Saint Petersburg State University Faculty of Physics Department of Quantum Magnetic Phenomena

International Symposium and Summer School in Saint Petersburg

Nuclear Magnetic Resonance in Condensed Matter

10th meeting: "NMR in Life Sciences" July 8 – 12 2013

Book of Abstracts

an AMPERE event

Saint Petersburg, Russia 2013



International Symposium and Summer School in Saint Petersburg

Nuclear Magnetic Resonance in Condensed Matter

10th meeting: "NMR in Life Sciences" July 8 – 12 2013 an AMPERE event

ББК В334.2, Г512 **М**43

Department of Quantum Magnetic Phenomena Faculty of Physics Saint Petersburg State University Saint Petersburg, 198504, Russia

http://nmr.phys.spbu.ru/nmrcm/

M43 Nuclear Magnetic Resonance in Condensed Matter: Abstracts of the International Symposium and Summer School, 10th meeting: "NMR in Life Sciences" – Saint Petersburg: "Solo" Publisher, 2013. – 128 p.

ISBN

Symposium and Summer School are supported by:

- Saint Petersburg State University
- German-Russian Interdisciplinary Science Center
- Russian Foundation for Basic Research
- Dynasty Foundation
- Bruker Biospin Russia

International Advisory Board

V. Balevicius (Vilnius, Lithuania)
V. I. Chizhik (Saint Petersburg, Russia)
J. Fraissard (Paris, France)
H. Haranczyk (Kraków, Poland)
S. Jurga (Poznań, Poland)
O. B. Lapina (Novosibirsk, Russia)
D. Michel (Leipzig, Germany)

Organizing Committee

Co-Chairmen:

V. I. Chizhik R. Z. Sagdeev (Novosibirsk)

Vice-Chairmen:

A. V. Egorov M. G. Shelyapina

- V. I. Minkin (Rostov-on-Don, Russia) K. V. Ramanathan (Bangalore, India)
- R. Z. Sagdeev (Novosibirsk, Russia)
- K. M. Salikhov (Kazan, Russia)
- A. V. Skripov (Ekaterinburg, Russia)
- N. R. Skrynnikov (Purdue, USA)
- M. S. Tagirov (Kazan, Russia)

Members:

- S. F. Boureiko A. V. Donets V. V. Frolov V. V. Matveev S. M. Sukharzhevskii P. M. Tolstoy Layout of Abstracts Book:
- A. A. Levantovsky

Registered names, trademarks, etc. used in this book, even without specific indication thereof, are not to be considered unprotected by law.

ББК В334.2, Г512

© Organizing Committee NMRCM 2013, Saint Petersburg, 2013. © "Solo" Publisher, Saint Petersburg, 2013. Printed in Russian Federation.

ISBN

Contents

١.	Lectures	11
	E. V. Charnaya, C. Tien, M. K. Lee, D. Nefedov, Y. A. Kumzerov, J. Haase, D. Michel NMR studies of nanostructured sodium and sodium-potassium alloy	. 13
	Denis Grebenkov Theoretical and numerical methods for DWMRI	. 14
	<i>Uwe Eichhoff</i> Recent developments in animal MRI. A personal review of the 21 th annual meeting of ISMRM 2013 in Salt Lake City	. 15
	Jacques Fraissard A "pot-pourri" of ¹²⁹ Xe NMR technique	. 16
	Sergio Fuentes Inorganic-Fullerenes based on MS ₂ dichalcogenides (M=Mo, W, Ta, Nb) and TiO ₂	. 17
	Valerij Kiselev Tracking neuronal fibers using diffusion-weighted MRI	. 18
	Boris B. Kharkov, Sergey V. Dvinskikh Fine art of packing: Solid State NMR study of surfactants at solid interfaces	. 19
	Olga Lapina, Eugine Papulovsky, Dzhalil Khabibulin, and Alexandre Shubin Multinuclear SSNMR/DFT GIPAW for molecular structure and reactivity relationships for supported oxide catalysts	. 20
	<i>Dieter Michel</i> Proton and deuteron ordering and dynamics in solids and in molecules adsorbed in porous materials	.21
	<i>Dmitry Novikov</i> Characterizing tissue microstructure with time-dependent diffusion	. 22
	<i>Rita G. Nunes</i> Diffusion-weighted imaging pulse sequences: Echo planar imaging and alternative methods	. 23
	A. F. Privalov Recent developments in Field Cycling NMR	. 24
	A. V. Skripov Nuclear magnetic resonance studies of atomic motion in borohydride-based hydrogen storage materials	. 25
	<i>Murat Tagirov</i> Fullerene like nanoparticles of PrF ₃ : from creations to medical applications	. 26
	Sergey Vasiliev, Jarno Järvinen, Denis Zvezdov, Janne Ahokas, Sergey Sheludyakov, Otto Vainio, Takao Mizusaki, Yutaka Fujii, Seitaro Mitsudo, Minchan Gwak, SangGap Lee Dynamic nuclear polarization at ultralow temperatures	. 27
	<i>Vitaly I. Volkov</i> Pulsed Field Gradient NMR for biological membranes and polymeric electrolyte investigations	. 28
	<i>Matthias Weigel</i> Extended Phase Graphs: What they mean and how to include diffusion	. 29

II. (Oral Reports	31
۸ ر	Nikolay V. Anisimov, Ekaterina I. Shalamova, Svetlana S. Batova, Andrey A. Samoylenko Jse of MRI database for analysis of evolution of magnetic field of superconducting magnet	34
V A N	/yacheslav A. Chertkov, Dmitriy A. Cheshkov, Tatiana A. Ganina, Sergey S. Nechausov, Kirill F. Sheberstov, Alla K. Shestakova Novel high resolution NMR techniques for elucidation of molecular structure and dynamics	, 35
R ⊢	Rinat G. Dzhambulatov, Alexey V. Donets Hydration properties of carboxylic acid functional groups in aqueous solutions	36
J 7	an Gabriel, Michael Vogel Li NMR field-cycling relaxometry as tool to investigate lithium ion dynamics in solid-state electrolytes	37
C	Oksana Ilina Concomitant gradient terms in low-field MRI	38
V F	/adim V. Kachala, Elena A. Khokhlova and Valentine P. Ananikov High-resolution NMR studies in ionic liqiuds	39
К Т s	Kerstin Kämpf, Beke Kremmling, Michael Vogel Temperature dependence of internal protein backbone dynamics studied by ² H NMR and random-walk Nimulations	40
B P	Boris B. Kharkov Phase behavior of CTAB bilayer intercalated into magadiite	41
II L C	lya A. Khodov, Mikhail Yu. Nikiforov, Gennady A. Alper, Sergey V. Efimov, Vladimer V. Klochkov, uís A. E. Batista de Carvalho Conformation preference of ibuprofen in chloroform by 2D-3D NMR and GIAO quantum chemistry calculation	42
А С (I	Alexandr A. Khrapichev Chemical Exchange Saturation Transfer (CEST) for intracellular pH-sensitive Magnetic Resonance Imaging MRI)	43
K ⊦	K. Klyukin, M. G. Shelyapina, D. Fruchart Hydrogen diffusion in various structures of MgH _x : a DFT study	44
А Е р	Anastasia Y. Kultaeva, Artem I. Antipov, Stanislav M. Sukharzhevskii Effect radiation annealing on the kinetics of accumulation of electron-hole centers in paleontological objects	45
V N	/yacheslav V. Kuzmin, M. E. Hayden, G. Tastevin, PJ. Nacher New insight on nonlinear spin dynamics in highly polarized liquids	46
V 13	/ladimir Matveev, Denis Markelov, Vladimir Chizhik, Petri Ingman, Erkki Lähderanta ³C and ¹H NMR Relaxation and segmental mobility in [emim]CH₃COO Ionic Liquid	47
/ı N	van V. Pleshakov, Nikolay S. Klekhta NMR signal operation in magnetic substances by the external field pulses	48
۸ R iı	M. Podrecca, G. Grolet, V. Delsinne & J. M. Colet Regulation of trophoblast migration: from a fingerprinting view to a mechanistic prospect n bioassay design	49
S ⊦	Sevastyan O. Rabdano, Alexey V. Donets Hydrophobic and hydrophilic effects in aqueous solutions of organic molecules	50

V. A. Ryzhov, I. V. Pleshakov, A. A. Nechitailov, N. V. Glebova, E. N. Pyatyshev, A. V. Malkova, I. A. Kiselev, V. V. Matveev Magnetic study of nanostructural composite material based on cobalt compounds and porous silicon5	1
<i>Ago Samoson</i> Hot spinning	2
M. A. Shevtsov, L. Yu. Yakovleva, B. P. Nikolaev, Ya. Yu. Marchenko, A. V. Dobrodumov, K. V. Onokhin, A. L. Mikhrina, I. V. Guzhova, M. G. Martynova, O. A. Bystrova, A. M. Ischenko, B. A. Margulis Magnetic Resonance Study of SPIONs conjugated with Hsp70 in C6 glioma intracranial model55	3
<i>Timur A. Sibgatullin, Frank J. Vergeldt, Henk Van As</i> Spin-spin relaxation-diffusion correlation analysis for estimation of distribution of membrane permeability and cell size in plant tissues	4
Nikolai Skrynnikov Ensemble-restrained MD simulations: accurate structure leads to accurate dynamics	5
Sergey G. Vasil'ev, Vitaly I. Volkov, Elena A. Tatarinova, Aziz M. Muzafarov A solid-state NMR investigation of MQ silicone copolymers5	5
Anna V. Vyvodtceva, Marina G. Shelyapina, Alexey Privalov, Daniel Fruchart ¹ H NMR study of hydrogen diffusion in disordered Ti-V-Cr alloys5	7
III. Poster Session	9
E. M. Alakshin, R. R. Gazizulin, A. V. Klochkov, K. Kono, S. L. Korableva, V. V. Kuzmin, A. M. Sabitova, T. R. Safin, K. R. Safiullin, M. S. Tagirov Magnetic coupling in system ³ He – PrF ₃ nanoparticles6	1
Nikolay V. Anisimov, Olga V. Isaeva, Svetlana S. Batova Simplification of MRI contrast by inversion recovery method6	2
Hike Asatryan, Darya Kramushchenko, Yulia Uspenskaya Registration of "antisite" defects in Y ₃ Al ₅ O ₁₂ by electron paramagnetic resonance6	3
Mariia I. Averina, Andrei V. Egorov Concentration effect on cations solvation in Ca(NO ₃) ₂ – LiNO ₃ – H ₂ O ternary system at normal conditions. A molecular dynamics simulation study64	4
<i>Eduard Baibekov</i> To the possibility of the high-temperature spin-photon coherence in a microwave cavity6	5
A. G. Bazir, O. S. Vezo, B. P. Nikolaev, Ya. Yu. Marchenko, L. Yu. Yakovleva, V. I. Rolich, V. V. Vojtylov NMR and Optical Properties of Dextran coated magnetic Nanosols6	5
Eduard V. Bocharov, Konstantin S. Mineev, Dmitry M. Lesovoy, Sergey A. Goncharuk, Olga V. Bocharova, Pavel K. Kuzmichev, Pavel E. Volynski, Alexander S. Arseniev Structural and thermodynamic aspects of specific interactions of transmembrane domains of bitopic proteins6	7
Olga V. Bocharova, Anatatoly S. Urban, Ilia S. Chaplygin, Kirill D. Nadezhdin, Pavel E. Volynski, Eduard V. Bocharov, Alexander S. Arseniev Structural insight on the dimerization of transmembrane domain of amyloid precursor protein66	8
Yury V. Bogachev, Julia S. Chernenco, Kamil G. Gareev, Irina E. Kononova, Lev B. Matyushkin, Vyacheslav A. Moshnikov Study of NMR relaxation in suspensions of magnetite-silica nanocomposite	Э

Yu. Bogachev, Yu. Chernenko, L. Grunin, V. Drapkin, M. Knyazev, Ya. Marchenko, A. Naumova Compact combined EPR/NMR/DNP Equipment70
Inna G. Borodkina, Anatolii S. Burlov, Gasan M. Abakarov, Konstantin A. Lyssenko, Igor S. Vasilchenko, Ali I. Uraev, Gennadii S. Borodkin, Dmitryi A. Garnovskii, Pavel B. Chepurnoy, Yuriy F. Mal'tsev, <u>Mikhail Yu. Antipin</u> , Vladimir I. Minkin Structure of Te-containing salen-type complexes with transition metals in solution and solid state
Inna G. Borodkina, Vera A. Anisimova, Ivan E. Tolpygin, Gennadii S. Borodkin, Igor S. Vasilchenko, Pavel B. Chepurnoy, Yuriy F. Mal'tsev, Vladimir I. Minkin Prototropic tautomerism 1(10)H-2,3,4,10-tetrahydropyrimido72
Eugenia A. Burilova, Anna B. Ziyatdinova, Rustem R. Amirov Paramagnetic NMR-probing of polymeric solutions73
Anna S. Dmitruk, S. G. Vasil'ev, E. A. Tatarinova Synthesis and characterization of Hexa(trimethylsiloxy)disiloxane using ¹ H, ¹³ C and ²⁹ Si NMR spectroscopy 74
Andrei V. Egorov, Mariia I. Averina Multinuclear NMR relaxation as a tool of investigating local structure and dynamics of ternary aqueous solutions of nitrate salts
Galina N. Fedyukina, Boris V. Sakharov, Pavel Ch. Kopilov, Sergey A. Ivanov, Andrey P. Anisimov H ¹ -NMR relaxation study of an amorphous state of the freeze-dried powders76
Dmitry Furman Detection of foreign bodies in the object using magnetic resonance imaging77
Ramil R. Gainov, Vera V. Klekovkina, Farit G. Vagizov, Alexander V. Dooglav, Vladimir A. Golovanevskiy, Ivan N. Pen'kov First-principles calculations of CuFeS ₂ : characterization based on the nuclear-resonance spectroscopy data
<i>Egor Gerts, Andrei V. Komolkin, Vladimir A. Burmistrov, Victor V. Alexandriysky, Sergey V. Dvinskikh</i> Influence of hydrogen bonding on macro- and microscopic parameters of cyanobiphenyls. The comparative study
H. Harańczyk, E. Baran, M. Florek-Wojciechowska, P. Nowak, J. Nizioł, T. Okuda, K. Strzałka, S. Knutelski, J. Tarasiuk
<i>H. Harańczyk, P. Nowak, M. Florek-Wojciechowska, E. Baran and M. A. Olech</i> Magnetisation transfer in <i>Cetraria aculeata</i> (Schreb.) Fr. thalli observed by ¹ H-NMR
A. V. Ievlev, Y. S. Chernyshev Molecular mobility in multi-component solutions
Valeria Ievleva, Alexei Baryshev, Elena Kurenkova, Alexander Ievlev, Sergey Lavrov, Marina Shelyapina, Anait Alexanyan ¹ H NMR study of hydrides of disordered binary Ti _{1-x} Nb _x alloys (with x = 0.5, 0.6 and 0.3)
A. U. Karseev, V. V. Davidov, V. I. Dudkin Nutation nuclear-magnetic magnetometer
Boris B. Kharkov Sign-sensitive measurement of heteronuclear dipolar couplings to spin-1

Ilya A. Khodov, Mikhail Yu. Nikiforov, Gennady A. Alper, Nugzar Zh. Mamardashvili Structural analysis of porphyrin complex of Sn(IV)porphyrinatesin with 4-imidazolylphenol in benzene by 2D ROESY and 2D DOSY NMR spectroscopy
Nikolay S. Klekhta, Ivan V. Pleshakov NMR in domain walls of magnetically ordered material: the information from the field pulses effect
Pavel A. Kupriyanov, Vladimir I. Chizhik NMR in the Earth magnetic field: Pre-polarization of Nuclei with Alternating Magnetic Field
<i>G. S. Kupriyanova, V. V. Molchanov, E. A. Severin, I. G. Mershiev</i> The method of signal detection of nuclear magnetic resonance in inhomogeneous magnetic field by using of composite pulses
Sergey E. Kurnikov, Alexey V. Donets Features of the ²³ Na quadrupole NMR-relaxation in aqueous solutions91
Vyacheslav V. Kuzmin, K. R. Safiullin, PJ. Nacher Signal feedback in NMR and MRI92
V. Loskutov, S. Zhakov, Y. Dolomansky Determination of the effective magnetic field gradient in a porous medium by CPMG sequence
Katerina Makarova, Ekaterina V. Rokhina, Elena Golovina and Henk Van As DFT calculations for identification of FDMPO radical adducts from fast isotropic Electron Spin Resonance and F ¹⁹ Nuclear Magnetic Resonance spectra
Denis A. Markelov, Maria V. Popova The temperature effects in different surfactant systems by means ¹³ C NMR
Denis A. Markelov, Mariya E. Mikhailova, Stanislav G. Falkovich, Igor M. Neelov, Vladimir V. Matveev, Anatolii A. Darinskii Hydrodynamic and aggregation properties of 4 th -generation poly-L-lysine dendrimers in aqueous NaCl solution by ¹ H NMR, light scattering, and molecular dynamics simulation
Thomas Meier, Jürgen Haase Ultra-High Pressure NMR Investigation on Elemental Liquid Gallium up to 25 kbar
Ivan Mershiev, Galina Kupriyanova Broadband composite pulses for Spin=1NQR in powders
B. P. Nikolaev, Ya. Yu. Marchenko, L. Y. Yakovleva A novel approach of antidote drug "Ferrocin" for clinical MR imaging of digestive system
K. Paradowska, O. Stefaniak, I. Wawer Solid state NMR study of cell wall materials100
Victoria Parshina, Svetlana levleva Preparation of agar phantoms which are designed mimic human tissues and theirs comparing with real tissues in medical MR images
Maria V. Popova, Philip S. Bubnov, Anna A. Vorontsova NMR study of Sodium Lauroyl Sarcosinate in Solution and Binary Mixtures
Filipp Riabchun, Vyatcheslav Frolov Field-shifting method for Magnetization Transfer Contrast in Iow-field (6.8 mT) Magnetic Resonance Imaging

S. A. Ruzheva, A. V. Bogaychuk The use of two-dimensional COSY and NOESY methods for the identification of the NMR signals of organic dyes
Ivan A. Rykov, Marina G. Shelyapina, Vladimir I. Chizhik Proton magnetic resonance in multiple metal hydrides107
<i>Boris V. Sakharov, Tatiana Kornushina, Sergey N. Viryasov, Mikhail Khramov</i> Effect of water on molecular mobility in protein and peptone powders studied by pulsed ¹ H NMR108
Andrey V. Savinkov, Alexander V. Dooglav, Boris Z. Malkin, Murat S. Tagirov, Dmitry P. Pavlov, Vera V. Klekovkina Magnetic properties of the rare-earth trifluorides RF3 (R = Tm, Eu) studied by ¹⁹ F NMR
M. Schäfer, A. F. Privalov, F. Fujara, I. V. Murin, V. N. Postnov, D. V. Postnov ¹ H diffusion in chemically functionalized fullerene doped Nafion proton electrolyte membranes measured by SFG-NMR
Kirill F. Sheberstov, Dmitriy A. Cheshkov, Vyacheslav A. Chertkov Orientation effects of aromatic compounds in isotropic media as studied by total-line-shape analysis of ¹ H NMR spectra
Sergey Sheludiakov, Janne Ahokas, Sergey Vasiliev, Jarno Järvinen, Vladimir Khmelenko, Shun Mao and David Lee Magnetic resonance study of atomic hydrogen and deuterium in solid H2 and D2 matrixes below 1K112
Alla K. Shestakova, Vyacheslav A. Chertkov A comparison of solid state and solution structure for a complex between hydrated lanthanum triflate and [221]cryptand
M. A. Shevzov, B. P. Nikolaev, Ya. Yu. Marchenko, L. Yu. Yakovleva, V. T. Lebedev Magnetic Resonance Imaging of Rat Glioma Model enhanced by using water-soluble Gadolinium Fullerene
A. V. Soloninin, A. V. Skripov, D. B. Ravnsbæk, T. R. Jensen, Y. Filinchuk NMR study of hydrogen dynamics in mixed-metal borohydride LiZn₂(BH₄)₅
Elena Tupikina, Sergev Smirnov, Peter Tolstoy A weak hydrogen bond donors: geometry and NMR properties of complexes of 1,1-dinitroethane116
Alina A. Uskova, Andrei V. Komolkin Site-site potential in coarse-grain model of the benzene117
Tatyana A. Vasilenko, Andrey K. Kirillov, Alexander N. Molchanov, Grigoriy A. Troitsky, Andrey V. Vyshnyakov, Igor G. Kostenko, Tatyana V. Pichka Emission of methane from fossil coal in the condition of enhanced moisture contents
Vladimir Y. Volkov Restore FID using modified CPMG pulse sequence119
A. I. Zhernovoy, S. V. Dyachenko, M. A. Vaseshenkova Investigation of dependence the Curie constant in colloidal solution from induction of magnetic field of superparamagnetic nanoparticles
Author Index
List of Participants 125

Part I

Lectures



E. V. Charnaya, C. Tien¹, M. K. Lee¹, D. Nefedov, Y. A. Kumzerov², J. Haase³, D. Michel³

Physics Department, St. Petersburg State University, St. Petersburg 198504, Russia E-mail: charnaya@mail.ru ¹Physics Department, National Cheng Kung University, Tainan 70101, Taiwan ²Ioffe Physiko-Technical Institute RAS, St. Petersburg 194021 Russia ³Faculty of Sciences and Geosciences, Leipzig University, Leipzig D-04103, Germany

on the Knight shift, melting and freezing phase transitions, in solid and liquid metals.

Experimental data of NMR studies on metallic sodium and and spin relaxation in liquid and solid sodium and its alloy sodium-potassium alloy embedded into nanoporous matrices are revealed. Alterations in atomic mobility were evaluated are presented. Size-effects and influence of nanoconfinement within the framework of theoretical models of spin relaxation



Laboratoire de Physique de la Matiere Condensee, CNRS – Ecole Polytechnique F-91128 Palaiseau Cedex France http://pmc.polytechnique.fr/pagespeso/dg E-mail: denis.grebenkov@polytechnique.edu

widespread experimental technique that relies on encoding of the random trajectories of diffusing nuclei by inhomogeneous magnetic fields. The non-invasive character of DWMRI made this technique the gold standard in material sciences, neurosciences and medicine. A geometrical confinement considerably affects the diffusive motion of the nuclei and the consequent signal attenuation under inhomogeneous

Diffusion Weighted Magnetic Resonance Imaging is a magnetic fields. In this lecture, we focus on theoretical and numerical aspects of resticted diffusion in NMR. We will present probabilistic, PDE and spectral approaches to describe restricted diffusion and the consequent signal formation. These approaches provide complementary views onto DWMRI and suggest efficient numerical techniques for simulating DWMRI in artificial or image-reconstructed porous media.



NMRCM Recent developments in animal MRI. A personal review of 2013 the 21th annual meeting of ISMRM 2013 in Salt Lake City

Uwe Eichhoff^{1,2}

¹Bruker HTS GmbH, D-63755 Alzenau (scientific consultant) ²M. V. Lomonosov Moscow state university (honorary professor) E-mail: Uwe.Eichhoff@bruker-biospin.de

1. Introduction

The 21th meeting of the ISMRM (International Society of Magnetic Resonance in Medicine) took place 20-26 April 2013 in Salt Lake City. The society brings together leading physicists, chemists, biologists and medical doctors in a highly successful interdisciplinary approach. Besides an extensive teaching program, 883 oral lectures, 1983 traditional posters and 1708 electronic posters have been presented. There were participants from all major countries all over the world (for example 600 from China) with one exception: the Russian Federation. It seems, that an extremely interesting and important field of science is almost completely neglected by the Russian scientists.

2. Intention of the review

The intention of this review is to pinpoint the importance of this field of science mainly to the Russian audience, to outline the for my personal opinion most important directions of development. As well the up to date state of hardware developments at Bruker BioSpin MRI GmbH will be discussed.

3. Important directions of animal MIRI

3.1. Brain mapping

During the last years atlases of the animal and human brain with sub-millimeter resolution have been created by various MRI methods such as functional MRI, resting state functional MRI and diffusion tensor imaging.

Functional MRI (fMRI) relies on signal intensity changes in the brain images resulting from changes in blood oxygenation due to the impact of external stimuli (visual, acoustic, mechanical) and/or performance of designated tasks. This allows to assign special functions to designated brain areas.

Resting State Functional fMRI (rs-fMRI) analyses the frequencies of signal intensity fluctuations in the resting brain and find connectivities between the voxels. This allows to obtain information about connections between different brain areas.

Diffusion Tensor Imaging is based on diffusion weighted imaging with varying gradient strength and gradient orientation. In neuronal fibres diffusion is comparably free in the fibres direction and restricted in the perpendicular directions. The DTI images reflect main diffusivity, fractional diffusion anisotropy and the direction of the diffusion tensor. From the direction of selective fibres can be extracted, leading to so called tractograms.



Figure 1. Example for DTI: DTI Reveals Neuroplastical Seasonal Changes in Songbird Brain

3.2. Molecular imaging, stem cell tracking, targeted drug delivery

Today gene-knock-out- or genetically modified animal are available for almost any human disease, expressing genes for a particular pathology. Cells can be transfected and loaded with smart MRI-contrast agents with minimal or no alteration of their functioning and proliferation. This enables insight into the nature of disease on a cellular/molecular level. Embryonal or reprogrammed adult stem cells can be marked with paramagnetic contrast agents or supersmall iron particles (SPIO) and tracked on their way to pathological locations. This opens the way to check and monitor stem cell therapy in animal models. Drugs can be incapsulated in special carriers, also marked with contract agents, and released in the targeted organ or pathology (like cancer) by external modalities like laser irradiation or ultrasound.

4. Summary and Outlook

Many important aspects of NMR in medicine remain beyond the scope of this short report, like in vivospectroscopy, spectroscopic imaging, metabolic studies by ¹H-NMR and ¹³C-NMR (with dynamic polarization), NMRhistology (by HRMAS), disease screening by High Resolution NMR of bodyfluids.

NMRCM A "pot-pourri" of ¹²⁹Xe NMR technique 2013 Jacques Fraissard

Université Pierre et Marie Curie Laboratoire de Physique Quantique, Paris, France E-mail: jacques.fraissard@upmc.fr

The ¹²⁹Xe NMR technique introduced in 1980 allows the determination of pore size, location and charge of compensating cations, structural defects, distribution of adsorbed species, etc. It is applied for the characterization of a lot of solids: mesoporous silica, clays, liquid crystals, metal-organic framework compounds (mainly their elasticity), carbons, polymers, diffusion in porous structures and even in archaeology.

Saint Petersburg, Russia

Since 2000, this technique has taken a new turn with the advent of laser-hyperpolarized xenon (HP-Xe) in the characterization of materials and organisms. The use of HP-Xe increases the sensitivity for the detection of xenon by several orders of magnitude. The range of its applications becomes wider each day. Now this monotonic probe allows

for remarkable explorations ranging from intricate experiments on single-crystal surfaces to the study of the complex nature of gas exchange in mammalian lungs. For example, encaged in a cryptophane cage bearing a ligand, xenon is a very sensitive sensor for detecting biomedically relevant protein targets or metal cations involved in many pathological and physiological processes. Medical applications increase each day, such as: xenon dissolved in the blood for the measurement of the rate of blood in arteries and veins, xenon imaging in brain or human lungs collected *in vivo*.

We will give some applications of this universal probe for material and biological characterizations.



NMRCM Inorganic-Fullerenes based on MS₂ dichalcogenides 2013 (M=Mo, W, Ta, Nb) and TiO₂

Sergio Fuentes

Center of Nanosciences and Nanotechnology of UNAM, Apartado Postal 2681, Ensenada, Baja California, México E-mail: fuentes@cnyn.unam.mx

Transition metal dichalcogenides MS_2 (M= Mo, W, Ta, Nb) have been extensively used as catalysts and lubricants due to their anisotropic behavior related with their layer structure where basal planes are very stable and border planes very reactive. Indeed, MS_2 closed structures have been synthesized as multilayer nanotubes, ribbons and onion-like nanostructures and have named the Inorganic Fullerenes (IF) by Tenne [1, 2]. Some of these materials such as the hollownanoparticles of WS_2 present entirely new properties for lubrication. On the other hand, titania nanotubes, can be considered other type of inorganic fullerenes which have large potential for applications in environmental protection and health care [3] due to their photocatalytic and nanostructural properties.

In this work, the synthesis methods, the physicochemical properties and the nanostructure characterization of several types of IFs will be presented. The application to areas of catalysis [4], lubrication, health care, impact protection will also be discussed.

- [1] Y. Rapoport, Y. Bilik, M. Feldman, S.R. Homyonfer, R. Cohen and R. Tenne, Nature, 387, (1997) 791-793.
- [2] R. Tenne and G. Seifert, Annu. Rev. Mater. Res., 39 (2009) 387–413.
- [3] Batur Ercan, Erik Taylor, Ece Alpaslan, Thomas J Webster, Nanotechnology, 29 (2011)22.
- [4] A. Olivas, S. Fuentes, A. Camacho and M.J. Yacaman, J. Materials Research, vol 19, 2176-2184, (2004).

NMRCM Tracking neuronal fibers using diffusion-weighted MRI

2013 Valerij Kiselev

Saint Petersburg, Russia

Dpt. of Radiology, Medical Physics, University Medical Center Freiburg E-mail: kiselev@ukl.uni-freiburg.de

Neuronal fibers forming brain white matter realize connections between different cortical areas and other parts of the brain. In vivo knowledge of the individual-specific configuration of neuronal fibers would be of great value for the diagnostics, for the surgical planning, and for the fundamental neuroscience. There has been a significant progress towards this goal during last decade inspired by the development of diffusion-weighted magnetic resonance imaging (dMRI) of the brain. This technique exploits the fact that diffusion of water molecules is strongly anisotropic within the neuronal fiber bundles.

An inherent problem of dMRI is its relatively coarse resolution of a few millimeters, often resulting in a number of fiber bundles placed within one voxel of an MRI image. This puts more weight on the biophysical modeling of the MRI signal in order to resolve the fiber content of each voxel, and to reconstruct the global fiber connectivity map.

We address this challenge by utilizing the self-consistency conditions resulted from the global nature of neuronal tracts stretching across many voxels. This strategy is pursued in the algorithm which we call "Global fiber tracking", inspired by the parallels with statistical physics of disordered systems. At its core, our algorithm employs the global "energy" minimization for the interacting segments with a tendency to polymerize into long fibers, placed in an external "field" locally orienting them in accord with the measured diffusion anisotropy. The resulting fiber configuration is a "ground state" into which such interacting segments freeze. This algorithm has been successfully validated by reconstructing fiber configuration in an artificial phantom, and demonstrates good performance on clinical dMRI data.



Boris B. Kharkov^{1,2}, <u>Sergey V. Dvinskikh¹</u>

¹Department of Chemistry and Industrial NMR Centre, Royal Institute of Technology - KTH, SE-10044 Stockholm, Sweden ²Department of Quantum Magnetic Phenomena, St. Petersburg State University - SPbGU, 198504, St. Petersburg, Russia E-mail: sergeid@kth.se

Mesostructured materials possess unique surface, structural, and bulk properties that lead to important practical applications. Theoretical and experimental studies of hydrocarbons confined in, intercalated between or adsorbed to inorganic surfaces report significant differences in structure and dynamics compared to those in the bulk. Understanding the molecular origin of confinement-induced changes is of fundamental interest to a wide range of applications.

In our work, new characterization tool for molecular structure and dynamics of organic component in mesostructural materials is developed. Aim is to provide general approach in term that broad array of systems with wide range of mobility can be characterized within single experimental technique. It should also provide quantitative information without relying on model assumptions.

In the present talk, we focus on surfactant-containing mesostructural organic-inorganic composites. Due to amphiphilic molecular properties, surfactants exhibit strong tendency to self-assemble in solution as well as to adsorb onto various interfaces such as solid surfaces. Surfactants are also widely used in design of organic-inorganic composites and in synthesis of mesoporous materials.

We apply solid state NMR spectroscopy to quantitatively characterize the surfactant conformational dynamics. Magic-

angle-spinning dipolar recoupling technique is used to study surfactant conformational motion in a wide dynamic range from essentially immobilized rigid state to highly flexible state with significant degree of conformational and rotational freedom. Dipolar recoupling combined with two-dimensional ¹³C separated local field spectroscopy allows for direct estimations of C–H bond order parameter profiles in hydrocarbon chains. Such approach does not require assumptions and adjustable parameters and reflects the changes in conformational dynamics without relying on specific motional model.

Dynamics of surfactant molecules adsorbed at solid surfaces, confined in ordered mesopores, and intercalated into inorganic layered structures is compared. The study shows that in surfactant bilayers intercalated in aluminophosphate layered structure molecules undergo fast rotation around molecules axis while chain is highly ordered and adopts transconformation. Both in cylindrical pores of hexagonal mesoporous silica and in adsorbed layer on silica nanoparticles the order parameter is gradually decreasing towards the end of the chain. Experimental order parameter profiles are also compared to those in surfactants aggregated in concentrated aqueous solution, in hexagonal and lamellar mesophases.

Saint Petersburg, Russia

NMRCM Multinuclear SSNMR/DFT GIPAW for molecular structure and 2013 reactivity relationships for supported oxide catalysts

Olga Lapina, Eugine Papulovsky, Dzhalil Khabibulin, and Alexandre Shubin

Boreskov Institute of Catalysis, 630090, Novosibirsk, Russia E-mail: olga@catalysis.ru

catalytic materials that are technologically indispensable in the 21st century: environmental control, production of energy, petrochemicals and pharmaceuticals, and the destruction of toxic agents. The wide range of catalytic applications reflects the versatile reactivity/selectivity characteristics of supported vanadia catalysts that have their origins in the ability to tune the molecular/electronic structures of the catalytic active vanadia nano-domains formed on the surfaces of oxide substrates (surface functional diversity).

In this lecture we are going to present multinuclear SSNMR/DFT GIPAW data of the molecular structure and reactivity/selectivity relationships for supported vanadium oxide catalysts. Step by step characterization of molecular structure of the catalytic vanadia nano-domains formed in supported binary VOx/MOx systems and in multilayered VOx/M₁Ox/M₂Ox catalysts, where M₁, M₂ - Si, Al, Ti, Zr, Nb, will be given. Special attention will be paid to solid-state NMR in its modern applications (High magnetic Field - HF and High Speed- HS MAS). According to these data the versatile types of vanadia domains could be formed, their structural characteristics are determined by a number of factors (vanadium content, nature of the support, structure of the support surface, nature of the layers in multilayered materials, structure of the layers, sequence of deposition, treatment conditions and so on). It is clear that it is rather difficult or even impossible to realize all the types of vanadia sites and to estimate their catalytic characteristics experimentally, especially due to the simultaneous formation of several vanadia species. However, this problem could be solved by quantum chemical simulations. Using the combination of finite cluster and periodic DFT quantum mechanical calculations of structural/spectral properties, the adequate structures for the most basic systems were obtained. Reactivity of the chosen adequate sites was also estimated.

As an example, here are shown experimental ⁵¹V NMR spectra of different vanadia sites formed on silica supported binary VOx/SiO₂ catalysts prepared by grafting technique from VOCl₃ (Fig.1A). Simulated ⁵¹V NMR spectra with nmr parameters for vanadia sites obtained by quantum chemical calculations are also given (Fig.1B). As could be seen, experimental and simulated spectra are rather similar. This allows us to assign each experimental spectrum to the specific vanadium sites. Thus after VOCl₃ deposition VOCl₂(OSi) sites are formed, which transform to VO(OSi)₃ species after hydration/dehydration procedure.

Using this approach the great number of vanadia sites

Supported vanadia catalysts belong to a large class of which could be formed in different systems at different conditions were calculated and their structure - reactivity relations were exemined. These fundamental relationships the molecular/electronic structures between and reactivity/selectivity of catalytic active vanadia nanodomains are critical for the molecular engineering of novel catalytic materials for targeted applications.



Figure 1. A – Experimental ⁵¹V NMR spectra at 105.15 MHz of: 1 - VOCl₃ at 173°C, 2, 3, 4 - of VOCl₃/SiO₂ prepared by grafting of $VOCl_3$ from the gas phase, (1) - after $VOCl_3$ deposition (line at 6 ppm corresponds to physically adsorbed VOCl₃, anisotropic line with $\delta_{iso} = -290$ ppm corresponds to VOCl₂(OSi)); (3) after hydration; (4) after evacuation at 100°C. (spectra adapted from refs. [1, 2]). $B-Simulated {}^{51}VNMR$ spectra with nmr parameters computed by GIPAW for VOCl₃, VOCl₂(OSi), VOCl(OSi)₂ and VO(OSi)₃ structures obtained by DFT.

Acknowledgements

This work was partly supported by the Russian Foundation for Basic Research (grant 13-03-00482) and by The Ministry of education and science of Russian Federation (project 8429). Siberian Supercomputer Centre, Novosirirsk, Russia (http://www2.sscc.ru) is acknowledged for the access to its computational facilities (integration grant no. 130).

- [1] Lapina O.B, Mastikhin V.M., Shubin A.A., Krasilnikov V.N., Zamaraev K.I., ⁵¹V Solid State NMR Studies of Vanadia Based Catalysts, Prog.NMR spectr., 24(1992) 457-525.
- [2] Mastikhin V.M., Lapina O.B., Vanadium Catalysts: Solid State NMR, in Encyclopedia of Nuclear Magnetic Resonance; Grant D.M., Harris R.K., Eds.; John Wiley&Sons Ltd.; Chichester, UK, 8(1996)4892-4904, emrstm0585



NMRCM Proton and deuteron ordering and dynamics in solids and in 2013 molecules adsorbed in porous materials

Dieter Michel

Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstr. 5, 04103 Leipzig, Germany E-mail: michel@physik.uni-leipzig.de

Proton ordering and exchange dynamics play an important role in hydrogen bonded solids and are also important for molecules adsorbed in porous materials. In the lectures previous and recent results are discussed which are related to the application of spin relaxation studies for adsorbed water, two-dimensional deuteron-exchange spectroscopy and orderdisorder phenomena in solids.

As an introduction to the lecture, former results are characterized which are concerned with proton exchange in adsorbed water, proton mobility in systems with strong acidic sites obtained by means of proton spin relaxation.

Then proton mobility is investigated with respect to the high ionic conductivity in crystals with hydrogen bonds. This is interesting, on the one hand, due to the practical applications of these crystals and, on the other hand, it gives the possibility to contribute in general to the understanding of the microscopic mechanism of electric conductivity. From this point of view, a particular interest is devoted to crystals with the structural peculiarity of quasi one-dimensional chains of atomic groups bound by hydrogen bonds showing a high conductivity. Such crystals serve as very appropriate model objects in order to study the proton ordering and to verify various assumptions about the microscopic mechanisms of proton conductivity. Substances with a surprisingly high ionic (protonic) conductivity are, among others, single crystals of ammonium hydrogen selenate NH₄HSeO₄ (AHSe), betaine phoshate (BP), betaine phoshite (BPI) and mixed crystals if the type BP_{1-x}BPI_x, containing quasi one-dimensional chains of SeO₄-, PO₄-, and PO₃tetrahedra connected by hydrogen bonds. The role of structural defects for the conductivity process is discussed.

In a third part, NMR spectroscopy is applied to investigate proton ordering in various crystals in relation to structural phase transitions.

Comments and support of my former colleagues, in particular professor Rolf Boettcher and professor Georg Voelkel, are greatly acknowledged.

NMRCM Characterizing tissue microstructure with time-dependent 2013 diffusion

Dmitry Novikov

New York University Medical School, New York E-mail: Dmitry.Novikov@nyumc.org

Molecular diffusion measurements are widely used to probe microstructure in materials and living organisms noninvasively. The precise relation of diffusion metrics to microstructure remains a major challenge: In complex samples, it is often unclear which structural features are most relevant and can be quantified. Here we classify the structural complexity in terms of the long time tail exponent in the molecular velocity autocorrelation function. The specific

values of the dynamical exponent let us identify the relevant tissue microanatomy affecting water diffusion measured with MRI in muscles and in brain, and the microstructural changes in ischemic stroke.

Our framework presents a systematic way to identify the most relevant part of structural complexity using transport measured with a variety of techniques.



NMRCM Diffusion-weighted imaging pulse sequences: Echo planar imaging 2013 and alternative methods

Rita G. Nunes

Institute of Biophysics and Biomedical Engineering, Faculty of Sciences, University of Lisbon, Lisbon, Portugal E-mail: rgnunes@fc.ul.pt

1. Introduction

The simplest diffusion-weighting module consists of a pair of diffusion gradients separated by a 180° refocusing pulse. In the presence of motion, phase accrued while the first gradient is applied is not perfectly cancelled by the second gradient. Incoherent motion associated to diffusion therefore leads to a distribution of phases within each voxel resulting in signal loss.

Diffusion-Weighted (DW) images need to be sensitive to the microscopic motion of water molecules (of the order of a few microns) which renders them extremely sensitive to bulk motion. Rigid-body motion can lead to global phase shifts and spatial phase gradients [1], while pulsatile brain motion [2] produces non-linear phase patterns.

2. Echo Planar Imaging

Single-shot echo planar imaging (ssEPI) is the most used sequence for DWI as it samples the whole of k-space following a single excitation, avoiding phase inconsistencies between different data points. Unfortunately, the long readout window means ssEPI is very sensitive to field inhomogeneities with images displaying spatial distortions and signal loss particularly at tissue-air interfaces. Geometric distortions due to eddy currents generated by the diffusion module are also problematic [3]. Strategies to minimize and correct for these effects will be discussed.

Image resolution attained with ssEPI is limited due to relaxation and so multi-shot approaches are needed for highresolution imaging. In this case, it is essential to correct for phase inconsistencies between shots, which can be measured using navigators. To increase efficiency, self-navigated sequences based on EPI, radial or spiral trajectories have been suggested.

3. Alternative Methods

3.1 Fast Spin Echo

Fast Spin Echo (FSE) techniques are robust to field inhomogeneities, but require precise control of the signal phase at the start of the refocusing pulse train (CPMG condition [4]). This is particularly challenging to achieve with DW. The sequence can be modified so that the FSE signal becomes phase insensitive but at the cost of a 50% signal reduction [5]. A different strategy consists in correcting for motion-induced phase patterns ensuring that the CPMG condition is satisfied following the diffusion sensitisation

module. Norris et al. demonstrated real time correction for linear phase patterns induced by rigid-body motion [6]. To correct also for the residual non-linear patterns, tailored RF excitation pulses can be used [7].

3.2 Steady-State Free Precession

Diffusion contrast is achieved by sacrificing signal-tonoise (SNR). Steady-State Free Precession (SSFP) sequences are very promising as they use very short repetition times and take advantage of the contribution from multiple coherence pathways to achieve high SNR per unit time. As will be discussed in the presentation, the downside is that signal depends also on the flip angle and relaxation times, making diffusion quantification more complicated. A review of DW-SSFP methods is presented in [8].

Acknowledgements

Portuguese Foundation for Science and Technology (PEst-OE/SAU/UI0645/2011).

