spins in the peptide group. Theoretical results are in very good agreement with the experimental data, very well reproducing the selectivity of the CIDNP transfer and the characteristic frequencies of the oscillations. The mechanism of the transfer is explained as follows: when the field switching is sufficiently fast the population difference between two coupled levels at high field can be transformed into spin coherence at low field. Evolution of such coherences results in redistribution of the initial polarization among the spins. It is possible to excite only particular coherences in our experiments with the result of selective CIDNP transfer between particular spins. The features in the dependence of the transfer efficiency on the field  $B_{int}$  can be explained as originating from nuclear spin level anti-crossings.

We also ran experiments for the dipeptide Trp-Trp where only the residue at the C-terminus is directly polarized at high field. At low magnetic field CIDNP can be redistributed coherently among all protons of the C-terminal residue in the same way as for the free amino acid and is even transferred to protons of the N-terminal residue. The results of our work have direct relevance for the correct interpretation of various field-cycling NMR experiments and for manipulating spin hyperpolarization, namely, for selectively directing it to target nuclei of choice and for creating long-lived states to save the non-equilibrium polarization over a time much longer than the longitudinal spin relaxation time  $T_1$ .

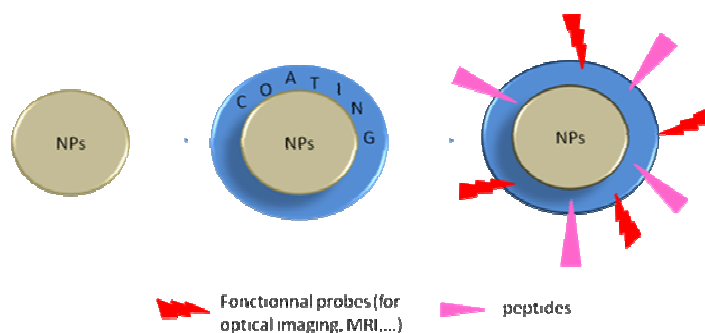
The project was supported by the RFBR (projects No. 11-03-00296a, 09-03-91006-FWF and 09-03-00837-a). K.L.I. and A.V.Y. acknowledge support from the Alexander von Humboldt Foundation.

## Synthesis of magnetic nanoparticles with narrow size distribution

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*During the last decades, researchers succeeded to reduce the size of the materials until nanometer. Thanks to their size, several nanosystems were elaborated for biomedical applications as contrast agents, hyperthermia mediators for cancer ablation and drug delivery vehicles<sup>1,2,3</sup>. The size of material is a key factor for nanosystems biodistribution. Recently, news applications appeared in the biomedical field, in particular, in multifunctional imaging which combines two complementary imaging techniques as MRI-optical imaging or MRI-PET imaging. In general, the development of multifunctional nanoparticles is realized in three steps. In the first step the nanoparticles are produced. After the synthesis, the particles are coated with stabilizing molecules. Finally, the particles are coupled with functional molecules bringing them new properties (peptides, luminescent molecules, paramagnetic complexes).*



***Picture 1*** : General method to produce multimodal probes for molecular imaging

*In this study, iron oxide nanoparticles (NPs) were synthesized by thermal decomposition<sup>4,5</sup> of a medium containing acetylacetonate precursor and surfactants. A narrow size distribution was obtained by this method which produced nanoparticles coated with oleic acid at the end of the synthesis. The next step is focused on the NPs surface modification to render them hydrophilic. We studied the physicochemical properties depending on the reaction conditions as the synthesis time, temperature and precursors concentration. The physicochemical properties were characterized by photon correlation spectroscopy, NMRD profiles, relaxometry measurements, transmission electron microscopy and thermogravimetry analyses.*

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## Relaxation in Bulk Polymer Melts at very low frequencies