- [1] Anderson AW, Gore JC. Analysis and correction of motion artifacts in diffusion weighted imaging *Magn Reson Med*, **32**, 379-387 (1994).
- [2] Miller KL, Pauly JM. Nonlinear phase correction for navigated diffusion imaging. – *Magn Reson Med*, 50, 343-353 (2003).
- [3] Jezzard P, Barnett AS, Pierpaoli C. Characterization of and correction for eddy current artifacts in echo planar diffusion imaging. – *Magn Reson Med*, **39**, 801-812 (1998).
- [4] Meiboom S, Gill D. Modified Spin-Echo Method for Measuring Nuclear Relaxation Times. – *Rev Sci Instrum*, 29, 688-691 (1958).
- [5] Alsop DC. Phase insensitive preparation of single-shot RARE: application to diffusion imaging in humans. – Magn Reson Med, 38, 527-533 (1997)
- [6] Norris DG, Driesel W. Online motion correction for diffusion-weighted imaging using navigator echoes: Application to RARE imaging without sensitivity loss. – *Magn Reson Med*, 45, 729-733 (2001).
- [7] R.G. Nunes, S.J. Malik, J.V. Hajnal. Single shot Fast Spin Echo diffusion imaging with correction for nonlinear phase errors using tailored RF pulses. – *Magn Reson Med*, In Press, (2013).
- [8] J.A. McNab, K.L. Miller. Steady-state diffusionweighted imaging: theory, acquisition and analysis. – *NMR Biomed*, 21, 783–793 (2010).



Institut für Festkörperphysik, TU Darmstadt, Hochschulstr. 6, 64289 Darmstadt, Germany E-mail: alexei.privalov@physik.tu-darmstadt.de

1. Introduction

Recent developments of Field Cycling (FC) NMR have opened new possibilities for the studies of condensed matter. Together with the availability of commercial relaxometers [1, 2] it renders the FC technique increasingly attractive for scientists. The main advantage of FC is the possibility to investigate the evolution of a spin system in a broad frequency range using a magnetic field which can be quickly switched (cycled). The goal of this contribution is to present some new developments of our group in the instrumentation and to give an overview of new techniques thereby further developing FC NMR.

2. Instrumentation

A typical FC experiment is best understood by considering the basic three steps of the magnetic field setting: First, the "polarization" of the sample in a magnetic field B_{pol} ; second, the "evolution" of the spin system in an adjustable field B_{ev} in which the nuclear spin polarization relaxes towards its new equilibrium state with a corresponding rate $T_1^{-1}(B_{ev})$; third, "detection" of the evolving polarization in a field B_{det} . This experiment is repeated in cycles as a function of the hold time t_{ev} of the evolution field B_{ev} .

For the reliability of an FC relaxometer the following parameters are of importance: a) the value of B_{pol} and B_{det} should be as high as possible, b) the range of B_{ev} should as broad as possible, c) the switching time should be as short as possible, d) the stability of the B_{det} should be good and e) the magnetic field homogeneity should be high. Depending on the experimental requirements not all of these conditions have necessarily to be fulfilled. In any case the accuracy of field regulation after the switching from B_{pol} to B_{ev}, especially if B_{ev} is in the range of μT or even below, is of a great importance. The field regulation over six orders of magnitude is a challenging problem [3]. Nevertheless, if signal averaging is required the stability of B_{det} during the NMR detection phase is a challenge. Compensation of magnetic field instabilities in FC NMR by reference deconvolution is a promising solution [4]. All these points will be discussed explicitly.

3. Experimental techniques

Results of several types of FC experiments on various nuclei will be presented and discussed:

- 1. Analysis of the T₁ dispersion in the solid state over a broad temperature range: In the case of an exponential relaxation the nuclear polarization will approach its new equilibrium with a corresponding rate $T_1^{-1}(B_{ev})$ which can be related to the spectral density of local magnetic field fluctuations, $J(\omega)$, which in turn is related to the correlation function of the dynamic processes. This method allows tracing correlation times over a very broad range from 10^{-3} to 10^{-10} s [5].
- Double NMR-NQR FC: With this method one can detect ¹⁴N quadrupolar transitions in various systems. Drugs and explosives can be detected with a sensitivity much higher as with pure NQR [6].
- 3. Investigation of slow molecular dynamics in polymers in ultralow magnetic fields: FC NMR can be applied for B_{ev} down to about 10⁻⁶ T corresponding to Larmor frequencies down to several tens of Hz [7].
- Rotational resonance in the laboratory system: Using FC is possible to mechanically rotate samples with NMR frequency corresponding to Bev [8].

- [1] http://www.stelar.it/
- [2] http://www.spinscope.com/
- [3] B. Kresse, A. F. Privalov, F. Fujara, Solid State NMR 40, 134, 2011
- [4] S. Reutter, A. Privalov, Appl. Magn. Res. 44, 55, 2013
- [5] A. F. Privalov, O. Lips, F. Fujara, J. Phys. Cond. Matter, 14, 4515, 2002
- [6] M. Nolte, A. Privalov, J. Altmann, V. Anferov, F. Fujara, J. Phys. D, 35, 939, 2002
- [7] A. Herrmann, B. Kresse, J. Gmeiner, A.F. Privalov, D. Kruk, F. Fujara, E. A. Rössler, *Macromolecules* 45, 1408, 2012
- [8] S. Reuter, A. Privalov, G. Buntkowsky, F. Fujara. Solid State NMR, 41, 74, 2012



A. V. Skripov

Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia E-mail: skripov@imp.uran.ru

Development of new sustainable and environmentfriendly energy systems requires safe and efficient ways of energy storage. Renewable energy can be stored directly as electricity in batteries or indirectly as hydrogen in solid-state hydrides. Metal borohydrides have received recent attention as promising hydrogen-storage materials due to their high hydrogen densities. However, practical use of the known metal borohydrides is hindered by their stability with respect to thermal decomposition and the slow hydrogen sorption kinetics. Elucidation of the complex structures and hydrogen dynamics in these materials may give a key to improving their

hydrogen-storage properties. This lecture presents a review of the dynamical properties of borohydrides and the related compounds. It is based mainly on recent experimental results obtained by the NMR group at the Institute of Metal Physics (Ekaterinburg). We will discuss the relations between the motional parameters derived from NMR experiments and the structural features of the borohydrides. A special emphasis will be made on novel borohydride-based systems showing both fast reorientational motion of BH₄ groups and fast translational diffusion of ions.



NMRCM Fullerene like nanoparticles of PrF₃: from creations to medical 2013 applications

Murat Tagirov

Kazan Federal University Kazan, Russia E-mail: murat.tagirov@kpfu.ru

Recently, the interest in nanoparticles has been steadily increasing owing to their unique physical and chemical properties. Deposition from colloid solutions is a well elaborated method, which makes it possible to obtain nanosized samples of double and triple rare-earth fluorides [1]. A modification of this technology with the use of microwave radiation is described in [2], where it was shown that there are internal cavities in the synthesized particles (suchnanoparticles are called fullerene like nanoparticles).This technology was used to synthesize a series of crystalline fullerene like PrF₃ nanoparticles [3, 4]. Since the hydrothermal synthesis is performed in an aqueous solution, it is possible to suppose that water is located in the internal cavities of such nanoparticles. According our results

of experiments this hypothesis was demonstrated by using nuclear magnetic resonance cryoporometry and highresolution transmission electron microscopy methods [5].

Finally some possible application for medicine will be presented.

- X. Wang and Y. D. Li, Angew. Chem. Int. Ed. 42, 3497 (2003).
- [2] L. Ma, W. Chen, Y. Zheng, et al., Mater. Lett. 61, 2765 (2007).
- [3] M. S. Tagirov, E. M. Alakshin, R. R. Gazizulin, et al., J. Low Temp. Phys. 162, 645 (2011)
- [4] M. S. Tagirov, E. M. Alakshin, R. R. Gazizulin, et al., J. Low Temp. Phys. 162, 645 (2011).
- [5] E. M. Alakshina, D. S. Blokhina, A. M. Sabitova, et al., JETP Letters, 2012, Vol. 96, No. 3, pp. 181–183.



NMRCM **Dynamic nuclear polarization at ultralow temperatures**

<u>Sergey A. Vasiliev</u>¹, Jarno Järvinen¹, Denis Zvezdov^{1,2}, Janne Ahokas¹, Sergey Sheludyakov¹, Otto Vainio¹, Takao Mizusaki³, Yutaka Fujii³, Seitaro Mitsudo³, Minchan Gwak⁴, SangGap Lee⁴

¹Department of Physics and Astronomy University of Turku, 20014 Turku, Finland E-mail: servas@utu.fi ²Kazan Federal University, 420008 Kremlyovskaya str., Kazan, Russia ³Research Center for Development of Far-Infrared Region, University of Fukui, Fukui, Japan ⁴Division of Materials Science, Korea Basic Science institute

1. Introduction

Dynamic nuclear polarization (DNP) is an important tool in magnetic resonance, which provides versatile control of the nuclear polarization and substantial enhancement of the sensitivity of NMR. Very interesting systems where the effects of DNP can be studied are shallow donors (P, As, Bi) in Si. Magnetic resonance studies of these samples have a long history starting from pioneering work of Feher [1]. Recently the interest to this system has been raised by the proposal of Kane [2] to utilize these impurity atoms for quantum computing with the nuclear spin serving as a memory qubit and electron spin for readout.

In this work we report on the first experimental study of DNP of ³¹P donors in silicon performed in strong magnetic field and temperatures below 1K. At these conditions donor electron spins are fully polarized, electron and nuclear relaxation times are extremely long. All these factors substantially change the efficiency of DNP: pumping with extremely low RF powers (<1 μ W) for reasonably short time (\approx 1 hour) very high values of DNP of ³¹P were reached.

2. Samples and methods

We performed experiments with the samples of silicon of normal isotopic abundance, having 4.7% of ²⁹Si with nuclear spin $\frac{1}{2}$. Due to rather sparse electron could of ³¹P, there is roughly 70²⁹Si nuclear spins effectively interacting with the donor electron via the dipole-dipole and exchange interactions. This interactions lead to the inhomogeneous broadening of the ³¹P ESR lines with the line width of 4 G. ESR spectra were recorded using a cryogenic 128-GHz heterodyne spectrometer [3], which is optimized for reaching highest sensitivity at very low (pW range) excitation powers. The spectrometer does not use field modulation and provides true absorption and dispersion components. ESR spectrum of ³¹P consists of two hyperfine lines: *a*-line (low field), and *b*line (high field) as shown in Fig. 1. Samples were mounted on one of the mirrors of a Fabry-Perot resonator, placed in a 4.6 T field inside high homogeneity superconducting magnet, and cooled down to 100 mK by a dilution refrigerator.

3. Results

At temperatures below 1K electron relaxation time of ³¹P is ≈ 0.1 sec, which caused easy saturation of the samples by

extremely low excitation powers. We found that stopping the sweep on the ESR line "burns" a hole in the spectrum already after several seconds of pumping. The holes were very narrow with the width of ≈ 15 mG, defined by the $1/T_2$ of ${}^{31}P$ electrons. The hole relaxation time after pumping ranged from several tens of minutes to tens of hours, depending on the pumping time and sample temperature. The holes were created in both lines of ³¹P, and can be explained by the DNP of ²⁹Si surrounding donor atoms via the Overhauser effect. Instead of burning holes we also pumped the whole ESR lines applying frequency modulation of the mm-wave source with appropriate deviation. Pumping b-line leads to the DNP of ³¹P (traces 1 and 2 in Fig. 1), while pumping the a-line leads to the DNP of 29 P (traces 3 and 4). In the latter case the *a*-line of ³¹P is shifted to the higher fields, and gets strongly narrowed. We discuss possible physical mechanisms of the observed phenomena and potential utilization of these effects for quantum computing.



Figure 1. ESR spectra with DNP of ³¹P and ²⁹Si after pumping at 128 GHz with $\approx 1 \mu W$ power: trace 1-moderate DNP of ³¹P after several min. of pumping of b-line; trace 2- full polarization of ³¹P nuclear spins after ≈ 1 h pumping of b-line; trace 3 - partial polarization of ²⁹S after pumping the a-line; trace 4 - strong polarization of ²⁹Si after several hours of pumping the a-line

- [1] G. Feher, Phys. Rev. vol. 114, 1219 (1959).
- [2] B.E. Kane, Nature, vol. **393**, 133 (1998).
- [3] S. Vasilyev, J. Järvinen, E. Tjukanoff, A. Kharitonov, and S. Jaakkola, Rev. Sci. Instrum. 75, 94 (2004).



NMRCM Pulsed Field Gradient NMR for biological membranes and 2013 polymeric electrolyte investigations

Vitaly I. Volkov

Institute of Problems of Chemical Physics RAS, Chernogolovka, Moscow Region, 142432, Russia E-mail: vitwolf@mail.ru

1. Introduction

The self-diffusion measurements, especially the techniques using the pulsed field gradient NMR following by Fourier transforms, are the unique methods for direct structural and dynamic studies in systems with the fast ionic and molecular transport. For diffusional water permeability in biological systems, pulsed field gradient NMR (PFG-NMR) spectroscopy has become the method of choice due to its remarkable sensitivity to molecular displacements in the range of 10nm–100 mm and to its non-invasive character.

In order to interpret the experimental data correctly, the model investigations are necessary.

The results were obtained at the Laboratory of Membrane Processes, Karpov Institute of Physical Chemistry, Moscow, Russia; Laboratory of NMR, Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow Region Russia and at Laboratory of Food and Biomaterial Science and Engineering, Graduated School of Life Science and Biotechnology, Korea University, Seoul, Korea. This presentation devotes to investigations of ionic and water transport in biological cells (chlorella, yeast and erythrocytes), in cation-exchange membranes and polymeric electrolytes for the lithium cells. Well known perfluorinated cation-exchange memdranes, sulfocationexchange styrene bivinyl benzene resin CU-2 with different amount of crosslinked agent and aromatic bi sulfocontaining polyamides were stidied. Two polyamide isomer compositions iso (μ PA) and tere (π PA) were investigated. Lithium and solvating molecules self-diffusion processes in polymeric electrolytes on the basis of polyester di-acrylate, lithium perchlorate and ethylene carbonate were investigated. The investigation of the polymeric electrolyte systems on the basis of LiBF4 diacrylatenic with ionic liquid 1- butyl-3methyl imidazole tetra fluorine borate (BMIBF4) was carried out.

2. Polymeric electrolytes

Sulfo-, carboxyl-, aminogroups containing ion exchange membranes were investigated as model systems. The hydration of fixed groups and alkaline and alkaline – earth ions were studied in details in perfluorinated Nafion membranes. The mechanism of charge group – counter ion or water molecule interactions were understood from high resolution hetero nuclear NMR data. Microscopic ionic and water molecule mobilities were determined by NMR relaxations. Self-diffusion coefficients of protonic molecules and lithium and fluorine counter ions in different spatial scales were measured directly by PFG NMR. It was concluded that the macroscopic electro – mass transfer is controlled by local ion and molecule jumps between adjacent charge groups. The interconnection between ionogenic channel structure, mobile ion or molecule-charge groups

binding and translational ionic and molecular mobility was determined. On the basic of this knowledge, the main particularities of water behaviour in proteins and gels have been understood. It was shown that hydrogen bond is very important for proton and water molecules motions in biological ionic channels. The degree of lithium perchlorate dissociation was estimated from the comparison of calculated and measured conductivity values. The Li⁺ cation solvation processes in polymeric electrolytes (PE) on the basis of polyester di-acrylate, lithium perchlorate and ethylene carbonate (EC) were investigated. It was revealed that the high ionic conductivity was realized when the amount of EC molecules per Li⁺ more than 4 and the lithium cations were solvated of EC molecules. At these conditions the dissociation degree of LiClO₄ molecules (Li⁺ concentration) strongly increses and the cation translation transfer is occured together with EC molecules. The fast exchange between the ions and the neighboring solvation sphere molecules following high ionic mobility occurs by at the same time [1].

3. Biological cell membranes

Water self-diffusion in cells of chlorella, yeast and red blood cell was investigated. These cells were selected as model systems with different cell membrane permeabilities. The apparent self-diffusion coefficients of intracellular and extracellular water were measured dependent on diffusion time. The regions of restricted diffusion and hindered diffusion were observed. Scaling approach and two compartment exchange model were applied to calculate cell sizes and permeabilities [2, 3]. The values of permeability calculated by these two ways are very close to each other. The correctness of these theoretical interpretations was also demonstrated by good agreement of cell sizes obtained from PFG NMR and electron microscopic data. The permeabilities are 3.10⁻⁶, 6.10⁻⁶ and about 10⁻⁴ m/s for chlorella, yeast and red blood cells, respectively, depending on cell growing conditions and physical chemistry treating. The average cell sizes are varied from 2 to 4 microns. The water exchange mechanism in biological cells is discussed.

Acknowledgements

The investigation was supported by Russian Basic Research Foundation, grant № 13-03-00698-a.

- V.I. Volkov, A.A. Marinin Russian Chemical Reviews 82(3) 248-272 (2013)
- [2] Suh K.J., Hong Y.S., Volkov V.I., Skirda V.D. et.al Biophys. Chem. 104, 121-130, (2003).
- [3] Cho J.H., Hong Y.S., Volkov V.I., Skirda V.D. et. al. Magnetic Resonance Imaging 21,1009-1017 (2003).



Matthias Weigel

University Medical Center Freiburg, Dept. of Radiology, Medical Physics Freiburg, Germany www.matthias-weigel.net E-mail: Matthias.Weigel@uniklinik-freiburg.de

are generated in and after a sequence of multiple gradients and RF pulses, and what the corresponding echo intensities Fourier space and the action of the RF pulses on these Fourier prerequisites are necessary for adding diffusion effects.

The essence of phase graphing is to predict when echoes components is characterized. If care is taken, further effects of diffusion can be included and quantified.

My talk will shed some light on the meaning and are. In the modern interpretation magnetization is depicted in interpretation of extended phase graphs and what

Part II

Oral Reports



NMRCM Use of MRI database for analysis of evolution of magnetic field of 2013 superconducting magnet

<u>Nikolay V. Anisimov</u>¹, Ekaterina I. Shalamova¹, Svetlana S. Batova¹, Andrey A. Samoylenko²

E-mail: anisimovnv@mail.ru ¹Lomonosov Moscow State University, Moscow, Russian Federation ²Semenov Institute of Chemical Physics

1. Introduction

The field strength of a horizontal bore magnet depends both on the current through the solenoid and the Earth magnetic field. It is useful to trace the evolution of the Larmor frequency to estimate the dynamics of both fields.

2. Materials and Methods

Materials of a database of MRI studies within 14 years were used for analysis of evolution of the Larmor frequency of a 0.5T MR-scanner (Bruker Tomikon S50) with a horizontal bore (north-east orientation) superconducting (SC) magnet (Magnex Ltd). This database [1] contents not only images but also pulse sequences parameters and results of automatic definition of operating frequency (F) of the MR scanner. This operation is made in the beginning of each MRI study to determine isocenter frequency. To do this the free induction signal is registered and position of the maximal peak is determined by Fourier analysis. Typical NMR spectrum of human organ contents two strong peaks from water and fat divided by 3.5 ppm. Value F depends on a water/fat proportion in organ under study as organ specific receiver coils are used and their locations are adapted to the investigated organs.

3. Results

Curves F(t) for receiver coils which were used for research of different organs (head, neck, etc.) are shown on Fig.1. Dispersion of the data is up to 10^2 Hz. Therefore each point on the graph is the result of month averaging. Graph points for head coil are higher than for the other coils around 70-80 Hz, i.e. just 3.5 ppm. This means that the adjustment of operating frequency is made on a water signal only for the head, while for other body parts – on fat signals. This should be taken into account by scanning with frequency-selective signal suppression [2].

Time constants of decay for all F(t) curves are identical - $\tau \ge 1.25 \cdot 10^5$ years. Magnetic field is mainly determined by the current through the SC solenoid. Hence if we know inductance of the solenoid (L=10.8 H) we can estimate its electric resistance as R=L/ τ . To define specific resistance of a material of which it is made one must know the wire's diameter and length. These parameters one can estimate from geometrical proportions of the solenoid. For our model of magnet one can propose that the top estimation of specific resistance of a superconductor made of niobium-titanic

(Nb₃Ti) cable is $1.4 \cdot 10^{-20}$ OM·cm. This value is typical for the type 2 superconductors [3].

Curves F (t) have the local «spikes» up to $\sim 10^2$ Hz. Probably they are connected with the changes of the magnetic field in the location of the magnet. These changes can be connected with the technogenic reasons. But it is impossible to exclude disturbance of the magnetic field of the Earth because of global seismic activity - the most powerful "splash" on curve F(t) concurs with a peak of seismic activity in 2007 [4].



Figure 1. Evolution of F (top) and seismic activity (down)

4. Conclusions

Information about the evolution of the Larmor frequency is useful for assessing the quality of a magnet and calculating the conductivity of a superconductor. Analysis of this information from NMR equipment in different geographic locations is useful for Earth magnetometry.

- N. V. Anisimov, E. B. Shilov, V. V. Gladun. Proc. NMRCM-2010; 59 (2010).
- [2] B. R. Rosen, V. J. Wedee, T. J. Brady. J. Comput. Assist. Tomogr.; 8, 813-818 (1984).
- [3] Y. B. Kim, C. F. Hempstead, A. R. Strnad. Phys. Rev. Lett.; 9 (7), 306-309 (1962).
- [4] http://earthquake.usgs.gov.



NMRCM Novel high resolution NMR techniques for elucidation 2013 of molecular structure and dynamics

<u>Vyacheslav A. Chertkov</u>¹, Dmitriy A. Cheshkov^{1,2}, Tatiana A. Ganina¹, Sergey S. Nechausov¹, Kirill F. Sheberstov^{1,3}, Alla K. Shestakova²

¹Department of Chemistry, Moscow State University, 1 Leninskie Gory, Moscow, 119992, Russia ²State Research Institute of Chemistry and Technology of Organoelement Compounds, 38 Shosse Entuziastov, Moscow, 111123, Russia

³Faculty of Materials Science, Moscow State University, 1 Leninskie Gory, Moscow, 119992, Russia E-mail: chertkov@org.chem.msu.ru

1. Introduction

Spin-spin coupling constants (SSCC) are the key NMR parameters for structure determination nowadays. However, direct measurement of these parameters is difficult in many cases due to peaks overlapping, short relaxation times and/or second order effects (see [1-2]). Theoretical description for SSCC needs also to be developed in practical aspects. We showed recently [3], that dynamic behavior of many important molecular systems can be described in terms of vibrations with large amplitude. Accurate structure studies of saturated four- and five-membered cycles imply solving specific problem of quantitative description of dynamic processes with very low barriers in them. Here we present application of few new effective techniques for extraction information on the dynamic structure [3, 4] via the high precision analysis of NMR multiplets and theoretical description of the NMR parameters.

2. Methods

We developed a practical method for evaluation of the parameters of conformational dynamics in terms of vibrations with large amplitude. The method based on: (*i*) the results of complete analysis of high resolution NMR spectra, (*ii*) ab'initio calculations of a reaction path and surfaces of potential energy and spin-spin coupling constants, (*iii*) a numerical solution of corresponding vibration problem and (*iv*) refinement for the parameters of the energy surface based on the best fit of experimental (see e.g. [1-2]) and calculated spin-spin couplings.

As a starting point, the undistorted potential energy surface (PES) of inner rotation for the compounds studied was built by applying the scanning technique to skeletal dihedral angles [3]. This allows us to get a trial "reaction path" for the pseudorotation process. Conformational dependencies for spin-spin coupling constants (SSCC) for principal points on the reaction path were calculated using FP DFT technique [5]. ¹H NMR spectra were recorded for a series of solvents and "Bruker AV-600" spectrometer at room temperature, and were treated using total lineshape analysis technique (program VALISA [1]) which allows to get very accurate estimates of experimental SSCC values. Finally, the reverse spectral problem was solved to adjust experimental and calculated data and build up the "true" potential of pseudorotation. We developed REVIBR program [3, 6],

which solves numerically corresponding vibration problem and models the dynamic averaging using the technique of convolution of the spin-spin coupling surfaces using the whole set of vibration energies and eigenvectors (normally, 200 lowest ones). Convolution criterion used in REVIBR program allows to get calculated SSCC for given temperature. Nonlinear optimization (Levenberg-Marquart techniques) of the estimated parameters for the "true" pseudorotation PES (modeling difference of ground states of main conformers ΔE and heights for the conformational barriers ΔE^{\neq}) used to get best fit of experimental and calculated SSCC values.

3. Results

Advantages of the technique developed demonstrated on a of monosubstituted cyclobutanes, series trans-1.2dihalocyclopentanes, tetrahydrofuran [3, 6], tetrahydrothiophene, tetrahydrothiophene-1-oxide, pyrrolidine, proline and ribonucleosides. The data obtained shows, that the pseudorotation process in every four- and five-membered system under study is carrying out by the mechanism with high amplitude of vibration. Major conformations of tetrahydrofuran and terahydrothiophene are twists ⁴T₅ and ${}^{5}T_{4}$, for pyrrolidine – envelope E₁ with equatorial NH-bond, for terahydrothiophene-1-oxyde – envelopes E_3 and with axial oxygen and for proline - envelope E5 with axial COOHgroup. Method used also for characterization of internal rotation in acyclic systems: styrene, substituted cis- and trans-azobenzenes, cinnamic aldehyde as well as in natural endogenic hormones noradrenaline and adrenaline.

References

- [1] S.V. Zubkov, S.S. Golotvin, V.A. Chertkov. *Russ. Chem. Bull.*, **51**, 1222-1230 (2002).
- [2] S.V. Zubkov, V.A. Chertkov IJMS, 4, 107-118 (2003).
- [3] A.V. Chertkov, O.I. Pokrovsky, A.K. Shestakova, V.A. Chertkov *Chem. Heterocycl. Comp.*, **44**, 782-784 (2008).
- [4] J.W. Blanchard, M.P. Ledbetter, T. Theis, M.C. Budker, D. Budker, A. Pines, J. Am. Chem. Soc., 135, 3607-3612 (2013).
- [5] W. Deng, J.R. Cheeseman, M.J. Frisch, J. Chem. Theory and Comput., 2, 1028-37 (2006).
- [6] A.V. Chertkov, A.K. Shestakova, V.A. Chertkov, *Chem. Heterocycl. Comp.*, **48**, 412 421 (2012).

- 35 -



NMRCM Hydration properties of carboxylic acid functional groups in 2013 aqueous solutions

Rinat G. Dzhambulatov, Alexey V. Donets

Department of Physics, St. Petersburg State University, St. Petersburg, Russia E-mail: ren6415@yandex.ru

1. Introduction

This work is directed on the solution one of the most important problem of biochemistry - development of method for studying the hydration properties of organic molecules. Analysis of concentration and temperature dependences of spin-lattice relaxation rates of solvent nuclei allows us to solve this problem. Firstly this method was developed for the investigation the electrolyte solutions [1] and later was used for the solution of acetic acid [2] and the solutions of amino acids [3]. In the present work the method was developed for aqueous solutions of carboxylic and dicarboxylic acids. For the first time the hydration properties of different functional groups of acids were separated.

2. Experiment and methods

The samples of solution of acetic, propionic, butyric, malonic and succinic acids in heavy water D2O were prepared. Measurements of the spin-lattice times of deuterium nuclei of solvent were carried out on Bruker SPX 4-100 or Bruker Avance 500 MHz by "inversion-recovery" method.

The water forms ordered structure around acid molecules. Water molecules are characterised by the certain dynamics and structure of hydrogen bonds near each functional group of organic molecule. In the case of the fast exchange of solvent molecules in the solution the relaxation rate of the solvent nuclei is given by the formula [1].

$$\frac{1}{T_1} = \sum_{i=1}^{N-1} \frac{mn_i}{M} \frac{1}{T_{1i}} + \left(1 - \sum_{i=1}^{N-1} \frac{mn_i}{M}\right) \frac{1}{T_{10}},$$

where m is the molality, M is the number of moles in 1000 grams of solvent, T_{1i} is the solvent nuclei relaxation time in the structure number *i*, T_{10} is the relaxation time of free solvent, n_i is the number of molecules in the *i* - structure (coordination number).

The formula predicts the linear concentration dependence, but distinct deviations from linearity have been observed. The bends may be explained by the change in solution structure. The first bend corresponds to the disappearance of free solvent structure. The position of the bend gives number of the water molecules in the hydration shell of acid molecule and coordination number of methylene group. The quantum chemical calculations confirmed these parameters. The linear approximation of experimental dependences and detailed analysis of slopes allow to determine the relaxation rates of the ²H nuclei of water near each functional group. The

activation energies in the different substructures of the solutions can be determined from the temperature dependences of relaxation rate.

3. Results

The analysis of concentration and temperature dependences of spin-lattice relaxation rates of the ²H nuclei of solvent molecule gives the following significant characteristics of hydration properties of carboxylic acids:

• An acetic, propionic and butyric acids molecules coordinate 20, 27 and 34 molecules of D₂O respectively.

• The coordination number of the methylene group is 7. This result agrees with result for amino acids obtained by NMR-relaxation data and quantum chemical calculations [2].

• The deuteron relaxation rates of water molecules in hydration shells of the methylene, methyl and carboxylic group were determined at different temperatures.

• The mobility of the water molecules near the hydrophobic methylene and methyl groups are less than in the pure water at different temperatures.

• The deuteron relaxation rate of solvent near the hydrophilic carboxylic group is similar with rate in pure water at low temperature T=276 K.

• Activation energies of water mobility for acetic and propionic acids solutions were determined.

The obtained parameters give information about structure and dynamic features of water near each functional group of organic molecules.

Acknowledgements

NMR data were obtained in department of Quantum Magnetic Phenomena and Magnetic Resonance Center of SPbSU.

This work is supported by the Russian Foundation for Basic Research (grant N_{2} 10-02-01043-a). The authors acknowledge Saint-Petersburg State University for a research grant.

- V. I. Chizhik, NMR relaxation and microstructure of aqueous electrolyte solutions, Mol. Phys., 1997, Vol. 90, No. 4, p. 653-659
- [2] M. A. Vovk, M. S. Pavlova, V. I. Chizhik, A. A. Vorontsova. Models of acetate ion hydration shells according to nuclear magnetic relaxation and quantum chemical calculations. Russian Journal of Physical Chamistry, 2011, V. 85(9), 1715-1720.
- [3] Rabdano S., Bachelor work, 2012.



NMRCM ⁷Li NMR field-cycling relaxometry as tool to investigate lithium 2013 ion dynamics in solid-state electrolytes

Jan Gabriel, Michael Vogel

Institut für Festkörperphysik, Technische Universität Darmstadt, Germany E-mail: gabriel@nmr.physik.tu-darmstadt.de

The main component of current batteries are Li-based materials. We use ⁷Li NMR to study lithium ion dynamics in glass with $0.5Li_2S+[(1-x)GeS_2+xGeO_2]$. Fast Field-cycling (FFC) relaxation is employed in combination with stimulated-echo (STE) experiments and line shape (LS) analysis to cover a time window over 10 orders of magnitude [1, 2]. The stimulated-echo is suitable to measure the correlation function $F_2(t)$ of lithium ion dynamics in solids in a range from 10^{-5} to 10^1 s. The motional narrowing of NMR spectra is sensitive to correlation times from 10^{-4} to 10^{-5} s. Finally we show that field-cycling relaxometrie has a time window from 10^{-9} to 10^{-5} s.

These three methods probe translational motion of lithium ions. The field-cycling and stimulated-echo data reveal a nonexponentiality of the lithium ion dynamics in the studied glasses. The shape of the spectral density $J_2(\omega)$ is well described by a Gaussian distribution of energy barriers and the decay of the correlation function of $F_2(t)$ is well interpolated by Kohlrausch-William-Watts function. Observation of T₁ minima for a broad range of Larmor frequencies allow us to determine temperature-dependent correlation times and thus, the activation energy of lithium ion dynamics. When the dynamics of lithium ions is too slow to be observed at sufficiently low temperatures, field-cycling relaxometry probes the nearly constant loss which is considered as a universal phenomenon of disordered solids.

Acknowledgements

We thank S. W. Martin for providing samples.



Figure 1. Data for 0.5Li₂S+GeS₂ a) mean correlation times from FFC, LS and STE. The correlation times for LS and FFC were obtained from fits under the assumption of Gaussian distributed energy barriers;
b) distribution of correlation times from FFC

- R. Böhmer, K. R. Jeffrey, and M. Vogel. Solid-state Li NMR with applications to the translational dynamics in ion conductors. Progress In Nuclear Magnetic Resonance Spectroscopy, 50(2-3):87-174, MAR 30 2007
- [2] M. Graf, B. Kresse, A. F. Privalov, and M.Vogel. Combining ⁷Li NMR field-cycling relaxometry and stimulated-echo experiments: A powerful approach to lithium ion dynamics in solid-state electrolytes. Solid State Nuclear Magnetic.


Faculty of Physics, Saint Petersburg State University E-mail: oxana.iljina@gmail.com

1. Introduction

The most common MR images obtaining method is a combination of the selective irradiation and two-time Fourier transform of the data. Usually we assume the coordinates has linear spatial dependence from the frequency. But whenever a linear gradient is activated there are concomitant gradients, and magnetic field has non-linear dependence result.

2. Concomitant gradients

Concomitant gradients are an unavoidable consequence of Maxwell's equations. When the one diagonal components of the gradient tensor was created (for example, $G_{zz} = \frac{\partial B_z}{\partial z}$) the

other diagonal components G_{xx} and G_{yy} inevitably appear. Creation of the off-diagonal component also lead to the appearance of transverse with respect to the static field

component (for example, $\frac{\partial B_z}{\partial x} = \frac{\partial B_x}{\partial z}$). These concomitant

gradients result in undesired phase accumulation during MRI scans and as a consequence a number of image artifacts including geometric distortion.

3. Example

The source of a gradient field is Maxwell coil. The distance between the coils are 1,7 of a diameter.

One can see that absolute value of field has not linear dependence on the coordinate. In a low-field MRI this effect increases.

- [1] P.A. Rink. Magnetic resonance in medicine (in Russian) - "GEOTAR-MED", Moscow, 2003
- [2] B.L. Alievsky, V.L. Orlov. The calculation of the axially symmetric coils magnetic field parameters (in Russian) – "Energoatomizdat", Moscow, 1983



Figure 1. Z – component of field (for one coil; the dotted lines) and absolute value of field for the different distance r from axis of coil (large scale)



Figure 2. Absolute value of field B (distance from axis of coil r=0.2 a.u.) for the different $B_0(0,01; 0,02; 0,03; 0,04)$



NMRCM High-resolution NMR studies in ionic liquids

Vadim V. Kachala^{1,2}, Elena A. Khokhlova² and Valentine P. Ananikov²

¹Bruker Ltd, Moscow, Russia E-mail: kachala@bruker.ru ²N. D. Zelinskii Institute of Organic Chemistry, Moscow, Russia

1. Introduction

The growing interest to reactions in ionic liquids (ILs) can be esplained by their features, especially, high stability at lelevated temoperatures, tuneable chemical and physical properties, and development methods of product extraction, purification and recycling of ionic liquids allow fulfilling high standards of Green chemistry. NMR spectroscopy can be used for online and offline reaction monitoring in ILs In order to perform studies of chemical reactions, extraction, quality control. The number of NMR measurements in ionic liauids rapidly expand. Well-known carbohydrate transformation into 5-hydroxymethylfurfural (5-HMF) is reviewed.

2. Chemical transformations reaction kinetics studies

Continuing our study that was started in 2011, we focused on different tasks. Our first step was the identification and quantification of reaction components. We successfully utilized carbon-13 spectra that have wide signal spread and extra loss overlap compared to 1H spectra. After determination of T1 relaxation times for carbon-13 of ionic liquid media and solutes we optimized experimental conditions. As the mechanism of the conversion of carbohydrates to 5-hydroxymethylfurfural (5-HMF) was studied at the molecular level with the detection of anomers and intermediate species, we continued our studies by investigation of reaction kinetics and further product trasnformation. The nowel Bruker software, Dymanic center was used for these purposes and tested on these objects.

Further research was focused on identification of minor compounds and byproducts.

3. Summary

1D and 2D NMR spectra for a broad range of IL systems open possibilities for quantification. This approach was useful for conducting mechanistic studies in native-state ionic liquids. Reaction kinetic studies showed competetive processes of 5-HMF formation and further degradation (Fig.1). Following the analuzed data, it became possible to optimize reaction conditions for maximum yeld of target product.

Acknowledgements

Authors thank Dr. Anna Codina (Bruker UK) for Dynamic Center support and consultations

- [1] Khokhlova E. A., Kachala V. V., Ananikov V. P., ChemSusChem, 2012, 5, 783-789.
- [2] Ananikov V. P., Chem. Rev., 2011, 111, 418-454.



Figure 1. Reaction kinetics for glucose \rightarrow 5-HMF transformations calculated by Dynamic Center



NMRCM Temperature dependence of internal protein backbone dynamics 2013 studied by ²H NMR and random-walk simulations

Kerstin Kämpf^{1,2}, Beke Kremmling¹, Michael Vogel¹

¹Institute for solid state physics , Technical University Darmstadt, Darmstadt, Germany ²E-mail: kerstin.kaempf@physik.tu-darmstadt.de

1. Introduction

Although possessing an ordered structure, proteins have shown to exhibit versatile but common internal dynamics, which is indispensable for protein function [1, 2]. The precise nature, hydration dependence and geometry of this motion remains, however unclear [3]. In order to improve the understanding of the internal protein backbone dynamics, a combined approach of solid state ²H NMR and random-walk simulations (RWS) is used.

2. Methods and Materials

Solid state ²H NMR is a valuable tool to investigate dynamics over a wide range of time scales $(10^{-9}-10^{1} \text{ s})$. It is sensitive to the time scale as well as the geometry of motion [4, 5]. Spin-lattice relaxation, line shape (c.f. Fig. 1) and stimulated echo experiments have been performed on samples of fully deuterated cyano phycocyanin (CPC) at two degrees of hydration (h=0 g/g, h=0.3 g/g) and varyious temperatures between 150-310 K. Suppressing the contribution of the fast methyl groups based on their different time scale, we find that the protein backbone exhibits a temperature-dependent small angle amplitude motion.

The NMR parameters of the backbone motion are calculated quantitatively by RWS for two limiting scenarios (s. Fig. 2): A heterogeneous scenario with a distribution of temperature dependent correlation times and a homogeneous scenario, in which the amplitude of motion increases with temperature, while the temperature dependence of its time scale is negligible.



Figure 1. ²H spectra of d-CPC at h=0.0 g/g and h=0.3 g/gat different echo delay times (20, 50, 100, 200 µs). The inner Pake spectrum results from the methyl groups, the outer Pake spectrum from the protein backbone



Figure 2. Two limiting models of temperature dependence of motion

3. Results

The RWS show that the existence of a temperature dependent amplitude of the motion is a main feature of internal protein dynamics. Nevertheless a single temperature dependent angle, roughly increasing from 0° to 15° in the range 200-300 K, cannot explain all experimental observations

A distribution of angles is required for a good description of the observations in ²H NMR. Thus, the present study reveals that internal protein dynamics is a complex motion with an amplitude that strongly depends on temperature [6].

Acknowledgements

This work is supported by the Verband Chemischer Industrie, Germany.

- [1] Xie, Single Molecule enzymatic dynamics, Science, 282, 1877, (1998).
- [2] Flomenbom, Stretched exponential decay and correlations in the catalytic activity of fluctuating single lipase molecules, PNAS, 102, 2368, (2005).
- [3] Michael, Single-molecule fluorescence studies of protein folding and conformational dynamics, Chem. Rev., 106, 1785, (2006).
- [4] Vogel, Effects of various types of molecular dynamics on 1D and 2D ²H NMR studied by random walk simulations, J.Magn.Res.,147,43, (2000).
- [5] Lusceac, 2H and 13C NMR studies on the temperaturedependent water and protein dynamics in hydrated elastin, myoglobin and collagen, BBA, 1804, 41-48, (2010).



NMRCM Phase behavior of CTAB bilayer intercalated into magadiite

Boris B. Kharkov^{1,2}

¹Department of Chemistry, Royal Institute of Technology - KTH, SE-10044 Stockholm, Sweden ²Department of Quantum Magnetic Phenomena, St. Petersburg State University - SPbGU, 198504, St. Petersburg, Russia E-mail: kharkov@kth.se

1. Introduction

Intercalation of ionic surfactant bilayers into inorganic solids has been a subject of considerable interest during past decades. These organic-inorganic materials have found application as adsorbents of organic pollutants in water remediation, as crystalline models of lipid bilayers, and as artificial membranes [1]. In these systems surfactant molecules are bounded via Coulombic interaction to the internal surface of the galleries of the layered solid. The variety of structures, including monolayers, bilayers, paraffin-like structures, can be achieved by adjusting grafting density and synthesis conditions. Various spectroscopic techniques along with MD simulations have been applied for studying structural parameters and dynamics of the organic component of the system [2].

In the present study, we apply two-dimensional ¹³C separated local field spectroscopy (SLF) under MAS conditions to quantitatively characterize conformational dynamics of the cetyltrimethylammonium bromide (CTAB) intercalated into layered magadiite.

2. Order parameter profiles

Due to its well-defined orientational and distance dependence, heteronuclear dipole-dipole interactions provide sensitive probe to characterize dynamics and ordering of the internuclear bond. Proton-detected local field spectroscopy under MAS conditions (R-PDLF) is one of the most powerful methods to measure and assign heteronuclear dipolar couplings [3].

Order parameter profiles obtained from R-PDLF experiments in CTAB intercalated into layered magadiite for three different temperatures are presented in Fig.1. The profile measured at room temperature and denoted by circles in Fig.1 indicates that the majority of alkyl chains of the CTAB molecules adopt all-trans conformation. Moreover, no rotation about the molecular axis is observed in the system, since S_{CH} is close to unity. With increasing the temperature gradual transition to the more mobile state was observed.

At 75 °C, all CTAB molecules in the sample were in the "rotating" state, i.e. an alkyl chain of a molecule is in relatively stiff all-trans conformation (with only a small fraction of gauche segments) in the presence of fast rotation about the molecular axis (triangles in Fig.1).



*Figure 1. CH bond order parameters S*_{*CH*} *along CTAB molecule for three different temperatures*

Upon further sample heating, sharp phase transition was observed at about 85 °C. Stars in Fig.1 depict order parameters for different carbons along the molecule in this highly mobile "liquid-crystalline"-like state at 110 °C. Very high conformational and rotational dynamics was shown by both R-PDLF and conventional one-dimensional ¹³C NMR.

Acknowledgements

This work was supported by Swedish Research Council VR and by Russian Foundation for Basic Research.

- [1] Y. Okahata, A. Shimizu Langmuir, 5(4), 954 (2012).
- [2] V.V Naik, S. Vasudevan J. Phys. Chem. C, 115(16), 8221 (2011).
- [3] S.V. Dvinskikh et al. J. Magn. Reson., 168(2), 194 (2004).

NMRCM Conformation preference of ibuprofen in chloroform by 2D-3D 2013 NMR and GIAO quantum chemistry calculation

<u>Ilya A. Khodov</u>, Mikhail Yu. Nikiforov, Gennady A. Alper, Sergey V. Efimov¹, Vladimer V. Klochkov¹, Luís A. E. Batista de Carvalho²

G.A. Krestov Institute of Solution Chemistry of RAS, Ivanovo, Russian. E-mail: iakh@isc-ras.ru ¹Institute of *Physics Kazan Federal University, Kazan, Russian.* ²*Faculty of Science and Technology, University of Coimbra , Coimbra , Portugal*

1. Introduction

Our studies are dedicated to conformational details for drugs in solutions. It is well known that polymorphism of drug compounds affects the solubility and plays an important role in the production of pharmaceuticals. In turn, properties of polymorphs are connected with molecular structures of compounds and their ability to exist in different conformational forms in the solvent, from which recrystallization occurs. Therefore, search for new polymorphic forms of drug is closely associated with the study of the conformational state of drugs in solutions.

We are now studying (S)-ibuprofen is the active enantiomer of ibuprofen. Ibuprofen (Fig. 1) is a nonsteroidal anti-inflammatory drug (NSAID) used for reduce fever and treat pain or inflammation.

2. Results and discussion

We performed a proper assignment of lines in the ¹H and ¹³C NMR spectra with the aid of experiments 2D HMBC, 2D NOESY, HSQC, TOCSY; NOESY, INADEQUATE and 3D HMQC-TOCSY.



Figure 1. Structure of ibuprofen

In our case, the HSQC and HMBC showed similar patterns for aromatic protons in ibuprofen. In order to obtain unambiguous assignment of proton and carbon resonances, we decided to record (13C,13C)-INADEQUATE spectrum (Fig. 2).

It allows us to trace the connectivities of carbon atoms: 9-8-7-2-5-4-3-6 (atom numbering is as in Fig. 1). Evidently, signals of carbons 4 and 5 are interchanged, as compared to the AIST database [1].

M.L. Vueba,M.E. Pina, and L.A.E. Batista de Carvalho in 2007 published the result of a theoretical study of ibuprofen using density functional theory (DFT) calculations[2]. Eight different geometries were found to be energy minima. Might assume that the NMR measurements and the DFT conformer structures are accurate, but that the populations conformers are not.



Figure 2. 2D INADEQUTE for ibuprofen in chloroform

Comparing the chemical shifts ¹³C (δ (R) = Tr σ TMS– Tr σ (R)) of the calculations GIAO and experimental determination ¹³C, we obtain estimates of the conformational preferences (fig 3) by partial correlation method.



Figure 3. Conformational preferences of ibuprofen in chloroform

Evidently, conformer G and H predominate, are E and F also present but to a lesser extent than conformer G and H. Conformers proportion of A,B,C,D is relatively small. Such conformers preference because the concentration of ibuprofen in chloroform saturated.

- [1] Spectral Database for Organic Compounds SDBS. http://sdbs.riodb.aist.go.jp
- [2] M.L. Vueba, M.E. Pina, L.A.E. Batista de Carvalho. *J Pharm Sci.*, 97(2), 845-859 (2007).



NMRCM Chemical Exchange Saturation Transfer (CEST) for intracellular 2013 pH-sensitive Magnetic Resonance Imaging (MRI)

Alexandr A. Khrapichev

CR/UK Gray Institute for Radiation Oncology & Biology Department of Oncology, University of Oxford, Churchill Hospital, OX3 7DQ Oxford, United Kingdom. E-mail: alexandr.khrapichev@oncology.ox.ac.uk

1. Introduction

CEST is an MRI technique in which saturation is applied at the frequency of exchangeable labile protons with readout being performed from water protons. Through chemical exchange of saturated protons from the labile group to the unsaturated protons in the bulk water, a detectable signal reduction can be measured [1, 2]. This mechanism provides an indirect way to detect dilute labile protons that would otherwise be undetectable due to their low concentration.

2. Methods

A typical magnetization transfer (MT) imaging sequence consists of a long rectangular saturation pulse followed by a fast echo-planar imaging (EPI) readout (Fig. 1a). The saturation pulse is applied off-resonance and the MT effect is acquired on the base frequency, usually water peak. The same approach is used in CEST experiments, but the effect is evaluated for a range of the saturation frequencies.

In this study a series of narrow band Gaussian pulses was used instead of a long rectangular pulse for the saturation to provide compatibility with clinical MRI systems, which have restrictions on the length of the radio frequency pulses. Also EPI was replaced by a robust gradient echo technique to improve image quality. However, a simple combination of these two substitutions would significantly increase the experimental time. In order to save time, the saturation pulses were interleaved with the imaging readout as outlined in Fig. 1b.





3. Results and discussions

The transfer of saturation from amide protons to water protons depends on the pH level, and therefore could be exploited to measure intracellular acidity, which is of particular interest in the brain. Here we have used a metastatic rat model to test the CEST technique. Rats were injected intracerebrally with breast cancer cells and underwent MR imaging at two different stages of tumour development: 14 days (Fig. 2 top) and 21 days (Fig. 2 bottom). CEST maps were constructed on a point by point basis and results (Fig. 2 left) correspond well with tumour locations as assessed with standard T₂ weighted imaging (Fig. 2 right), clear changes of the imaging contrast are visible.



Figure 2. MR Images: a,b - CEST-maps; $c,d - T_2$ -weighted. Tumour development: a,c - 14 days; b,d - 21 days

However, in order to achieve fully quantitative results it should be taken into account that amide proton transfer depends not only on the level of acidity, but also on the concentration of amide present, therefore further analysis, based on an advanced computational model, is required.

Acknowledgements

This work is funded by Medical Research Council and Cancer Research UK.

- J. Zhou, P.C.M.V. Zijl. Prog. Nucl. Magn. Reson. Spectrosc., 48, 109-136 (2006).
- [2] P.C.M.V. Zijl, N.N. Yadav. Magn. Reson. Med., 65, 927-948 (2011).



¹St.Peterburg State University, 3, Ulyanovskaya, Petrodvorets, 198504, St.Peterburg, Russia ²Institut Néel, CNRS, 25 avenue des Martyrs, BP 166, 38042 Grenoble cedex 9, France *E-mail: konstantin.klyukin@gmail.com*

1. Introduction

Magnesium is one of the most promising candidates for hydrogen storage, mainly because of its high hydrogen storage capacity (up to 7.6 w%), low cost, large reserves and high reversibility of the hydrogen sorption reaction. Unfortunately, a rather high temperature of the hydrogen release, very low hydrogenation/dehydrogenation rates and a high reactivity toward air and oxygen essentially limit its application for practical uses.

Nevertheless, it was found that the limited dissociation rate of hydrogen on the metal surface may be improved by additions of transition metal catalysts (TM). Investigations by means of in situ X-ray [1] and neutron [2] diffraction of Mg/Nb thin films and nanocrystallites showed that hydrogen atoms penetrate inside Mg through the so-called Nb "gates". However, up-to-now there is no complete description of such a phenomenon on the microscopic level.

In our previous works [3, 4] we proposed one of the possible explanations of such hydrogen kinetic improvements in magnesium. We found that Nb additives stabilize the Mg bcc structure on interface border that could exhibit a much better hydrogen diffusion rate reference to other possible structures (hcp, fcc, rutile) of Mg.

In this contribution we report on the results of our theoretical studies of hydrogen diffusion in different structures of magnesium. To calculate diffusion coefficients and energy activation barriers we considered various possible diffusion paths in bulk Mg. Zero point energy (ZPE) contributions to energy barriers were also calculated.

2. Method of calculations

Calculations were performed within the framework of density functional theory (DFT) using the plane-wave pseudopotential method and the Perdew–Burke–Ernzerhof GGA exchange and correlation potential as implemented in Quantum Espresso package [5]. For all calculated structures we optimized the lattice parameters and the atomic positions. The kinetic energy/charge cut-off was equal to 70/260 Ry, the $12 \times 12 \times 12$ k-point mesh was used. To estimate ZPE contributions we performed phonon calculations using the linear-response method. The Nudged Elastic Band (NEP) method was used to locate the minimum energy path for H-

diffusion. As the initial and final hydrogen states the tetrahedral and octahedral sites were selected.

3. Results and discussion

The calculations of the activation energy barriers for hcp, fcc and bcc structure of MgH_x at low hydrogen concentration are still in progress. But preliminary results have shown that bcc-MgH_x has the minimal activation barriers, wheras hcp-MgH_x has the biggest ones. Such theoretical results were experimentally confirmed by faster hydrogen diffusion through the bcc lattice observed experimentally in Mg_{1-x}Nb_xH₂ [6].

Also using the scheme presented in Ref. [7] we calculated diffusion coefficient for all magnesium structures. The ZPE contributions to diffusion coefficient proved to be rather insignificant.

Our early calculations [4] showed that in the bcc-MgH_x structure hydrogen atoms tend to be randomly distributed over the interstitial sites. We assume that this may reduce the so-called "blocking" hydride layer effect. Our present calculations revealed that the bcc-MgH_x structure also has the smallest activation energy barriers. From our point of view these two factors may be responsible for faster hydrogen diffusion through the bcc lattice as observed experimentally in Mg_{1-x}Nb_xH₂ [6] and may explain the catalytic effect of TM additions in magnesium.

- J.F. Pelletier, J. Huot, M. Sutton, R. Schulz, A.R. Sandy,L.B. Lurio and S.G.J. Mochrie, Phys. Rev. B, 63, (2001) 052103.
- [2] P. de Rango, A. Chaise, J. Charbonnier, D. Fruchart, M. Jehan, Ph. Marty, S. Miraglia, S. Rivoirard, N. Skryabina, J. Alloys Compd., 445-447 (2007) 52.
- [3] K. Klyukin, M.G. Shelyapina, D. Fruchart, Solid State Phenomena, 170 (2011) 298.
- [4] K Klyukin, MG Shelyapina, D Fruchart, Journal of Alloys and Compounds (2013), http://dx.doi.org/10.1016/j.jallcom.2013.02.089
- [5] Giannozzi, Paolo, et al., Journal of Physics: Condensed Matter 21.39 (2009): 395502.
- [6] X.H. Tan , L. Wang , C.M.B. Holt, B. Zahiri , M.H. Eikerling and D. Mitlin, Phys. Chem. Chem. Phys.,14 (2012) 10904.
- [7] K. W. Kehr, in Hydrogen in Metals I, edited by G. Alefeld and J. Völkl (Springer, Berlin, 1978), p. 197



NMRCM Effect radiation annealing on the kinetics of accumulation of 2013 electron-hole centers in paleontological objects

<u>Anastasia Y. Kultaeva</u>, Artem I. Antipov¹, Stanislav M. Sukharzhevskii²

Faculty of Physics, Saint-Petersburg State University, Department of Quantum Magnetic Phenomena E-mail: anastasia.kyltaeva@gmail.com ¹E-mail: artemis198@mail.ru ²E-mail: stas@nmr.phys.spbu.ru

1. Introduction

The problem of determining the paleontological age was always acutely in various fields of knowledge. For scientists such as historians, archaeologists, paleontologists, geologists question of dating is fundamental. Of particular interest is the study of the researchers of Periodo Quarternario, covering the last 2 million years, since it is a special period in the history of the Earth - in this period of emerging life on Earth and on the stage of history is primitive man (approx. 11,500 years ago).

2. The principles of dating

For solving problem of determining the age throughout the scientific world are beginning to use the technique of EPR - dating. This is due to the fact that all objects in the lithosphere, voluntarily or involuntarily exposed to ionizing radiation - the sun's rays, radioactive elements in the Earth's crust, etc. As a result of this interaction in materials produced electron and hole centres, which is proportional to the amount of time and intensity of the radiation exposure to the substance.

3. EPR-dating

Unique direct method of recording and study of electron and hole centres (EHC) in the matter is the method of electron paramagnetic resonance (EPR).

For determining paleontological dose to relate the values the intensity of the EPR-dosimetry signal to the values received dose. [1]

In this work we used the method "additional doses", which was first proposed in [2, 3] (Fig. 1). The intensity of the EPR signal from the natural dose contains information about the process of the formation kinetics of radioinduction centres.

The error in determining the dose does not exceed 10%.

The intensity of the dosimetric signal is described by the function:

$$y = 269.31 \left(1 - e^{(2.54E - 4)(x + 122.43)} \right).$$

If the resulting function to take into account the parameters

of electron and hole in the radioactive annealing, it is a more accurate model to estimate the age of paleontological objects.



Figure 1. The intensity of the dosimetry signal by tooth enamel from additional radiation doses

4. Conclusions

As a result of the resulting model behaviour of electron and hole centres with radiation annealing of biological samples.

Building a more accurate model for the determination of the paleontological age.

Acknowledgements

Samples for dating were provided by V. Ivanova, Institute of Oceanology.

Author is grateful to for help in creating this work Varvara

V. Ivanova, A. Avenirovu and Vladimir V. Lomasovu.

- Morgan H., Wilson R.M., Elliott J.C. et al. Preparation and characterization of monoclinic hydroxyapatite and its precipitated carbonate apatite intermediate // Biomaterials.- 2000.- V. 21.- P. 617-627.
- [2] Grün R., Stringer C.B. Electron spin resonance dating and the evolution of modern humans// Archaeometry V. 33, № 2. Great Britain, 1991. P. 153-199.
- [3] Hennig G.J., Grün R. ESR dating in Quaternary geology // Quat Sci Rev 2, 1983. P. 157-238.



NMRCM New insight on nonlinear spin dynamics in highly polarized liquids 2013 Vyacheslav V. Kuzmin^{1,3}, M. E. Hayden², G. Tastevin, P.-J. Nacher

¹Laboratoire Kastler Brossel, ENS – CNRS – UPMC, 24 rue Lhomond, 75005 Paris, France ²Permanent address: Simon Fraser University, 8888 Univ. Drive, Burnaby BC, V5A 1S6 Canada ³E-mail: slava.kuzmin@lkb.ens.fr

1. Introduction

The tools used to increase sensitivity in liquid NMR (high-Q probes, hyperpolarisation (HP), very high field) contribute to enhance, also, the effects of radiation damping (RD) and distant dipolar field (DDF). This leads to ill-controlled non linear dynamics due only to DDF (precession instability, spectral clustering, multiple spin echoes: MSEs) or to both RD and DDF (bizarre signals and cross-peaks, spatial-temporal chaos, multiple maser emissions: MMEs) [1].

We report investigations of precession instabilities, with and without RD, that characterize the development of unstable magnetization patterns and probe the effect of the sample size and shape on spin dynamics at high DDF.

2. Techniques

We perform systematic low field (3 mT) studies with condensed laser polarised ${}^{3}\text{He}{}^{4}\text{He}$ mixtures at low temperature (1 K). The dilute sample (0.3-5% of ${}^{3}\text{He}$, with 10% polarization) partly fills a 4-mm i. d. tube. We use an active feedback scheme to control RD. Numerical simulations (on desktop computer) rely on time integration of the nonlinear Bloch equations (with DDF, RD, diffusion, and applied gradients) for magnetic moments on a cubic lattice. Finite size samples effects are taken into account using 3D unit cells (up to 10^7 sites) that include distributions of moments (up to 10^6) with variable aspect ratios.

3. Results

3.1. Seeded instability: finite size effects

Without RD, 90° FID signals collapse because of the development of inhomogeneous magnetisation patterns that grow exponentially in time during transverse precession. Simulations show that the growth rate depends on the spatial wavevector (k) of the initial magnetization pattern, sample shape and size, and diffusion (Fig. 1).



Figure 1. Examples of computed rates changes with wavevector (k) (w: transverse size of the 3D sample). Decrease at high k occurs for finite D

3.2. Development of unstable patterns

We have developed MRI-based techniques to probe the evolution of the magnetization patterns. Parametric amplification of the imprinted pattern and spatial harmonic generation are observed, in experiments and simulations.





3.3. Multiple maser emissions

Interplay between RD and DDF leads to the emission of a single (for high RD) or multiple (for moderate RD, as recently observed in HP ¹²⁹Xe) rf bursts. Our new experimental and simulation tools allow a detailed characterization of the MMEs.



Figure 3. Spontaneous MMEs (main plot) observed at moderate RD. The shape of the 1st burst departs from that of a usual maser (no DDF, single emission), which is attributed to the onset of DDF-induced instability at large transverse magnetization

4. Conclusion

This work on precession instabilities directly probes the sample size and shape effects that have previously only been inferred from MSE features in HP ¹²⁹Xe and ³He and are expected to be important whenever strong DDFs are encountered.

References

 H. Desvaux, Non-linear liquid-state NMR, Progress in NMR Spectroscopy, 70, (2013).

V. V. K.'s work is supported by the *P*-*G* De Gennes (FPGG) Foundation and the French National Research Agency.



NMRCM ¹³C and ¹H NMR Relaxation and segmental mobility in 2013 [emim]CH₃COO Ionic Liquid

<u>Vladimir Matveev</u>, Denis Markelov, Vladimir Chizhik, Petri Ingman¹, Erkki Lähderanta²

Faculty of Physics, Saint-Petersburg State University, Russian Federation E-mail: vmatveev@nmr.phys.spbu.ru ¹Instrument Center, University of Turku, Finland ²Section of Physics, Lappeenranta University of Technology, Finland

1. Introduction

3. Correlation times, τ_c

The purpose of the current work is carrying out the comparative analysis of relaxation rates of 13 C and 1 H nuclei in [emim]CH₃COO ionic liquid (IL) and determination of reorientation characteristic times of the counterions.

2. Relaxation rates

Relaxation rates for some groups of the studied IL are shown in Fig. 1, and numbering of lines corresponds CS increasing in ¹H spectrum (below).



Figure 1. Examples of ¹H&¹³C relaxation rates

Using well known BPP formula we have calculated τ_c for each group of the IL on both ¹H and ¹³C data.



Figure 2. An example of τ_c calculated using ¹H&¹³C data for CH₃-group of anion (2) and N-CH₃ of cation (3)

The comparison have shown that (i) ¹H and ¹³C relaxation rates reveal equal values of correlation times as well as of activation energies of molecular motion for all groups of the counterions and (ii) spin-diffusion contribution becomes the prevailing one in the ¹H relaxation at low temperature.

Acknowledgements

This work was supported by Research Programme of Saint-Petersburg State University.

NMRCM NMR signal operation in magnetic substances by the external field 2013 pulses Saint Petersburg, Russia Luca V. Pleabaland 2 Nikolan C. Klakhta?

Ivan V. Pleshakov^{1,2}, Nikolay S. Klekhta²

¹Ioffe Physical-Technical Institute of the Russian Academy of Sciences, 194021 St. Petersburg, Russia E-mail: ivanple@yandex.ru ²Saint-Petersburg State Polytechnic University, 195251 St. Petersburg, Russia

1. Introduction

The problem of nuclear spin echo control attracts an attention because of growing interest to the feasibilities to operate with NMR signal by external actions. It is especially important for the magnetically ordered materials, where the signal forms in the domain walls and it is possible to manipulate with them by application of magnetic field pulses, [1-2]. This report is devoted to the principles of such an operation and its potential for the obtaining of information on the properties of substance.

2. Experiment

The situation, when the echo signal, excited in magnetic sample ($Li_{0.425}Fe_{2.425}Zn_{0.15}O_4$) by a standard non steady-state NMR technique, using radio frequency (rf) pulses, and subjected also by an additional sequence of magnetic (video) pulses, is under discussion. The different variants of video pulses effect are examined: i) the action of single pulse; ii) the action of two unidirectional pulse sequence; iii) the action of the sequence of two pulses can be applied both in the interval between rf pulses and simultaneously with them.

3. Results

It was observed that, as in [3], the single video pulse depresses the nuclear spin system response because of the displacement of domain walls, which was experimentally proved by the obtaining of the constant field dependence of the echo intensity. It was shown that the phenomenon can be described by so-called 'optical model', where the individual spin isochromates are considered as optical beams, and the depression as their 'defocusing'. An example of two-pulse and stimulated echo signals (with amplitudes I_e and I_{se} correspondingly) quenching by the single video pulse with the input time t_v , is demonstrated in Fig. 1 (here the delay time between the first and second rf pulses is 185 µs, and between the second and third ones is 790 µs).

The model implies a number of other effects, for instance, the restoring of the depressed two-pulse echo under the action of the sequence of two video pulses. It is illustrated by the Fig. 2, where an increasing of restoration effect is shown, when the durations of video pulses (τ_{v1} , τ_{v2}) become equal.

It was also revealed, that in the case of the coincidence of video and rf pulses the spin system can be excited in different places of sample, which means that it is possible to scan the material near the domain wall positioning.



Figure 1. Echo-signals depression by single video pulse



Figure 2. Echo-signal restoring by two video pulses

Acknowledgements

The work was supported by the Presidium of Russian Academy of Sciences, Program P-03.

- L.A. Rassvetalov, A.B. Levitski. Sov. Solid State Phys., 23, 3354-3359 (1981)
- [2] G.I. Mamniashvili, T.O. Gegechkori; A.M. Akhalkatsi, C.A. Gavasheli. – Low Temperature Physics, 38, 466-472 (2012)
- [3] I.V. Pleshakov, N.S. Klekhta, Yu.I. Kuzmin. Technical Physics Letters, 38, 853-855 (2012)



NMRCM Regulation of trophoblast migration: from a fingerprinting view to 2013 a mechanistic prospect in bioassay design

M. Podrecca, G. Grolet, V. Delsinne & J. M. Colet

Faculty of Medicine and Pharmacy, University of Mons, Belgium Department of human biology and toxicology E-mail: manuel.podrecca@umons.ac.be

1. Introduction

In parallel to the many efforts recently devoted to clinically understand the early onset of preeclampsia, emergence of new strategies are also needed to discover and/or evaluate new potential therapies. Therefore, we combined classical migration and immunofluorescence assays to metabolomic analysis of mouse Trophoblast Stem cells (TS) to figure out mechanistic outcomes on trophoblast migration.

2. Objective

The aim of this work was to set up an integrated procedure to evaluate in vitro stimulation / inhibition of trophoblast migration.

3. Methods

Mouse TS cells were used due to their easily inducible and reproductible in vitro differentiation into migratory cells. Inhibition and stimulation of their migration were respectively induced by addition of growth factors (FGF4/TGF β 1) and sarcosine. Their effects were evaluated by the use of transwells assays and confocal microscopy (Na/K-ATPase and E-Cadherin). These results were then compared to 1H-NMR analysis of cell media and M/C cell extracts.

4. Results and conclusion

Pro-migratory effect of sarcosine [1] on the trophoblast has been highlighted by transwells assays and confirmed by confocal microscopy. At a concentration of 10 μ M, it induced a 30% increase of cell migration (fig. 1). Modifications in the expression and localization of β 1 Na/K-ATPase and Ecadherin were also observed in the same conditions in correlation with a higher EMT. Metabolomics was not only a usefull fingerprinting tool of trophoblast migration but revealed unsuspected metabolic changes associated with a potential role in epigenetic mechanisms [2]. For instance, variations in relative concentrations of glycerphosphocholine and dimethylglycine were observed (fig. 2).

- [1] Sreekumar A., et al., 2009 "Metabolomic profiles delineate potential role for sarcosine in prostate cancer progression". Nature , 457/7231: 910-914
- [2] Chang, C-J & M-C Hung, 2012 "The role of EZH2 in tumour progression". British journal of cancer, 106/2: 243-247.



Figure 1. Increased TS cells migration induced by sarcosine



Figure 2. Variations in relative concentration of metabolites correlated w/ cell migration acquisition and/or epigenetic mechanisms in cell media (MC0, MD0, MC24, and MD24) and M/C cell extracts (TS, GTC and GTC+Sar)



NMRCM Hydrophobic and hydrophilic effects in aqueous solutions 2013 of organic molecules

Sevastyan O. Rabdano, Alexey V. Donets

Faculty of Physics, Saint-Petersburg State University, Russia E-mail: sevastyan@rabdano.ru

1. Introduction

A clear understanding of interaction of organic molecules functional groups with different environment allows us to understand the formation of the spatial structure of proteins in complicated biological solution and live tissues. It can be supposed the formation of biological nanostructures due to mutual influence of hydrophobic and hydrophilic interactions in complex solutions.

The hydration parameters of the different functional groups and the hydrocarbon skeleton can be calculated from the solvent nuclei (¹H, ²H, ¹⁷O) NMR-relaxation and results of quantum chemical calculations. The hydration properties of the hydration shells of the hydrophobic methylene and methyl and hydrophilic amino and carboxylic group were carried out by ²H nuclei relaxation at various temperatures.

Also the microstructure of the hydration shells of glycine ($^{+}H_{3}N$ -CH₂-COO⁻) and β -alanine ($^{+}H_{3}N$ -CH₂-CH₂-COO⁻) were studied by quantum chemical calculations.

2. Relaxation and HF/DFT calculations

The deuteron spin-lattice relaxation rates (R_1) of the water were measured at 13.8 MHz on Bruker SXP4-100 and at 76.8 MHz on Bruker Avance^{III}/500 spectrometers. The solutions of carboxylic and amino acids were prepared at concentration diapason from 0 mole / 55.5 mole D₂O and to the limit of solubility.

The water molecules in the investigated solutions with organic molecules can be divided into several groups: hydration shells of carboxylic, amino, methylene groups and pure solvent. For example, see Fig. 1. Relaxation rate of the solvent nuclei should be calculated as a sum of contributions of each substructure. In the case of the fast exchange of the water molecules between substructures, the R_1 of the solvent nuclei in the investigated system is given by formula:

$$R_1 = \sum_i p_i R_i \tag{1}$$

here R_i – is the relaxation rate of deuterium in the *i*-th substructure and p_i – is the relative concentration of the *i*-th substructure [1, 2]. The values of p_i can be easily calculated from concentration and hydration numbers of the functional groups. Last ones are determined from molecular dynamics and/or quantum chemical calculations.

At the same temperatures the concentration dependences can be described by system of the equations like (1) for the relaxation rates of deuterons of water in aqueous solutions with the different organic molecules. This system was solved for the R_i of deuterons near methyl, methylene, amino and carboxylic groups.

3. Results

1. The mobility of water molecules in the hydration shells of the hydrophobic groups is less than in pure D_2O by a factor of 1.7 at 3°C and 1.4 at 55°C. The hydrophobic effect decreases with increase of temperature.

2. The deuteron relaxation rate of water molecules near the hydrophilic groups at 3° C is approximately the same with the relaxation in the bulk water. But at 55° C it is greater than in pure D₂O by factor of 1.4. It seems that at the high temperatures the mobilities of water near the hydrophobic and hydrophilic fragments are similar.



Figure 1. Scheme of hydration shells of hydrophobic groups (double line) and hydrophilic groups (single line) of glycine, propionic acid and malonic acid molecules

3. Energies of interaction between H₂O molecule in the hydration shells of COO⁻, NH₃⁺ and CH₂ and solute molecule were calculated at DFT/6-31++G(d,p) level of theory in [glycine (H₂O)₅₇] and [β-alanine (H₂O)₇₀] clusters. The averaged values are 13.3 and 13.4 kkal/mole for NH₃⁺ groups of glycine and β-alanine respectively, 9.2 and 10.4 kkal/mole for COO⁻ groups, 2 and 3.8 kkal/mole for CH₂ groups. The energy of interaction between two water molecules is equal 5.6 kkal/mole ((H₂O)₆₀ cluster at the same level of theory with PCM bulk solvation).

4. We analyzed angles X-O-H between solute fragment X and the water molecule (H-O-H). The orientation of water molecules near the hydrophobic groups are almost random. CH₂ and CH groups don't influence on the orientation of H₂O molecules. Distribution of angles for the hydrophilic groups are typical for systems with hydrogen bonds.

Acknowledgement

This work is supported by the Russian Foundation for Basic Research (grant N_{2} 10-02-01043-a). The authors acknowledge Saint-Petersburg State University for a research grant.

- [1] Zimmerman J., Brittin W. J.Phys.Chem., 1957, 61, 1328.
- [2] Chizhik V.I. Molec. Phys., 1997, 90(4), 653.

NMRCM Magnetic study of nanostructural composite material based on 2013 cobalt compounds and porous silicon

<u>V. A. Ryzhov</u>¹, I. V. Pleshakov², A. A. Nechitailov², N. V. Glebova², E. N. Pyatyshev³, A. V. Malkova⁴, I. A. Kiselev¹, V. V. Matveev⁴

¹Petersburg Nuclear Physics Institute, NRC Kurchatov Institute, Gatchina, 188300, Russia
E-mail: ryzhov@omrb.pnpi.spb.ru
²Ioffe Physical Technical Institute, Russian Academy of Sciences, St. Petersburg, 194021 Russia
E-mail: ivanple@yandex.ru
³St. Petersburg State Polytechnical University, St. Petersburg, 194021 Russia
E-mail: pen@mems.ru
⁴Faculty of Physics, St. Petersburg State University, St. Petersburg, 199164 Russia
E-mail: vmatveev@nmr.phys.spu.ru

Heterogeneous system, consisted of a semiconductor and magnetically ordered substance, is one of topical problem of solid state physics, which attracts an attention of experts because the magnetic parameters of matter may be transformed by the confinement and interplay of cluster surface with supporting body [1,2]. This work presents the results of investigation of a composite material obtained by the filling of cylindrical cavities of porous silicon, by an initial Co-containing compound (CoCl₂·6H₂O) followed by its reduction to a magnetic phase via chemical reaction with sodium tetraborohydride (NaBH₄) (por-Si). This process can lead to the formation of two main phases, metallic cobalt and cobalt boride (Co₂B) [3], the latter also possessing ferromagnetic (F) properties [4]. The tasks of this work were: (i) to confirm an origination of magnetic nanoparticles in pores; (ii) to specify what kinds of substances are formed in the pores. Expecting that a state of magnetic material in the pores is mainly determined by described above chemical reactions we repeated them in a glass test tube instead of Si matrix (Ref-sample) to obtain a larger amount of material for study. It was very lightweight (that indicates a porous character of product), easy electrifiable insulator powder. Comparative study of magnetic properties of por-Si, Refsample and a submicron bit of metal Co (Co-bulk) was carried out.

Registration of second harmonic of magnetization (M_2) generation in the parallel steady (H) and harmonic magnetic fields h(t) (f=15.7 MHz) [5] as well as X-range electron magnetic resonance (EMR) spectrometer, in which the recording signal is proportional to off-diagonal element of the magnetic susceptibility tensor, $M_y(\omega) = \chi_{yx}(\omega)h_x(\omega)$, [6] were employed for study of the magnetic properties. Symmetry properties of M_2 allows one to detect the appearance of a remanent magnetization, M_{rem} , in a sample at arising Hhysteresis (symmetric relative to the point H=0 H-scan was used).

The obtained results of comparative study of the por-Si, Ref-sample, and Co-bulk reveal the following features. The M_2 signals of all three samples exhibit the *H*-hysteresis that suggests the presence of F ordered regions with M_{rem} in all the samples. The Im(Re) $M_2(H)$ curves for por-Si and Ref-sample

reveal a close *H*-form and a close $M_2(H)$ dependence on *T* (at least, in ReM2 component) and on frequency of H-scan $(F_{\text{scan}}=0.01 \div 10 \text{Hz})$. The latter implies a necessity of using a conception of blocking temperature to explain the Fdependence of the responses. The decreasing of field hysteresis in the M_2 response at heating (at fixed F_{scan}) and at decreasing of F_{scan} (at fixed temperature) evidences a single domain regime of the formed F clusters in these samples. Some difference in T-behavior of $Im M_2(H)$ can be mainly referred to pore surface effect on a magnetic dynamics of a material, forming inside the pores. The found temperature dependences of "coercivity", H_C , in Re M_2 component of the por-Si and Ref-sample responses at lowest $F_{\text{scan}} = 0.01 \text{ Hz}$ allow us to estimate the values of blocking temperatures for these compounds as $T_{Bp} \sim 473$ K and $T_{BR} \sim 471$ K accordingly. The essentially larger *H*-hysteresis and "coercivity", H_C , as well as much weaker dependences on T and F_{scan} are found in metallic Co-bulk. Besides, the huge difference in EMR signals of Co-bulk and Ref-sample (a reproductible EMR signal is not found for por-Si) is also detected. The obtained results let us to conclude that in the composite as well as in the reference substance ferromagnetic clusters of predominantly insulating compounds of cobalt and boron (Co₂B, $T_C \approx 440$ K [4] or Co₃B, $T_C \approx 760$ K [7]), appear as a result of chemical reaction. In the former sample they form on the inner surface of matrix and for both cases the single domain state of particles is realized. The closeness of the estimated values of blocking temperature values together with the other experimental results obtained for por-Si composite and Ref-sample provides an evidence of the similarity of the physical properties of clusters in both investigated materials.

- [1] J. P. Chen et al. J. Appl. Phys., 76, 6316 (1994).
- [2] N.V. Glebova et al. Tech. Phys. Lett., 36, 878 (2010).
- [3] G. N. Glavee et al. *Inorg. Chem.*, **32**, 474 (1993).
- [4] C. Petit and M. P. Pileni. *JMMM*, **116**, 82 (1997).
- [5] A.V. Lazuta et al.- Sov. Phys. JETP, 73, 1086 (1991).
- [6] V.A. Ryzhov et al. *Tech. Phys.*, **40**, 71 (1995).
- [7] L. Yiping et al. *JMMM*, **79**, 321 (1989).



NMR Institute and Tallinn University of Technology, Estonia E-mail: ago.samoson@nmri.eu

Study of biological polymers in water solution has arguably become the raison d'être of NMR. Sadly however, the technical progress is leading this activity to thermal death. While increase in magnetic fields requires shorter motional correlation times, the research logic gravitates to larger and with that slower molecular systems. We shall argue that coherent mechanical spinning is beginning to substitute random thermal motion and solid state experiments will adopt experimental hierarchy and protocols of "high resolution". With a new generation of µ-rotor, bio-VT probe

technology [1] we have observed breakdown of manyspin systems at 100kHz rates, leading to resolution, adequate for the assignement of ca 100 residue proteins within minutes.

New technology offers also convenient solutions for sample heating, some examples of a reaction monitoring by natural abundance ¹³C through-flow at 400C are given.

References

[1] www.nmri.eu

NMRCM Magnetic Resonance Study of SPIONs conjugated with Hsp70 in 2013 C6 glioma intracranial model

<u>M. A. Shevtsov</u>¹, L. Yu. Yakovleva², B. P. Nikolaev², Ya. Yu. Marchenko², A. V. Dobrodumov³, K. V. Onokhin¹, A. L. Mikhrina⁴, I. V. Guzhova¹, M. G. Martynova¹, O. A. Bystrova¹, A. M. Ischenko², B. A. Margulis¹

¹Institute of Cytology of the Russian Academy of Sciences (RAS), St. Petersburg, Russia ²Research Institute of Highly Pure Biopreparations, St.Petersburg, Russia ³Institute of Macromolecular Compounds of the Russian Academy of Sciences (RAS), St. Petersburg, Russia ⁴I.M. Sechenov institute of evolutionary physiology and biochemistry of the Russian Academy of Sciences (RAS), St. Petersburg, Russia

E-mail: shevtsov-max@mail.ru

1. Introduction

The superparamagnetic iron oxide nanoparticles (SPIONs) have the ability to function as a platform for development of theranostic agents. For therapeutic potency and specific delivery to the tumor site of SPIONs we conjugated the latter with recombinant heat shock protein Hsp70. The possibility for the MRI monitoring of targeted delivery of the magnetic conjugate of Hsp70 was analyzed in rat C6 glioma model.

2. Materials and methods

The dextran-coated SPIONs were prepared by coprecipitation from Fe⁺², Fe⁺³ salt solutions as was described earlier [1]. Recombinant human heat shock protein Hsp70 was prepared from E. coli transformed with a pMSHsp70 plasmid. Magnetic conjugates were formed from SPIONs and Hsp70 by coupling COO protein groups to carbodiimide activated surface dextran. The biological activity of Hsp70 in the conjugate was assessed by the chaperone ELISA-assay. Magnetic characteristics of conjugate were analysized by proton relaxometry. Proton magnetic relaxation times T_2 were measured with the help of the NMR-spectrometer (CXP-300, Bruker) in magnetic field 7.1 T. The in vitro distribution of SPIONs was assessed on the C6 glioma cell culture with the help of confocal and electron microscopy. The in vivo traffic was analyzed in the rat model of intracranial C6 glioma. MR images (gradient echo (FLASH), T_1 - and T_2 -weighted, multisc and multi-echo (MSME T_2 -map) of rat glioma were obtained by Bruker Avance II NMR spectrometer 11 T.

3. Results

The measured coefficients of the relaxation efficiency $R_1=0.37 \text{ mM}^{-1}\text{s}^{-1}$, $R_2=113 \text{ mM}^{-1}\text{s}^{-1}$, $R_2^*=230 \text{ mM}^{-1}\text{s}^{-1}$ of SPIONs and its conjugates correspond to values of negative contrast agents. The results suggest the strong relaxation efficiency of magnetic Hsp70 conjugates in aqueous dispersions. The magnitude of magnetic relaxation rate of Hsp70 conjugates matches well with their appreciable contrast manifestation in phantom study made by MRI. In in vitro studies Hsp70 conjugates sedimented onto C6 cells and passed through the plasma membrane in the endosome-like structures. Visual examination of the confocal and electron microscopy images demonstrated more endosome-filled or not included into the endosomes nanoparticles in case of the Hsp70 conjugates. MRI study of experimental animals confirms the contrast effect of iron oxide nanoparticles conjugated with Hsp70 in the procedure of targeted administration. After magnetic nanoparticles infusion the most significant change in contrast was observed in the tumor

on T₂-weighted images. Following intravenous infusion of the SPIONs after 24 h there was a decrease of the T₂ relaxivity time in comparison to the control animals (P<0.05). Application of the Hsp70-SPIONs further reduced the relaxivity time in the T₂-weighted regimen and numerous zones of conjugate dispersion could be observed as the areas of signal drop (especially in the *FLASH* regimen) (P<0.001) (Figure 1). On the subsequent *postmortem* fluorescence images of the brain sections in the reflecting-laser light scanning on confocal microscope we could confirm the accumulation of the Hsp70-SPIONs in the glioma tumor. The study demonstrated that Hsp70-SPION conjugates being intravenously injected in the tumor model accumulate in the glioma and enhance the contrast of their MRI images.



Figure 1. MR T₂-weighted images of control and animal treated with intravenous injection of Hsp70-SPIONs. Presented the axial sections of the brain. The tumor in control animal is pointed by white solid arrow. Red arrows point the zones that correspond to the nanoparticles accumulation

4. Conclusions

The contrast efficiency of SPIONs conjugated with Hsp70 in MRI diagnostics is confirmed in a rat model of grafted intracranial glioma tumor. Magnetic Hsp70 conjugate intravenously injected in C6 glioma rat model accumulates in the tumor and exhibit as strong T_2 relaxation agent.

Acknowledgements

This study was supported by the grant of the Program of Russian Academy of Sciences (RAS) "Molecular and Cell Biology" and grant of Russian Fund for Basic Research №10-0401049.

References

 B.P. Nikolaev, Y.Y. Marchenko, L.Y. Yakovleva et al. Magnetic epidermal growth factor for targeted delivery to grafted tumor in mouse model – IEEE Transactions of magnetic, 49, 1-7 (2013).

- 53 - NMRCM 2013, Saint Petersburg, Russia, July 8 - 12, 2013



NMRCM Spin-spin relaxation-diffusion correlation analysis for estimation 2013 of distribution of membrane permeability and cell size in plant tissues

Timur A. Sibgatullin¹, Frank J. Vergeldt², Henk Van As²

¹Kazan Institute of Biochemistry and Biophysics, 420111, str. Lobachevsky 2, Kazan, Russia. E-mail: timsdance@mail.ru ²Wageningen NMR Centre, Wageningen University, 6703 HA, Dreijenlaan 3, Wageningen, The Netherlands E-mail: Henk.vanAs@wur.nl

1. Introduction

The measurements of membrane permeability of plant and animal cells are essential for solving a wide range of fundamental and applied problems. The most of methods of water membrane permeability measurements used up to date are restricted as they measure either a characteristic of only a single cell or an averaged over the sample parameter. But a study of physiological processes has to be performed preferably on a living intact organism - an object with complex and heterogeneous structure.

A new method is suggested for estimate of the distribution of cell size and membrane permeability of cells in heterogeneous plant tissues. This method is based on the analysis of correlation between rates of spin-spin relaxation of magnetization of water protons and apparent self-diffusion coefficient of water.

2. Materials and Methods

Measurements were performed on the ¹H NMR spectrometer operating at 30 MHz. T2-D correlation (DRCOSY) was measured using a modified stimulated echo (STE) pulse sequence with a train of 180° RF-pulses for acquisition of the relaxation signal decay following the diffusion encoding of signal. A maximum pulsed field gradient strength was 1 T/m. T₂-D correlation maps were obtained using 2D Fast Laplas Inversion of measured 2D dataset of signal attenuation as a function of b-value (diffusion encoding) and time for transverse relaxation during a train of 180° RF-pulses. For demonstrative purposes the inner part of apple parenchyma tissue was chosen as an object of experiments. Temperature of the sample was kept constant at $T = 25^{\circ}C$.

3. Theory

An alteration of permeability (P) of membrane of plant cell leads other things being equal to i) an alteration of apparent spin-spin relaxation time of water protons and ii) an alteration of time dependence of apparent mean diffusion coefficient of water in the long-time limit in biological tissues. Both, T₂ and D, can be measured by NMR method. However, they are also sensitive to the variation of cell size R. As a result, measuring either T₂-relaxation or diffusion alone doesn't allow the

evaluation of the distribution of membrane permeability in heterogeneous biological objects.

In present work a new approach offered for analysis of T₂-D correlation at short diffusion labelling time (t) when the displacement of water molecules is much less compared to the cell size. In approximation of spherical geometry of a cell a following equation can be derived

$$\frac{1}{T_2^{app}} - \frac{1}{T_2^{bulk}} = \frac{9\sqrt{\pi}}{4} H \frac{1 - (D(t)/D_0)}{\sqrt{D_0 t}},$$

where H – magnetization sink strength $H \propto P$; T_2^{bulk} and T_2^{app} – spin-spin relaxation time of water protons measured in pure water and in plant cell respectively; D_0 – selfdiffusion coefficient of bulk water. If the relaxation time in the extracellular space is infinitely short, H equals the true membrane permeability P.

This equation shows that at given membrane permeability $\frac{1}{T_2^{app}} - \frac{1}{T_2^{bulk}} \quad \text{is linearly correlate with} \quad \frac{1 - (D(t)/D_0)}{\sqrt{D_0 t}}.$

Permeability of membrane of pant cell can be determined even if cell size is unknown.

4. Results

Analysis of T₂-D correlation maps measured at diffusion labelling time t = 12, 25 and 50 ms shows that the distribution of membrane permeability is narrow in apple parenchyma tissue. This finding is well agreed with the role of the apple parenchyma as a homogenous storage tissue. As far as magnetization sink strength H is determined the cell size a distribution can be derived from T2-D correlation. A measured cell size distribution is in good agreement with microscopy of apple parenchyma.

Finally, applications of given approach range from a fundamental research on the field of adaptive strategies of plants to the environmental stress (for example, drought) to applied purposes like a quality control of foodstuffs.

Acknowledgements

The reported study was partially supported by RFBR, research projects No. 12-04-31677, 13-04-01203.



NMRCM Ensemble-restrained MD simulations: accurate structure leads to 2013 accurate dynamics

Nikolai Skrynnikov

Department of Chemistry, Purdue University, USA E-mail: nikolai@purdue.edu

Currently, the best existing MD force fields cannot accurately reproduce the global free-energy minimum which realizes the experimental protein structure. As a result, long MD trajectories tend to drift away from the starting coordinates (e.g. crystallographic structures). To address this problem, we have devised a new simulation strategy aimed at protein crystals. An MD simulation of protein crystal is essentially an ensemble simulation involving multiple protein molecules in a crystal unit cell (or a block of unit cells). To ensure that average protein coordinates remain correct during simulation, we introduced crystallography-based the restraints into the MD protocol. Since these restraints are aimed at the ensemble-average structure they have only minimal impact on conformational dynamics of the individual protein molecules. So long as the average structure remains reasonable, the proteins move in a native-like fashion

as dictated by the original force field. To validate this approach we have used the data from solid-state NMR spectroscopy, which is the orthogonal experimental technique uniquely sensitive to protein local dynamics. The new method has been tested on human ubiquitin and SH3 domain from chicken α -spectrin. The ensemble-restrained MD simulations produced lower crystallographic R factors than conventional simulations; they also led to more accurate predictions for solid-state chemical shifts and backbone order parameters. Taken together, these results suggest that the presented trajectories may be among the most realistic protein MD simulations ever reported. In this context the ensemble restraints based on high-resolution crystallographic data can be viewed as protein-specific empirical corrections to the standard force fields.