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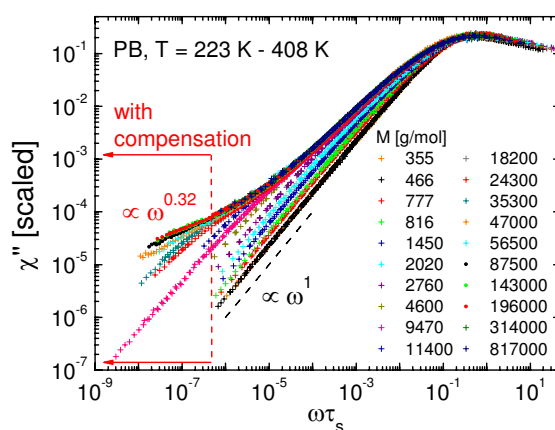
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Fast field cycling (FC)  $^1\text{H}$  NMR is applied to study segmental reorientation dynamics in melts of linear 1,4-polybutadiene (PB) with different molecular weights ( $M$  in g/mol). By applying frequency-temperature-superposition (FTS) for each  $M$  we create master curves  $\chi''(\omega\tau_s)$  ( $\tau_s$ : segmental correlation time) in the susceptibility representation  $\chi''(\omega) = \omega/T_1(\omega)$  and therefore extend the accessible frequency range to cover more than 8 decades. This enables us to observe the different dynamic regimes of the tube-reptation model for the high  $M$  limit ( $M \gg M_e$ ,  $M_e$ : entanglement  $M$ ) [1-4].

The susceptibility master curves reflect segmental ("local") as well as collective polymer dynamics. The scaling by  $\tau_s$  yields "isofrictional" spectra (see Fig. 1) and the common peak at  $\omega\tau_s \approx 1$  represents the primary relaxation governed by the glass transition. While a simple liquid (PB with  $M = 466$  in Fig. 1) only exhibits glassy dynamics represented by the  $\alpha$ -peak, for polymers with higher  $M$  an excess intensity is discernible on the low frequency side ( $\omega\tau_s < 1$ ) which is due to the slower,  $M$  dependent polymer dynamics. For low frequencies or long times where polymer dynamics contribute predominantly, the datasets can be supplemented with FC experiments compensating earth and stray fields (cf. Fig 1) or with  $^1\text{H}$  double quantum NMR data (cf. [5]), respectively.

As a result we find that the crossover from Rouse to fully established tube-reptation dynamics is highly protracted. Only for very large  $M$  ( $Z = M/M_e > 100$ ) the power law exponent approaches the predicted value from the model. Moreover, by investigating blends of protonated and deuterated PB we are able to separate intra- and intermolecular contributions to relaxation [6].



**Fig. 1.** Susceptibility master curves as a function of the reduced frequency for 1,4-polybutadiene (PB) with different  $M$  and in the temperature range as indicated.

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## Kinetic $^{19}\text{F}$ Fast Field Cycling NMR study of a liquid crystal

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Fast Field Cycling Nuclear Magnetic Resonance is getting more popular with time as new applications are being explored.

For sensitivity reasons, most FFC applications published so far refer to protons.

Nevertheless, the use of a broadband RF console, operating in the range of 2-80 MHz, offers the possibility to observe, under optimal conditions, other interesting nuclides with smaller gyromagnetic ratios  $\gamma$ , such as  $^2\text{H}$ ,  $^{31}\text{P}$ ,  $^{23}\text{Na}$ ,  $^{19}\text{F}$ .

The possibility to maintain indefinitely  $B_0$  turn on further increases the breadth of FFC-NMR experiments and applications on SpinMaster2000.

In present work, we propose a novel approach to use SpinMaster2000 as a “permanent” magnet (maintaining  $B_0$  turn on) to uniformly align a liquid crystalline sample by slow cooling from the isotropic to the nematic phase.

Fast field-cycling NMR was then applied to investigate the field dependence of the  $^{19}\text{F}$  longitudinal relaxation rate of sample in the isotropic phase (90 °C) and at five temperatures (80, 75, 70, 65 and 60 °C) in the nematic phase of 4DBF2.

In classical FFC experiment the field has to be turned off to permit the effective action of the cooling systems. Thus a nematic sample which presents a macroscopically uniaxial phase in the presence of an external magnetic field, referred to as a nematic monodomain, will suffer a mesoscopic disorder due to thermal fluctuations when the external field is turned off [1].

The obtained dispersions verified a  $\nu^{-1/2}$  dependence of  $R_1$  at low frequency in the nematic phase [2], [3] which disappeared in the isotropic phase. Moreover, in the nematic phase dips due to the presence of the quadrupolar nucleus  $^{11}\text{B}$  were also detected.