NMRCM A solid-state NMR investigation of MQ silicone copolymers

Sergey G. Vasil'ev¹, Vitaly I. Volkov¹, Elena A. Tatarinova², Aziz M. Muzafarov²

¹Institute of Problems of Chemical Physics, Academician Semenov Avenue 1, Chernogolovka 142432, Russian Federation ²Institute of Synthetic Polymeric Materials, Profsoyuznaya street 70, Moscow 117393, Russian Federation

E-mail: viesssw@mail.ru

1. Introduction

Silicones are compounds of silicon that possesses at least one silicon-carbon bond and have a siloxane linkage. The designation M, D, T and Q, respectively, are used for mono-, di-, tri-, and quaternary coordination of oxygen around silicon in silicones. MQ silicone copolymers (also called the MQ resins) are the best examples of commercial hybrid organic– inorganic materials with nanoscale dimensions [1]. These siloxane copolymers are composed of clusters of densely linked quadrifunctional silicate Q (SiO_{4/2}) groups end-capped with monofunctional trimethylsiloxy M (Me₃SiO_{1/2}) groups. Most silicone resins will contain residual silanol (SiOH), which allows them to react further at some point.

MQ resins are used in a large variety of silicone products ranging from cosmetics components to composite materials. Silicone resins are used extensively in coating applications, most prominent among these are pressure sensitive adhesives, plastic hardcoats and paper release coatings [2].

2. Characterization of MQ resins

The composition of MQ copolymers greatly affects the physical properties of the final product, such as appearance, density, transmittance, viscosity, softening point and tackability. The structure of an MQ resin molecule is defined by three characterization parameters: M/Q ratio, molecular weight, and %OH. Silicon 29 solid-state NMR has proved to be a powerful tool in determination of mono-, di-, tri- and tetrafunctional cross-linked groups and various substituents in polysiloxanes. Cross-polarization (CP) and directpolarization (DP) excitation methods in concert with magic spinning (MAS) allows to obtain qualitative and quantitative information on composition, surface and bulk properties, local molecular environment of diverse silicon containing materials such as silica gels, organosilicon polymers and resins, mesoporous materials, hybrid inorganic-organic materials.

3. Experimental

The samples of MQ copolymers were obtained by the hydrolytic polycondensation of the alkoxysilanes in the presence of acetic acid as an active medium [2].

Solid state NMR experiments were performed on Bruker Avance III spectrometer with a 9.4 T widebore superconducting magnet. The spectrometer operated at 400.22 MHz for ¹H, 100.64 MHz for ¹³C and 79.51 MHz for ²⁹Si. Samples were placed in 3.2 mm rotor in diameter for spinning at magic angle.

The direct polarization is the straightest way to obtain quantitative spectra, but this technique is time-consuming method especially in the case of ²⁹Si nuclei. By the reason of long repetition time requirements for quantitative analysis the only limited number of scans could be acquired in acceptable time of experiment, so DP spectra have low signal to noise ratio which affects the resulting accuracy. Cross polarization allows to obtain the more intense signal with respect to DP spectra (the CP gain of signal is proportional to the ratio of gyromagnetic ratios of nuclei pair, which in the case of ²⁹Si and ¹H is about 5) in the more shorter time (the required repetition time depends on T_1^H rather than T_1^{Si}). The intensities of the lines in CP spectra are affected by the crosspolarization dynamics. The variable contact time experiments were performed to restore the intensities.

Spin-lattice relaxation times T_1 measurements of ²⁹Si nuclei and analysis of ²⁹Si {¹H} variable contact time signal intensities allowed to obtain quantitative data on the relative content of different sites in MQ copolymers.

Acknowledgements

This work is supported by the Russian Foundation of Basic Research (Project No. 13-03-00698-a).

- [1] Arkles, B. MRS Bulletin. 2001, 26, 402-408.
- [2] Egorova, E.V., Vasilenko, N.G., Demchenko, N.V., Tatarinova, E.A., Muzafarov, A.M., Dokl. Chem., 424, 15 (2009).

NMRCM 2013 Saint Petersburg, Russia

NMRCM ¹H NMR study of hydrogen diffusion in disordered Ti-V-Cr alloys 2013 Anna V. Vyvodtceva¹, Marina G. Shelyapina¹, Alexey Privalov², Daniel Fruchart³

¹*Faculty of Physics, Saint-Petersburg State University, Russia* ²*Institut für Ferstkoerperphysik, TU Darmstadt, 64289, Hochschulstarsse 6, Darmstadt, Germany* ³*MCMF Institut Néel, CNRS, BP 166, 38042 Grenoble Cedex 9, France E-mail: annavyvod@gmail.com*

Metal hydrogen systems have been studied extensively due to their ability to be used as hydrogen storage materials. For such applications hydrogen dynamics in a metal lattice is an important parameter. The most direct way to obtain information about the hydrogen mobility is to measure the hydrogen self-diffusion coefficient.

Here we report on the results of hydrogen self-diffusion coefficient measurements in Ti-V-Cr hydrides of different composition, namely TiV_{0.8}Cr_{1.2}H_{5.29}, Ti_{0.33}V_{1.27}Cr_{1.4}H_{1.13}, Ti_{0.5}V_{1.9}Cr_{0.6}H_{5.03}. The TiV_{0.8}Cr_{1.2}H_{5.29} and Ti_{0.5}V_{1.9}Cr_{0.6}H_{5.03} hydrides have fcc structures, whereas Ti_{0.33}V_{1.27}Cr_{1.4}H_{1.13} has bcc structure because the amount of hydrogen is not enough for a structural phase transition [1]. We have studied also alloys with Zr₇Ni₁₀ additives to ascertain the effect of catalysts on hydrogen mobility in the lattice [2]. The relevant dynamic parameters, e.g., the self-diffusion coefficients *D* and the activation energies E_a were determined.

All hydrogen diffusion measurements have been performed employing the static field gradient nuclear magnetic resonance (SFG NMR) method [3]. Such a technique allows us to measure proton self-diffusion coefficients even for short spin-spin relaxation times T_2 , when the pulsed field gradient method is not applicable. To enable application of long diffusion times and, thus, small diffusion coefficients, the stimulated echo sequence was used.



Figure 1. Hydrogen diffusivity in studied hydrides $Ti_{0.5}V_{1.9}Cr_{0.6}H_{5.03}$, $TiV_{0.8}Cr_{1.2}H_{5.29}$ in $Ti_{0.33}V_{1.27}Cr_{1.4}H_{1.13}$. The solid lines represent fitting by Arrhenius expression

Sometimes the apparent self-diffusion coefficient measured in experiments is lower than the real one. This is the case if the diffusion is restricted by geometry factors of studied samples, usually by the size of pores, inside which particles diffuse. In our case this restriction factor is the crystallite size. To eliminate this effect we have also measured the diffusion coefficients with varying times between pulses to optimize the experiment conditions.

Figure 1 shows the self-diffusion coefficient as a function of the inverse temperature for samples of different compositions. We see that the temperature dependence is well described by the Arrhenius law. Both hydrogen self-diffusion coefficients at room temperature and the activation energies of hydrogen diffusion are presented in Table 1.

Table 1. Dynamic parameters of hydrogen atoms

Compound	$D_0 \times 10^{-8}$ (cm ² /s)	$D^{294K} \times 10^{-11}$ (cm ² /s)	E _a (eV)		
TiV _{0.8} Cr _{1.2} H _{5.29}	0.53	1.43	0.15		
$Ti_{0.33}V_{1.27}Cr_{1.4}H_{1.13}$	6.98	2.62	0.20		
Ti _{0.33} V _{1.27} Cr _{1.4} + 4 wt.% Zr ₇ Ni ₁₀	7.65	0.91	0.23		
Ti _{0.5} V _{1.9} Cr _{0.6} H _{5.03}	0.43	3.74	0.12		
Ti _{0.5} V _{1.9} Cr _{0.6} + 4 wt.% Zr ₇ Ni ₁₀	0.65	3.87	0.13		

It has been obtained that the value of the activation energy strongly depends on the composition of the alloys. In the sample with bcc structure the activation energy of hydrogen diffusion is highest (0.2 eV). Among the samples with fcc lattices this value is decreasing when the vanadium fraction is increasing.

Acknowledgements

This work supported by G-RISC, the program "Mobility funds for excellent young Russian students". We are grateful to Prof. Dr. Franz Fujara and Prof. Dr. Michael Vogel for very helpful discussions.

- S. Miraglia, D. Fruchart, N. Skryabina, M. Shelyapina, J. Alloys Compd. 442, 49-54 (2007).
- [2] H.T. Takeshita, N. Fujiwara, T. Oishi, D. Noréus, N. Takeichi, N. Kuriyama, J. Alloys Compd. 360, 250-255 (2003).
- [3] G. Fleischer, F. Fujara, NMR-basic Pr. and Progr., 30, 159 (1994).

Part III

Poster Session

NMRCM Magnetic coupling in system ³He – PrF₃ nanoparticles 2013 E. M. Alakshin¹, R. R. Gazizulin¹, A. V. Klochkov¹, K. Kono², S. L. Korableva¹, Saint Petersburg, Russia V. V. Kuzmin¹, A. M. Sabitova¹, T. R. Safin¹, K. R. Safiullin¹, M. S. Tagirov¹

¹Institute of physics, Kazan Federal University, Kazan, Russia ¹E-mail: alakshin@gmail.com ²RIKEN, Wako, Saitama, Japan

1. Introduction

The resonance magnetic coupling between ³He and van Vleck paramagnet TmES was discovered earlier [1]. The later on the magnetic coupling between liquid ³He nuclei and the ¹⁴¹Pr nuclei of microsized (45 μ m) Van Vleck paramagnet PrF₃ powder has been observed [2, 3]. The usage of nanosized PrF₃ powder as a solid substrate in contact with ³He should create highly coupled system¹⁴¹Pr–³He.

2. Experiment and Results

The nanosized samples of PrF_3 and LaF_3 were synthesized [method described in 4, 5]. The spin kinetics of ³He in contact with synthesized nanoparticles has been studied (Fig. 1, 2).



Figure 1. The dependence of longitudinal relaxation rates of ³He in systems «LaF₃- adsorbed ³He» (\circ , \bullet) and «PrF₃ - adsorbed ³He» (∇ , ∇) on magnetic fields at 1.5 K

According to experimental data in Fig. 1 the low-field ³He relaxation mechanism in systems «PrF₃– adsorbed ³He» can be explained as a cross-relaxation mechanism between ¹⁴¹Pr and ³He nuclei. An additional proof of this fact comes from the equality of nuclear magnetic relaxation times of ¹⁴¹Pr and ³He at low magnetic fields. Also in system «LaF₃– adsorbed ³He» the relaxation rates are significantly smaller than in case of «PrF₃– adsorbed ³He», which is also supports the idea about magnetic coupling ¹⁴¹Pr - ³He. In Fig. 2 the correlation

between estimated cross-relaxation effect [2] and our experimental data is shown.



Figure 2. The dependence of longitudinal relaxation rates of ³He in systems «PrF₃ – adsorbed ³He» (□) on magnetic fields (the ³He relaxation mechanism in inhomogenious magnetic field is subtracted [5]). Solid line – the NMR ¹⁴¹Pr signal intensity at ³He Larmor frequency of non-oriented PrF₃ powder [2]

3. Summary

Thus, magnetic coupling in system ${}^{3}\text{He} - PrF_{3}$ nanoparticles have been observed.

Acknowledgements

This work is partly supported by the Russian Foundation for Basic Research (project no. 12-02-00372-a) and the Ministry of Education and Science of the Russian Federation (project no. 02.G25.31.0029).

- [1] A.V.Egorov et al. JETP Lett., 39, 584 (1984)
- [2] A.V. Egorov et al. JETP Lett, 86, 6, 416 (2007)
- [3] A.V. Egorov et al. *Journal of Physics: CS*, **150**, 032019 (2009)
- [4] L. Ma et al. Materials Letters, 61, 2765 (2007)
- [5] Tagirov M.S. et al. J. Low Temp. Phys. 162, 645 (2011)
- [4] Cowan B.P. J. Low Temp. Phys., 50, 135-142 (1983)



NMRCM Simplification of MRI contrast by inversion recovery method

Nikolay V. Anisimov, Olga V. Isaeva, Svetlana S. Batova

Lomonosov Moscow State University, Moscow, Russian Federation E-mail: anisimovnv@mail.ru

1. Introduction

Inversion-recovery method is widely used in MRI for contrast control [1]. It is used to suppress signals of normal tissues with known longitudinal relaxation times T_1 , such as cerebrospinal fluid (CSF) or/and fat. In addition, it is used to enhance the contrast between tissues with similar T_1 , for example, white matter (WM) and gray matter (GM) of the brain. The use of phase-sensitive images increases the efficiency of this method.

Inversion-recovery method is useful for simplification of the picture of tissue contrast. This simplification can be achieved by aligning the contrast between normal tissues, for example, between the CSF and GM or WM. It is useful for identifying lesion zones, particularly in the case when the total attenuation of normal tissue results in excessive weakening of the useful signal [2].

In this paper we propose a method for calculating the inversion time (TI) to align the contrast between tissues A and B with different values of T_1 and proton density ρ -respectively, T_{1A} , T_{1B} and ρ_A , ρ_B . It is interesting that contrast equalization may be accompanied by loss of the signal at the boundary between tissues with different T_1 . This is analogous to the "border effect" for tissues with different chemical shifts, which is observed in gradient echo pulse sequences (an artefact of the 2nd kind).

2. Materials and Methods

For the calculation of TI, in which contrast alignment is achieved, it is necessary to consider the evolution of the longitudinal magnetizations (M_z) for A and B and to equate them to the module at t=TI. For TR>>TI we have

 $M_z(TI)=M_0(1-2exp(-TI/T_1))$.

Then we obtain two equations corresponding to the antiparallel (I) and parallel (II) orientations of M_{zA} and M_{zB} :

 $X^{k}+X-(m+1)/2=0$ (I) and $X^{k}-X+(m-1)/2=0$ (II),

where X=exp(-TI/T_{1A}), $k=T_{1A}/T_{1B}$, $m=M_{0A}/M_{0B}=\rho_A/\rho_B$.

Solving the equation for X, we find TI, and the detected signal which is proportional to $M_z(TI)$ and hence (1-2X).

3. Results

The results of calculations are shown on Figure 1. There are curves $-\ln X(k)$ and (1-2X(k)) for several values of *m*. Well known values of *k* for the main intracranial structures (CSF, GM, WM, fat) are marked by vertical dashed lines [1]. The intersections of these lines and the curves give the desired values of TI and M_z(TI).

From the graphs, it follows that the alignment of the contrast is useful only for tissues with sufficiently differing

 T_1 . In this case, the desired result can be obtained at small signal loss and acceptable value of TI.



Figure 1. Diagrams TI and M_z for antiparallel (high) and parallel (low) orientations of M_z for intracranial structures

Several variants of contrast alignment for CSF and brain matter at 0.5T (Bruker Tomikon S50) are shown on Figure 2. There are: A - T2WI (no alignment), B - CSF/GM, C,D,E -CSF/WM, F - result of A and E multiplication. In cases B and C we have a parallel orientation of the M_z for CSF and for WM. In the case of D and E we have antiparallel orientation for them. This orientation gives good tissue contrast differentiation on phase-sensitive image (D). The result of antiparallel orientation of the M_z is the loss of signal on the border of tissues (marked by arrows) on the magnitude image (E).

TI values experimentally chosen are less than those graphically calculated. It is due to the fact that the condition TR>>TI is not satisfied.



Figure 2. Variants of contrast alignment between brain structures(TR/TE=5.0/0.1 s, ETL=8). Normal volunteer

4. Conclusions

Simplification of tissue contrast by aligning the signals of normal tissues can be combined with the mapping of the areas where tissues with different T_1 are adjacent to each other. Inversion-recovery method gives possibility to do it.

- [1] E. M. Haacke, et al. Magnetic Resonance Imaging: Physical Principles and Sequence Design (1999).
- [2] N. V. Anisimov, et al.- Proc. NMRCM-2007; 51(2007).



NMRCM Registration of "antisite" defects in Y₃Al₅O₁₂ by electron 2013 paramagnetic resonance

Hike Asatryan, Darya Kramushchenko, Yulia Uspenskaya¹

A.F. Ioffe physical-technical institute, St. Petersburg, Russian Federation E-mail: hike.asatryan@mail.ioffe.ru ¹Saint Petersburg State Institute of Technology (Technical University)

1. Introduction

Among of solid-state laser materials yttrium aluminum garnet ($Y_3Al_5O_{12}$), attracted attention by a number of unique features. Over the past few years, interest in such objects, doped with cerium increased significantly due to the prospect of the use of this crystals, as an effective and fast scintillators in positron emission tomography (PET-imaging) in medicine. One of the most direct and informative methods for studying the properties of these materials is the electron paramagnetic resonance (EPR), which allows to determine the spin and the valence of the impurity ion, its local symmetry and composition of the immediate environment, and etc.

2. Experimental

EPR spectra of single crystals $Y_3Al_5O_{12}$: Ce³⁺ were recorded on a standard X - range EPR-spectrometer JEOL. In EPR spectra beside the usually observed Ce³⁺ lines [1] a large number of resonances has been revealed with intensities by two orders lower. New lines are undoubtedly attributed to Ce³⁺ ions occupying the same lattice dodecahedrally coordinated Y³⁺ sites. One part of these lines grouped near to the main lines referred as "satellite".



Figure 1. EPR spectra of Ce^{3+} ions in $Y_3Al_5O_{12}$ single crystals at $\mathbf{B} \parallel [001]$ and $\mathbf{B} \parallel [110]$, T = 4.2K and v = 9.35GHz

In fig. 1a and b spectra of main and satellite lines at $\mathbf{B} \parallel [001]$ and $\mathbf{B} \parallel [110]$ (high magnetic field) orientations are presented. Satellite lines can be divided by intensities at least into two groups, A and B as it shown in fig. 1.

3. Discussion

Natural cerium does not have odd isotopes, therefore the EPR spectra of this ions do not exhibit a magnetic hyperfine structure; consequently, all apparent line are due to magnetically nonequivalent positions of Ce^{3+} in the $Y_3Al_5O_{12}$ lattice. So low intensity lines may be caused by such Ce^{3+} ions which are localized in the same c-sites, but in the immediate nearest cationic surrounding of which located a defect. One possibility is that in nearest surrounding of such Ce^{3+} centres one of Al^{3+} ions in a-site is substituted by Y^{3+} with considerably greater ionic radius. Such centres (fig. 1a, group of lines B) are associated with deviation of crystal composition from stoichiometrye. These are so-called "antisite" defects.

The possibility of such substitution in the range of 1 - 1.5%in the high temperature crystal growth was reported in [2]. On the substitution of Y³⁺ ions by Al³⁺ in the dodecahedral sites there is no evidence, however, in our opinion are also possible. The group of lines A (fig. 1a) corresponds to the centers of Ce³⁺, which has in surrounding Y³⁺ ions replaced by Al³⁺ in dodecahedral positions. The concentration of centers A is much less than the centers of B. The probability of formation of A centers is much less than the B. It is clear that the replacement of $Y^{3+} \rightarrow Al^{3+}$ or $Al^{3+} \rightarrow Y^{3+}$ will lead to different distortions of Ce3+ surroundings: compression and decompression, respectively. Because of the differences of ionic radii ($R_{Al}^{3+} = 0.53$ Å, $R_Y^{3+} = 1.02$ Å), this will lead to a change in the interatomic distances. This will result in dissimilar crystalline fields to those of Ce³⁺ ions in the cation environment of which formed a "antisite" defect.

Acknowledgements

This work has been supported by Ministry of Education and Science, Russia, under the Contracts No. 8017 and No. 8568; by the programs of the Russian Academy of Sciences: "Spin Phenomena in Solid State Nanostructures and Spintronics" and "Fundamentals of nanostructure and nanomaterial technologies" and by the Russian Foundation for Basic Research under Grant nos. 12-02-01011, 13-02-00821 and 13-02-00802.

- [1] H.R. Lewis. J. Appl. Phys., 1966, v.37, N 2, p.739-741.
- [2] S. Geller, G.P. Espinoza, L.D. Fullmer, P.B. Grandall. Mater. Res. Bull. V. 7, 1219 (1972).



NMRCM Concentration effect on cations solvation in Ca(NO₃)₂ – LiNO₃ – 2013 H₂O ternary system at normal conditions. A molecular dynamics ^{jourg, Russia} simulation study

Mariia I. Averina, Andrei V. Egorov

Faculty of Physics, Saint-Petersburg State University, Ulianovskaya 1, 198504, Saint-Petersburg, Russia E-mail: maryaverina@gmail.com

1. Introduction

Understanding the microstructure of ternary aqueous solutions is a problem of fundamental interest in chemistry and chemical engineering. One of the most puzzling group of substances is nitrate systems which exhibit extremely high solubilities. Khripun et al. [1] explained this by microheterogeneity implementation in solutions. In this context, computer simulations, capable to provide a detailed molecular-level description of solution structure, should be very fruitful for further investigation of the problem.

2. Molecular Dynamics simulations

To describe the peculiarities of cations solvation in ternary systems with fixed concentration ratio of the salts $[Ca(NO_3)_2]:[LiNO_3]:[H_2O]=1:2:n$ molecular dynamics simulations were carried out over the wide concentration range from n=36 to 8.5. MDynaMix package [2] was used. Five lithium-water interaction potentials [3-7] predicting the different hydration of Li⁺ ion were considered in order to understand the effect of lithium cation on the properties of the ternary system. Potentials for all other interacting atoms were taken from Refs. [7,8]. The SPC/E water model [9] was used in the simulations. Cross terms were calculated using the Lorentz-Berthelot combining rules. The geometry of nitrate anion was kept rigid [8,10]. All simulations were carried out in an isothermal-isobaric (NPT) ensemble in a cubic periodic cell at 1 atm and 25°C. Temperature was kept constant by using the Nosé-Hoover thermostat and pressure was regulated by the Hoover barostat. The equations of motion were solved using the Verlet algorithm with a time step of 2.0 fs. The SHAKE procedure was employed to constrain all the bond lengths. The Coulomb interactions were calculated using the Ewald summation method.

3. Results

The most concentrated solution $[Ca(NO_3)_2]:[LiNO_3]:$ $[H_2O] = 1:2:8.5$ was simulated using five types of Li⁺ ion potential parameters, concentration dependence – for the parameters taken from Refs. [3,5] only. Radial distribution functions, coordination numbers, self-diffusion coefficients of ions and water molecules, mean residence time of water molecules in various solution sub-structures were estimated. With increasing nitrate salts concentration the redistribution of water molecules between solvation shells of cations was observed: calcium cation is mostly surrounded by water molecules with a small admixture of nitrate anions, lithium cation – by nitrate anions with a dash of water molecules. It was shown that for concentrated ternary systems the structure of the ions solvation shells weakly depend on Li^+ ion potential parameters: share of water oxygens in the Li^+ cation first solvation shell does not exceed 40% and nitrate-anion oxygens predominate (see fig. 1). Change of Li^+ cation potential does not affect the solvation of Ca^{2+} ion.



Figure 1. Number of oxygen atoms in the Li⁺ cation first solvation shell (n=8.5)

Acknowledgements

The financial support of the Dynasty Foundation (Stipend Program for Students), The Russian Foundation for Basic Research (grant 13-03-01073a), and Saint-Petersburg State University are gratefully acknowledged.

- M.K. Khripun, K.Yu. Chervonenko, A.Yu. Efimov, et al., *Rus. J. Gen. Chem.* 70, 200 (2000).
- [2] A.P. Lyubartsev, A. Laaksonen, Comp. Phys. Comm. 128, 565 (2000).
- [3] K. Heinzinger, P.C. Vogel, Z. Naturforsch. A 29, 1164 (1974).
- [4] J. Chandrasekhar, D.C. Spellmeyer, W.L. Jorgensen, J. Am. Chem. Soc. 106, 903 (1984).
- [5] L.X. Dang, J. Chem. Phys. 96, 6970 (1992).
- [6] B.M. Pettitt, P.J. Rossky, J. Chem. Phys. 84, 5836 (1986).
- [7] J. Åqvist, J. Phys. Chem. 94, 8021 (1990).
- [8] T. Megyes, S. Bálint, E. Peter, et al., J. Phys. Chem. B 113, 4054 (2009).
- [9] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, *J. Phys. Chem.* **91**, 6269 (1987).
- [10] C. Ebner, R. Sansone, M. Probst, Int. J. Quant. Chem. 70, 877 (1998).



NMRCM To the possibility of the high-temperature spin-photon coherence 2013 in a microwave cavity

Eduard Baibekov

Kazan Federal University, 420008 Kazan, Russian Federation E-mail: edbaibek@gmail.com

1. Introduction

Quantum coherence is a fundamental concept of modern physics that reveals itself in wide range of phenomena either of matter or light origin. In cavity quantum electrodynamics, the photons in a reflective cavity are coupled to the atoms or spins [1] thus providing an opportunity to combine and observe both light and matter coherence. Recently, several experimental groups reported the observations of magnetictype coupling that involved interactions of light with the particles bearing electron spin [2, 3]. The coupling with the cavity mode was achieved with standard electron paramagnetic resonance instrumentation. Well-resolved splitting of the cavity mode was an indication of the strong coupling regime based on the coherence of the spin and photon states. Since each cavity photon interacts simultaneously with all the spins in the cavity, there is an opportunity to transfer information coherently from the photons to the spin ensemble as a whole, with obvious applications in quantum computing and quantum holography [4].

2. Tavis-Cummings model

Let us consider an ensemble of $N \gg 1$ identical noninteracting spins-1/2 coupled with the single-mode radiation field of a lossless microwave cavity. We adopt Tavis-Cummings model [5] and write the system Hamiltonian as

$$\hat{H} = \omega_0 \hat{a}^+ \hat{a} + \omega_s \hat{S}_z + g \left(a \hat{S}_+ + a^+ \hat{S}_- \right)$$

where ω_0 is the photon frequency, ω_s is the spin excitation energy, \hat{a}^+ and \hat{a} are the photonic creation and annihilation operators. The last term represents the spin-photon interaction. The coupling constant g is the same for all spins in the host sample in case when the sample dimensions are much smaller than the field wavelength. Supposing that the number of photons in the cavity is << N, one can obtain the corresponding energy spectra either numerically (for $N \sim 10$) or analytically. In the latter case, the spin ensemble must be very close to its highest polarization state, i.e. $S_z = -N/2$. If the spins are under thermal equilibrium, this corresponds to zero temperature ($\tau = 0$). The emission spectrum of the cavity at resonance ($\omega_0 = \omega_s$) consists of a single line at frequency ω_0 split by a gap of $2g\sqrt{N}$ (vacuumfield Rabi splitting) [6].

3. Calculation of the cavity emission spectrum at high temperatures

If the spins belong to paramagnetic atoms distributed in a solid, the zero-temperature approximation is inadequate even for τ of a few Kelvin. Utilizing Holstein-Primakoff transformation in the basis of Dicke states [7], we calculate the cavity emission spectrum for low polarization states and obtain the generalized Rabi splitting $\Delta = 2g\sqrt{2|\langle S_z \rangle|}$, where $\langle \ldots \rangle$ denotes thermal averaging. The lineshapes of the split lines are Gaussian with the standard deviation of $\frac{\Delta}{2} \sqrt{\frac{N}{\langle S \rangle^2}} - \frac{4}{N}$. We show that the splitting is observable under the condition $0 \le \tau \ll \omega_s \sqrt{N}$. This means that the spinphoton coherence in a microwave cavity can be partially preserved even if the spins are randomly directed. For X-band cavity with $\omega_0/2\pi = 10$ GHz and at room temperature the splitting is observable if $N > 10^6$. The further increase of τ diminishes the Rabi splitting and broadens both of the split lines in the emission spectrum that indicates the temperatureinduced loss of coherence.

Acknowledgements

This work was supported by RFBR (grant no. 12-02-31336) and by Dynasty Foundation. The author thanks B. Z. Malkin for advice and useful discussions and B. Barbara whose suggestions had motivated this work.

- H. Walther, B.T.H. Varcoe, B.-G. Englert, T. Becker. *Rep. Prog. Phys.*, 69, 1325-1382 (2006).
- [2] E. Abe, H. Wu, A. Ardavan, J.J.L. Morton. Appl. Phys. Lett., 98, 251108(1-3) (2011).
- [3] I. Chiorescu, N. Groll, S. Bertaina, T. Mori, S. Miyashita. - Phys. Rev. B, 82, 024413(1-7) (2010).
- [4] H. Wu, R.E. George, J.H. Wesenberg, K.Mølmer, D.I. Schuster, R.J. Schoelkopf, K.M. Itoh, A.Ardavan, J.J.L. Morton, G.A.D. Briggs. *Phys. Rev. Lett.* – 105, 140503(1-4) (2010).
- [5] M. Tavis, F.W. Cummings. Phys. Rev. 170, 379-384 (1968).
- [6] J.J. Sanchez-Mondragon, N.B. Narozhny, J.H. Eberly. *Phys. Rev. Lett.* – 51, 550-553 (1983).
- [7] R.H. Dicke. Phys. Rev. 93, 99-110 (1954).

NMRCM NMR and Optical Properties of Dextran coated magnetic Nanosols 2013 A. G. Bazir, O. S. Vezo, B. P. Nikolaev, Ya. Yu. Marchenko, L. Yu. Yakovleva, Saint Petersburg, Russia V. I. Rolich, <u>V. V. Vojtylov</u>

St. Petersburg State University, St.Petersburg, Russia, and Research Institute of Highly Pure Biopreparations, St.Petersburg, Russia E-mail: Vladislav.Voitylov@paloma.spbu.ru

1. Introduction

The prognostic value of diagnosis by MRI with contrast enhancement by magnetic nanosols strongly depends on the ratio between fine and crude of nanoparticle conglomerates in solution that has to be controlled. Some NMR and optical methods are applied to magnetic characteristic control and sizing of suspended particles of Fe_3O_4 in aqueous solutions of dextran [1, 2].

2. Materials and methods

The magnetic nanosol of iron oxide magnetic nanoparticles were synthesized and stabilized by dextran (Sigma,10 kDa). NMR spectra and magnetic relaxation times T₁, T₂, T₂^{*} were measured with the help of spectrometer *CXP*-300 (Bruker) under magnetic field of 7,1 T. The coefficients of relaxation rate R₁, R₂, R₂* (relaxivity) were determined from the slopes of the concentration plots. The T₁, T₂ – weighted images of gel phantom were obtained under *RARE*- T_1 and *Turbo-RARE*- T_2 scanning regimes at Avance II NMR tomographic accessory at 11 T.

The sizing is carried out by transmission electron microscopy, SFI-method, electro-optical dynamics, *Photocor-FC* correlation spectrophotometer and *Zetasizer Nano* (Malvern Instruments, UK).

3. Results

3.1. Magnetic relaxometry



Figure 1. Magnetic relaxation time T₂ of water protons in MNPs dispersion as function of time "stand by" t of different centrifuge fractions MNPs in field 7.1 T. (centrifugation (12×10³ rpm) at 5 min(1), 2 min(2), 1 min (3), 0 min (4))

The coefficients of magnetic relaxivity correspond to negative contrast agents. The spin-spin relaxation rates r_2 and r_2^* are much higher than spin lattice relaxation rate r1. Stable fine fractions of MNPS had the time of relaxation of magnetic momentum 1-10 ms (Fig.1).

3.2. Electro-optical relaxation



Figure 2. Optical anisotropy (EO-effect) induced by electric field of 1 kV/cm (1) and 2 kV/cm (2)

The time of EO relaxation is 10-20 ms (Fig. 2). It correlates with time of magnetic relaxation (Fig. 1).

3.3. SFI-measurements

The autocorrelation function of light scattering is described by contributions of small MNPs with dimension 6-10 nm in fraction of clusters with average diameter 100 nm. The fine fraction of MNPs gives the dominant contribution in concentration dependence of refractive increment.

4. Conclusion

Relaxation of electric and magnetic dipoles of MNPs in magnetic nanosol implemented in general mechanism of rotational movement of MNP as whole entity.

Acknowledgements

The work was supported by FMBA RF (grant 40.002.12.0). Authors thank I.N.Voevodina for synthesis of MNPs.

- E. Lima et al. Size dependence of the magnetic relaxation and specific power absorption in iron oxide nanoparticles J. Nanopart. Res. (2013), vol. 15, p.1654.
- [2] K. V. Erin. Electro and Magneto Optical Measurements of Electric Field Strength in Magnetic Colloids Based on Liquid Dielectrics. Optics and Spectroscopy, 2011, vol. 111, No. 1, pp. 79–84.



NMRCM Structural and thermodynamic aspects of specific interactions of 2013 transmembrane domains of bitopic proteins

<u>Eduard V. Bocharov</u>, Konstantin S. Mineev, Dmitry M. Lesovoy, Sergey A. Goncharuk, Olga V. Bocharova, Pavel K. Kuzmichev, Pavel E. Volynski, Alexander S. Arseniev

Laboratory of Biomolecular NMR-Spectroscopy, Department of Structural Biology, Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry RAS, Mikluho-Maklaya str 16/10, Moscow, Russia E-mail: bon@nmr.ru

1. Introduction

Bitopic proteins having only one helical transmembrane domain are a class of biologically significant membrane proteins, including the majority of receptor protein kinases, immune receptors and apoptotic proteins, which are involved in regulating the development and homeostasis of multicellular organisms. Recent studies have been making it increasingly clear that specific helix-helix interactions of single-span transmembrane domains are critical for lateral dimerization and modulation of biological function of bitopic proteins. Establishing structure-function relationship as well as rational design of new types of drugs targeting membrane proteins requires precise structural information about this class of objects.

2. Methods

To investigate spatial structure and internal dynamics of such transmembrane helical dimers in membrane mimic environment, detergent micelles and lipid bicelles, we have developed the robust strategy using a combination of modern methods of solution NMR spectroscopy and molecular modeling. First, using cell-free and bacterial expression and purification systems we obtained the C13,N15-isotope labeling protein fragment. Next, varying solution buffer, detergent or lipid composition we selected the optimal NMR-sample condition using different physical-chemical methods, by means of which we controlled the size of supramolecular micellar and bicellar systems (having effective molecular mass up to ~ 50 kDa) as well as the protein secondary structure and oligomerization. Then, the standard set of heteronuclear NMR spectra was acquired for spatial structure calculation and internal dynamics description. The intermolecular contacts in the interfacial region of the transmembrane dimers were directly identified by preparing an "isotopic heterodimer" and carrying out experiments, which select NOEs arising between C13,N15 and C12,N14 bound protons of isotopic labeled and natural abundance monomers, respectively. Finally, the resulting NMR structures of the transmembrane dimers were subjected to energy relaxation using molecular dynamics in explicit lipid bilayers with the imposed NMR-derived constraints. That provided the precise information about atomic-scale details of protein-protein and protein-membrane interactions.

3. Results

We investigated transmembrane fragments of several bitopic proteins from different families: Bcl-2 proapoptotic protein Bnip3, amyloid precursor protein APP, and receptor tyrosine kinases ErbB, Eph, FGFR, which play important roles in normal and in pathological conditions of human organism.



Figure 1. Effects of the lipid/protein (L/P) ratio and temperature on the free energy of weak dimerization of the transmembrane domain of the ErbB receptor tyrosine kinase in lipid bicelles

As a result, we established spatial structure and internal dynamics of the homo- and heterodimeric transmembrane domains, characterized diverse transmembrane helix-helix packing interfaces and obtained detailed picture of intra- and intermolecular interactions in membrane. We showed that the helix association undergoes usually through a structural "tuning" of the dimer subunits with the formation of the net of inter-monomeric polar contacts. The quantitative analysis of observed monomer-dimer equilibrium (Fig. 1) gave an insight into kinetics and thermodynamics of folding processes of helical transmembrane domain in model membrane mimic environment and perhaps in cellular membranes. The already available information about structural-dynamic properties of the dimeric transmembrane domains of studied bitopic proteins along with the available biophysical and biochemical data provides useful insights into their functioning in the human organism.

Acknowledgements

This work was supported by the Program "Molecular and Cellular Biology" of RAS and the Russian Foundation for Basic Research, grant 12-04-01816-a to EVB.



NMRCM Structural insight on the dimerization of transmembrane domain 2013 of amyloid precursor protein

<u>Olga V. Bocharova</u>, Anatatoly S. Urban, Ilia S. Chaplygin, Kirill D. Nadezhdin, Pavel E. Volynski, Eduard V. Bocharov, Alexander S. Arseniev

Laboratory of Biomolecular NMR-Spectroscopy, Department of Structural Biology, Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry RAS, Mikluho-Maklaya str 16/10, Moscow, Russia E-mail: o.bocharova@gmail.com

1. Introduction

Neurodegenerative Alzheimer's disease is the one of leading causes of death among the elderly, especially in developed nations. For appropriate therapy of Alzheimer's disease it is essential to determine the molecular basis of the pathogenesis. Amyloid β -peptide which forms amyloid plaques in brain during Alzheimer's disease is the product of sequential cleavage of a single-span bitopic membrane amyloid precursor protein (APP). More than half of mutations of APP found to be associated with familial forms of Alzheimer's disease are located in its transmembrane domain. The pathogenic mutations presumably affect structural-dynamic properties of the APP transmembrane domain, changing its conformational stability and/or lateral dimerization in the neuron's membrane.

2. Methods

Sufficient quantities of ¹⁵N and ¹³C isotope enriched samples of the recombinant APP transmembrane fragments were obtained using cell-free and bacterial expression systems. The set of heteronuclear NMR spectra was acquired for spatial structure calculation and internal dynamics description of the APP transmembrane fragments embedded into detergent micelles, supramolecular membranemimicking complexes. MD-relaxation of the NMR structures in hydrated explicit lipid bilayers provides a detailed atomistic picture of the protein-protein and proteinmembrane interactions. In addition, possible helix-helix packing interfaces were studied in model implicit and explicit membranes.

3. Results

Two recombinant peptides, corresponding to APP fragments Asp⁶⁷¹-Lys⁷²⁶ and Asp⁶⁸⁶-Lys⁷²⁶ including the APP transmembrane domain with adjacent N-terminal juxtamembrane sequence and metal binding site, were investigated in the dodecylphosphocholine micelles. NMRderived dimer structure consists of two α -helices (Fig. 1): a short surface-associated juxtamembrane one Lys687-Asp694 and a long transmembrane one Lys⁶⁹⁹-Lys⁷²⁴; the α -helices are connected via a mobile loop region. A minor bending of the transmembrane α -helix takes place near tandem residues Gly⁷⁰⁸-Gly⁷⁰⁹. Binding of Zn²⁺ ions with metal-chelating region does not perturb the transmembrane dimerization motif. The APP membrane-spanning α -helix self-associates in a left-handed parallel dimer through extended heptad repeat motif $I^{702}xxxM^{706}xxG^{709}xxxA^{713}xxI^{716}xxxI^{720}xxI^{723}$ whereas alternate tetrad motif $G^{700}xxxG^{704}xxxG^{708}$ apparently assigned for interaction with cholesterol. The cholesterol-binding hydrophobic cavity is formed under the loop region where the juxtamembrane α -helix contacts with the membrane surface near N-terminus of the transmembrane α -helix. Dimerization mechanism of APP transmembrane domain has been described at atomic resolution for the first time that is important for understanding molecular events of APP sequential proteolytical cleavage resulting in amyloid β peptide.



Figure 1. Dimeric structure of the APP transmembrane fragment Asp⁶⁸⁶-Lys⁷²⁶. Cylinders illustrate the juxtamembrane JM- and transmembrane TM-helices. Sequential γ-secretase cleavage sites and mutations associated with familial forms of Alzheimer's disease are indicated by arrows at the APP amino acid sequence

Acknowledgements

This work was supported by the Program "Molecular and Cellular Biology" of RAS and the Russian Foundation for Basic Research, grant 11-04-01795-a to OVB.



NMRCM Study of NMR relaxation in suspensions of magnetite-silica 2013 nanocomposite

<u>Yury V. Bogachev</u>, Julia S. Chernenco, Kamil G. Gareev, Irina E. Kononova, Lev B. Matyushkin, Vyacheslav A. Moshnikov

Saint-Petersburg Electrotechnical University "LETI", 197376, Saint-Petersburg, Russia E-mail: kggareev@yandex.ru

1. Introduction

Magnetic nanoparticles are of interest to biomedicine, as they can be used in systems of diagnostics and targeted drug delivery. It is known that one of the promising T₂-contrast agents is superparamagnetic Fe₃O₄ core stabilized by biologically inert shells. Being dispersed in an aqueous medium, magnetite particles accelerate the diffusion of protons and reduce the spin-spin relaxation time T₂ [1, 2]. Despite the overall aggregative stability, the magnetic nanoparticles can form linear chains under a constant magnetic field [3].

2. Experimental methods

Synthesis of magnetite nanoparticles is consisted of several stages. To stabilize the grain size of Fe_3O_4 precipitation was carried out directly in the presence of mesoporous silica obtained by sol-gel method. Isopropyl alcohol tetraethoxysilane solution was prepared and then gelation was provided by addition of aqueous ammonia, dried at room temperature and annealed at 300 °C for 15 minutes. Obtained powder was added to a solution of ferric chloride and ferric sulfate (molar ratio of Fe^{3+} and Fe^{2+} in proportion 2:1) and precipitated by adding ammonia hydroxide.

Transmission of dilute suspensions were analyzed on a spectrophotometer UV-5400 PE ("Ecohim", Ltd) in the measurement mode of the spectra (190 - 1000 nm) and kinetic measurements on fixed wavelength.

To measure the protons relaxation rate NMR relaxometer "Spin Track" ("Resonance Systems", Ltd.) was used. Magnetic field induction equaled 0.33 T, resonant frequency - 14 MHz. The sample volume was 1000 μ l in test tubes with a diameter of 10 mm. For the measurement of the spin-spin relaxation time T₂ Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was applied.

Scanning probe microscopy system "INTEGRA THERMA" ("NT-MDT", Ltd.) in semi-contact mode was used to analyze particles microstructure and grain size.

3. Experimental results

Mean diameter of composite particles was estimated by transmission kinetics measurement and AFM independently. It equals ~ 100 nm, so in the absence of magnetic field specimens demonstrate constant aggregative stability after sedimentation of large fractions. T₂-measurement process takes about a few seconds, so it doesn't significantly affect the system. But just in the first 2 minutes the constant field provokes two-fold decrease in the rate of relaxation (fig. 1).



Figure 1. Time dependence of spin-spin relaxation rate for specimen after various storage times

If we continue on measurement, we find the values of r_2 stabilize at 50-60 l/mM*s with a slow reduction during storage. AFM revealed the formation of linear aggregates of nanoparticles in the field direction (fig. 2). It was found that effect appears in the fields over ~10 mT.



Figure 2. AFM image of Fe_3O_4/SiO_2 particles dried in magnetic field of 0.2 T, image size $40x40 \ \mu m^2$ (left) and $2x2 \ \mu m^2$ (right)

Further study should explain the role of silica mesoporous structure in the aggregative stability and relaxation efficiency of composites. To solve this problem we can investigate the effect of the TEOS solution concentration on the specific surface area of the silica powder and the time of sedimentation.

- [1] Rink P.A. Magnetic resonance in medicine / P.A. Rink // Blackwell Scientific publication. 1993. 246 p.
- [2] D.-X. Chen et al. J. of Magn. and Magn. Mater., 322, 548–556 (2010)
- [3] O.N. Sorokina et al. Appl. Sci., 2, 342-350 (2012)



NMRCM Compact combined EPR/NMR/DNP Equipment

2013 Yu. Bogachev¹, Yu. Chernenko¹, L. Grunin², V. Drapkin¹, M. Knyazev¹, ^{yurg, Russia} Ya. Marchenko¹, <u>A. Naumova¹</u>

> ¹Department of Physics, Saint-Petersburg Electrotechnical University, 5, prof. Popova st., Saint-Petersburg, 197376, Russia; ²Department of Physics, Volga State University of Technology, 3, Lenin sq., Yoshkar-Ola, Republic of Mari El, 424000, Russia E-mail: spin_Itd@mail.ru, mobilenmr@hotmail.com

1. Introduction

New compact combined EPR/NMR/DNP equipment is developed both for research and for routine applications. The described instrumentation can be characterized by low cost, reliability and simplicity, small size and high level of measurement automation, the wide selection of functional modules and units. The hardware features are based on the latest developments in electronics, computer technology, original design and schematic solutions.

2. Specifications of the EPR part of equipment



Parameter	Value				
Sensitivity	2x10 ¹⁰ spin/G				
Operating frequency	(9.09.6) GHz				
Maximum microwave power	0,15 W				
Induction of magnetic field	0.050.7 T				
Maximum ampoule diameter	11 mm				

3. Specifications of the NMR part of equipment

Parameter	Value
Working frequency	580 MHz
RX sensitivity	Better than 1 μ V (when S/N ratio = 3)
Adjustable TX output power	Up to 500 W
Three selectable bandwidths of analog filter	From 100 Hz up to 1 MHz
Pulse sequence length	Up to 64K events with resolution 100 ns
Probe tube diameter	Up to 40 mm

4. Original/Custom instrumentation

Among original instrumentation developments there are:

• Compact high-stability microwave units of homodyne and threshold type, low-noise Gunn oscillator being used as a microwave oscillator;

• Handheld magnet systems based on electromagnets and permanent magnets with high uniformity of magnetic field;

• Digital systems for recording and processing the EPR and NMR data.

For DNP measurements at 0.35 T an electromagnet and special cylindrical microwave cavity with TE 011 mode have been used. Also the portable DNP system based on Halbach type permanent magnet has been developed.

5. Applications

Various modifications of the described compact combined EPR/NMR instrumentation are successfully used not only in stationary research or educational laboratories but also in mobile applied laboratories as well as in industrial conditions to control continuous technological processes.





NMRCM Structure of Te-containing salen-type complexes with transition 2013 metals in solution and solid state

<u>Inna G. Borodkina</u>¹, Anatolii S. Burlov¹, Gasan M. Abakarov², Konstantin A. Lyssenko³, Igor S. Vasilchenko¹, Ali I. Uraev¹, Gennadii S. Borodkin¹, Dmitryi A. Garnovskii¹, Pavel B. Chepurnoy¹, Yuriy F. Mal'tsev⁴, Mikhail Yu. Antipin³, Vladimir I. Minkin¹

¹Institute of Physical and Organic Chemistry of Southern Federal University, Stachki str., 194/2, Rostov-on-Don, 344090 Russian Federation, e-mail: nmr@ipoc.sfedu.ru ²Dagestan State Technical University, I. Shamil str., 70, Makhachkala, 367015 Republic of Dagestan, Russian Federation

 ³N.A. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str., 28, Moscow, 119991 Russian Federation
⁴Physical Faculty of Southern Federal University, Zorge str., 5, Rostov-on-Don, 344090 Russian Federation

1. Introduction

The ligand chemistry of tellurium has been a subject of growing interest [1]. Among various types of tellurium donor atom ligands capable of bonding with metals, the focus has largely been on telluroethers [1e, 2, 3].

In continuation of our study of the coordination chemistry of tellurium-containing azomethines we synthesized tellurium containing salen-type ligands which might coordinate to hard metal ions resulting in the rarely observed bonding between 'hard' metal ions with 'soft' tellurium in absence of any "macrocyclic or compartmental effect".

2. Goals of the Investigation

We report herein on a systematic study of the synthesis and structure of the complexes of acyclic hybrid N_4Te and O_2N_2Te salen type ligands (1) with well-known 'hard' transition metals leading to the formation of novel metallosalen structures. Included are the first examples of the penta- and hexadentate metallochelates involving Co(II), Ni(II), Cu(II) and Zn(II) along with softer Cd(II) ions (2).



X = NTs, O; R = phenyl, pyrazolM = Co, Ni, Cu, Zn, Cd

In particular, we describe the single-crystal X-ray and detailed NMR studies which serve to establish the presence of coordinative interaction between 'hard' metal and the 'soft' tellurium.

3. Results and Discussion

3.1. NMR Investigations

We have performed ¹H, ¹³C, ¹⁵N and ¹²⁵Te NMR investigations of compounds **1**, **2**, and obtained results revealed that ligating systems **1** undergo total deprotonation under formation of complexes **2** whose structure involves addition coordination of tellurium atom on the central metal ion.

3.2. X-ray Study

X-ray reveals that chelates **2** possess a pentacoordinated structures with N_4 Te or O_2N_2 Te environment of the central ion (see, for instance, Fig 1).



Figure 1. Structures of complexes 2·CH₃OH (X = O, R = pyrazole, M = Ni, Zn)

Therefore we have demonstrated that metallocomplexes on the basis of Salen-like tellurium-containing azomethines possess the same type structure in solution and in the solid state.

Acknowledgements

All measurements were performed on the equipment of the Joint Science Centre SFU "Molecular Spectroscopy".

- (a) Murray, S.G.; Hartley, F.R. Chem. Rev. 1981, 81, 365-414. (b) Gysling, H.J. Coord. Chem. Rev. 1982, 42, 133-244. (c) Hope, E.G.; Levason, W. Coord. Chem. Rev. 1993, 122, 109-170. (d) Singh, A.K.; Sharma, S. Coord. Chem. Rev.2000, 209, 49-98. (e) Levason, W.; Orchard, S.D.; Reid, G. Coord. Chem. Rev.2002, 225, 159-199.
- [2] Karlin, K.D.; Arnold, J. *Progress in Inorganic Chemistry* 2007, 43, 353-417.
- [3] Levason, W.; Reid, G.; Zhang, W. Dalton Trans. 2011, 40, 8491-8506.



NMRCM Prototropic tautomerism 1(10)H-2,3,4,10-tetrahydropyrimido 2013 [1,2-*a*]benzimidazole

<u>Inna G. Borodkina</u>¹, Vera A. Anisimova¹, Ivan E. Tolpygin¹, Gennadii S. Borodkin¹, Igor S. Vasilchenko¹, Pavel B. Chepurnoy¹, Yuriy F. Mal'tsev², Vladimir I. Minkin¹

¹Institute of Physical and Organic Chemistry at Southern Federal University, Rostov-on-Don, Stachki Ave., 194/2, Russian Federation, e-mail: nmr@ipoc.sfedu.ru ²Physical Faculty of Southern Federal University, Zorge str., 5, Rostov-on-Don, 344090 Russian Federation

1. Introduction

Derivatives of 1- and 10-N-substituted 2,3,4,10tetrahydropyrimido[1,2-a]benzimidazole exhibit an antioxidant, hypoglycemic, and antiaggregant activity [1,2]. At the same time the properties and preferential tautomeric forms of 1(10)H-2,3,4,10-tetrahydropyrimido[1,2-a] benzimidazole still have been not investigated.

2. Tautomerism

Model 1- and 10-N-substituted tautomeric forms of 2,3,4,10-tetrahydropyrimido[1,2-a]benzimidazole were prepared based on corresponding substituted 2- aminobenzimidazoles [1]. To get insight into the structure of unsubstituted 2-aminobenzimidazole existing in solution in two tautomeric forms (1H and 10H - 1a and 1b respectively).



Figure 1. Tautomerism and atom's labelling of tetrahydropyrimido[1,2-a]benzimidazole

3. Results and Discussion

3.1. NMR Investigations

Investigations have been performed on the spectrometer AVANCE-600 by the heteronuclear and multidimensional NMR spectroscopy. Classification of signals in the spectrum of ¹H was made using the technique of correlation spectroscopy COSY.

Chemical shift of NH has been detected upon deuteration with D_2O . The employment of correlation methods HSQC and HMBC allowed detecting positions of the chemical shifts of ^{13}C and ^{15}N nuclei. Identification of the tautomeric

Table 1. Chemical shifts of ¹H, ¹³C, ¹⁵N NMR in DMSO-d₆

equilibrium has been performing using the correlation spectrum $^1\mathrm{H-^{15}N}$ HMBC.



Figure 2. Correlation spectrum ¹H-¹⁵N HMBC of 1 in DMSO-d₆

This spectrum (Fig. 2) exhibits cross-peaks in the crossing of chemical shifts in 2.03 for H_{12} and 61.00 for N_{10} that corresponds to the constant of spin-spin interaction through three bonds and in the crossing of chemical shifts in 7.25 for H_{13} and 61.00 for N_{10} the results prove localization of the NH hydrogen atom at the N_{10} nitrogen atom.

Acknowledgements

All measurements were performed on the equipment of the Joint Science Centre SFU "Molecular Spectroscopy".

- V. A. Anisimova, M. M. Osipova, A. A. Spasov, A. F. Turchaeva, G. P. Dudchenko, N. P. Larionov, S. G. Kovalev. – *Pharm. Chem. J.*, 36, 468-473 (2002).
- [2] V. A. Anisimova, I. E. Tolpygin, A. A. Spasov, D. S. Yakovlev, N. A. Kolobrodova, N. A. Gurova, O. A. Salaznikova, L. V. Naumenko, V. A. Kosolapov, L. V. El'tsova, T. M. Mitina, M. P. Voronkova, K. V. Lenskaya. – Pharm. Chem. J., 46, 325-330 (2012).

Nucleus	1(¹⁵ N)	2	3(¹⁵ N)	4	5	6	7	8	9	10(¹⁵ N)	11	12	13
$^{1}\mathrm{H}$				7.07	6.93	6.85	7.12			7.25	3.32	2.03	3.94
¹³ C/ ¹⁵ N	188.30	152,73	120.50	106.74	120.37	117.57	114.34	142.62	133.86	61.00	38.59	21.05	39.75



Chemical Institute, Kazan Federal University, Kazan, Russia E-mail: salmonella@fresh.marine.ac.ice

1. Introduction

NMR-paramagnetic probing (NMR-PP) is a unique method for investigation of organized media, which makes possible controlling complexation and association processes, monitoring substrate-receptor interactions, development of new contrast agents for magnetic resonance imaging on the basis of stable metal complexes with high values of the relaxation efficiency parameter (REP).

The complexation of paramagnetic metal ions is usually accompanied by the decrease of REP. However, in solutions of Gd³⁺, Mn²⁺ and some other ions, an unexpected significant increase in the rate of relaxation was revealed in presence of anionic or nonionic surfactants [1]. From the NMR theory the proton relaxation rate in solutions of the named ions is known to be controlled by the rotational correlation time τ_r . Therefore the REP rise in polymeric solutions should be evidence on the probe ions binding to the oppositely charged macromolecules.

2. Objects and methods

Gadolinium(III) and manganese(II) salts were used to produce Gd^{3+} and Mn^{2+} ions in water. Next polymers (Fig. 1) and their mixtures were used in current investigation.



Figure 1. Formulae of used polymers

3. Results of NMR paramagnetic probing

We have run NMR-PP of the probe ion containing of PSS, PVP and PEI alone aqueous solutions as well as of their binary mixtures.

Polyvinylpyrrolidone does not react with Gd³⁺ and Mn²⁺ ions and the relaxivity values in this systems are very close to the REP magnitudes of corresponding aqua-ions.

Polyethyleneimine contains amino groups which are known to be very poor donors for both Gd(III) and Mn(II).

Nevertheless in PEI solutions both probe ions showed decrease of relaxivity - behavior more corresponding to common complex formation than to simple adsorption.

Only polystyrene sulfonate solution revealed behaviour corresponding to ion binding to nano object (Fig. 2).



Figure 2. Proton relaxivity in solutions of PSS alone and PSS-PVP mixed aqueous solutions in presence of Mn^{2+} ions

The REP rise on the Fig. 2 ("PSS" curve) is a result of more slow rotation of the Mn^{2+} probe ions bound to the negatively charged PSS macromolecule. This binding is reversible and addition of excess sodium ions led to liberation of Mn^{2+} ions into bulk solution and as a result - to lowering of relaxivity.

In PVP-PEI mixture no difference with PEI alone system was detected. Oppositely, addition of PSS to PVP-containing solution of Mn(II) in wide pH range resulted in sharp rise of R_1 up to 25000 M⁻¹s⁻¹ (Fig. 2, curve "PVP+PSS"), and R_2 - up to 60000 M⁻¹s⁻¹. This effect may be the result of formation of interpolymer complex, where the manganese ions bind in new environment than on PSS molecule.

Acknowledgements

This work was supported by the RF Ministry of education and science government order (KFU theme "Budget 12-12").

References

[1] R.R. Amirov. Metal compounds as magnetic-resonance probes for highly-organized media. Application in MR imaging and solution chemistry [Soedinenia metallov kak magnitno-resonansnyie zondy dlya vysokoorganizovannyh sred. Primenenie v MRtomographii i khimii rastvorov"]. Kazan: "New Knowledge" ("Novoye Znanie"), 2005. 316 pp.


^a <u>Anna S. Dmitruk^{1,2,3}, S. G. Vasil'ev³, E. A. Tatarinova²</u>

E-mail: anitadmitruk@gmail.com

¹Lomonosov Moscow State University, Faculty of Fundamental Physical and Chemical Engineering, Moscow, 119991, Russian Federation

²Institute of Synthetic Polymeric Materials, Profsoyuznaya street 70, Moscow 117393, Russian Federation

³Institute of Problems of Chemical Physics, Academician Semenov Avenue 1, Chernogolovka 142432, Russian Federation

1. Introduction

The successful practical use of so-called MQ-copolymers caused the active development of this area and the emergence of new applications of these polymeric materials. The MQ copolymers are organosiloxane copolymers composed of quadrafunctionalsilicate (Q) units end-capped with monofunctional trimethylsiloxy (M) groups. The simplicity of obtaining and versatility of properties of these MOcopolymers allowed using them in various areas, ranging from cosmetics to additives in coating and composite materials of various purposes [1,2]. Despite the great interest in these materials, their structure has not been studied yet. This work describes the synthesis of the monomer hexa(trimethylsiloxy)disiloxane _ by the catalytic polycondensation route. This study will provide an opportunity to clarify the more complex structure of the MQ polymers. Due to the fact that the choice of the reagents to produce various kinds of resins is currently made empirically, knowing the architecture of these molecules will allow obtaining them through more effective routes, to control the final structure of the product and its chemical properties.

2. Synthesis

Hexa(trimethylsiloxy)disiloxane was obtained by catalytic polycondensation of hexaethoxydisiloxane in the presence of an acetic acid as an active media [3].

3. Experimental

The ¹H, ¹³C, ²⁹Si NMR spectra were recorded on a Bruker Avance III 500 instrument in CDCl₃ as a solvent using the residual solvent peak as an internal standard (¹H, ¹³C) and TMS as an external standard (²9Si).



Figure 2. ²⁹Si NMR spectrum of hexa(trimethylsiloxy) disiloxane

Signals of CH₃ groups appear at $\delta 0.22$ -0.11 ppm in ¹H and at $\delta 2.13$ -1.45 ppm in ¹³C spectra. The ²⁹Si spectra shows the signals of trimethylsiloxy groups between 8.5-4.5 ppm. Most intense of them corresponds to hexa(trimethylsiloxy) disiloxane. The silicate groups of hexa(trimethylsiloxy) disiloxane appears at -110 ppm. The presence of set of different lines in spectra indicates that the higher molecular weight products are also formed in the reaction.

References

CH₃

- Guillaume, K.; Xavier, T.; Jean-Luc, G. (Loreal). WIPO Patent WO2011/001217, January, 2011
- [2] Serobian, A.K. (The Clorox Co.). U.S. Patent 2007/0128962A1, June7, 2007
- [3] Ye.V. Egorova, NG Vasilenko, Demchenko, NV, Tatarinova, EA, AM Muzafarov; Dokl. Chem. 2009. T. 424. Number 2. p. 200-204.

CH₂



Figure 1. The general scheme of synthesis



NMRCM Multinuclear NMR relaxation as a tool of investigating local 2013 structure and dynamics of ternary aqueous solutions of nitrate

salts

Andrei V. Egorov, Mariia I. Averina

Faculty of Physics, Saint-Petersburg State University, Ulianovskaya 1, 198504, Saint-Petersburg, Russia E-mail: egorov@nmr.phys.spbu.ru

1. Introduction

Describing the microstructure and dynamics of ternary aqueous solutions at the molecular level is of importance to the understanding of the solvation phenomenon. Complexity of the problem requires a variety of methods to be employed. NMR relaxation is one of an important means of investigating the properties of binary solutions (see [1] and reference wherein). In order to ascertain whether or not relaxation measurements may be effectively used to describe concentrated ternary systems the study of ternary aqueous solutions of nitrate salts Ca(NO₃)₂–LiNO₃–H₂O was carried out.

2. Experimental

The nitrate salts (LiNO₃ from Sigma-Aldrich and Ca(NO₃)₂·4H₂O from Fluka) were preliminary dried at 160^oC. Solutions were prepared by weighing out appropriate amounts of the salts and diluting volumetrically with heavy water (99.97% of deuterium). Concentrations of the components were determined by NMR quantification using the external concentration standards. The list of the systems studied is given in Table 1. All NMR measurements were performed on a Bruker Avance 500 SB spectrometer. The temperature was maintained at $25.0\pm0.1^{\circ}$ C. Spin-lattice relaxation times (T_1) were measured by using the inversion-recovery technique. The error in relaxation times measurements does not exceed 5 %.

Solution	Ca(NO3)2 conc. mol/l	LiNO3 conc. mol/l
1	3.0	2.8
2	3.6	3.1
3	4.0	3.7
4	4.8	4.3
5	5.0	4.9
6	5.0	5.3
7	5.0	6.1

3. Results

The spin-lattice relaxation times of the ⁴³Ca, ⁷Li, and ¹⁴N nuclei are collected in Table 2. To obtain structural of dynamical parameters from experimental measurements it is necessary to make assumptions on the local structure of the ions environment. Such assumptions highly influence the interpretation of the relaxation data. The results indicate that NMR relaxation technique should be used as a complement to the results obtained by other methods. In particular, it can be a validation method for Molecular dynamics computer simulations.

Solution	T_1 , sec		
	⁴³ Ca	⁷ Li	¹⁴ N
1	0.066	10.1	0.0085
2	0.049	7.7	0.0062
3	0.033	5.3	0.0040
4	0.022	3.6	0.0026
5	0.013	2.5	0.0016
6	0.010	1.9	0.0011
7	0.005	1.1	0.0005

Table 2. Relaxation times of the nuclei studied $(25^{\circ}C)$

Acknowledgements

We are indebted to Dr. Sergey Dvinskikh, Royal Institute of Technology, Sweden for his help with experiments. The financial support of The Russian Foundation for Basic Research (grant 13-03-01073a), and Saint-Petersburg State University are gratefully acknowledged.

References

[1] V.I. Chizhik, Mol. Phys. 90, 653 (1997).



Galina N. Fedyukina, Boris V. Sakharov, Pavel Ch. Kopilov, Sergey A. Ivanov, Andrey P. Anisimov

FBUN State Research Centre for Applied Microbiology & Biotechnology, Obolensk 142279, Russia E-mail: galafed@mail.ru

1. Introduction

A common way of stabilizing the biological objects (proteins, vaccines, microbial preparations) is freeze-drying. H¹-NMR relaxation technique is known to be the best method to estimate an amorphous state of dry preparations. Here are presented the results of the study of the freeze-dried subunit plague vaccine by ¹H-NMR relaxation technique.

2. Instrumental

The subunit plague vaccine F1+V and D-mannitol were used in our work. The dry samples were rehydrated in the glass container with the saturated solution of KCl (a_w =0.82) during 2 h at the room temperature.

NMR parameters were taken on the relaxometer "Chromatec-Proton-20M" (Russia) at a resonance frequency of 20 MHz and temperature 40°C. The "dead time" of the receiver channel was 12 μ s. Proton free induction decays (FID) were acquired using the following parameters: a 90°pulse of 2.4 μ s, a dwell time of 0.5 μ s between two successive data points, 64 scans of 8000 data points and a recycle delay of 30 s (vaccine) and 120 s (D-mannitol) between each scan. T₁ was measured by using Hahn pulse sequence 90°- τ -90°-FID. The patterns were sealed in 10-mm NMR-tubes. The quantity of powdered samples was controlled (average weight 0.4 g).

3. Results

The experimental results can be seen in the fig. 1. All the FIDs were analyzed by fitting to relaxation functions consisting of a fast (solid) and a slow (mobile) relaxing components (1) [1]:

$$I(t) = A_{S0} \left((1 - f_g) e^{(-t/T_{2Sa})^2} \sin(bt) / (bt) + f_g e^{(-t/T_{2Sg})^2} \right) + A_{m0} e^{-t/T_{2m}} e^{(-t/T_{2mv})^2}$$
(1)

where: I(t) is the signal intensity observed, A_{S0} and T_{2S} are the amplitude (the initial intensity) and characteristic times of solid crystalline phase (low mobility protons), *b* characterizes a forced damped oscillation and A_{m0} and T_m represent the amplitude and T_2 of the high mobility protons component. All parameters in formula 1 were determined.

The fig. 2 shows the best fitting of the experimental curves to the theoretical functions according eq. 1.

It was found that the solid component parameters were the same for three samples. This fact says about similar structural dynamical state of the glass matrix in all studied formulations.

The FID liquid component was not registered for dry and wet mannitol. But it was clearly seen in dry vaccine signal where its proton population was 3%. After wetting this component increased considerably in vaccine and reached 12.6%. It was in good accordance with the adsorbed water content (9%).



Figure 1. The experimental FIDs for D-mannitol (1), the freeze-dried (2) and rehydrated (3) vaccine. The signals were normalized to the signal at 12 µs. The insert represents the first 100 µs of the FIDs





References

[1] Sakharov B.V., Volkov V. Ya., Bogush V.G. NMR Relaxation Studies of Fibers from Bombyx mori and Artificial Silk –Like Proteins. // Abstracts of the Int. Conf. "Modern Development of Magnetic Resonance", Kazan, August 15-20. – 2004. P. 282-283.



Dmitry Furman

St. Peterburg State University, 1 Ulyanovskaya st., Petrodvorets, 198504, St.Peterburg, Russia E-mail: dm.furman.nmr@mail.ru

1. Introduction

Development of methods for non-invasive study of the internal structure of objects is an important scientific problem. MRI and other radiological techniques are used in medicine and industry. Modern MRI techniques help not only to study the internal structure of objects, but also their chemical composition. The use of low field MRI scanner (6.8 mT) allows you to explore protic samples with ferromagnetic inclusions. This is their advantage over scanners with stronger fields.

2. Experiment

Determination of inclusions was performed using different staining techniques. There changes in the duration of the RF pulse and the time between them were obtained. In the experiment, the base sequence was GRE-sequence. Due to the fact that the gradient sequences are more sensitive to local inhomogeneities of the field than the SE sequence.

3. Results

The experiment had shown the influence degree of the inclusions parameters on MRI images. Optimal parameters sequences were produced for the study different inclusions. Had studied quantitative and qualitative factors of influence on the signal inclusions (fig.1, 2).



Figure 1. The dependence of the signal intensity of the integrated type inclusion



Figure 2. The dependence of the integrated signal intensity of the inclusion of volume. For iron

- [1] Maja Musse, François De Guio, Stéphane Quellec, Mireille Cambert, Sylvain Challois, Armel Davenel. Quantification of microporosity in fruit by MRI at various magnetic fields: comparison with X-ray microtomography.- Magnetic Resonance Imaging 28 (2010) 1525–1534
- [2] Cheng-Jin Du, Da-Wen Sun. Recent developments in the applications of image processing techniques for food quality evaluation. - Trends in Food Science & Technology 15 (2004) 230–249
- [3] Peter A. Rinck Magnetic Resonance in Medicine.-Blackwell Wissenschafts – Verlang Berlin Vienna 2001.



NMRCM First-principles calculations of CuFeS₂: characterization based on 2013 the nuclear-resonance spectroscopy data

<u>Ramil R. Gainov</u>¹, Vera V. Klekovkina¹, Farit G. Vagizov¹, Alexander V. Dooglav¹, Vladimir A. Golovanevskiy², Ivan N. Pen'kov¹

¹Institute of Physics, Kazan Federal University, Kazan, Russia ²Curtin University, Perth, Australia E-mail: ramil.gainov@kpfu.ru; vera.klekovkina@kpfu.ru

1. Introduction

Various complex chalcogenide materials, including Cu-Fe-S and Cu-Fe-Se systems, are intensively studied by numerous experimental and theoretical methods. This fact is due to a wide range of chalcogenide properties and, as a consequence, potentially area of practical application. However, both the phase-structural and the magnetic transformations are often quite subtle and are impossible to detect by a single method. Instead, a combination of different methods is required. Ternary compound CuFeS₂ (referred to as chalcopyrite) is being example of this. Actually, CuFeS2 has insufficiently known properties; among them are uncertain valence states of Cu and Fe and their distribution over the structure, details of phase transitions at about 50 K and low-temperature magnetic state below 50 K [1,2]. These aspects present a strong motivation for a complementary study of CuFeS₂.

2. Results and discussion

The CuFeS₂ compound contains two nuclei probes suitable for nuclear-resonance studies. Both Mössbauer spectroscopy on the ⁵⁷Fe nuclei and NMR spectroscopy on the ^{63,65}Cu nuclei provide information on the local fields felt by the Fe and Cu nuclei as well as their relaxation characteristics, pointing the fluctuations around the critical points (e.g. phase transitions). The comparison of Mössbauer and NMR data can help explain the exchange interactions, dynamics of local fields and internal fluctuations along the polymeric -Cu-S-Fechemical bonds. On the other hand, calculations on the basis of density functional theory (DFT) should show the uncertain band structure and the details of the low-temperature phase transitions obtained from the Mössbauer and NMR experiments.

Our preliminary plane wave pseudo-potential calculations using local spin density approximation (LSDA) showed the density of states (DOS) for CuFeS₂ (Fig. 1) in agreement with earlier calculations [3]. The calculated dipole contribution in the local magnetic field on the Cu nuclei is approximately 2kOe [4]. This value is significantly lower than ~16kOe experimental values obtained from the NMR spectra measurements. Therefore, the local magnetic field on the Cu nuclei is produced mainly due to the hyperfine magnetic field. Hyperfine field on the Cu nuclei due to the covalence effect was computed as in [5] and found to be approximately 14kOe, making up the total field of 16kOe which corresponds perfectly with the experimental value. The total magnetic field on the Fe nuclei, as follows from the Mössbauer studies, is approximately 370kOe, which is larger compared with the magnetic field of the Cu nuclei.



Figure 1. Calculated total and partial electron density of states

This large value of the hyperfine field on the Fe nuclei is due to the core polarization effect. Calculations predict the Fe electronic magnetic moment value of $3.29\mu_B$ [4] (experimental value of $3.85\mu_B$). In order to calculate the value of the hyperfine field on the Fe nuclei the full potential methods are required. As a further step, it is interesting to apply generalized gradient approximation (GGA), a method generally considered more suitable for magnetically ordered materials, for comparison with the LSDA results.

Acknowledgements

This work is partly supported by RFBR grant under No. 12-02-31282 (mol_a).

- J.C. Wooley et al. J. Magn. Magn. Mater., 162, 347-354 (1996).
- [2] S.W. Lovesey et al. J. Phys.: Cond. Mat., 24, 216001(1)-216001(7) (2012).
- [3] R. Edelbro et al. Appl. Surf. Sci., 206, 300-313 (2003).
- [4] R.R. Gainov et al. European J. Mineralogy, in press.
- [5] A. Abragam. The principles of nuclear magnetism. -Clarendon Press, Oxford, 1961.
- [6] G. Donnay et al. Phys. Rev., 112, 1917-1923 (1958).



NMRCM Influence of hydrogen bonding on macro- and microscopic 2013 parameters of cyanobiphenyls. The comparative study

<u>Egor Gerts</u>^{1,4}, Andrei V. Komolkin¹, Vladimir A. Burmistrov², Victor V. Alexandriysky³, Sergey V. Dvinskikh¹

¹*Faculty of Physics, Saint-Petersburg State University, Russian Federation* ²*Ivanovo State University of Chemical Technology, Ivanovo, Russian Federation* ³*Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russian Federation* ⁴*E-mail: gerts-e-d@yandex.ru*

1. Introduction

The interest in materials with non-covalent interactions is greatly increased for the last few years. In particular hydrogen-bonded systems are of great practical importance as they influence the mobility and ordering of the material. Two liquid crystals (LCs) of cyanobiphenyl series (HO6OCB, also referred as HOC6B or H6CBP, and 7OCB (Fig. 1)) have been studied by virtue of NMR and molecular dynamics simulations methods. Both LCs have approximately the same length, however HO6OCB can form hydrogen bonds between terminal groups, while 7OCB can not. That influences drastically on the properties of LCs.



Figure 1. ω -hydroxy-4-n-hexiloxy-4'-cyanobiphenyl (HO6OCB, upper) and 4-n-heptyloxy-4'-cyanobiphenyl (7OCB, lower)

Dew to the temperature dependence of chemical shift spectral lines correlation should be done for the spectra in liquid crystalline phase. Method described in the paper of Guo and Fung [1] has been applied for that purpose.

2. Experiment

Experimental part was carried out at Royal Institute of Technology, Stockholm, Sweden by prof. S. V. Dvinskikh.

¹H and ¹³C NMR spectra were obtained using PDLF technique on a Bruker Avance III 500MHz spectrometer. Proton NMR with pulsed-field-gradient has been applied to obtain self-diffusion coefficients [2].

3. Simulation details

Fully atomistic model has been chosen to carry out a reliable study of hydrogen bonding. MuScaT method [3], which allows "on the fly" transition between more and less detailed models (fully atomistic and united atoms models in our case), has been applied to speed up the equilibration. 784 molecules have been placed in cubic cells with periodic boundary conditions for both LCs. OPLS and OPLS-AA force fields and the canonical (NVT) ensemble have been used. Temperature has been kept at $0.98T_{\rm NI}$ (the temperature of nematic to isotropic transition) for each LC. After the equilibration the analysis was performed on trajectories of 10 ns for both systems. More information on the simulation details could be found in our poster.

4. Results and discussion

The purpose of this work is to determine the influence of hydrogen-bonding on several macro- and microscopic parameters, such as order parameters, self-diffusion coefficients and conformations of the above mentioned LCs, which will be discussed in details in our poster.

- [1] Guo, W., Fung, B. M. (1991). *The Journal of chemical physics*, **95**, 3917.
- [2] Dvinskikh, S. V. (2013). Applied Magnetic Resonance, 44(1-2), 169-180.
- [3] Neverov, V. S., Komolkin, A. V. (2012). The Journal of Chemical Physics, 136, 094102.



NMRCM Residual moisture behavior in extremophilic *Polypedilum* 2013 *vanderplanki* monitored by ¹H-NMR

H. Harańczyk¹, <u>E. Baran¹</u>, M. Florek-Wojciechowska¹, P. Nowak¹, J. Nizioł², T. Okuda³, K. Strzałka⁴, S. Knutelski⁵, J. Tarasiuk²

Jagiellonian University, Cracow, Poland ¹Institute of Physics, 31-059 Cracow, Reymonta St. 4 ²AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Cracow, Poland ³National Institute of Agrobiological Sciences, 1-2 Ohwashi, Tsukuba, Ibaraki 305-8634, Japan ⁴Faculty of Biotechnology, Jagiellonian University, Cracow, Poland ⁵Institute of Zoology, Jagiellonian University, Cracow, Poland E-mail: ewelina.motyka@uj.edu.pl

1. Introduction

African chironomid *Polypedilum vanderplanki* in its larval form is the largest multicellular animal capable of anhydrobiosis [1]. It populates the temporary completely dried pools in Northern Nigeria and Uganda. Its maggot may survive deep desiccation during the prolonged dry season [2].

We analysed water content in dehydrated larva, a number and an arrangement of water binding sites on inner surfaces of its organism, and formation of tightly and of loosely bound water fractions at different temperatures.

2. Materials and methods

Dehydrated larvas of the chironomid *Polypedilum* vanderplanki were grown in a laboratory conditions [3].

Microtomography crossections were recorded using Nanotom S (General Electric). X-ray tubes with a power up to 57 W and a maximum operating voltage of 180 kV were used. The lamp is an open type with replaceable cathode and window. Max. voxel resolution (depending on object size), < 500nm (0.5µm).

¹H-NMR spectra were acquired on a Bruker Avance III 300 spectrometer, Bruker Biospin. The resonance frequency was 300 MHz, bandwidths 300 kHz. The pulse length was $\pi/2 = 2.1$ ms.

3. Results

3.1. Microtomography

Microtomograms of dried *P. vanderplanki* larva revealed the inner structure of the organism with the arrangement altered as compared with the actively living organism (Fig. 1).

3.2. ¹H-NMR

¹H-NMR spectra show superposition of the solid component well fitted by Gaussian function ($v \approx 44$ kHz), coming from protons of dried tissues of *P. vanderplanki*; and Lorentzian line component (with $v \approx 1.6$ kHz) coming from water tightly bound on inner and outer surfaces of solid tissue. This behaviour of bound water resembles that for Coleoptera alytron [4] or in DNA-CTMA complex [5].

NMR spectra temperature dependence show the gradual immobilizing of bound water without the formation of the ice crystallites, as it is detected in thalli of Antarctic lichenized fungi expiring very low temperatuere [6]. The detected by us contribution of liquid signal in dry form of *P. vanderplanki* maggot is unexpectedly high.



Figure 1. Crossection of dehydrated larva of Polypedilum vanderplanki

- M. Sakurai, T. Furuki, K. Akao, D. Tanaka, Y. Nakahara, T. Kikawada, M. Watanabe, T. Okuda, vol. 105 no. 13, 5093–5098.
- [2] R. Cornette, Y. Kanamori, M. Watanabe, Y. Nakahara, O. Gusev, K. Mitsumasu, K. Kadono-Okuda, M. Shimomura, K. Mita, T. Kikawada, T. Okuda., J Biol Chem. 2010 Nov 12;285(46):35889-99.
- [3] T. Okuda. O. Gusev, 2012, 121-138
- [4] H. Harańczyk, P. Nowak, M. Florek, S. Knutelski, APP, 2011
- ¹H-NMR spectra show superposition of the solid [5] H. Harańczyk, J. Kobierski, J. Nizioł, E. Hebda, J. Pielichowski, D. Zalitacz, M. Marzec, and A. El-Ghayoury, Journal of Applied Physics, 113, 044702 (2013)
 - [6] H. Harańczyk, P. Nowak, M. Bacior, Ł. Pater, M.A. Olech, APP, 2011
 - [7] H. Harańczyk, P. Nowak, M. Bacior, M. Lisowska, M. Marzec, M. Florek, M.A. Olech, Antarctic Science, Volume 24, Issue 04, August 2012, pp 342-352



NMRCM Magnetisation transfer in *Cetraria aculeata* (Schreb.) Fr. thalli 2013 observed by ¹H-NMR

H. Harańczyk¹, P. Nowak¹, M. Florek-Wojciechowska¹, <u>E. Baran¹</u> and M. A. Olech²

¹Institute of Physics, Jagiellonian University, 30059 Cracow, Poland ²Institute of Botany, Jagiellonian University, 31501 Cracow, Poland *E-mail:* hubert.haranczyk@uj.edu.pl

1. Introduction

Lichenized fungi are extremophilic organisms which survive freezing and/or deep dehydration [1-3]. The understanding of the molecular mechanism of freezing and dehydration resistance requires a knowledge on formation of tightly and loosely bound water fractions for different steps of hydration process [5, 6]. ¹H-NMR is one of the methods which allows to observe both: signal coming from water molecules binding to the thallus and solid signal coming from protons of solid matrix of the thalii. Magnetization transfer experiment allows one to get the exchange rate for the proton transfer between solid matrix of the thallus and bound water reservoir.

2. Materials and methods

Thalli of fruticose lichenized fungi *Cetraria aculeata* were collected in the vicinity of Arctowski Polar Station, King George Island, Maritime Antarctic during a sunny and cloudy weather conditions.

Proton spectra were collected on Bruker Avance III spectrometer (Bruker Biospin), operating at the resonance frequency 300 MHz (at $B_0 = 7$ T). The length of the soft π pulse was 100 µs with the transmitter power used equal to 3.7 W. The hard $\pi/2$ pulse power was 400 W and the pulse lasted 2.1 µs. Repetition time was 2 s.

3. Results

The recorded ¹H-NMR spectra are superpositions of a Gaussian component ($\Delta v_G \approx 50$ kHz) coming from protons of solid matrix and an averaged Lorentzian component ($\Delta v_L \approx 3000$ Hz) coming from protons of bound water.

The hard-hard sequence $(\pi_x - \tau - \pi/2_y)$ acts on the all proton spins. Magnetization recovery of solid fraction is described by two exponents characterized by recovery times equal to T_{1s} = (130.5±9.1) ms and T_{2s} = (679±12) ms. Magnetization recovery of liquid fraction is described by two exponents characterized by times equal to T_{1L} = (53.5±9.8) ms and T_{2L} = (604±13) ms.

The B_1 of soft pulse in the soft-hard sequence $(\pi_x - \tau - \pi/2_y)$ does not exceed local fields in solid matrix of thallus, thus, only liquid magnetization is reversed. The detection, hard, pulse rotates whole proton magnetization of the sample. The

exchange rate may be calculated from the reversed component of relaxation function, and for *Cetraria aculeata* thallus hydrated to $\Delta m/m_0 = 0.089$ equals of 312.5 1/s. The fraction of transferred magnetization (exchangeable protons of the thallus) may be estimated as 55%.



Figure 1. ¹H NMR spectra recorded after soft hard-hard $\pi - \tau - \pi/2$ pulse sequence (black) and soft-hard sequence (red)

Acknowledgements

The research was carried out with the equipment purchased thanks to the financial support of the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (contract no. POIG.02.01.00-12-023/08).

- [1] H. Harańczyk, On water in extremely dry biological systems, Wyd. UJ 2003.
- [2] H. Harańczyk, A. Pietrzyk, A. Leja, M. A. Olech, Acta Phys. Polon. A, **109**, 411 (2006).
- [3] H. Harańczyk, M. Bacior, P. Jastrzębska, M.A. Olech, Acta Phys. Polon. A, 115, 516-520 (2009).
- [4] H. Harańczyk, Ł. Pater, P. Nowak, M. Bacior. M.A. Olech, Acta Phys. Polon., A, 121, 480-484, (2012).
- [5] H. Harańczyk, M. Bacior, M.A. Olech Antarctic Science 20, 527-535 (2008).
- [6] Harańczyk H., Nowak P., Bacior M., Lisowska M., Marzec M., Florek M., Olech M.A., "Bound water freezing in Antarctic Umbilicaria aprina from Schirmacher Oasis", Antarctic Science, 343-352, (2012).



NMRCM Molecular mobility in multi-component solutions

A. V. Ievlev, Y. S. Chernyshev

Department of Quantum Magnetic Phenomena, Physical Faculty, St.-Petersburg State University, 198504 St.-Petersburg, Russia E-mail: alexandr ievlev@nmr.phys.spbu.ru

1. Introduction

The need to update the molecular mechanism of diffusion and relaxation electrolyte ions, finding the optimal conditions to increase the mobility of charge carriers (ions) in nonaqueous electrolytes. That is not a full range of tasks that need to be addressed for such class of substances, as ionic liquids.

2. Methods used in the experiment

To measure the diffusion coefficients used the technique of pulsed magnetic field gradient. Experimental temperature dependences were obtained on a spectrometer BRUKER AVANCE 400 applicable to the method using stimulated echoes at temperatures ranging from 298 K to 353 K. The solvent used deterred water. The concentration of the ionic liquid was 6 CMC. High resolution spectra of the samples prepared on the spectrometer BRUKER AVANCE 500, at room temperature.

3. Measurements

Figures 1 and 2 show the effect of carbon nanotubes on the mobility in the multi-component solutions.



Figure 1. Temperature dependence KD ionic liquid and solvent



Figure 2. Temperature dependence KD ionic liquid and solvent with carbon nanotubes

4. Results and discussions

Analyzing the experimental results obtained for the temperature dependence of the CD and high-resolution spectra recorded by the spectrometer BRUKER AVANCE 500. We came to the conclusion that the presence of carbon nanotubes affects our multi-component mixture, this is manifested in the broadening of the spectral lines and a small deviation in the temperature dependence of the CD.

Acknowledgements

This work is supported by Russian Foundation of Basic Research (grant N_{2} . 10-03-01043-a), and St. Petersburg State University grant to support expeditions and trips to the Russian and international organizations to conduct basic research (grant N_{2} 11.42.507.2011). The author expresses his thanks to Vitaly I. Volkov and his team for hosting high-quality experiments.



NMRCM ¹H NMR study of hydrides of disordered binary $Ti_{1-x}Nb_x$ alloys 2013 (with x = 0.5, 0.6 and 0.3)

<u>Valeria Ievleva</u>, Alexei Baryshev, Elena Kurenkova¹, Alexander Ievlev, Sergey Lavrov, Marina Shelyapina, Anait Alexanyan²

Dept. of Quantum Magnetic Phenomena, St. Petersburg State University, St. Petersburg, Russia E-mail: shelyapina@nmr.phys.spbu.ru ¹Center for magnetic resonance, Saint-Petersburg State University, St. Petersburg, Russia ²Institute of Chemical Physics of Armenian NAS, 5/2 P. Sevak str.,Yerevan 0014, Armenia

Transition metal alloys belong to a class of hydrogen storage materials. Appreciable enlightening of main characteristics both static and dynamics can be provided using nuclear magnetic resonance (NMR) method which is an especially powerful tool to investigate metal hydrogen systems. Here we report on the results of our ¹H NMR study of Ti_{1-x}Nb_xH_y hydrides (x = 0.5, 0.6 and 0.3 and $y \approx 2$). All the samples under study were prepared using the Self-propagating High-temperature Synthesis method [1].

The ¹H NMR line shapes of the samples were tested with home-built cw NMR spectrometer at 43 MHz at room temperature. The pulse ¹H NMR signals were registered within the temperature range from 190 to 360 K using homebuilt NMR spectrometer (at 20 MHz). The spin-lattice relaxation times T_1 were measured using the inversion recovery techniques.

Fig. 1 provides an example of ¹H NMR spectrum in the Ti_{0.4}Nb_{0.6}H_{1.9} hydride. As it is seen, for hydrides of binary alloys the NMR spectra consist of two lines: a broad and a narrow. The broad line characterizes hydrogen rigidly bound to the lattice, whereas the narrow one is associated with mobile hydrogen. Such a proton NMR line shape is rather typical for hydrides of transition metal alloys, and was observed in hydrides of Ti-V and Ti-V-Cr alloys [2].





For all studied hydrides and over all temperatures the magnetization recovery curves were described by two exponents with different intensities. The temperature

dependences of the both components of the proton spinrelaxation rates in $Ti_{0.5}Nb_{0.5}H_{1.91}$ are shown in Fig. 2. Similar to hydrides of binary Ti-V alloys [2] temperature dependence of R_1 have a rather complicated character that reflect structural phase transitions in this hydrides.



Figure 2. Two components of the spin relaxation rates R_1 (a) and their intensities (b) in $Ti_{0.5}Nb_{0.5}H_{1.91}$ as functions of inverse temperature

- A.G. Aleksanyan et al. J. Alloys Compds. 509 (2011) S786-S789.
- [2] E. Kurenkova et al. Solid State Phenom. 194 (2013) 254-257.