In the findings obtained the field-cycling method has given evidence for significant changes in molecular dynamics and order: a good reason for the use of field-cycling in studies of liquid crystals which show also strong relaxation dispersion and the strong differences in the dispersions corresponding to different mesophases.

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## A complete platform for PHIP method

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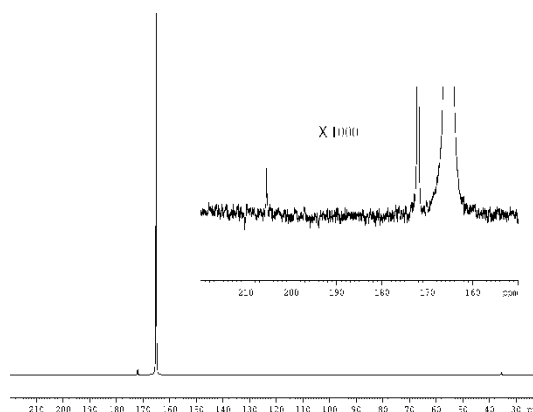
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In recent years many efforts have been devoted to the development of MR-hyperpolarization methods.

Parahydrogen-Induced Polarization (PHIP) is an efficient technique that permits to achieve high signal enhancement on <sup>1</sup>H and heteronuclear signals of molecules that derive from parahydrogenation reaction. This allows to overcome the low sensitivity problem of NMR spectroscopy and to increase the wideness of Nuclear Magnetic Resonance (NMR) experiments and applications (1, 2).

The PHIP method permits high polarization percentages on molecules to which parahydrogen can be added by means of catalytic hydrogenation; therefore small unsaturated organic molecules are usually chosen as hydrogenation substrates. The parahydrogenation reaction must be carried out very quickly, few seconds, in order to prevent hyperpolarization losses due to fast relaxation, furthermore the hydrogenation must be very efficient in order to achieve high hydrogenation yield with little amount of catalyst. In order to achieve these tasks, a very efficient hydrogenation catalyst must be used, a relatively high parahydrogen pressure, and is necessary the mixing between parahydrogen, substrate and catalyst. Furthermore, the application of pulse sequences to hyperpolarized molecules has also been developed to allow manipulation of specific hyperpolarization features. For instance, polarization lifetime can be lengthened by means of sequences that allow maintaining the singlet state (3), or net (longitudinal) polarization on heteronuclei (<sup>13</sup>C) can be obtained by means of appropriate pulse sequences (4).

In this work we present some results obtained from a complete platform for PHIP that allowed us to obtain in few seconds strongly hyperpolarized parahydrogenated molecules with very high reaction yield. The PHIP polarizer used combines an improved para-hydrogenation reactor with a highly reliable pulse programmer (Stelar S.r.l., Mede (PV), Italy) for manipulation hyperpolarization at low magnetic field. A double-tuned RF circuit operating at 2.27 MHz (<sup>1</sup>H) and 0.57 MHz (<sup>13</sup>C) allows RF transmission of pulse sequence acting on <sup>1</sup>H and <sup>13</sup>C as well as direct NMR detection of PHIP signal.



The enhancement factor of the hyperpolarized <sup>13</sup>C signal is about 20000, corresponding to 20% polarization.

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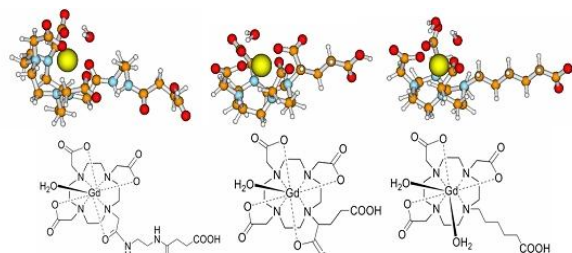
## Relaxivity Enhancement of Gd(III)-Chelates Anchored on Mesoporous Silica Nanoparticles

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### Introduction

The use of mesoporous silica nanoparticles as Gd-complexes carriers for the development of MR-enhancing hybrid materials has been recently explored in order to enhance the relaxivity per Gd and per particle.<sup>1</sup> A detailed study on the chemical role of the porous support on the magnetic properties of different Gd(III)-chelates (Scheme 1) immobilized on nanosized (20-50 nm) MCM-41 nanoparticles was carried out.<sup>2</sup>