National Research University — St. Petersburg State Polytechnical University, Russia, 195251, St.Petersburg, Polytechnicheskaya, 29, Institute of Physics, nanotechnology, and telecommunications E-mail: antonkarseev@gmail.com, davydov_vadim66@mail.ru, vidoodkin@mail.ru

1. Introduction

Measuring devices which operating principle is based on the nuclear-magnetic resonance (NMR) are widely adopted in scientific researches and technology [1, 2]. At the present quantum magnetometers, especially time, Hanle magnetometers, are successfully used for ultra-weak magnetic fields measurement [3], such as magnetic fields in space, ferromagnetic screens fields, etc. But in case of high irregularity of the weak magnetic field, observed NMR signal is unsuitable for accurate measurements [4]. Therefore, weak magnetic fields with high irregularity (more the part of percent per centimetre), widely spread in present time, cannot be measured with required accuracy by modern quantum magnetometers. One of solutions for this problem, namely measurement of such fields, is use of NMR-magnetometer, based on the nutation method. Its application gives essential benefits in accuracy.

2. Experimental technique

Accuracy of weak magnetic fields and their irregularity measurement by nutation method depends on two quantities: width and slope of nutation line in points, where amplitude of registered NMR signal comes up to zero value. Before nutation NMR magnetometers developers are set two tasks – decrease width and increase slope of nutation line.

In the presented research a method, based on spatial separation of two nutation coils, was developed. Such a design of nutation sensor bears a resemblance to propagation of the atomic beam in an atomic-ray tube [5]. According to the atomic beams technique, impact of electromagnetic field leads to the spectral line contour formation. To prevent the spectral line spread, Ramsey developed an installation. In this installation, the atomic beam communicates with a high-frequency field twice in two remote areas of small size. As a result of this impact, fine structure (Fig. 1), that resembles the intensity distribution under the interference of quasimonochromatic light passed through narrow slits, positioned apart from each other, occurs on the peak of resonance curve



Figure 1. Shape of the spectral line in the installation with separated impact areas

In order to attain an analogy with Ramsey experiment, the optimal balance between nutation coils size and the distance between them, and also additional conditions in impact areas were fitted.

3. Results

The results obtained have shown that the nutation line slope increases, and the width decreases. This allows to increase the weak irregular magnetic field parameters measurement accuracy.

- Jesse Russel. Nuclear magnetic resonance Moscow: LLC «Kniga po trebovaniyu», 2012, 107
- [2] M.P. Borodin. Application of the phenomenon of nuclear magnetic resonance. SPbU, 2003, 316
- [3] N.M. Pomerantsev, V.M. Ryzhkov, G.V. Skrotskii Physical basis of quantum magnetometry, Moscow: Nauka, 1972, 316
- [4] E.B. Alexandrov, G.I. Khvostenko, M.P. Chayka Interference of atomic states, Moscow: Mir, 1991, 246
- [5] V.V. Grigoryants, M.E. Jabotinsky, V.F. Zolin. Quantum frequency standards. Moscow: Nauka, 1968, 288



NMRCM Sign-sensitive measurement of heteronuclear dipolar couplings 2013 to spin-1

Boris B. Kharkov^{1,2}

¹Department of Chemistry, Royal Institute of Technology - KTH, SE-10044 Stockholm, Sweden ²Department of Quantum Magnetic Phenomena, St. Petersburg State University - SPbGU, 198504, St. Petersburg, Russia *E-mail: kharkov@kth.se*

1. Introduction

Due to its well-defined orientation and distance dependence, the through-space dipole-dipole coupling represents one of the most informative parameters in studies of molecular geometry, orientational ordering and internal dynamics by NMR. Wide range of solid state NMR experiments in both static and rotating samples have been developed during last decades for determination of internuclear dipole-dipole couplings. One of the shortcomings of the conventional techniques is that sign of the dipolar interaction is unavailable due to inherent symmetry of the dipolar multiplets.

In the present contribution, the approach to obtain the sign and the magnitude of the interaction of $spin-\frac{1}{2}$ to spin-1nuclei in oriented static samples is described.

2. Selective decoupling

Due to anisotropy of the molecular magnetic susceptibility many systems of high importance, such as liquid crystals and biomembranes, can be aligned in the external magnetic field. In this case, symmetric triplets appear in the spectrum of spin-¹/₂ nucleus (e.g. ¹³C, ¹⁵N) due to heteronuclear dipole-dipole couplings to spin-1 nuclei (e.g. ²H, ¹⁴N). Moreover, quadrupolar interaction leads to appearance of a doublet in the spectrum of spin-1. Irradiation of one of the transitions in the quadrupolar spectrum will mix up two of the three lines in the spectrum of spin-¹/₂ and, thus, leads to breaking the symmetry in the spectrum. Which pair of lines would collapse depends on the relative signs of the dipole-dipole and quadrupolar couplings.

The effect of single-quantum (SQ) selective decoupling is demonstrated in Fig.1 [1]. The spectrum of Fig.1(a) exhibits several triplets for carbon sites in the vicinity of ¹⁴N nucleus. Spectrum was obtained in the presence of only proton decoupling. The additional ¹⁴N SQ-decoupling results in asymmetric doublets (Fig. 1(c) and 1(d)) and indicates the same sign of dipolar interaction to ¹⁴N spin for C1, C2, and C3 carbons and opposite sign for trimethyl ammonium group. Clearly, the technique is rather straightforward to implement in practice and generalization of the approach for the multidimensional correlation studies is possible.



Figure 1. (a) ¹³C proton decoupled NMR spectrum in lamellar CTAB/hexanol/D₂O mesophase with C1, CN, C3, and C2 carbon signals expanded (b). The effect of selective SQ nitrogen decoupling is shown on the spectra (c) and (d). Signals due to hexanol in the spectrum (a) are labelled with stars

Detailed quantum mechanical description, employing Average Hamiltonian Theory and single-transition operator formalism, will be presented along with experimental results in various mesophases.

Acknowledgements

This work was supported by Swedish Research Council VR and by Russian Foundation for Basic Research.

References

 B.B. Kharkov, V.I. Chizhik, S.V. Dvinskikh – J. Chem. Phys., 137, 234902 (2012).



NMRCM Structural analysis of porphyrin complex of 2013 Sn(IV)porphyrinatesin with 4-imidazolylphenol in benzene by Saint Petersburg, Russia 2D ROESY and 2D DOSY NMR spectroscopy

Ilya A. Khodov, Mikhail Yu. Nikiforov, Gennady A. Alper, Nugzar Zh. Mamardashvili

G.A. Krestov Institute of Solution Chemistry of RAS, Ivanovo, Russian E-mail: iakh@isc-ras.ru

1. Introduction

Ability porphyrinates coordinatively unsaturated cations Sn (IV) axial coordinate additional electron donor molecules or fragments of molecules allows them to serve as a basis for the design of multifunctional supramolecular assemblies [1-3]. In most cases, these processes are based on the donoracceptor interaction of the metal cation of the reaction center porphyrinates with oxygen atoms of the substrate molecule

NMR spectroscopy applied to the study of structure of the complexes and measurement of diffusion coefficients of Sn(IV)porphyrinates and its complex with 4-imidazolylphenol in benzene Thus, the synthesis and NMR study identified of the Sn(IV)porphyrinatesin with 4-imidazolylphenol (Fig 1).

These results extend the use of multi center substrate receptor interactions to construct supramolecular porphyrin ensembles of varying difficulty.

2. Results and discussions



Figure 1. Chemical structures Sn(IV)porphyrinatesin, 4-imidazolylphenol and their complex

Methods of two-dimensional ROESY (Fig. 3) and DOSY (Fig. 2).



Figure 2. 2D DOSY complexe of Sn(IV)porphyrinatesin with 4-imidazolylphenol in benzene



Figure 3. 2D ROESY complexe of Sn(IV)porphyrinatesin with 4-imidazolylphenol in benzene

These results of the research reveal the possibility of design on base of the tetrapyrrolic compounds new macrocyclic receptors for the detection and binding of substrates of different nature.

Acknowledgements

Financial support was from the Russian Foundation for Basic Research, Project No.HK 12-03-00775/13.

- [1] T. Mizutani, T. Ema, T. Yoshida, Y. Kuroda, H Ogoshi. - Inorg. Chem., 2(10), 2072-2078.(1993)
- [2] G.R. Deviprased, F D'Souza. Chem. Commun. 19, 1915-1916 (2000)
- [3] G. M. Mamardashvili, N. Zh. Mamardashvili, O.I.Koifman - Macroheterocycles 6(1) 67-73 (2013)



NMRCM NMR in domain walls of magnetically ordered material: the 2013 information from the field pulses effect

¹ <u>Nikolay S. Klekhta</u>¹, Ivan V. Pleshakov^{1,2}

¹Saint-Petersburg State Polytechnic University, 195251, St.-Petersburg, Russia ²Ioffe Physical-Technical Institute of the Russian Academy of Sciences, 194021 St.-Petersburg, Russia E-mail: ivanple@yandex.ru

1. Introduction

The action of magnetic field pulses on the NMR signal observed in magnetically ordered material can be regarded as a method for investigation of the substance properties. The signal suppression effect and its applications for the study of magnetic parameters of a compound were revealed some of tens years ago [1], and recently it was developed for a number of particular cases, [2-4]. Here we discuss the influence of multi-pulse sequence on the spin echo in a ferric material and the data, which can be extracted form such an experiment.

2. Experiment and discussion

A number of possible experimental scenarios were analyzed in this work: the action of video pulses, both coincident and not coincident with the radio frequency (rf) pulses exciting the spin system, and possesses as positive and negative amplitudes.

The NMR was observed in lithium-zinc ferrite as a spin echo signal of Fe-57. It was experimentally confirmed, that predictions for the different situations are realized in the stuff. The echo suppression and restoring was observed. The most interesting case is an experiment with the sequence of two video pulses, act on the sample simultaneously with rf pulses in such a mode, when the nuclear spin system excited in a certain previously defined area. This kind of operation is possible because of domain wall control by the video pulses. The model for the effect explanation is demonstrated in Fig. 1, where x is a spatial coordinate and η_w is NMR enhancement coefficients in the domain wall.



Figure 1. The model of NMR excitation in the movable domain walls. a - Bloch wall at initial position; the wall, shifted on the distance Δx under the action of pulse field h_V . b - the corresponding spatial distributions of the enhancement coefficients



Figure 2. Action of the sequence of video pulses, coincident with the rf pulses, in different cases (shown in insert)

A representative experimental result is shown in Fig. 2. Here the difference in the signal behavior for the cases of acting of video pulses with the same or different signs is displayed. They correspond to the physical situations when the domain wall shifts to the same or opposite directions during the spin system excitation by the first and second rf pulses.

The possible implications of the observed phenomena were studied in the work. The results of magnetometric and NMR experiments were putted into connection. It was shown that some of parameters of material can be extracted from the experimental data, like, for example, an estimation of the domain wall thickness.

Acknowledgements

The work was supported by the Presidium of Russian Academy of Sciences, Program P-03.

- L.A. Rassvetalov, A.B. Levitski. Sov. Solid State Phys., 23, 3354-3359 (1981)
- [2] G.I. Mamniashvili, T.O. Gegechkori; A.M. Akhalkatsi, C.A. Gavasheli. – *Low Temperature Physics*, 38, 466-472 (2012)
- [3] A.M. Akhalkatsi, T.O. Gegechkori, G.I. Mamniashvili et al. – *Physics of Metals and Metallography*, **105**, 351-356 (2008)
- [4] I.V. Pleshakov, N.S. Klekhta, Yu.I. Kuzmin. Technical Physics Letters, 38, 853-855 (2012)

NMRCM NMR in the Earth magnetic field: Pre-polarization of Nuclei with 2013 Alternating Magnetic Field Saint Petersburg, Russia David A. Kunzivanov Madimir J. Chiphile

Pavel A. Kupriyanov, Vladimir I. Chizhik

Faculty of Physics , Saint-Petersburg State University, Russia E-mail: p.kupriyanov@nmr.phys.spbu.ru

There are many interesting applications of nuclear magnetic resonance in the Earth magnetic field [1, 2]. To compensate the decrease of the NMR signals in weak magnetic fields, including Earth's magnetic field, the different techniques are used. In this work some peculiarities of the polarization of nuclei with an additional strong magnetic field have been considered. In particular, the polarization of nuclei with an alternating magnetic field at a very low frequency F (but $F \gg 1/T_1$, where T_1 is the spin-lattice relaxation time) has been investigated. It is convenient and useful to turn the additional magnetic field on the perpendicular direction relatively B₀. We have been shown that in this case it is possible to fulfil the conditions of the adiabatic change of the summary field direction:

$$f_m \ll \frac{\gamma}{2\pi} \cdot \frac{B_0^2}{B^*},$$

where f_m is the frequency of the polarizing field, γ is the gyromagnetic ratio, B_0 is the Earth magnetic field, B^* is the applied alternating magnetic field.

The description of the process can be carried out on the basis of the Bloch equations using the "shaking" frame. The process of growth of macroscopic magnetization at the application of different magnetic field – as a sine wave and square wave – was modeled.



Figure 1. The growth of nuclear magnetization in the case of the sine-shaped pre-polarization

The application of the alternating magnetic field can help to decrease transient processes in an NMR sensor if the polarization current is switched off at the certain phase. The

There are many interesting applications of nuclear amplitude of damping transients can be approximately in 50 agnetic resonance in the Earth magnetic field [1, 2]. To times less than in the case of switching continuous current off.



Figure 2. Minimum transient processes in the LC resonant circuit

The experimental results confirming the theoretical predictions are presented in Fig. 3.



Figure 3. The amplitude of the NMR signal in the Earth field on the frequency and amplitude of the polarizing magnetic field

The work is supported by the grant of the Saint-Petersburg University and grant of RFBR #13-03-91372 CT_a.

- P.M. Borodin, A.V. Melnikov, A.A. Morozov, Yu.S. Chernishev: Nuclear Magnetic Resonance in Earth. 232 p. Leningrad: Izd. LGU 1967 (in Russian).
- [2] N.M. Vecherukhin, A.V. Melnikov, and P.M. Borodin. Applied Magnetic Resonance, 22,483-496 (2002).



NMRCM The method of signal detection of nuclear magnetic resonance in 2013 inhomogeneous magnetic field by using of composite pulses

G. S. Kupriyanova, V. V. Molchanov, E. A. Severin, I. G. Mershiev

Immanuel Kant Baltic federal university

1. Introduction

In recent years, a tendency to minimize the equipment with compact permanent magnet in low field nuclear magnetic resonance (NMR) has been developed [1]. Although high resolution NMR in high field has excellent possibilities for chemical analysis of liquids, the mobile applications are based on low field NMR relaxometry. The introduction of the permanent magnets leads to a number of problems associated with the low intensity of signals in a weak magnetic field, the need to eliminate distortions caused by a static magnetic field inhomogeneity and heterogeneous sample excitation RF field, the lack of stability in frequency due to the heating of the magnet. Additionally the frequency shift produces the phase distortions caused by off-resonant irradiation of the sample. One way to solve these problems is an application of composite pulses [2].

2. Composite pulses

A composite pulse consists of a set of RF pulse sequences with different phases and duration. The action of the composite pulse can be equivalent to the usual 90°- or 180°pulses, but an additional rotation of the magnetization vector with the varying phase pulses can compensate for the effect of the magnetic field inhomogeneity in the sample volume or the effect of the resonance offsets.

3. Experimental results

We experimentally investigated the conditions of effective excitation signal through composite pulses in NMR installation created on the basis of the NMR/ NQR Apollo console. Nuclear magnetic resonance of the protons was observed at a frequency of 13.99 MHz. We used a permanent magnet without temperature stabilization with homogeneity of the magnetic field near $\Delta B/B \sim 10^{-4}$.

Preliminary experiments on the relaxation times measurements by inversion-recovery method and spin-echo using the conventional $\pi/2$ and π pulses of different durations have showed that the relaxation times are highly dependent on the duration of the 90° τ pulse and offset resonance frequency.

In order to select the best set of composite pulses for effective excitation signal and relaxation measurements in samples of different origin the NMR signals have excited by composite pulses, equivalent to 90° and 180° pulses have been investigated. In order to investigate the most effective compensation phase the intensity and the line width of the NMR signal were studied as a function of the type of composite pulse, the residual magnetization after inversion under 180° pulse are determined with the use of conventional 180°, and composite 180° pulses with offset resonance.



Figure 1. The dependence of the residual magnetization level after the single 180° pulse and equivalent 180° composite pulse, depending on the resonance offset

Table 1. The relative value of the line width B obtained for the effects of 180° composite pulse and the relative value of signal-to-noise ratios C, obtained with composite pulse sequences and to conventional ones

Commonito mulas	$\Delta \omega^{j}$	Oil	
Composite puise	Ω_1^0	В	С
180	-0.94, 1,06	1	1
9090180 0 90 90	-0.81, 1.19	0.75	1
$\frac{27_099_{180}180_0211_{180}386_0}{211_{180}180_099_{180}27_0}$	-0.86,0.86	0.9	0.8
ASBO-9(7A)	0.428	1.5	1.1
ASBO-9(7C)	0.332	0.8	0.8
, i			

 $\frac{\Delta\omega^{\prime}}{a_1^0}$ is equal to the ratio of the resonance offset to received signal to the pulse bandwidth, which can be determined from

the 90° pulse duration.

- B.Blümich, F.Casanova, S.Appelt, NMR at low magnetic fields, Chemical Physics Letters 477 (2009) 231–240
- [2] M.H. Levitt, Composite pulses, in: D.M. Grant, R.K. Harris (Eds.), Encyclopedia of Nuclear Magnetic Resonance, Wiley, Chichester, (1996) 2694–2711.



Sergey E. Kurnikov, Alexey V. Donets

St. Petersburg State University E-mail: serkurnikov@gmail.com

1. Introduction

Investigation of microstructure of aqueous electrolyte solutions attracts great interest due to their important role in various physical, chemical, technological and biological processes. The method developed in the Department of Quantum Magnetic Phenomena [1] makes it possible to determine important parameters of the microstructure of electrolyte solutions. The results, obtained for ²³Na ion, make it possible to find out several laws which describe the formation of ion hydration shells: monatomic ions are surrounded by the highly symmetrical shells, hydration shells of cations are characterized by two layers usually.

2.²³Na NMR-relaxation

The Fig. 1 shows the concentration dependence of the spin-lattice relaxation time ²³Na in NaNO₃ aqueous solution. The slope of the experimental curve changes at concentration $m = 2,3 \text{ mol } ([\text{NaNO}_3]:[\text{D}_2\text{O}] = 1:24)$. The main reason is the disappearance of zone of free solvent in the solution. The first hydration shell of the sodium consists of 6 water molecules, second shell – 12. The NO₃⁻ ion coordinates 6 molecules. The bend at concentration $m = 4,6 \text{ mol } ([\text{NaNO}_3]:[\text{D}_2\text{O}] = 1:12)$ indicates complete disappearance of the second layer of the hydration shell of the ion Na+. With further increase in concentration does not exclude the formation of contact ion pairs. The experimental results are in good agreement with data previously obtained on the basis of relaxation of the solvent nuclei.

3. Quantum-chemical calculation

Quantum-chemical calculation water clusters around the sodium cation were carried out. Some structures characterizing by minimum potential energy were used for estimating significant properties Na-H₂O system. Calculation of the electric field gradient (EFG) allows us to get full information about nearest environment of the cation and realize distribution theory of structures in aqueous solutions. Time of spin-lattice relaxation was estimated summing all contribution from each complex with corresponding probability weight. The calculations confirm experimental results. Thus, we were able to obtain fundamental knowledge using two complementary and independent methods.



Figure 1. Concentration dependence of the ²³Na spin-lattice relaxation in aqueous solutions NaNO₃ and NaCl at different temperatures



Figure 2. Structures of Na $^+(H_2O)_n$ clusters (n = 6, 18) with the corresponding type of symmetry. The method: DFT B3LYB, basis the 6-31G (3df, 3pd)

Acknowledgements

This work is supported by the Russian Foundation for Basic Research (grant N_{2} 10-02-01043-a). The authors acknowledge Saint-Petersburg State University for a research grant.

- Donets A. V., Chizhik V.I., Structural Chemistry, 2011.
 V. 22, № 2. 465-470
- [2] Chizhik V.I., Molec. Phys., 1997. V.90, 653.



NMRCM Signal feedback in NMR and MRI

Vyacheslav V. Kuzmin^{1,3}, K. R. Safiullin², P.-J. Nacher¹

¹Laboratoire Kastler Brossel, ENS – CNRS – UPMC, 24 rue Lhomond, 75005 Paris, France ²Present address: Kazan Federal University, Institute of Physics, Kazan, Russia. ³E-mail: slava.kuzmin@lkb.ens.fr

1. Introduction

Tuned pick-up (PU) coils with high quality factors O are used in NMR and MRI for high-sensitivity and low-noise detection. However they limit the signal bandwidth (BW) and the enhanced currents cause strong radiation damping (RD) effects in the samples. Signal feedback (FB) can be used to actively control these currents and adjust the BW and RD without resistive losses and noise penalty [1, 2].

2. Techniques

We use an inductive coupling scheme to feed a suitably amplified phase-adjusted signal back into the PU coils of our low-field NMR systems. Different types of high-impedance (high-Z) amplifiers, matched to our high-Z tuned circuits $(Z\sim10-100k\Omega)$, are compared. One system is used for NMR studies in liquid ³He, where the use of a cryogenic coaxial connection limits the open-loop (OL) Q-factor to a low value (Fig. 1). The other one is used for MRI, with a pair of Litzwire PU coils separately tuned with Q_{OL} ~150. This elementary coil-array allows parallel data acquisition with a field of view (FoV) smaller than the object for accelerated imaging. The sensitivity encoding (SENSE) information obtained from the independent coils is used for image reconstruction [3].

3. Results

Figure 1 illustrates that the *Q*-factor of a given tuned circuit can be efficiently controlled using FB. We have observed that most high-Z amplifiers actually introduce significant uncontrolled FB, possibly by internal capacitive coupling. This can result in unstable OL operation at high positive gain, but appropriate FB can be used to solve this issue.



scheme, with capacitive or inductive² coupling

Figure 1. Principle of FB into the NMR coil (left) and electrical resonance curves recorded around $f_0=74.7$ kHz (right). The moderate OL Q-factor ($Q_{OL}=8.8$) is strongly reduced by negative FB ($Q_{FB<0}=1.3$) or increased by positive FB ($Q_{FB>0}=110$)

When two coils are closely coupled to a sample, they are usually coupled to each other as well. This induces split resonances and strongly correlated currents in both coils (Fig. 2, left). Negative FB in each detection channel broadens the detection BW and decouples the detected signals by reducing the currents in the coils (Fig. 2, right).



Figure 2. Resonance curves for a pair of inductively coupled detection (PU) coils independently tuned at $f_0=87$ kHz $(Q_{OL}=150)$. An emf is injected in PU1 and the signals of the two detections channels are recorded for OL and negative FB operations

Figure 3 shows a reconstructed image obtained with FBdecoupled coils and SENSE acquisition. The artifact-free final (unfolded) image demonstrates the efficiency of the decoupling scheme.





The $4.5 \times 4.5 \times 3.5$ cm³ water sample containing plastic shapes used for MR imaging

Figure 3. 2D projection image (left) obtained from the water sample (right) by ¹H MRI at 87 kHz (2mT). A FLASH sequence was used for MRI with a 3-cm FoV in the vertical direction (smaller than the sample) and a 1.5-mm in-plane resolution. Image reconstruction uses the computed sensitivity maps of the coils

4. Conclusion

Signal FB in NMR and MRI has various applications and offers efficient noiseless broadening of BW [2], flexible control of coil-sample interactions and hence of RD [4], and suppression of coil-coil interactions for parallel imaging. It is conveniently implemented at low NMR frequency, but can also be used at high field using suitable FB schemes.

V. V. K.'s work is supported by the FPGG Foundation.

- [1] D.I. Hoult. Rev. Sci. Instrum., 50, 193 (2009).
- [2] E. Baudin et al. J. Phys.: Conf. Ser., 294, 012009 (2011).
- [3] K.P. Pruessmann et al. Magn. Reson. Med, 42, 952 (1999).
- [4] V.V. Kuzmin et al., this conference.



Saint Petersburg, Russia <u>V. Loskutov</u>^{1,2}, S. Zhakov^{1,3}, Y. Dolomansky^{1,4}

¹Baker Hughes, Russian Science Center, Kutateladze 4A, Novosibirsk, 630128, Russia
 ²IMary State University, Yoskar-Ola, Lenin sq.1, Russia
 ³Institute of Metal Physics, The Ural Branch of Russian Academy of Science, Ekaterinburg, ul. S.Kovalevskaya, 18, 620990, Russia
 ⁴Institute of Geophysics, The Ural Branch of Russian Academy of Science, Ekaterinburg,ul. Amundsena, 100, 620016, Russia,
 E-mail: val_losk@rambler.ru

1. Introduction

NMR well logging is finding wide use in formation evaluation. Due to logging speed requirements, NMR CPMG T_2 measurements are used to estimate formation parameters like porosity, permeability, and capillary bound water. The purpose of this work is to examine the possibility of determining the value of effective internal magnetic field gradient in the measurement of the transverse relaxation time of liquid in the presence of fluid flow in porous media using a CPMG sequence.

2. Theory

If the fluid-saturated porous medium applied external pressure gradient in the sample there is fluid motion. The fluid flow permeability, κ , is defined by Darcy's law: $v = -(\kappa/\eta)\nabla p$ where v is the flow velocity, ∇p is the pressure gradient and κ/η , the ratio of permeability to viscosity, is the fluid mobility. If the pressure gradient ∇p is known, to determine the permeability of the medium is necessary to determine the fluid flow rate in this porous media.

As shown earlier [1], at the low fluid flow velocity and taking into account the time dependence of the self-diffusion coefficient D [2], the transverse relaxation time T_2 of Carr-Purcell-Meiborn-Gill (CPMG) echo train is proportional to flow velocity. The explicit form of this dependence can be defined as

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2D}} + \frac{4(\sqrt{2} - 0.5)}{35}\gamma^2 G^2 \sqrt{D} v \tau^{5/2}, \qquad (1)$$

where first term T_{2B} is the contribution from the fluid bulk relaxation mechanism, the second term

$$1/T_{2D} = \gamma^2 G^2 D \tau^2 / 12$$
 (2)



Figure 1. Dependence of the average transverse relaxation rate on τ^2 at different values of magnetic field gradient

reflects the relaxation due to the self-diffusion of a liquid in the presence of a magnetic field gradient, G, where time τ refers to the time delay between the radio frequency pulse and the refocusing RF pulse in the spin echo pulse sequence and γ is the nuclear gyromagnetic ratio [3].

However, at interpretation of measurement results of relaxation times in porous systems there is some ambiguity in definition of a fluid flow velocity associated with an unknown value of an efficient gradient G.

3. Experiments

Fig.1 show the dependence of the transverse relaxation rate of aqueous solution $CuSO_4$ in the Berea core (provided by «Baker Hughes B.V.») on $(2\tau)^2$. According to Eqs. (1) and (2), in the absence of fluid flow this dependence must be linear, as shown in Fig.1. The linear approximation of the experimental data to determine the explicit form of the dependence of the type Eq. (2).

Fig. 2 shows the dependence of the second term of the linear approximation on the magnetic field gradient as a function of the applied gradient.

Then
$$\frac{D\gamma^2}{12} (G_0 + G_{int}) = -0.0265 + 0.022G_0$$
, where the

value of the internal gradient G_{int} of the order of 12 Gs and is approximately equal to the applied gradient.

- V. Loskutov, S. Zhakov, Y, Dolomansky. NMRCM, 2012. – SPb., "Solo" 2012. (p.98).
- [2] V.V. Loskutov, V.A. Sevriugin. J.Magn.Reson. 230, 1– 9 (2013).
- [3] M. D. Hurlimann at al. J.Magn.Reson. A113, 260-264 (1995).



Figure 2. Linear approximation of the dependence $(\gamma G)^2 D/12$ on magnetic field gradient



NMRCM DFT calculations for identification of FDMPO radical adducts 2013 from fast isotropic Electron Spin Resonance and F¹⁹ Nuclear ^{Durg, Russia} Magnetic Resonance spectra

<u>Katerina Makarova^{1,2}</u>, Ekaterina V. Rokhina², Elena Golovina² and Henk Van As²

¹Department of Physical Chemistry, Faculty of Pharmacy, Warsaw Medical University, Zwirki i Wigury 61, 02-091 Warsaw, Poland, kmakarova@wum.edu.pl; ²Laboratory of Biophysics and Wageningen NMR Centre, Wageningen University, Dreijenlaan 3, 6703 HA Wageningen, The Netherlands

1. Introduction

The anti-oxidant properties of various compounds could be shown by their influence on the formation of free radicals in Fenton reaction. The formation of free radicals during the Fenton reaction is usually studied by the ESR spin trapping technique. 4-hydroxy-5,5-dimethyl-2-

trifluoromethylpyrroline-1-oxide (FDMPO) is widely used for such measurements due to the long life time of the FDMPO spin adducts and high reactivity with various free radicals. Additional information about trapped radicals as well as concentrations of the formed spin adducts could be obtained from F¹⁹ NMR spectra. However, the identification of the trapped radicals based on parameters extracted from ESR and NMR spectra are quite complicated. In this work we propose the use of DFT calculations as a powerful tool for identification of trapped radicals.

2. Materials and methods

DFT Calculations

Quantum chemistry calculations using density functional theory (DFT) were performed on a set of FDMPO radical adducts and corresponding to them hydorxilamines to acquire F-hfcs and N-hfcs values (ESR parameters) and chemical shifts (F¹⁹ NMR). All calculations were carried out using the GAUSSIAN 09 program [1].

3. Results and discussion

DFT calculations of ESR parameters

It was found that DFT calculations at B3LYP/6-31G++ level of theory using PCM model for solvent together with 2 solvent molecules as well as accounted rotation of the CF₃ group result in very accurate values of hyperfine splitting (ESR parameters) [2]. We use this approach to identify the new FDMPO radical adduct observed in Fenton reaction with methanol in the presence of taxifolin. The experimental hyperfine splitting constant (A_N=13.31G and A_F=2.94G) were obtained by ESR spectra simulations. The DFT calculations of FDMPO/taxifolin radical adduct results in A_N=13.37G and A_F=2.87G that confirms the origin of trapped radical. However, some radical adducts could be reduced to corresponding hydroxylamine quickly, so their contribution to the total ESR spectrum could be below 5% and could not be extracted via simulations. In this case, the F¹⁹ NMR could

be applied to identify the formed hydroxylamines [3]. The NMR spectra measured for various systems contains signal from FDMPO spin trap (-60ppm) as well as formed hydroxylamine molecules. In this work we propose to use DFT calculations of possible NMR shifts for identification of the formed hydroxilamines.

The same calculation procedure [2] was applied for the set of FDMPO hydroxylamine molecules. However, NMR calculations at B3LYP/6-31++G level of theory provides quite inaccurate values of chemical shifts for FDMPO spin trap (-88ppm) as well as its various spin adducts. Better results were obtained at pbe1pbe/6-31G++(d,p) level of theory (-72ppm), however further improvement of the accuracy is required (experimental values is -66ppm). Moreover, it was found that calculated NMR parameters are very sensitive to solvent molecules. Thus, in addition to the rotation of CF₃ the geometry optimization with fixed dihedral angle (of CF₃ group) should be used.

Acknowledgements

The DFT calculations were performed with the Gaussian 09 package in the Interdisciplinary Centre for Mathematical and Computational Modeling (Warsaw, Poland) under the computational Grant G14-6.

- [1] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, in, Wallingford CT, 2009.
- [2] K. Makarova, E.V. Rokhina, E.A. Golovina, H. Van As, J. Virkutyte, The Journal of Physical Chemistry A, 116 (2011) 443-451.
- [3] V.V. Khramtsov, V.A. Reznikov, L.J. Berliner, A.K. Litkin, I.A. Grigor'ev, T.L. Clanton, Free Radic. Biol. Med., 30 (2001) 1099-1107.

NMRCM The temperature effects in different surfactant systems by means 2013 ¹³C NMR Saint Petersburg, Russia Denis A. Markolay, Maria V. Denava

³¹⁴ Denis A. Markelov, Maria V. Popova

Department of Quantum Magnetic Phenomena, St. Petersburg State University E-mail: mariavpopova@nmr.phys.spbu.ru

1. Introduction

Surfactants have broad applications in many areas. For example, surfactants are major constituents of detergents, industrial cleaners, and cosmetics. Some surfactants are used aswetting, emulsifying, defoaming, or solubilizing agents in the pharmaceutical,food, and textile industries.

Nuclear magnetic resonance (NMR) has been provento be one of the most powerful techniques for probing structure, dynamics and conformation of the surfactant molecules.

Over the past decade another area of surfactant chemistry that has been studied extensively. This is the association of surfactant molecules with dendrimers.

Dendrimers are a new class of monodisperse, globular polymer with treelike structures. Due to such structure dendrimers are of interest for many chemical and biomedical applications. For example, dendrimers have been used as sensors in diagnostics; as catalyst scaffolds; as nonviral gene carries; as anticancer, antimicrobial and antiviral agents; as drug capsules, synthetic hosts in host-guest systems; in imaging techniques based on magnetic resonance and computer tomography and others.

Surfactants are ideal guests for dendrimers because of the hydrophobic and hydrophilic parts in their structure.

We have studied the effect of the temperature on the aggregation and de-aggregation surfactants with different hydrophobic length in solution and hydrophobic dendrimer-water-surfactant systems. For investigation we used four surfactants with chemical formula $CH_3(CH_2)_nCOOR(n=4, 6, 8 \text{ and } R=Na \text{ or } K)$ and carbosilanedendrimers with first ("I") and fourth ("IV") generation.

2. Results

The temperature increase of surfactant solutions results in a gradual upfield of the chemical shifts for all carbon atoms in the aliphatic chain (see, for example Fig. 1). We conclude that the demicellization process takes place in this case.



Figure 1. The temperature dependence of ¹³C chemical shifts for different carbons in hexanoate solution relative to 26⁰C

In ternary systems in addition to surfactant aggregates in solution exist also the dendrimer-surfactant supramolecular aggregates. With increasing temperature, in addition to the growth of the exchange rate is a reduction of the micellar aggregation numbers in solution and the simultaneous increase of the surfactant molecules associated with dendrimers.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Grant No. 12-03-33155-mol-a-ved).



NMRCM Hydrodynamic and aggregation properties of 4th-generation poly-2013 L-lysine dendrimers in aqueous NaCl solution by ¹H NMR, light scattering, and molecular dynamics simulation

<u>Denis A. Markelov</u>^{1,2}, Mariya E. Mikhailova¹, Stanislav G. Falkovich², Igor M. Neelov², Vladimir V. Matveev¹, Anatolii A. Darinskii²

¹Faculty of Physics, St. Petersburg State University ²Institute of Macromolecular Compounds E-mail: markeloved@gmail.com

1. Introduction

One of most perspective practical applications of dendrimers is their use for gene delivery into a biological cell. Another possible application of dendrimers is the Alzgeimer's decease therapy based on their ability to prevent the aggregation of amiloid peptides

The new class of dendrimers is poly-L-lysine (PLL) dendrimers consisting of lysine aminoacid residues. L-amino acids are environmentally friendly materials due to their biocompatibility, biodegradation and non-toxicity.

In this work we studied hydrodynamic properties of 4thgeneration lysine dendrimers in aqueous NaCl solution. Concentration of the dendrimers and the salt were 0.2 and 0.9 weigh %, respectively. The presence of the salt in the solvent is necessary for neutralizing the effect of the polyelectrolyte. In molecular dynamics (MD) simulation the single PLL dendrimer considered and, therefore, no molecule salt were used.

2. Results

All methods give similar results for the size of dendrimer (Fig. 1). However, hydrodynamic radius, R_h , which obtained from NMR data, has a slight tendency to a decrease with increasing temperature. While the simulation and the light scattering experiment show an absence of a dependence of R_h on temperature. The difference between light scattering experiment and simulation results is within the error limits.

We suppose that R_h decrease trend from NMR data correspond to the destruction of aggregates consisting of

several dendrimers because the NMR method measures average diffusion coefficient of proton for all dendrimers i.e. both single and aggregated dendrimers. Then, decrease of R_h can be explained by the increase of the contribution of a single dendrimer to diffusion the coefficient due to destruction of the aggregates. This hypothesis is confirmed by light scattering experiment in which high size aggregates are observed at room temperature and practically disappear at 60 C.



Figure 1. The temperature dependence of hydrodynamic radius of 4th-generation PLL dendrimer

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Grants No. 12-03-33155, 12-03-31243 and 13-03-00524)

NMRCM Ultra-High Pressure NMR Investigation on Elemental Liquid 2013 Gallium up to 25 kbar Saint Petersburg, Russia

Thomas Meier, Jürgen Haase

Institute for Experimental Physics II, University of Leipzig, Linnestrasse 5, 04103 Leipzig E-mail: thomas.meier@physik.uni-leipzig.de, j.haase@physik.uni-leipzig.de

1. Introduction

The application of a new high pressure NMR technique in anvil cells has made the investigation of condensed matter under extreme conditions possible [1, 2]. Here we present the first ⁶⁹Ga- and ⁷¹Ga-NMR results of compressed liquid Gallium at pressures up to 25 kbar. Despite the observed validity of the Korringa relation, the apparent positive pressure coefficient of the Knight shift, $\partial K/\partial p$ cannot be explained within the theory of free electrons in a simple metal.

2. Motivation

The investigation of solid and liquid metals has been a focus of research over the last decades. Their mechanical, optical, and electronic properties under extreme conditions are not yet fully understood, and may reveal a wealth of interesting phenomena. Recently, investigations of elemental Aluminium under ultra-high pressures revealed a Lifschitz transition above 70 kbar [3], and put considerable doubt to our understanding of the electronic properties of simple metals. In theory, most metals do not change in electronic structure or long range - short range ordering under phase transisiton, and in accordance with the Landau-Fermi liquid theory, there should be an inverse pressure dependence of the Knight shift. Gallium, however, is known to exhibit electronic and structural pecularities under phase transition that cannot be explained with recent theories.

3. Experimental

All measurements were conducted with our home-built highpressure Moissanite anvil cells. The Moissanite anvils were of 800 and 1000 µm culet diameters, and a radiofrequency microcoil (5 turns of 18 µm copper wire) was placed in the middle of a preindented Beryllium-Copper gasket, together with the liquid Gallium samples and fine ruby powder as pressure senors. Hydrostatic pressures in the sample cavity were provided by paraffin oil.

4. Ultra-High Pressure NMR Technique

The resonating radio frequency microcoil is placed in the sample cavity of our home-built Moissanite anvil cell, leading to an increased sensitivity of several orders of magnitude, and, hence, allows for high sensitivity NMR-measurements on highly correlated electron systems. The whole cell is mounted onto a home-built series resonance probe head.Our Mao-Bell type pressure cells are composed of Titanium Grade 23, with dimensions of 20 mm in height and 17 mm diameter. Typically, thin Be-Cu disks were used as a gasket material, with extra low magnetic susceptibilities to minimise distortions of the external magnetic field.



5. Results

5.1. Pressure induced spectral shift

1) $\partial K/\partial p > 0$ is in accordance with early works from Cornell [4] (up to 5 kbar);

2) positive observed shift in resonance frequency hints towards an increase in the density of states at the Fermi level under volume compression, whereas theory predicts a $K_s(p)/K_s(0) \sim N(E_F)(p)$ / $N(E_F)(0) \sim (\Delta V / V_0)^{-3/2}$ behaviour.



5.2. Magnetic- & Quadrupolar spin relaxation times

1) Unique electronic structure of Gallium allows for rigorous decomposition of the magnetic and quadrupolar contributions to the spin-lattice relaxation times [5];

2) quadrupolar contribution increases under rising pressure, while T^m₁ decreases up to 19 kbar.



6. Conclusions

Application of the introduced ultra-high pressure NMR technique proved to be a versatile tool for investigation of strongly correlated electron systems. Gallium shows a distinct change in its electronic properties upon the liquid Ga - Ga II phase transition at 19 kbar. This is contradictory to our current understanding of simple metals under phase transitions. Furthermore, the distinct increase in Knight shift, and thus in the electronic density of s-states at the Fermi-level is even more suprising, since a three-dimensional Fermi-liquid should exhibit a decrease in N(E_F) under volume compression.

Acknowledgements

This research was funded by the International Research Training Group (IRTG) for Diffusion in Porous Materials and by the German Research Society (DFG). Additionally, we thank Marcus Anton from the University of Leipzig for the pressure calibration. We gratefully acknowledge the help from Prof. Dr. Dieter Michel from the University of Leipzig.

- [1] J. Haase et.al., Rev. Sci.Instr., 80(7), 073905/1-/4, 2009
- [2] T. Meissner et.al., J.Low. Temp. Phys., 159, 284-287, 2010
- [3] T. Meissner et.al, arXiv:1207.3702, 1-5, 2012
- [4] D.A. Cornell, Phys. Rev., 153(1), 208-216, 1967
- [5] W.W. Warren, W.G. Clark, Phys. Rev., 277(2), 171-180, 1969



NMRCM Broadband composite pulses for Spin=1NQR in powders

Ivan Mershiev, Galina Kupriyanova

Faculty of physics and technology, Immanuel Kant Baltic federal university E-mail: ivan.mershiev@gmail.com

1. Introduction

Composite pulse basically is a sequence of radiofrequency pulses with varying duration and phase. Composite pulses has been widely used in NMR as a tool for elimination of dipoledipole interactions, to increase signal-to-noise ratio and to reduce errors in quantum computing computation. In NQR, composite pulses can increase SNR [1], radiofrequency field homogeneity and effective volume of a detection coil for single-sided acquisition. It can be useful for NQR remote sensing applications. Our approach to composite pulses design based on use of NQR fictious spin operators for I=1 and product operator formalism.

2. Theory

In NMR, theory of composite pulses design is often straightforward. A possible way to create a composite pulce sequence is to use a geometrical vector approach or perturbation theory. However, simple vector model has no physical sense in NQR. Instead, it is possible to divide NQR density matrix to the set of independent orthogonal subspaces, corresponding to the NQR energy levels. This fictional spin-1/2 operators [2] may be presented as individual vector models for every NQR frequency. In single-frequency experiment it is possible to implement a vector model for single subspace and trace an evolution of magnetization vector, emerging under the radiofrequency field. The goal is to calculate a trajectory of magnetization vector which will lead to minimal variance. It is impossible in NQR to excite every crystallite in powder sample, so the calculations suggest directional averaging.

- Ramamoorthy A., Chandracumar N., Dubey A.K., Narasimhan P.T. Analysis or the performance of NQR composite pulses // Journal of Magnetic Resonance, 1993. Series A102, P. 274-286
- [2] Vega S., Pines A.: J. Chem. Phys. 66, 5624-5644 (1977)



NMRCM A novel approach of antidote drug "Ferrocin" for clinical MR 2013 imaging of digestive system

B. P. Nikolaev, Ya. Yu. Marchenko, L. Y. Yakovleva

Reseach Institute of Highly Pure Biopreparations, St.Petersburg, Russia E-mail: nikolaevhpb@gmail.com

1. Introduction

The medicine "Ferrocin" is prescribed as antidote against peroral nutrition of radioactive nuclides Cs, K and toxic rare earth elements. Antitoxic action of antidote strongly depends on the physiological state of organism. The clinical application of "Ferrocin"can be supported by MR imaging. The robust diagnosis depends on the detailed visualization of antidote in digestive tract. The paramagnetic properties of drug is the crucial demand for enhancement of visual resolution of digestive image in MRI. MR imaging of mouse model was done in dynamics after delivery of antidote per os. The results were discussed using the magnetic relaxometry data.

2. Materials and methods

The antidote "Ferrocine" was produced by "Farm Defence" (Moscow). The Prussian Blue is the main component of "Ferrocine" with general formula $Fe_4^{III}[Fe^{II}(CN)_6]_3nH_2O$ (n=14-16). The medicine was prepared as 1% aq. suspensions. Antidote intragastric dose 6 mg/mouse was administered to fasting mouse by feeding needle. MR imaging was fulfilled at 30 min time after administration.

Proton relaxation times T1, T2 were measured at CXP-300 spectrometer at proton resonance 300 MHz. MR images of mouse stomach-bowel tract were recorded at Avanch II spectrometer (Bruker). MR imagings of mouse stomach were made by gradient echo Flash (TR=5.4 мсек, TE=350 мсек, T1-weighted Rare T1 (TE=7.5 мs, TR=1.5 s, rare-фактор=4) and T2-weighted Rare T2 (TE=12 мs. TR=4.200 s, rare-factor=8, TEeff=36 мs).

3. Results

3.1. Relaxometry study

The measured T1, T2, T2 of water proton relaxation were reduced by influence of paramagnetic dispersion "Ferrocin". Relaxivity calculated from linear concentration plots (Fig. 1) suggests possible efficient contrast action of antidote in MRI experiments.

Acceleration of relaxation is caused by paramagnetic clustering of nanocrystals "Ferrocin". According the ratio r_2/r_1 "Ferrocin" is more preferred for MRI as T2 contrast agent.

3.2. MR imaging of mouse model

Loading of stomach by "Ferrocin" results in the decrease of NMR signal from voxels corresponding antidote locus. Contrast enhancement is visualized in the form of dark regions in T1-weigheted images Fig. 2. Images associated with presence of contrast agent reveal new anatomical details of stomach and duodenal bowel.



Figure 1. Spin-spin relaxation rate of protons in "Ferrocin" dispersion vs Fe content



Figure 2. T1-weighted images of mouse stomach loaded by antidote "Ferrocin" (left) and control polysaccharide solution (right)

4. Conclusions

1. Antidote "Ferrocin" promotes the contrast visualisation of mouse digestive system as efficient T2 contrast agent.

2. Detailed visualization of antidote treatment per os can be achieved by MR imaging.

Acknowledgements

This work was supported by FMBA RF (grant 40.002.12.0). Our great thanks A. Dobrodumov, I. Voevodina for assistance in experiments.

- [1] Mohammadreza Shokouhimehr, Eric S. Soehnlen, Anatoly Khitrin et al. Biocompatible Prussian blue nanoparticles: Preparation, stability, cytotoxicity, and potential use as an MRI contrast agent. Inorganic Chemistry Communications 13 (2010) 58–61.
- [2] M. Verdaguer , F. Villain , R. Ouahe's et al. Attractive magnetic Prussian blues. Polyhedron 24 (2005) 2906– 2908.



NMRCM Solid state NMR study of cell wall materials

K. Paradowska, O. Stefaniak, I. Wawer

The Medical University of Warsaw, Faculty of Pharmacy, Department of Physical Chemistry, Banacha 1, 02-097 Warsaw, Poland

1. Introduction

Numerous studies provided scientific support for a relationship between non adequate fibers consumption and heart disease, high cholesterol, obesity, diabetes and colon cancer. Dietary fiber (non-digestible carbohydrates and lignins that are found in plant) and "functional fiber" (nondigestible carbohydrates that have beneficial physiological effects) add to "total fiber", determined as an important feature of food. An adequate intake for total fiber was set at 25-38g/day, whereas average American and European diets cover less than half the requirement. An expanding market for high-fiber products stimulated research and development of new formulations. Responding to this trend, various plant materials, frequently waste or by-products of agro-industry are now considered as a source of precious components for functional food and nutraceutics. Fruits are usually characterized by an edible portion and moderate amounts of waste material such as peels, seeds and stones. Due to increasing production, disposal represents a growing problem since the plant material is usually prone to microbial spoilage. On the other hand, costs of drying and storage of by-products are economically limiting factors. The agro-industrial waste is often utilized as feed or as fertilizer. However, demand for feed may be varying. Thus, efficient and environmentally sound utilization of these materials is becoming more important. The preparations from by-products of apples and grapes containing dietary fiber and natural antioxidants have already found applications as dietary supplements.

Solid state NMR is widely used for characterization of crystalline powders but also amorphous samples and polymers, including various plant materials. The technique has been used to determine structure and properties of cellulose and cellulosic products

2. Materials and Methods

The materials included pomace from aronia (chokeberry, *Aronia melanocarpa E.*), black currant (*Ribes nigrum*) and bilberry (*Vaccinium myrtillus*) processing. The materials being the waste product of food industry, were dried and fine powdered (micronized) by Microstructure. In brief, waste were dried and milled (to size of less 100µm).

The ¹³C NMR spectra were recorded on a Bruker DMX-400 spectrometer with magic angle spinning (MAS) and cross-polarisation (CP) pulse sequences and high power proton decoupling. The samples were packed in 4 mm ZrO₂ rotor and spun at 10 KHz. Dipolar dephasing pulse sequence (with 50 μ s delay befor acquisition) was used to observe selectively the non protonated carbons. Variable contact time experiments provided data on mobility of fiber chains.

3. Conclusions

The standard ¹³C CPMAS NMR spectra of all micronised natural fibers show large signals in the carbohydrate region between 60 and 80 ppm (fig.1). These groups of resonances can be assigned to cellulose, the major component of cell walls. The spectra recorded in dipolar dephasing mode, enabled identification of further compounds, mainly polyphenolics. Characteristic resonances in the region of aromatic carbons indicated that in the fiber material obtained from aronia fruits there are significant amounts of antocyanidins, catechins and cutins.



Figure 1. ¹³C CPMAS NMR spectra of dietary fibers from: aronia, bilberry, cocoa, oat, apple, black currant, rasphberry

- Asp N., G., Johansson C., G., Hallmer H., et al. (1983). Rapid enzymatic assay of insoluble and soluble dietary fiber. *Journal of Agricultural and Food Chemistry*, 476-82.
- [2] Akiyama T. et al. (2003). *Phytochemistry*, 64, 1157– 1162
- [3] Atalla R. H.& VanderHart D.L. (1999). Solid State Nuclear Magnetic Resonance, 15, 1
- [4] Bardet, M., Robert, D., Lundquist, K., Von Unge, S. (1998). Distribution of *erythro* and *threo* forms of different types of b-O-4 structures in aspen lignin by ¹³C NMR using the 2D INADEQUATE experiment. *Magnetic. Resonance. Chemistry*, *36*, *597–600*.
- [5] Górecka D., Hęś M., Szymandera-Buszka K., Dziedzic K. (2009). Contents of selected bioactive components in buckwheat groats. *Acta Scientiarum. Polonorum.*, *Technol. Aliment.*, 8(2), 75-83.
- [6] Wawer I., Wolniak M., Paradowska K. (2006). Solid state NMR of dietary fiber powders from aronia, bilberry, black currant and apple. *Solid state Nuclear Magnetic Resonance*, 30, 106-113



NMRCM Preparation of agar phantoms which are designed mimic human 2013 tissues and theirs comparing with real tissues in medical MR

¹ images

Victoria Parshina, Svetlana Ievleva

Saint Petersburg State University, 198504 Saint Petersburg, Ulianovskaya st. 1 E-mail: parshenn@mail.ru

1. Introduction

Phantoms are increasingly important for standardizing and optimizing scanner performance, and calibrating data analysis [1]. And there are a some works devoted to applying agar phantom in this field theme [3]. But there is another applications of such phantoms like a imitations of human tissues in terms of their relaxation pathways, including T1, T2 [2] water and fat saturation for developing or approving Magnetic Resonance imaging (MRI) protocols. In this work were prepared several agar phantoms close by Magnetic Resonance (MR) properties to human muscles, fat and white and gray tissues of brain.

2. Methods

Samples were made from ultra-pure agar with concentrations 1.2-1.8% in solutions Cu₂SO₄ (2-4 micro moles per milliliter) and relaxation times were measured in University laboratory by spectrometer Bruker with value of constant magnetic fields is equal 2 T. When necessary parameters were achieved by varying of agar and paramagnetic concentrations samples were placed near human body in medical MRI system (Toshiba ExelArt Atlas Vantage XGV) for comparing with tissues on images. MR contrast was estimated by the brightness of the pixels of images in eFilm (program for viewing and processing DICOM images). There were obtained images of spine,knee and brain.

3. Results



Figure 1. Axial slice of brain and agar phantoms in T_1 contrast

In picture 1 is shown an image of axial slice of human brain obtained by protocol with short time repetition for $T_{1,}$ contrast where are images of two agar phantoms are two rectangles on the left side of image. The averaged values for brightness pixels in white and gray tissue of brain is 1171 and 938 for agar phantoms are 2063 and 2504 that is 21% intensity contrast for brain and 25% for agar phantoms.



Figure 2. Axial slice spine and agar phantoms in T_2 contrast

Figure 2 demonstrates an image of axial slice of human spine obtained by protocol with effective time echo is equal 100 msec for T2 contrast where are the images of two agar phantoms are two rectangles at the bottom of image. The averaged values for brightness pixels in muscles and fat tissues of spine is 1332 and 6879 for agar phantoms are 2233 and 5706 that is 516% intensity contrast for fat and muscles and 255% for agar phantoms.

Acknowledgements

This work was made with help of staff and patients of Children Hospital N5 named N.F. Filatov.

- [1] Graves et al. "JMRI", 28:278-281, 2008.
- [2] D. Mustafi, E. Peng, M. Heisen, A. M. Wood, J. Buurman, and G. S. Karczmar. World of Phantoms: Reference Standards for Bench to Breast MRI. "Proc. Intl. Soc. Mag. Reson. Med." 17 (2009) p. 2104.

NMRCM NMR study of Sodium Lauroyl Sarcosinate in Solution and Binary 2013 Mixtures Saint Petersburg, Russia Maria V. Danaval. Phillip C. Buknavil, Appa A. Varanteauz²

<u>Maria V. Popova¹</u>, Philip S. Bubnov¹, Anna A. Vorontsova²

¹Department of Quantum Magnetic Phenomena, St. Petersburg State University E-mail: mariavpopova@nmr.phys.spbu.ru ²FGU VNIIPO of EMERCOM of Russia, Saint-Petersburg

1. Introduction

As well know, commercially used surfactants are invariably mixtures of two or more types of surfactants. The understanding of the nature of macromolecular aggregates is consequently of great technological relevance. Although such systems have been used for a long time, knowledge of the detailed structure and size of different kinds of mixed surfactant molecules in the co-aggregates still requires further study. Besides, many problems on the conformational changes of molecules still remain unresolved. As well as despite a large number of studies of micellar systems direct microscopic investigations of surfactant dynamic and aggregate structure as their aggregation state changes from micellar to monomeric and back to micellar are still quite rare.

2. Results

We have performed NMR studies including ¹³C and ¹H chemical shift, ¹H relaxation time and self-diffusion coefficient measurements of binary surfactant solutions of sodium lauroyl sarcosinate (SLAS) and mixing systems (SLAS–D₂O-cosurfactant) at different surfactant concentration and/or temperature. As co-surfactant we used anionic amphiphiles with two different hydrophobic chains - potassium decanoate and potassium hexanoate.

In the ¹³C and ¹H spectra of SLAS every resolved carbon or proton nucleus causes two signals due to the existence of two isomers in solutions and binary mixtures. The population values of both isomers depend on the surfactant concentration and temperature. For example, the population of the trans configuration of surfactant molecules relative to that of the cis-configuration was found to increase with increasing concentration. This observation indicates that the transconfiguration of SLAS is more stable in the micelle state than in the monomeric state. The separation of the trans and cis resonance lines, which called internal chemical shift is influenced by the concentration of SLAS and/or co-surfactant as well as by the temperature. The temperature increase leads to the downfield change of external chemical shifts of ¹³C and ¹H nucleus (see. Figure 1).



Figure 1. The temperature dependence of ¹³C external chemical shift in SLAS solution

Acknowledgements

M. Popova is grateful to the Deutscher Akademischer Austauschdienst (DAAD) for financial support of the visit in Institute für Experimentelle Physik II und Organische Chemie of Universität Leipzig and also to Prof. Dr. Michel and Prof. Dr. Hennig from the Leipzig University for the scientific guidance and the help in all organizational questions. We are grateful to the Center for Magnetic Resonance of St. Petersburg State University for the part NMR measurements.



NMRCM Field-shifting method for Magnetization Transfer Contrast in low-2013 field (6.8 mT) Magnetic Resonance Imaging

Filipp Riabchun, Vyatcheslav Frolov

Department of Quantum Magnetic Phenomena, faculty of physics, Saint Petersburg State University E-mail: fryabchun@gmail.com

1. Introduction

Magnetization Transfer Contrast (MTC) is a well-known method of improving the informational content of Magnetic Resonance Images (MRI). Such images are affected by the spacial distribution of macromolecular component (low T2) in tissues

2. Basic principles

MTC method is based on homonuclear Overhauser effect between so-called free and bounded protons, the latter being present in macromolecules. The thing is that we can't directly observe MR signal of bounded protons because of extremely short T₂ (~ mks). But if we could somewise saturate the bounded protons magnetization, it would affect the signal from free protons (T₂ ~ ms) due to exchange processes.

There are two common ways to perform such saturation. The off-resonance method uses the difference between radiofrequency (RF) absorbtion linewidth of free and bounded protons. It consists in applying RF pulses with some offset from resonance frequency such that bounded proton spins absorb much more RF energy than those of the free protons. The on-resonance method involves specific pulse sequences (mostly binomial pulses), applied on resonance frequency but self-compensating for free protons.

3. Materials and Methods

In this work we represent an attempt to perform MTC with home-built 6.8 mT MRI scanner on 4% agar gel. We've decided to use slightly modified off-resonance method involving some B0 field shifting such that saturation and excitation pulses frequencies are equal and one can use the same RF transmitter for both.

- [1] S. J. Graham, R. M. Henkelman. Understanding Pulsed Magnetization Transfer — JMRI 1997: 7, 903–912.
- [2] S. J. Graham, R. M. Henkelman. Pulsed Magnetization Transfer Imaging: Evaluation of Technique — Radiology 1999: 212, 903–910.

NMRCM The use of two-dimensional COSY and NOESY methods for the 2013 identification of the NMR signals of organic dyes Saint Petersburg, Russia

S. A. Ruzheva, A. V. Bogaychuk

Physico-Technical Institute, Department of Radio Physics and Information Security, Immanuel Kant Baltic Federal Univnrsitet E-mail: fotinija_89@mail.ru

spectrum, which allows you to make some assumptions about the chemical composition of the substance.

Modern NMR spectrometry to determine not only the chemical composition, but also the spatial structure of the substance. Such an opportunity came through the use of twodimensional experiments.

If the chemical structure is known, it is possible to carry out the assignment of the corresponding resonance lines. If the structure is unknown, the structure can be selected from several alternatives. [2] In general, you should answer the question: "Which of the nuclear spins are linked together?" In principle it is possible to get an answer to this question is simple enough for even the structures using one-dimensional methods, such as using isolation or construction of theoretical spectra. However, in general there are more complicated cases when the spectra contain overlapping lines, these methods lead to success only if a large number of laborintensive and time-consuming experiments. With this method of two-dimensional information can be obtained from a single experiment [3].

The best-known examples of these experiments are COSY and NOESY.

The sample used in this paper the azo-dye, acid-base indikator.CI22120. C.I.Direct red 28 - Congo red.

For identification of the NMR signals of organic dyes we conducted three types of experiments:

1. Removal of the proton spectrum (PROTON);

- 2. COSY;
- 3. NOESY.

We got the exact values of the chemical shifts of hydrogen and spent the correlation signal for the dye Congo red by proton spectrum and the experiment COSY.

Also we received correlation maps NOESY, obtained with different mixing time 100, 300 and 500 ms. It was concluded that the growth of the correlation value τ_m improved card,

One of the basic experiment is to obtain a proton NMR namely the intensity of the cross peaks, all the peaks are more soluble and decreases the noise contribution. Were compared with theoretical and practical information for small molecules with large rotational correlation time.

> For small values of the mixing interval τ_m for the intensity of cross-peak between the lines that match the resonance of spins *i* and *j*, we have the formula

$$\sigma_{ij} \sim r_{ij}^{-6} \tau_m \,, \tag{1}$$

where σ_{ij} - intensity cross-peak, and r_{ij} - the corresponding distance between the nuclei.

Resulting in a practical way the intensity of the peaks on the mixing time suggests coordination between theory and practice, however, it is worth noting that the construction of further dependence is difficult because of the spin diffusion, which is evident when $\tau_m > 500$ ms and degrades the testimony of the experiment. Thus, based on the findings of the outcome of the experiment depends on the mixing time, we can choose an optimal value for a sample of Congo red τ_m = 500 ms. Then, using the formula

$$r_{ij} = r_0 \, \delta \! \left\{ \frac{\sigma_0}{\sigma_{ij}} \right\},\tag{2}$$

where σ_0 and r_0 - the calibration values, we have obtained the corresponding relative distance of the observed cross-peaks of the sample congo red, due to the experimental NOESY.

- [1] A. "Two-Dimensional Bax, Nuclear Magnetic Resonance in fluid", 1988, 160
- [2] H. Gunther, "Introduction to the course NMR Spectroscopy", 1984, 142-207
- A. Deroum, "Modern NMR techniques for chemistry [3] research," 1992. 145-188, 266-348
- [4] R. Ernst, G. Bodenhausen, A. Vokaun, "NMR spectroscopy in one and two dimensions", 1990, 342-353
- [5] S. Braun, H.-O. Kalinowski, S. Berger, "150 and more basic NMR experiments", 1998, 79-82, 92-93

NMRCM Proton magnetic resonance in multiple metal hydrides 2013 <u>Ivan A. Rykov</u>, Marina G. Shelyapina, Vladimir I. Chizhik

Faculty of Physics , Saint-Petersburg State University, Russia E-mail: ivan_rykov@nmr.phys.spbu.ru

The temperature dependences of spin-lattice relaxation (T_1) of the ¹H nuclei can provide information on hydrogen mobility in metallic lattice. However, for the adequate interpretation of experimental data one needs an appropriate model, which can provide an understanding of hydrogen state. Usually, the proton relaxation in metallic hydrides is analyzed using the isotropic model firstly proposed by Bloembergen, Purcell and Pound (BPP).

Metal-hydrogen systems are inhomogeneous, that leads to larger minima in T_1 temperature dependence. This smoothing is often treated by incorporating the distribution of hydrogen motion parameters. Moreover, some features of temperature dependencies of the proton relaxation in metallic hydrides cannot be explained within the framework of the BPP model even taking into account the distribution of activation energies and correlation times [1-3].

¹H NMR spectra of metallic hydrides show that hydrogen can exist in two states [4]: relatively mobile (m) and bounded to the lattice (b), and there is an exchange between these two states.

This paper presents the results of measurements of temperature dependences ¹H of spin-lattice relaxation rates in alloys $TiV_{0.8}Cr_{1.2}H_{5.29}$, $Ti_{0.33}V_{1.27}Cr_{1.4}H_{1.13}$, $Ti_{0.5}V_{1.9}Cr_{0.6}H_{5.03}$ and $Ti_{0.5}V_{1.9}Cr_{0.6}H_{5.03}$ +Zr₇Ni₁₀. For the interpretation of obtained data the exchange model, taking into account the temperature dependence of mobile hydrogen concentration (Fig. 1), was considered.



Figure 1. The example of temperature dependence of FID amplitude for mobile hydrogen in $TiV_{0.8}Cr_{1.2}H_{5.29}$

The fraction of mobile hydrogen was obtained from FID temperature dependence. Fraction of hydrogen bounded to the lattice was found from the relation $p_m+p_b=1$. Dependencies similar to that shown in Fig. 1 were obtained for all samples.

The results of the approximation temperature dependencies of spin-lattice relaxation rates using the exchange model with the distribution of mobile hydrogen fraction are shown in Fig 2 and Fig. 3.



Figure 2. Temperature dependence of the proton spin-lattice relaxation rate in the TiV_{0.8}Cr_{1.2}H_{5.29} hydride at 20 MHz

For both hydrogen states the approximation parameters were individual: the second moment, the activation energy and the correlation time.



Figure 3. Temperature dependencies of the proton spinlattice relaxation rate in all hydrides at 20 MHz

- [1] Hayashi S, Hayamizu K, Yamamoto O. J. Chem. Phys. 1982; 79:4392e7.
- [2] Ueda T, Hayashi S, Hayamizu K. Phys. Rev. B 1993; 48:5837e43.
- [3] Ueda T, Hayashi S. J All Comp 1995; 231:226e32.
- [4] V.S. Kasperovich, M.G. Shelyapina, B. Khar'kov, I. Rykov. J. of Alloys and Compounds, 509 (2011), 804– 808.



NMRCM Effect of water on molecular mobility in protein and peptone 2013 powders studied by pulsed ¹H NMR

Boris V. Sakharov, Tatiana Kornushina, Sergey N. Viryasov, Mikhail Khramov

State Research Center for Applied Microbiology & Biotechnology, Obolensk, Moscow reg., Russia E-mail: lab71@mail.ru

1. Introduction

Peptones (products of partial hydrolysis of proteins consisting mainly of mixtures of different polypeptides) are one of the main ingredients of nutrient media for the diagnosis of microorganisms and their properties depend on the quality and shelf life of product forms (powders) of these products. Water and temperature are known to be very important factors for physical stability of powders.

The aim of the present work is to investigate the dynamic properties (by ¹H NMR) of powders and compare the effects of water on proton mobility in powders bovine albumin (BSA) and beef peptone.

2. Experimental

All NMR data were obtained on NMR pulse analyzer "Chromatek-Proton-20M" (Russia) operating on line with PC at 20 MHz. The overall dead time of the spectrometer was 12 μ s; 8000 data points with a dwell time of 0.5 μ s were acquired to registration of free induction decay (FID) curves. 100 scans and recycle delay of 2 s were used for each FID measurement. The quantity of powdered samples in the NMR tubes was controlled. The water content values (W_d) are expressed as per cent water on a dry basis.

The complete fitting method (8 parameters) by Gauss/Sine, Gauss functions as models of crystal and amorphous phases of a solid-state component of decay, and Voite function for a liquid (water) component was introduced [1]:



Figure 1. Experimental FID and the best fit curves of peptone powder ($W_d = 6.2\%$)

$$I(t) = A_{S0} \left((1 - f_g) e^{(-t/T_{2Sg})^2} \sin(bt) / (bt) + f_g e^{(-t/T_{2Sg})^2} \right) + A_{I0} (e^{-t/T_{2I}} e^{(-t/T_{2Iv})^2})$$

3. Results and discussion

All the It was found out that FID of completely dried protein and peptone powders are very close in shape and are characterized by the existence of a crystalline phase with the second moment magnitude $M_2 \approx 7 \times 10^9 \text{ s}^{-2} (M_2 = 2/\text{ T}^2_{2\text{ Sa}} + b^2/3)$ and the amorphous phase $T_{2g} \approx 30$ s with a population of $f_g \approx 0,06$. After moistening samples beginning from a 2% hydration level, FID slowly decaying component of both powders was recorded, intensity A_{Wo} and relaxation time T_{2w} of which increased with hydration growth, and A_{Wo} increase strictly corresponded to the increase of water weight (Fig. 2).



Figure 2. The correlation between the population of the slowly component (A_{W0}/A_{S0}) and the water weight content for BSA

Changes in solid-phase decay of protein after moistening were insignificant, but they were authentically shown in gradual decrease of M₂ at a small growth of T_{2g} and constancy of f_g . Peptones showed similar behavior up to the hydration level 7-8%. Exceeding of this level led to a sharp decrease in the crystalline phase fraction, increase in proton population of the amorphous phase and appearance of an exponential component with the mobility rather high for polymers ($T_2 \approx 65 \ \mu s$) (Fig. 3).

References

 Takeshi Yamanobe, Hiroki Uehara, and Masaki Kakiag. Practical NMR Analysis of Morphology and Structure of Polymers // Annual Reports on NMR Spectroscopy. – 2010. - Vol. 70. - P. 203-239.



Figure 3. Comparison of experimental FIDs and their solid components for the powders with W_d =6.2% (a) and W_d =19.8% (b)



NMRCM Magnetic properties of the rare-earth trifluorides $RF_3 = 2013$ (R = Tm, Eu) studied by ¹⁹F NMR

<u>Andrey V. Savinkov</u>, Alexander V. Dooglav, Boris Z. Malkin, Murat S. Tagirov, Dmitry P. Pavlov, Vera V. Klekovkina

Institute of Physics, Kazan Federal University, Kazan, Russia E-mail: Andrey.Savinkov@gmail.com

1. Introduction

The heavy-rare-earth fluorides RF_3 (R = Sm,..., Yb) have the orthorhombic crystal structure Pnma (62) [1] with the C_s point symmetry of the rare-earth ion. These compounds are studied as a model system for testing theories of rare-earth magnetism in insulators. We report on magnetic properties of single crystals and powder samples of thulium and europium fluorides (TmF₃ and EuF₃) studied by ¹⁹F NMR. Spectra of the electronic excitations of Tm³⁺ and Eu³⁺ ions and the transferred hyperfine interaction between the rare-earth and fluorine ions have been on the focus of the study.

2. Magnetic relaxation of ¹⁹F

The energies of electronic excitations corresponding to gaps between the ground state and first excited states of Tm³⁺ and Eu³⁺ ions have been derived from the temperature dependences of the longitudinal relaxation rate T_1^{-1} of ${}^{19}\text{F}$ nuclei. In EuF₃, this rate was measured in the magnetic field 0.5965 T in the wide temperature range. At the temperatures 200 - 300 K, the $T_1^{-1}(T)$ behavior is clearly exponential and can be well described by the function $\sim \exp(-\Delta/T)$ with $\Delta = 670(40)$ K. At 77 – 200 K, the curve $T_1^{-1}(T)$ corresponds to $\Delta \sim 390$ K. These values give energy gaps between the ground state ${}^{7}F_{0}$ and sublevels of the excited ${}^{7}F_{1}$ multiplet of the Eu³⁺ ion. The $T_1^{-1}(T)$ behavior of ¹⁹F nuclei in TmF₃ was determined earlier as exponential with $\Delta = 9.3(4)$ K [2], giving the gap between the ground state and the first excited sublevel of the ³H₆ multiplet for the Tm³⁺ ion. Thus, the ¹⁹F nuclear longitudinal relaxation in EuF_3 (at 77 – 300 K) and TmF₃ (at helium temperatures) is determined by magnetic fields produced by Tm³⁺ and Eu³⁺ magnetic moments at ¹⁹F sites and fluctuating due to Orbach-Aminov processes.

3. The ¹⁹F NMR spectra

Angular dependences of ¹⁹F NMR spectra in the spherical TmF₃ sample were taken at temperatures 1.5 K and 300 K. The angular dependence at T = 1.5 K was obtained from measurements at the fixed frequency of 23.5 MHz in the applied magnetic fields B_0 (from 0 to 1.05 T) rotated in the *ac*-plane of the TmF₃ sample. The angular dependence of the ¹⁹F NMR spectrum at T = 300 K was measured in the static magnetic field $B_0 = 0.6139$ T directed in the *ac* crystallographic plane of the TmF₃ single crystal, but the NMR frequency was scanned in the range 24.0 – 25.0 MHz (Fig. 1).

To describe the results of NMR measurements in TmF₃,

we considered the following effective Hamiltonian of a single Tm^{3+} ion in the *j*-sublattice in the external magnetic field **B**₀:

$$H_j = H_0 + H_{CF,j} - \boldsymbol{\mu} \mathbf{B}_{loc,j}.$$

Here H_0 is the free-ion Hamiltonian, $H_{CF,j}$ is the crystal field Hamiltonian, μ is the magnetic moment of Tm³⁺ ion, $B_{loc,j}$ is the effective local magnetic field at the *j*-position. The NMR frequencies are determined by fields at ¹⁹F nuclei $\mathbf{B}_{loc,F} = \mathbf{B}_0 + \mathbf{B}_d + \mathbf{B}_t$, B_d and B_t are dipole and transferred hyperfine magnetic fields from Tm³⁺ ions. Parameters of the dipole-dipole and the transferred hyperfine interactions between Tm³⁺ and F⁻ ions were extracted from the angular dependences of ¹⁹F NMR spectra measured at 1.5 K and 300 K (the best fit is presented by solid lines in Fig. 1).



Figure 1. Angular dependence of ¹⁹F NMR spectra in TmF₃

The ¹⁹F NMR spectra were measured in EuF₃ powder in the temperature range 1.5 – 300 K, the ¹⁹F NMR line was found very narrow (~10 G at 1.5 K and ~7 G at 300 K). This suggests that the dipole and transferred hyperfine magnetic fields from Eu³⁺ moments are negligible, because the Eu³⁺ ions are mainly in the ground nonmagnetic state ⁷F₀ at low temperatures, and due to very fast fluctuations of Eu³⁺ magnetic moments at T = 300 K.

Acknowledgements

This work was supported by the RFBR grant 12-02-00372-a. VVK acknowledges the support from Ministry of Education and Science of Russian Federation (contract N 14.132.21.1413).

- A. Zalkin and D. H. Templeton. J. Am. Chem. Soc. 75, 2453 (1953).
- [2] A. V. Savinkov et. al. J. Phys.: Conf. Series 324, 012033 (2011).



NMRCM ¹H diffusion in chemically functionalized fullerene doped Nafion 2013 proton electrolyte membranes measured by SFG-NMR

<u>M. Schäfer</u>¹, A. F. Privalov¹, F. Fujara, I. V. Murin¹, V. N. Postnov², D. V. Postnov²

¹Institut für Festkörperphysik, TU Darmstadt, Hochschulstr. 6, 64289 Darmstadt, Germany E-mail: max@element.fkp.physik.tu-darmstadt.de ²Department of Chemistry St. Petersburg State University, Universitetskij pr.26, 198504, St. Petersburg, Russia

1. Introduction

Nafion[®] ionomers are solid polymer electrolytes with a high conductivity for protons when they are hydrated. Therefore they are well suited for the application in fuel cells. Nafion consists of a hydrophobic main chain with hydrophilic side chains having a sulfonic acid group at the ends. Hydration leads to a selforganisation of the hydrophilic and hydrophobic groups building up a nanostructured network of ionic clusters interconnected by channels where water molecules migrate along restricted pathways [1]. The conductivity increases with water content and temperature. A main problem of fuel cells is the temperature limitation of about 80°C due to a rapid loss of water [2].

The objective is the enhancement of the conductivity at low relative humidity as well as the improvement of the water management and hydration stability at high temperatures. This can be achieved by the addition of nanomaterials. Fullerenes are one of the dopants with the advantage of their spherical shape, such that a high density of chemical attachments is possible [3].

During this study we investigated the long range proton transport in dry and wet samples of Nafion doped with two fullerene-based materials $C_{60}(OH)_n$ and $C_{60}(SO_3)_n$ having different additional functional groups up to n=24. Diffusion in pure Nafion is presented for comparison.

2. Experimental

We used NMR diffusometry in an ultrahigh static field gradient (SFG) realized by a special NMR magnet with an anti-Helmholtz arrangement of superconducting field coils. The field B and the gradient g are presented in Fig. 1.



By using a ¹H Larmor frequency of 100 MHz four positions correspond to a magnetic field of 2.35 T. There are two positions z_{HG} where a gradient of 178 T/m is reached and two positions z_{LG} with 50.5 T/m. The diffusion measurement was done by stimulated echos at two different gradients to exclude the influence of T₁- and T₂-relaxation. Several data sets with different constant evolution times τ (t_M varied) and different mixing times t_M (τ varied) are recorded. The sample temperature has been stabilized by a cryostat.

3. Results

For different τ and t_M the results of the diffusion coefficients are consistent with each other. The resulting diffusion coefficients as a function of temperature, shown in Fig. 2, are described by an Arrhenius law. At low temperatures there is a change towards higher activation energy. In contrast to all wet samples where the diffusion is the same at high temperatures the dry samples show the strongest diffusion in the entire temperature range for the $C_{60}(SO_3)_n$ added Nafion. In comparison to pure Nafion the achieved diffusion in this functionalized fullerene doped sample is increased by a factor of 2. Thus the additive $C_{60}(SO_3)_n$ might be promising for practical application of Nafion.



Figure 2. Arrhenius plot of the diffusion coefficients

- [1] K. A. Mauritz, R. B. Moore, Chem. Rev., 104, 4535 (2004).
- [2] A. Wieckowski, J. Nørskov, Fuel Cell Science, Wiley, 388 (2010)
- [3] K. Tasaki, J. Gasa, H. Wang, R. DeSousa, Polymer 48, 4438 (2007)



NMRCM Orientation effects of aromatic compounds in isotropic media as 2013 studied by total-line-shape analysis of ¹H NMR spectra

⁴ <u>Kirill F. Sheberstov^{1,2}</u>, Dmitriy A. Cheshkov^{2,3}, Vyacheslav A. Chertkov²

¹Faculty of Materials Science, Moscow State University, Moscow, Russia ²Department of Chemistry, Moscow State University, Moscow, Russia ³State Scientific Centre of RF "GNIIChTEOS", Moscow Russia E-mail: kirillsheb@gmail.com

1. Introduction

Molecules with anisotropy of magnetic susceptibility exhibit partial orientation in strong magnetic field of the spectrometer. As a result, anisotropic nuclear spin interactions are incompletely averaged and thus residual couplings may show up in high-resolution NMR spectra [1, 2]. Thus, line widths, intensities and positions of peaks can be affected, and even additional line-splittings could be observed. Taking into account these orientation effects allows escape accuracy errors in interpreting spectra and also offers additional information about structure and properties of molecules studied.

2. Creating a computer program for calculating ¹H NMR spectra

For the first time, we designed a computer program for total-line-shape analysis of ¹H NMR spectra including dipoledipole residual constants in calculations. Our algorithm separates contributions of the indirect coupling from the direct dipole-dipole coupling. Dipolar couplings D linearly depend on the squared magnetic induction B_0^2 [2]. Thus, the program performs combine computation of the two spectra obtained in different magnetic fields.

3. Experimental aspects

In our work we studied ¹⁵N enriched *cis*- and *trans*azobenzene, substituted naphthalenes, styrene and tetrahydrofuran in different isotropic solvents. Degassed and sealed-off in vacuum samples were used. Experimental

spectra were pre-processed with reference deconvolution technique for getting narrower lines (Lorenzian-shaped, width at half-maximum ~ 0.1 Hz) [3].

4. Results

A series of high-resolution ¹H NMR spectra recorded at 7.04 T and 14.09 T magnetic fields were analyzed in the framework of a unified approach with highest possible accuracy, see figure 1. The spin-spin coupling constants and the dipole-dipole coupling constants for all pairs of ¹H nuclei of studied molecules were estimated (values of D constants achieve tenths of mHz, while accuracy of analysis is about 0.5 mHz). Taking into account, the orientation effects improves in all cases R-factors of the fit. Character of the slope for the linear dependences on the squared magnetic induction B_0^2 can be used for the determination of absolute signs of the spin-spin coupling constants. Thus we determined signs of a series of small but important for conformational analysis ¹H-¹⁵N constants in ¹⁵N enriched azobenzene.

- E.W. Bastian, C. MacLean, NMR basic Principles and Progress // 1991, v. 25, pp. 1–44.
- [2] A.K. Shestakova, A.V. Makarkina, O.V. Smirnova, M. M. Shtern, V.A. Chertkov, *Russ. Chem. Bull.*, // 2006, v. 55, pp. 1359—1367.
- [3] G.A. Morris, H. Barjat, T.J. Home, *Progress in NMR Spectroscopy* // **1997**, v. 31. pp. 197–257.



Figure 1. 300 MHz (left) and 600 MHz (right) ¹*H NMR experimental (peaks up) and calculated (peaks down) spectra* of trans-1-(phenyl-D₅) -2-phenyldiazido-1-¹⁵N



NMRCM Magnetic resonance study of atomic hydrogen and deuterium in 2013 solid H₂ and D₂ matrixes below 1K

<u>Sergey Sheludiakov</u>¹, Janne Ahokas¹, Sergey A. Vasiliev¹, Jarno Järvinen¹, Vladimir Khmelenko², Shun Mao² and David Lee²

¹Department of Physics and Astronomy, University of Turku, Finland E-mail: servas@utu.fi ²Department of Physics and Astronomy, Texas A&M University, College Station TX77843, USA

1. Introduction

Hydrogen and deuterium solids at low temperatures represent a special class of quantum crystals, where due to the large zero point oscillations and light mass, the effects of quantum tunnelling play important role. Behaviour of atomic impurities in these crystals attracted attention of researches because of the possibility of reaching collective quantum phenomena related with Bose-Einstein Condensation (BEC) or so-called supersolid behaviour. This may happen at high enough densities of atomic hydrogen. In our recent work [1] we succeeded in reaching record high densities of atoms $4 \cdot 10^{19}$ cm⁻³. This has been done by implementing a novel method of in-situ dissociation of H2 or D2 molecules by low temperature (<1 K) RF discharge. H and D are the simplest atomic systems where magnetic resonance methods may be utilized for the characterization of the sample properties. Having a non-zero proton and electron spins it provides a large variety of possibilities for NMR, ESR and double resonance methods. Our experiments are performed in strong magnetic field of 4.6 T, so that electron spins are fully polarized below 1 K. This simplifies the dynamic nuclear polarization (DNP) and offers several ways of measuring relaxation of allowed and forbidden magnetic resonance transitions. In this work we present the first ESR study of H/D-impurities stabilized in solid H₂ and D₂ matrices below 1K. We demonstrate that the chemical reactions of isotopic exchange play important role and help in reaching even higher densities of atomic hydrogen.



Figure 1. ESR spectra of D and H in a steady (blue) and polarized (red) states. 1. H-a-line, 2. D-α-line, 3. D-β-line 4. D-γ-line, 5. H-b-line

2. Experimental setup

Samples of H and/or D in solid H_2/D_2 crystals were created in two stages: 1) we deposited a thin film of solid molecular para-H₂ (ortho-D₂) onto a cold (<1 K) surface of quartz microbalance crystal, which served also as a mirror of 128 GHz Fabry-Perot resonator; 2) we dissociate part of the molecules in the film by running an RF discharge in the miniature helical resonator located nearby.

The ESR study was performed using a cryogenic 128-GHz heterodyne spectrometer [2] which is optimized for reaching highest sensitivity at very low (in the pW range) excitation powers. Helical resonator placed near the sample was used for making ENDOR (f=910MHz) and running RF-discharge in the sample cell.

3. Results

We found that the quantum isotopic exchange reactions D+H₂=H+HD, D+HD=H+D₂ go with sufficiently high rate even at temperatures below 1K, and effectively convert atomic deuterium into hydrogen. It turned out that H densities resulting after such conversion reach record high 8×10^{19} cm⁻³, twice higher than ever before reached in these systems. At such high densities the effects of the dipoledipole interactions between atoms lead to substantial homogeneous broadening of the ESR lines with the line widths exceeding 10 Gauss. High, nearly 100% nuclear polarization of H was created by means of solid- and Overhauser effects within one hour of irradiation by $<1 \mu W$ of mm-wave power. A noticeable decrease of the T₁ of the H nuclear spins in comparison with pure H:H₂ was observed. Pumping the second line of D (center of ESR spectrum) we created simultaneously positive DNP of D and negative DNP of H. We discuss possible explanations of this effect being due to the nuclear polarization transfer between H and D, or strong exchange effects between clusters of H atoms.

- J.Ahokas, O.Vainio, S.Novotny, V.V.Khmelenko, D.M. Lee and S.Vasiliev, Phys. Rev.B, vol. 81, 104516
- [2] S. Vasilyev, J. Järvinen, E. Tjukanoff, A. Kharitonov, and S. Jaakkola, Rev. Sci. Instrum. vol. 75, 94 (2004).


NMRCM A comparison of solid state and solution structure for a complex 2013 between hydrated lanthanum triflate and [221]cryptand

Alla K. Shestakova¹, Vyacheslav A. Chertkov²

¹State Research Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuiastov 38, 111123 Moscow, Russia E-mail: alla@nmrcenter.ru ²Department of Chemistry, Moscow State University, Leninskie Gory 1/3, 119992 Moscow Russia E-mail: chertkov@org.chem.msu.ru

1. Introduction

Stable complexes of azacrownethers and cryptands with metal ions are known more than two decades. Of special interest are the lanthanide derivatives The application of lanthanides in many fields is closely related to their unusually high co-ordination number and large charge density. Many uses require complexation of the lanthanide with suitable organic ligands, which then allow, for example, introduction of other functions into systems like chemical nucleases. There are not many structural investigations with such systems (see e.g. [1, 2]). Presently we report here the results for a complex between hydrated lanthanum triflate and [221]-cryptand obtained with three independent methods: X-ray diffraction, quantum chemistry calculations and NMR measurements of vicinal spin-spin coupling constants.

2. Results and discussion

Complexation leads to dramatic effect on conformation of the ligand. X-Ray diffraction data revealed the structure of innersphere almost C_{2v}–symmetrical complex with [221]cryptand and hydrated lanthanum triflate. We performed a series of ECP quantum chemical calculations (Lanl2dz approach), which support the structure of complexes under study. Experimental vicinal spin-spin coupling constants between protons of neighboring CH2groups for complexes of lanthanum salts with a series of model macrocyclic ligands (1,10-diaza-18-crown-6 [2] and [2,2,2]-cryptand [1]) in solutions (CDCl₃, CD₃OD and CD₃CN) are in good agreement with the *ab'inito* calculated ones (PFT DFT with Ub3lyp and 6G/311(d) basis set). The conformation of the biggest loop of the [221]-cryptand is close to that of 1,10-diaza-18-crown-6 in their lanthanum complexes.

The complex is of particular interest due to a specific coordination sphere with all seven binding sites of the cryptand (all five O and both N-atoms, see fig. 1) and extra three water molecules grouping from the same side of the compound (through the biggest loop of the cryptand). The analysis of the crystal packing revealed, that in crystal molecules are assembled into the two layers by O-H...O bonds (O...O 2.766(6)-2.867(6)Å) formed by the water molecules and CF₃SO₃ anions.



Figure 1. Scheme of the spatial structure for binding of La(3+) with [2,2,1]-cryptand extra three co-ordinated water molecules

ECP quantum chemical calculations (Lanl2dz approach) support the structure. Experimental vicinal spin-spin coupling constants between protons of neighbouring CH_2 -groups in solutions (CD₃OD and CD₃CN) are in good agreement with the *ab'inito* calculated ones (PFT DFT with Ub3lyp and 6G/311(d) basis set, see e.g. [3]). So, the specific conformation of the ligand in solutions of the complex and in the solid state is entirely the same.

- [1] A.K. Shestakova, V.A. Chertkov, H.-J. Schneider, *Tetr. Letters*, **41**, 6753-6756 (2000).
- [2] A.K. Shestakova, V.A. Chertkov, H.-J. Schneider, K.A. Lysenko, Org. Letters, 3, 325-327 (2001).
- [3] W. Deng, J.R. Cheeseman, M.J. Frisch, J. Chem. Theory and Comput., 2 1028-37 (2006).