**Scheme 1.** GdL1 (1), GdL2 (2) and GdL3 (3) complexes.

Considering the relaxivity per particle, the GdL2/MCM system showed  $r_{1p}$  of almost 15800  $\text{mM}^{-1}\text{s}^{-1}$  with respect to 9700 for GdL1/MCM and 3500 for GdL3/MCM, demonstrating that, although the number of GdL2 complexes grafted onto the mesoporous material is higher than in case of GdL1/MCM, part of the complexes are almost silent from the relaxometric point of view. This is probably due a chemical interaction from the MCM-41 surface and the complexes. In order to account for this result, the protonated amino groups present on the silica surface were reacted with acetic anhydride in DMF in order to transform the  $\text{NH}_3^+$  groups in neutral amide groups. The transformation of protonated amino groups into amides in GdL2/MCM resulted in a large increase of the longitudinal molar relaxivity (per Gd) of the material passing from 20.3 to 37.8  $\text{mM}^{-1}\text{s}^{-1}$  (86.2% enhancement). This high  $r_{1p}$  value, coupled to the high molar amount of grafted GdL2 onto the silica nanoparticle gives rise to a value of relaxivity per particle of 29500  $\text{mM}^{-1}\text{s}^{-1}$  which will allow a possible application of this hybrid material in molecular imaging procedure. For neutral GdL1 and GdL3 anchored on MCM, the relaxivity did not significantly change after acetylation.

In order to confirm the hypothesis that part of the GdL2 complexes are anchored inside the MCM-41 nanopores and thus do not influence the  $r_{1p}$  value of the material, we carried out the synthesis of mesoporous silica nanoparticles (MSN) with both surfactant and aminopropyl triethoxysilane to allow the presence of  $\text{NH}_2$  groups only on the external surface of the particles. The attachment of the GdL2 complexes followed by extraction of the surfactant would leave the Gd-complexes on the exterior of the MSNs and the pores empty. These GdL2-MSNs are slightly larger (80 nm by TEM and aggregates of 200 nm by DLS measurements) with a lower amount of GdL2 attached (ca. 10%) and a relaxivity per Gd ca. 40% higher than the previous GdL2-MCM-41 NPs. Transformation of the amino groups into amides enhances further the relaxivity.

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## Characterization of wide size rock cores by means of Field Cycling NMR Relaxometry

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<sup>1</sup>H-NMR relaxation times of water-saturated rock samples are widely employed to characterize the architecture of pore space and to estimate petrophysical properties, such as permeability and irreducible water saturation. These parameters are used both in laboratory studies and in well logging (NML).

So far, such NMR studies were always carried out at a fixed frequency (typically 10 or 20 MHz in laboratory and 2 MHz in NML). It is well known [1] that NMR relaxation rates are inherently field dependent, a fact which might represent a complicating factor in the above mentioned applications. Mono-exponential analysis of longitudinal relaxation curves so far published [2] indicate that the field dependence does exist, but is quite modest. However, it has been amply shown [3] that the mono-exponential hypothesis is rarely applicable to natural rocks, where one usually observes wide distributions of relaxation rates, due to the wide distributions of pore sizes and their physical and chemical properties.

For this reason, we have investigated the relaxation rate distributions in two sandstones with different porosity:

- 1) *feldspathic quartz Sandstone* with porosity 22.1
- 2) *quartzarenite Sandstone* with porosity 17.5
- 3)

Cylindrical rock samples (1') were saturated by water under vacuum. Their relaxation curves were measured on a Fast Field Cycling NMR Relaxometer equipped with wide bore probe, by of a number of relaxation field values, ranging from 20 kHz to 10 MHz.. Continuous distribution analysis of the curves was performed by UPEN [3].

The field dependence of the distribution curves was to be expected. The extent of the variations, however, exceeds intuitive expectations and is subject to further study. We believe that, in principle, analysis of a set of  $T_1$  distribution curves obtained at a number of relaxation field values can allow one to better separate different sample components and associate a distinct field-dependence profile with each of them. Work aimed at achieving this goal is at present in progress.

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