NMRCM Magnetic Resonance Imaging of Rat Glioma Model enhanced by 2013 using water-soluble Gadolinium Fullerene

<u>M. A. Shevzov</u>¹, B. P. Nikolaev², Ya. Yu. Marchenko², L. Yu. Yakovleva², V. T. Lebedev³

¹Institute of Cytology of RAS, St.Petersburg, Russia ²Reseach Institute of Highly Pure Biopreparation,St.Petersburg, Russia ³Institute of Nuclear Physics, St.Petersburg, Russia *E-mail: nikolaevhpb@gmail.com*

1. Introduction

In preliminary study we have shown that the high proton relaxivity of Gd-containing water soluble fullerene provide the enhancement of contrast of liver image in mouse MR imaging [1]. Antiangiogenesis activity of Gd@Ful is supplementary reason for using this paramagnetic agent for theranostic study of cancer [2,3]. The rat glioma is suitable model for study of Gd@Ful fitness for diagnostic application in brain cancer cases.

2. Materials and methods

Water soluble gadofullerene was synthesized as $Gd@C82(OH)x \ge 20$ as described [4]. Water solutions of Gd@Ful were used for magnetic relaxation measurements in vitro and for MR imaging of rat with implanted glioma. C6 glioma cells were injected into brain. Gd@Ful was delivered to animal intravenously and directly into tumor through intracranical hole after tumor formation at 3d week. Magnetic relaxation times and relaxivity of water protons under action of Gd@Ful were estimated with help CXP-300 spectrometer (Bruker). MR imaging of brain tumor was made by scanning by Avance II NMR spectrometer with microimaging accessory.

3. Results

MR scanning of experimental glioma demonstrated the enhancement of contrast tumor image after intravenous administration of Gd@Ful solution. The T1 weighted images of rat glioma are shown in Figure.1.



Figure 1. T1-weighted transvers images of rat glioma after iv injection Gd@Ful (right). Left image – control

The intravenous injection caused the shortening of T1 time relaxation in the area of blood vessels. The same effect of resonance was achieved after local injection into tumor Figure 2. The paramagnetic Gd inside Fullerene cage strongly affects the spin state of water protons in homogeneous magnetic field. The reduction of tumor angiogenesis doesn't inhibit the contrast action of Gd@Ful as contrast agent.



Figure 2. T1-weighted image of rat glioma after injection Gd@Ful into the tumor body

The scanning in T2-weighted regime represents the decrease of signal intensity of necrotic tissue Figure 3.



Figure 3. T2-weighted image of rat glioma after iv Gd@Ful injection (right). Control-left

The Gd@Ful administration promotes the improvement of lining tumor border due to accumulation of paramagnetic substance in tumor locus. The traffic of Gd@Ful into glioma is ensured by destruction of blood-brain barrier by cancereous cells. The contrast efficiency of Gd@Ful corresponds to the characteristics of negative contrast agent.

4. Conclusion

The Gd@Ful preparation is shown to be effective contrast enhancer for theranostic study of brain tumors.

Acknowledgements

This work was supported by the FMBA RF (grant 40.002.12.0). Authors thank A.Dobrodumov for MRI scanning.

- [1] Ya.Yu. Marchenko, B.P. Nikolaev et al. Magnetic Relaxation Study of Water–soluble Gadofullerene as potential contrast agent for theranostics. NMRCM 2012, St.Petersburg, Book of abstracts, p.102.
- [2] H. Meng et al. Potent Angiogenesis Inhibition by the Particulate Form of Fullerene Derivatives. // ACNano, 4(2010), № 5, p. 2773–2783.
- [3] Zhiyun Chen et al Applications of Functionalized Fullerenes in Tumor Theranostics.// Theranostics 2 (2012), №3, P.238-250.
- [4] Patent RF № 2396207.

NMRCM NMR study of hydrogen dynamics in mixed-metal borohydride 2013 LiZn₂(BH₄)₅

Saint Petersburg, Russia

<u>A. V. Soloninin¹</u>, A. V. Skripov¹, D. B. Ravnsbæk², T. R. Jensen², Y. Filinchuk³

¹Institute of Metal Physics, Ural Division of the Russian Academy of Scieinces, S. Kovalevskoi 18, Ekaterinburg 620990, Russia

E-mail: alex.soloninin@imp.uran.ru

²Center for Materials Crystallography, Interdisciplinary Nanoscience Center and Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark ³Institute of Condensed Matter and Nanosciences, Université Catolique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium

1. Introduction

Recently prepared mixed-metal borohydride $\text{LiZn}_2(\text{BH}_4)_5$ is considered as one of the most promising materials for hydrogen storage. The compound $\text{LiZn}_2(\text{BH}_4)_5$ has high hydrogen content of 9.5wt% and its decomposition temperature T_d is 400 K. This borohydride exhibits novel structure motifs built of doubly interpenetrated 3D frameworks consisting of dinuclear complex anions $[\text{Zn}_2(\text{BH}_4)_5]^-$ and Li^+ , which implies that there are no covalent bonds between them. The aim of the present work is to investigate the H jump motion in $\text{LiZn}_2(\text{BH}_4)_5$ using ¹H and ¹¹B NMR measurements of the spectra and spin-lattice relaxation rates over the temperature range of 18 - 300 K.

2. Results and discussion

The temperature dependences of the proton spin-lattice relaxation rates R_1 measured at three resonance frequencies for LiZn₂(BH₄)₅ are shown in Fig. 1. For the relaxation mechanism due to nuclear dipole-dipole interaction modulated by atomic motion, $R_1(T)$ typically exhibits a frequency-dependent maximum. This maximum is expected to occur at the temperature at which the atomic jump rate τ^{-1} becomes nearly equal to the resonance frequency ω . For parametrization of the proton spin-lattice relaxation data for LiZn₂(BH₄)₅ we have used the "three-peak" model with a Gaussian distribution of activation energies. We assume that, for each type of the motion, the temperature dependence of τ_i is governed by the Arrhenius law and the resulting R_1 is the sum of R_{1i} (i = 1, 2, 3) The parameters of model are the average activation energies (E_{ai}) , the activation energy dispersions (ΔE_{ai}) and the pre-exponential factors (τ_{0i}). The results of the simultaneous fit of this model to the data for $LiZn_2(BH_4)_5$ are shown by the solid curves in Fig. 1; the corresponding fit parameters are $\tau_{01} = (1.1 \pm 0.1) \times 10^{-14}$ s, $E_{a1} =$ 173±6 meV, $\Delta E_{a1} = 52\pm4$ meV; $\tau_{02} = (4.1\pm0.5)\times10^{-14}$ s, $E_{a2} =$ 207±12 meV; and $\tau_{03} = (1.5\pm0.1) \times 10^{-14}$ s, $E_{a3} = 302\pm5$ meV. A similar behaviour of $R_1(T)$ has been observed for α -Mg(BH₄)₂ [1].

Recent studies of the crystal structure of $LiZn_2(BH_4)_5$ [2] have shown that all BH₄ groups are coordinated by two metal atoms, and these groups occupy four inequivalent sites. A coexistence of strongly differing activation energies can be related to the nearly linear coordination of BH₄ groups by two

Zn atoms or one Li and one Zn atom. As in the case of α -Mg(BH₄)₂ [1], the lowest activation energy E_{a1} should correspond to the BH₄ rotation around the 'easy' 2-fold axis along the Zn – B – Zn(Li) line. For different BH₄ groups, the Zn – B – Zn(Li) angle shows a distribution from 165° to 176.5° [2]. In the temperature dependence of R_1 , this faster motion contributes to the low-*T* 'tail' described by E_{a1} and the distribution width ΔE_{a1} . The relaxation rate maximum near room temperature is due to the slowest jump process described by E_{a3} . This type of motion should correspond to the BH₄ rotation around the 2-fold axis perpendicular to the Zn – B – Zn(Li) line.



Figure 1. Proton spin-lattice relaxation rates measured at 14, 28, and 90 MHz for LiZn₂(BH₄)₅ as functions of the inverse temperature. The solid lines show the simultaneous fits of the "three-peak" model to the data

Acknowledgements

This work is supported by the Russian Foundation for Basic Research (grant 12-03-00078).

- A.V. Skripov, A.V. Soloninin, O.A. Babanova, H. Hagemann, Y. Filinchuk. *J. Phys. Chem. C*, **114**, 12370-12374 (2010).
- [2] D.B. Ravnsbæk, C. Frommen, D. Reed, Y. Filinchuk, M. Sørby, B.C. Hauback, H.J. Jakobsen, D. Book, F. Besenbacher, J. Skibsted, T.R. Jensen. – J. Alloys Compd. C, 509S, S698-S704 (2011).

NMRCM A weak hydrogen bond donors: geometry and NMR properties of 2013 complexes of 1,1-dinitroethane

Elena Tupikina¹, Sergev Smirnov², Peter Tolstoy^{1,2}

¹*Faculty of Physics, Saint-Petersburg State University, Ulyanovskaya str. 3, Saint-Petersburg E-mail: elenatupikina@gmail.com* ²*Center for magnetic resonance, Saint-Petersburg State University, Universitetskiy pr. 26, Saint-Petersburg Petersburg*

H-bonds are known to encompass a wide and continuous scale of bonding energies going from, say, 0.2 to 45 kcal mol⁻¹, the weakest bonds being barely distinguishable from van der Waals interactions and the strongest ones very similar to covalent bonds. Terms such as "weak" and "strong" contain an inevitable element of arbitrariness without establishing a precise energy borderline between them.

The importance of the hydrogen bond to the structure and function of biological molecules can hardly be overstated. Whereas the function of standard H-bonds such as NH…O and OH...O is now appreciated, the contributions of weaker interactions remain an active area of inquiry. For example, the approach of a OH-bearing group as a proton donor toward the electron cloud that hovers above an aromatic ring, in a so called OH π H-bond, is becoming more widely recognized. A particularly interesting unconventional H-bond makes use of a CH group as a proton donor. Early skepticism about this primarily phenomenon was based on the low electronegativity of carbon, which reduces the partial positive charge that is believed to be necessary to reside on the H if it is to act as a bridging atom. On the other hand, there are a number of features which can promote the acidity of a CH group.

In this work we focus on C—H···B (B – is proton acceptor group) bonds, formed by 1,1-dinitroethane (DNE) (Fig. 1) with various proton acceptors (such as aliphatic amines, pyridine derivatives etc.). Proton donating ability of DNE ($pK_a = 5.2[1]$) is sufficiently high to form complexes of various structures, including those with proton transfer, i.e. ion pairs of the C····HB⁺ type [2].



Figure 1. Structure of 1,1-dinitroethane and its anion (calculated by B3LYP/6-31++G(d,p) method)

Purpose of this work is the complex investigation of the geometry and properties of C—H···B complexes by NMR, X-ray and *ab initio* methods. During the work we obtained ¹H, ¹³C and ¹⁴N NMR spectra of complexes of DNE with proton acceptors at various temperature (180 – 330 K). Different correlations between NMR parameters with interatomic distances have been successfully used to define the geometry of the hydrogen bonds. To date there are very few experimental data about correlations between ¹*J*_{CH} coupling in the proton donor group and interatomic distance C···H. The stronger is the proton donating ability of the solvent B, the longer is the C···H distance in its C-H...B complex with DNE. We monitor the changes in the C···H distance by measuring ¹*J*_{CH} coupling constant.

Using DFT methods (GAUSSIAN09) were calculated geometry and NMR properties of this complex, shown the comparison with the experiment data. Also discussed X-Ray structures of complexes of DNE with diethylmine (Fig. 2) and dibuthylamine as proton acceptor group.



Figure 2. X-ray structure of complex DNE with diethylamine

Acknowledgements

This work is supported by RFBR grants (11-03-00237-a, 11-03-00346-a, 12-03-00215-a).

NMR data were obtained in Magetic Resonance Center of SPbSU, http://cmr.spbu.ru/.

X-ray data were obtained in X-Ray Diffraction Center of SPbSU, http://xrd.spbu.ru/.

- [1] George W. Gokel, Handbook of organic chemistry, McGraw-Hill, 2004.
- [2] P. M. Borodin, N. S. Golubev, G. S. Denisov, Yu. A. Ignatiev, Org. Magnetic Resonance, 7, 185-186, 1975.



NMRCM Site-site potential in coarse-grain model of the benzene

Alina A. Uskova, Andrei V. Komolkin

Physical Faculty, Saint-Petersburg State University, Russia E-mail: linka_ss@mail.ru

1. Introduction

In computer simulations of molecular dynamics of benzene molecules, a popular and effective representation of the short-range attractive and repulsive interactions is atomatom Lennard-Jones 6-12 potential functions. In such models, 12 atoms of one molecule interact with 12 atoms of another molecule. In this work we present new single-site potential functions for the benzene molecule.

2. Coarse-grained benzene molecule

There are a number of techniques to perform long simulations of large systems. One of the most common approaches is to reduce the number of interaction sites in molecules, resulting in fewer calculations at each molecular dynamics step.

In coarse-grain potential the groups of atoms close to each other (e.g., atoms belonging to benzene rings or to several methyl groups in the chain) are replaced by a single particle.

The Gay-Berne potential [1] is the most grained model, where the whole molecule is represented by one prolonged body that is treated as a single interaction center.

In our model the coarse-grained benzene ring consists of one site. A modified Lennard-Jones 6-12 potential is used for calculation of the Van-der-Waals interactions to imitate the interactions of benzene ring with other atoms [2]:

$$E_{ij} = 4\epsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij} - \Delta_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij} - \Delta_{ij}} \right)^{6} \right), (1)$$

where Δ_{ij} is shifting of the Lennard-Jones sphere, r_{ij} is the distance between centers of the rings. For benzene the parameters ϵ_{ij} , σ_{ij} and Δ_{ij} are functions of mutual orientation of two rings:

$$\epsilon = \epsilon(\theta, \varphi), \sigma = \sigma(\theta, \varphi), \Delta = \Delta(\theta, \varphi)$$
 (2)

due to molecular symmetry (see Figure).

To estimate parameters of (2) we calculate energy of two molecules using full-atomic model with parameters from optimized potentials for liquid simulation (OPLS-AA). Energy profiles were approximated with (1) by non-linear fitting. Final form of parameters in (2) is represented as

$$\epsilon = \sum_{k=0}^{6} \sum_{l=0}^{6} c_{kl} \sin k\varphi \sin l\theta$$



The modified single-site potential was developed to study properties of molecule of benzene with Monte-Carlo method.

In the report, method of the parameter optimization and the results of comparative simulation of full-atomic system and single-site system are discussed.

- J. G. Gay and B. J. Berne J. Chem. Phys. 74, 3316 (1981)
- [2] V. S. Neverov, A. V. Komolkin J. Chem. Phys. 136, 094102 (2012)



NMRCM Emission of methane from fossil coal in the condition of enhanced 2013 moisture contents

<u>Tatyana A. Vasilenko</u>, Andrey K. Kirillov, Alexander N. Molchanov, Grigoriy A. Troitsky, Andrey V. Vyshnyakov, Igor G. Kostenko, Tatyana V. Pichka

Institute for Physics of Mining Processes of the NAS of Ukraine R. Luxemburg str. 72, Donetsk 83114, Ukraine E-mail: tvasilenko@mail.ru

1. Introduction

Water moistening of a coal seam in the course of mining is a necessary requirement providing decrease in the content of methane in a stoping face. The last fact guarantees safer conditions of coal mining. Besides, estimation of the influence of natural humidity on gas capacity of coal is an actual practical and theoretical problem [1, 2]. Such physical parameter as binding energy of methane with the surface of porous coal structure will determine substantially the emission rate at sudden outbursts during mining and coal storage for a long time.

Therefore the aim of the present research is evaluation of parameters of methane transfer in previously moistened coal samples.

2. Experimental technique

The technique of experiments included saturation of the coal fraction of 2-2.5 mm in size by water vapor at the temperature of 30-35 °C with the subsequent saturation by methane in the high pressure chamber at P = 8-10 MPs for 1 - 3 months. Methane emission was measured by the method of proton magnetic resonance by means of continuous and spin-echo spectrometers and by the thermo-gravimetric method in a wide temperature range (from -155 to 80 °C). Component separation of fluids (methane and water) was carried out on the base of relaxation time T_2 for the spin-echo signal and the width of resonant lines of ¹H absorption ΔH (Fig.1). The effective diffusion coefficient D_{eff} for CH₄ was estimated by the inclination of kinetic curves of amplitude attenuation of NMR signal and mass loss of the samples in several hours similarly to [3].

3. Results

Experimental results indicate decrease in activation energy of adsorbed methane for moistened samples in comparison with the data for dry samples. So, the energy of activation $E_a = 6$ kJ/mol for watered coal of the early stage of coalification unlike 18 kJ/mol for dry coal is received.

Under long saturation of the samples with methane, D_{eff} is comparable with the diffusion coefficient of methane in

water. Thus, in the temperature range from-10 to + 80 °C, the Arrhenius temperature dependence of D_{eff} is weakly expressed. Water vapors present in the volume of coal pores substantially affect evaluation of self-diffusion coefficient of methane in the course of spin-echo measurements.



Figure 1. Temperature dependence of the time of spin-spin relaxation $T_2 \sim 1/\Delta H$ in Arrhenius for long-flame-coal. The autodyne spectrometry data for three components of coalwater-methane system are presented

4. Conclusions

On the basis of our research, it is possible to state that at large depths (800 - 1500 m) with high pressure and temperatures of the moistened coal seams, certain conditions are created for increased gas emission at the expense of redistribution of adsorbed fluids on pore walls. Among other parameters, the reduction of binding energy of CH₄ results in increase in the effective diffusion coefficient that characterizes the rate of gas emission.

- [1] E. Battistutta, et al. Energy & Fuels, 26, 746–752 (2012).
- [2] S. Day, R. Sakurovs, S. Weir. Intern. J. Coal Geolog, 74, 203–214 (2008).
- [3] A.D. Alexeev, T.A. Vasilenko, A.K. Kirillov, et al., High Pressure Physics and Technics, 20, № 3, 143 (2010) (in Russian).



Moscow State University for Equipment Engineering & Informatics, Moscow 107996, Russia E-mail: volkovobolensk@mail.ru

1. Introduction

Correction for inhomogeneity of the static magnetic field based on approximation a Gaussian function or using a FID of uniform liquid depends on the shape and size-sample, as well as its location in a magnetic field. Well known spin echo method to eliminate the influence of field inhomogeneity on FID is free from this disadvantage. In this report, the modified CPMG pulse sequence with the increasing time intervals between 180°-pulses was used to record the true shape of the total transverse magnetization decay.

2. Experiment

NMR relaxometer "Hromatek-Proton-20M" with resonance frequency 20 MHz, duration 180° -pulse 4,4 μ s, and "dead time" 10 μ s, was used for measurements. Pulse sequence:

 $90^{\circ} - \tau_{0} - (-\tau_{1} - 180^{\circ} - \tau_{1} -)_{N1}(-\tau_{2} - 180^{\circ} - \tau_{2})_{N2} \dots (-\tau_{j} - 180^{\circ} - \tau_{j} -)_{Nj} (1)$

as constructed by using special device "designer of pulses", which is part of relaxometer [www.chromatec.ru].



Figure 1. FID and echoes of almond protons at various intervals between 180 ° pulses in the neighboring cycles (eq.1): $\tau_0 = 0$, 1ms; $\tau_1 = 1$ ms (N₁=7); $\tau_2 = 2$ ms (N₂=10); $\tau_3 = 4$ ms (N₃=18)

For example, fig. 1 shows a typical result of the application this pulse sequence for measurement of proton transverse magnetization decay. Solid-phase part of FID was observed in the time up to 100 μ s, when the inhomogeneity of the magnetic field as yet has no effect on the free induction decay (fig.2). Switch-on delay of the first 180° pulse ($\tau_0+\tau_1$) provides to measure this part of FID without interference.

The effect of field inhomogeneity on the next part of the FID can correct by application closely spaced 180° pulses. Since the sum of the 180° -pulse duration and the "dead time" is 14.4 µs, the measurement of the FID amplitude can be made every 15 µs. This provides a good definition of intermediate relaxation times about 100 µs, which cannot be accurately measured without taking into account the inhomogeneity of the field.

When measuring the slow part of the transverse magnetization decay 180°-pulse repetition frequency is

reduced. This avoids the heating of the sensor coil and samples itself. In general, this technique allows you to record the total transverse magnetization decay (FID + echo amplitudes) in the form of a single curve (fig. 3).



Figure 2. The initial part of the FID in a non-uniform static magnetic field (solid line) and the restored FID (dashed line)



Figure 3. Common decays of the proton transverse magnetization: $\tau_0 = 80 \ \mu s$; $\tau_1 = 20 \ \mu s$ $(N_1 = 20)$; $\tau_2 = 200 \ \mu s$ $(N_2 = 20)$; $\tau_3 = 1 \ m s$ $(N_3 = 20)$; $\tau_4 = 4 \ m s$ $(N_4 = 120)$

3. Conclusion

Method for measuring amplitudes of the true FID and the echo signals using one multi-pulse sequence like CPMG but at increasing intervals between 180°-pulses was proposed. This method reduces the total number of 180° pulses and avoids the "heating" of the sample and the "saturation" of the spin system by lowering the RF power absorbed by the sample during the experiment. The method improves the accuracy of determining the relative amplitudes of the relaxation components as the effects of the instability the resonance conditions, the gain of the receiver and the baseline drift lower than if the separate measurement and processing of the FID and echo signals were used.

This technique is not sensitive to the form of magnetic field inhomogeneity and it is suitable for use in most bench top NMR relaxometer.



NMRCM Investigation of dependence the Curie constant in colloidal 2013 solution from induction of magnetic field of superparamagnetic nanoparticles

A. I. Zhernovoy, S. V. Dyachenko, M. A. Vaseshenkova

Saint-Petersburg State Technological Institute (TU), Russia E-mail: azhspb@rambler.ru

1.Introduction

In previously published experimental works [1-2] static magnetic susceptibilities of suspensions superparamagnetic nanoparticles was found by electromagnetic method. Thus it was received that experimental dependences of static magnetic susceptibility from thermodynamic temperature T obey the Curie-Weiss law in the initial sections of magnetization curves. In the work [3] is shown that if magnetization of the suspension J is found by formula: J = (B/μ_0) - H, where B and H - induction and intensity of magnetic field in suspension accordingly, then the magnetic susceptibility $\chi = J\mu_0/B$ at initial part of the magnetization curve (for small B) obeys the Curie law $\chi = C/T$. It provides the way measuring χ at unknown thermodynamic temperature T to determine this temperature by the formula $T = C/\chi$ tentatively identified C by the formula = $T_t \chi_t$ where T_t and χ_t , - corresponding values of the triple point of water.

Theoretically the Curie law follows from the Langevin formula $J = J_s La(\xi)$, where La - Langevin function, J_s – saturation of magnetization, $\xi = pB/kT$ - Langevin parameter, p - magnetic moment of nanoparticle.

From here:

$$C = J\mu_0 T/B = C_0 3La(\xi)/\xi,$$
 (1)

$$C_0 = J_s p \ \mu_0 / 3k \tag{2}$$

is the value of C at $\xi \ll 1$. Theoretical dependence C/C₀ from ξ constructed from the formula (1), shown in the curve 1 on Fig. 1. It should be compared with the experimental dependence C from induction B.

2. Experiment

The installation described in work [4] has been applied to carrying out of experimental researches of dependence the Curie constant from magnetic induction. Investigated suspension was colloidal solution of magnetite nanoparticles in water with mass concentration of solids of 14%. Frequencies f_1 and f_2 was measured with help of radiofrequency coils located in specific points of the sample. The signal of NMR was located in constant external MF at these frequencies. On these frequencies find $H = f_1/\gamma_{\text{H}}$ and $B = f_2/\gamma_{\text{B}}$, where $\gamma_{\text{H}} = 53.4$ - gyromagnetic ratio in units of Hz·m/A and $\gamma_{\text{B}} = 4,25 \cdot 10^7$ - gyromagnetic ratio in units of Hz/T. And the Curie constant is $C = (1 - f_1/f_2) \cdot T$.

3. Acknowledgements

Values of Curie constant C was experimentally received at several inductions of magnetic field B defined on frequencies f_2 . The value C=C₀ was found by averaging of 7 values of C received at B<1 mT. It is necessary to connect values of inductions B with values of Langeven parameter ξ for comparison of experimental results with a theoretical curve 1 in picture 1. And it is necessary to know value of a magnetic moment of nanoparticles p for this purpose. The magnetic

moment p can be found from the formula (2) having substituted in it experimental value of $C_0=171,6$ K and magnetization of saturation $J_{\mu}=8100$ A/m, received in work [4]. As a result p turns out 7 $\cdot 10^{-19}$ J/T. At such value of magnetic moment for each experimental point we find Langeven parameter ξ . With use of these parameters and values of C we receive the experimental points noted in the form of squares on fig. 1. It is possible to make sure, that experimental points do not satisfy the theoretical curve 1. The reason of this can be in distribution of nanoparticles on sizes leading to distinction of their magnetic moment. Expression for C in view of polydispersiveness of nanoparticles looks like:

$$C = (6C_0 / {\xi_M}^2) \ln(sh({\xi_M}) / {\xi_M},$$

where ξ_{M} – value of ξ for average size of nanoparticles.

The theoretical dependence constructed on this expression is presented on fig. 1 by curve 2, it satisfies to experimentally received datas. From that it is possible to make the conclusion, that speed of reduction of Curie constant with growth of B depends on polydispersiveness of nanoparticles. It can be used for assessment of polydispersiveness superparamagnetic nanoparticles.



Figure 1. Theoretical and experimental dependence the Curie constant suspension from magnetic induction of.superparamagnetic nanoparticles 1 - theoretical dependence of ξ without polydispersity of nanoparticles, 2 - theoretical dependence of C at medium values of ξ_{med} with polydispersity of nanoparticles. Experimental dependence is presented by experimental points

- [1] Y.I. Dikansky//Magnetohydrodynamics.1982.№3. P. 33-36
- [2] E.Y. Bloom, M.M. Mayorov, A.B. Cerberus Magnetic liquid. Riga. Zinatne, 1989. P. 386.
- [3] A.I. Zhernovoy, Y.R. Rudakov, S.V. Dyachenko // Scientific Instrumentation. 2012. V. 22, № 1. P. 52-54.
- [4] A.I. Zhernovoy, V.N. Naumov, Y.R. Rudakov // Scientific Instrumentation. 2009. V. 19, № 3. P. 57-61.

Author Index

Abakarov, Gasan M., 71 Ahokas, Janne, 27, 112 Alakshin, E. M., 61 Alexandriysky, Victor V., 79 Alexanyan, Anait, 83 Alper, Gennady A., 42, 87 Amirov, Rustem R., 73 Ananikov, Valentine P., 39 Anisimov, Andrey P., 76 Anisimov, Nikolay V., 34, 62 Anisimova, Vera A., 72 Antipin, Mikhail Yu., 71 Antipov, Artem I., 45 Arseniev, Alexander S., 67, 68 Asatryan, Hike, 63 Averina, Mariia I., 64, 75 Baibekov, Eduard, 65 Baran, E., 80, 81 Baryshev, Alexei, 83 Batista de Carvalho, Luís A. E., 42 Batova, Svetlana S., 34, 62 Bazir, A. G., 66 Bocharov, Eduard V., 67, 68 Bocharova, Olga V., 67, 68 Bogachev, Yury V., 69, 70 Bogaychuk, A. V., 106 Borodkin, Gennadii S., 71, 72 Borodkina, Inna G., 71, 72 Bubnov, Philip S., 104 Burilova, Eugenia A., 73 Burlov, Anatolii S., 71 Burmistrov, Vladimir A., 79 Bystrova, O. A., 53 Chaplygin, Ilia S., 68 Charnaya, E. V., 13 Chepurnoy, Pavel B., 71, 72 Chernenco, Julia S., 69, 70 Chernyshev, Y. S., 82 Chertkov, Vyacheslav A., 35, 111, 113 Cheshkov, Dmitriy A., 35, 111 Chizhik, Vladimir I., 47, 89, 107 Colet, J. M., 49 Darinskii, Anatolii A., 96 Davidov, V. V., 85 Delsinne, V., 49 Dmitruk, Anna S., 74 Dobrodumov, A. V., 53 Dolomansky, Y., 93 Donets, Alexey V., 36, 50, 91 Dooglav, Alexander V., 78, 109 Drapkin, V., 70 Dudkin, V. I., 85 Dvinskikh, Sergey V., 19, 79 Dyachenko, S. V., 120 Dzhambulatov, Rinat G., 36 Efimov, Sergey V., 42 Egorov, Andrei V., 64, 75 Eichhoff, Uwe, 15 Falkovich, Stanislav G., 96

Fedyukina, Galina N., 76 Filinchuk, Y., 115 Florek-Wojciechowska, M., 80, 81 Fraissard, Jacques, 16 Frolov, Vyatcheslav, 105 Fruchart, Daniel, 44, 57 Fuentes, Sergio, 17 Fujara, F., 110 Fujii, Yutaka, 27 Furman, Dmitry, 77 Gabriel, Jan, 37 Gainov, Ramil R., 78 Ganina, Tatiana A., 35 Gareev, Kamil G., 69 Garnovskii, Dmitryi A., 71 Gazizulin, R. R., 61 Gerts, Egor, 79 Glebova, N. V., 51 Golovanevskiy, Vladimir A., 78 Golovina, Elena, 94 Goncharuk, Sergey A., 67 Grebenkov, Denis, 14 Grolet, G., 49 Grunin, L., 70 Guzhova, I. V., 53 Gwak, Minchan, 27 Haase, Jürgen, 13, 97 Harańczyk, H., 80, 81 Hayden, M. E., 46 Ievlev, Alexander V., 82, 83 Ievleva, Svetlana, 101 Ievleva, Valeria, 83 Ilina, Oksana, 38 Ingman, Petri, 47 Isaeva, Olga V., 62 Ischenko, A. M., 53 Ivanov, Sergey A., 76 Järvinen, Jarno, 27, 112 Jensen, T. R., 115 Kachala, Vadim V., 39 Kämpf, Kerstin, 40 Karseev, A. U., 85 Khabibulin, Dzhalil, 20 Kharkov, Boris B., 19, 41, 86 Khmelenko, Vladimir, 112 Khodov, Ilya A., 42, 87 Khokhlova, Elena A., 39 Khramov, Mikhail, 108 Khrapichev, Alexandr A., 43 Kirillov, Andrey K., 118 Kiselev, I. A., 51 Kiselev, Valerij, 18 Klekhta, Nikolay S., 48, 88 Klekovkina, Vera V., 78, 109 Klochkov, A. V., 61 Klochkov, Vladimer V., 42 Klyukin, K., 44 Knutelski, S., 80 Knyazev, M., 70

Komolkin, Andrei V., 79, 117 Kono, K., 61 Kononova, Irina E., 69 Kopilov, Pavel Ch., 76 Korableva, S. L., 61 Kornushina, Tatiana, 108 Kostenko, Igor G., 118 Kramushchenko, Darya, 63 Kremmling, Beke, 40 Kultaeva, Anastasia Y., 45 Kumzerov, Y. A., 13 Kupriyanov, Pavel A., 89 Kupriyanova, Galina S., 90, 98 Kurenkova, Elena, 83 Kurnikov, Sergey E., 91 Kuzmichev, Pavel K., 67 Kuzmin, Vyacheslav V., 46, 61, 92 Lähderanta, Erkki, 47 Lapina, Olga, 20 Lavrov, Sergey, 83 Lebedev, V. T., 114 Lee, David, 112 Lee, M. K., 13 Lee, SangGap, 27 Lesovoy, Dmitry M., 67 Loskutov, V., 93 Lyssenko, Konstantin A., 71 Makarova, Katerina, 94 Mal'tsev, Yuriy F., 71, 72 Malkin, Boris Z., 109 Malkova, A. V., 51 Mamardashvili, Nugzar Zh., 87 Mao, Shun, 112 Marchenko, Ya. Yu., 53, 66, 70, 99, 114 Margulis, B. A., 53 Markelov, Denis A., 47, 95, 96 Martynova, M. G., 53 Matveev, Vladimir V., 47, 51, 96 Matyushkin, Lev B., 69 Meier, Thomas, 97 Mershiev, Ivan G., 90, 98 Michel, Dieter, 13, 21 Mikhailova, Mariya E., 96 Mikhrina, A. L., 53 Mineev, Konstantin S., 67 Minkin, Vladimir I., 71, 72 Mitsudo, Seitaro, 27 Mizusaki, Takao, 27 Molchanov, Alexander N., 118 Molchanov, V. V., 90 Moshnikov, Vyacheslav A., 69 Murin, I. V., 110 Muzafarov, Aziz M., 56 Nacher, P.-J., 46, 92 Nadezhdin, Kirill D., 68 Naumova, A., 70 Nechausov, Sergey S., 35 Nechitailov, A. A., 51 Neelov, Igor M., 96 Nefedov, D., 13 Nikiforov, Mikhail Yu., 42, 87 Nikolaev, B. P., 53, 66, 99, 114 Nizioł, J., 80

Novikov, Dmitry, 22 Nowak, P., 80, 81 Nunes, Rita G., 23 Okuda, T., 80 Olech, M. A., 81 Onokhin, K. V., 53 Papulovsky, Eugine, 20 Paradowska, K., 100 Parshina, Victoria, 101 Pavlov, Dmitry P., 109 Pen'kov, Ivan N., 78 Pichka, Tatyana V., 118 Pleshakov, Ivan V., 48, 51, 88 Podrecca, M., 49 Popova, Maria V., 95, 104 Postnov, D. V., 110 Postnov, V. N., 110 Privalov, Alexey F., 24, 57, 110 Pyatyshev, E. N., 51 Rabdano, Sevastyan O., 50 Ravnsbæk, D. B., 115 Riabchun, Filipp, 105 Rokhina, Ekaterina V., 94 Rolich, V. I., 66 Ruzheva, S. A., 106 Rykov, Ivan A., 107 Ryzhov, V. A., 51 Sabitova, A. M., 61 Safin, T. R., 61 Safiullin, K. R., 61, 92 Sakharov, Boris V., 76, 108 Samoson, Ago, 52 Samoylenko, Andrey A., 34 Savinkov, Andrey V., 109 Schäfer, M., 110 Severin, E. A., 90 Shalamova, Ekaterina I., 34 Sheberstov, Kirill F., 35, 111 Sheludiakov, Sergey, 27, 112 Shelyapina, Marina G., 44, 57, 83, 107 Shestakova, Alla K., 35, 113 Shevtsov, M. A., 53, 114 Shubin, Alexandre, 20 Sibgatullin, Timur A., 54 Skripov, A. V., 25, 115 Skrynnikov, Nikolai, 55 Smirnov, Sergev, 116 Soloninin, A. V., 115 Stefaniak, O., 100 Strzałka, K., 80 Sukharzhevskii, Stanislav M., 45 Tagirov, Murat S., 26, 61, 109 Tarasiuk, J., 80 Tastevin, G., 46 Tatarinova, Elena A., 56, 74 Tien, C., 13 Tolpygin, Ivan E., 72 Tolstoy, Peter, 116 Troitsky, Grigoriy A., 118 Tupikina, Elena, 116 Uraev, Ali I., 71 Urban, Anatatoly S., 68 Uskova, Alina A., 117

Uspenskaya, Yulia, 63 Vagizov, Farit G., 78 Vainio, Otto, 27 Van As, Henk, 54, 94 Vaseshenkova, M. A., 120 Vasil'ev, Sergey G., 56, 74 Vasilchenko, Igor S., 71, 72 Vasilenko, Tatyana A., 118 Vasiliev, Sergey A., 27, 112 Vergeldt, Frank J., 54 Vezo, O. S., 66 Viryasov, Sergey N., 108 Vogel, Michael, 37, 40 Vojtylov, V. V., 66 Volkov, Vitaly I., 28, 56 Volkov, Vladimir Y., 119 Volynski, Pavel E., 67, 68 Vorontsova, Anna A., 104 Vyshnyakov, Andrey V., 118 Vyvodtceva, Anna V., 57 Wawer, I., 100 Weigel, Matthias, 29 Yakovleva, L. Yu., 53, 66, 99, 114 Zhakov, S., 93 Zhernovoy, A. I., 120 Ziyatdinova, Anna B., 73 Zvezdov, Denis, 27

List of Participants

Aktas Bekir

Gebze Institute of Technology Gebze Turkey *aktas@gyte.edu.tr*

Aleksashina Nadejda Alekseevna

Institute Metal Physics Ekaterinburg Russia nadejda.aleksashina@gmail.com

Alexandriysky Viktor, V.

Research Institute of Macroheterocyclic Compounds, Ivanovo State University of Chemistry and Technology Ivanovo Russian Federation nmr@isuct.ru

Aminova Roza

Kazan Federal University Kazan Russia raminova@rambler.ru

Amirov Rustem

Kazan Federal University Kazan Russia ramirov@ksu.ru

Andrey Gurinov

Saint Petersburg State University Saint Petersburg Russia andrey.gurinov@spbu.ru

Anisimov Nikolay

Lomonosov Moscow State University Moscow Russia anisimovnv@mail.ru

Asatryan Hike

A.F. Ioffe physical-technical institute St. Petersburg Russia hike.asatryan@mail.ioffe.ru

Averina Mariia

Saint Petersburg State University Saint Petersburg Russia maria080389@mail.ru

Babailov Sergey

A.V.Nikolaev's Institute of Inorganic Chemistry Novosibirsk Russian Federation *babajlov@niic.nsc.ru*

Baibekov Eduard Il'darovich

Kazan Federal University Kazan Russia edbaibek@gmail.com

Baran Ewelina

Institute of Physics, Jagiellonian University Kraków Poland ewela0203@wp.pl

Barzilovich Petr Yurievich

Institute of Problems of Chemical Physics Chernogolovka Russia pjetro@yandex.ru

Bazir Anna Russian Federation *anya.bazir@gmail.com*

Benkevich Vladimir

Russia hem0@yandex.ru

Bocharov Eduard Valerievich

Laboratory of Biomolecular NMR-Spectroscopy, Department of Structural Biology, Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry RAS Moscow Russia bon@nmr.ru

Bocharova Olga Vladimirovna

Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry RAS Moscow Russia o.bocharova@gmail.com

Borodkin Gennadii Sergeevich

Institute of Physical and Organic Chemistry at Southern Federal University, Rostov-on-Don Russia nmr@ipoc.sfedu.ru

Borodkina Inna Gennadyevna Institute of Physical and Organic Chemistry at Southern Federal University, Rostov-on-Don

Russia nmr1@ipoc.sfedu.ru

Bubnov Philipp Saint Petersburg State University Saint Petersburg Russia

fill192@mail.ru

Céspedes-Camacho Isaac Fabián

Leiden Institute of Chemistry, Universiteit Leiden Leiden The Netherlands *i.f.cespedes.camacho@chem.leidenuniv.nl*

Charnaya Elena V. Saint Petersburg State University Saint Petersburg Russia *charnaya@mail.ru*

Chernyak Alexander

Institute of Problem of Chemical Physics RAS Chernogolovka Russia sasha_cherniak@mail.ru

Chernyshev Yuri Saint Petersburg State University Saint Petersburg Russia cherni@nmr.phys.spbu.ru

Chertkov Vyacheslav Alekseevich

Chemistry department M.V. Lomonosov Moscow State University Moscow Russia vchertkov@hotmail.com

Chizhik Anna

Saint Petersburg State Universiry Saint Petersburg Russia *afrancuzova@mail.ru*

Chizhik Vladimir Ivanovich Saint Petersburg State University Saint Petersburg Russia vchizhik@mail.ru

Davydov Vadim Vladimirovich

Saint Petersburg state politechnical university Saint Petersburg Russia davydov_vadim66@mail.ru

Dmitruk Anna Sergeevna

Moscow State University Moscow Russia anitadmitruk@gmail.com

Dolinenkov Filipp

Baltic Federal University of Immanuel Kant Kaliningrad Russian Federation *dolinenkov@mail.ru*

Donets Alexey V.

St. Petersburg State University Saint-Petersburg Russian Federation *aldonets@mail.ru*

Dvinskikh Sergey V.

Royal Insitute of Technology KTH Stockholm Sweden sergeid@kth.se

Dyachenko Semen

Saint Petersburg State Technological Institute Saint Petersburg Russia samyon2008@yandex.ru

Dzhambulatov Rinat

Saint Petersburg State University Saint Petersburg Russia ren6415@yandex.ru

Egorov Andrei Saint Petersburg State University Saint Petersburg Russia *egorov@nmr.phys.spbu.ru*

Eichhoff Uwe Bruker HTS GmbH, MGU im. M.V.Lomonosova Gaggenau Germany *Uwe.Eichhoff@bruker-biospin.de*

Fedyukina Galina Nikolaevna

FBUN State Reseach Centre for Applied Microbiology and Bionechnology Obolensk Russia galafed@mail.ru

Fraissard Jacques

University P. and M. Curie, and ESPCI Paris France jacques.fraissard@upmc.fr

Frolov Viatcheslav

Saint Petersburg State University Saint Petersburg Russia vfrolovv@bk.ru

Fuentes Sergio

CNyN-UNAM Ensenada Mexico fuentes@cnyn.unam.mx

Furman Dmitry

Saint Petersburg State University Saint Petersburg Russia dm.furman.nmr@mail.ru

Gabriel Jan

TU Darmstadt, Institut für Festkörperphysik Darmstadt Germany jan.p.gabriel@gmx.de

Gareev Kamil

Saint-Petersburg Electrotechnical University "LETI" Saint-Petersburg Russia kggareev@yandex.ru

Gerts Egor Saint-Petersburg State University Saint-Petersburg Russia gerts-e-d@yandex.ru

Golovina Eugeniia

Saint Petersburg State University Saint Petersburg Russia Jn.Golovina@gmail.com

Grebenkov Denis

CNRS Palaiseau France denis.grebenkov@polytechnique.edu

Ievlev Alexandr

Saint Petersburg State University Saint Petersburg Russia alexandr_ievlev@nmr.phys.spbu.ru

Ievleva Valleriya Olegovna

Saint Petersburg State University Saint Petersburg Russia valeriya_ievleva@nmr.phys.spbu.ru

Ilina Oksana

Saint Petersburg State University Saint Petersburg Russia oxana.iljina@gmail.com Isaeva Olga Lomonosov Moscow State University Moscow Russian o.v.isaeva@gmail.com

Kachala Vadim V.

Bruker Ltd/N.D. Zelinskii IOC Moscow Russia kachala@bruker.ru

Kämpf Kerstin

Technical University Darmstadt Darmstadt Germany kerstin.kaempf@physik.tu-darmstadt.de

Karseev Anton

St. Petersburg State Politechnical University Saint-Petersburg Russia antonkarseev@gmail.com

Kharkov Boris Saint Petersburg State University Saint Petersburg Russia kharkov@kth.se

Khodov Ilya

G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences Ivanovo Russia *ilya.khodov@gmail.com*

Khrapichev Alexandr Alexandrovich

University of Oxford Oxford United Kingdom a.khrapichev@gmail.com

Kirillov Andrey Kuzmich

Institute for Physics of mining processes NAS of Ukraine Donetsk Ukraine *kirillov@fti.dn.ua*

Klehta Nikolay Sergeevich

Saint-Petersburg State Polytechnic University Saint-Petersburg Russia klekhta@mail.ru

Klekovkina Vera Vadimovna Kazan Federal University, Institute of Physics Kazan Russia Vera.Klekovkina@gmail.com

Klyukin Konstantin

Saint Petersburg State University Saint Petersburg Russia konstantin.klyukin@gmail.com

Komolkin Andrei V.

Saint Petersburg State University Saint Petersburg Russia komolkin@nmr.phys.spbu.ru

Koriakina Vladilina

Institute of Oil and Gas Problems Yakutsk Russia *kvladilina@mail.ru*

Kultaeva Anastasia Yur'evna

Saint Petersburg State University Saint Petersburg Russia anastasia.kyltaeva@gmail.com

Kupriyanov Paul

Saint Petersburg State University Saint Petersburg Russia *p.kupriyanov@physicist.net*

Kurnikov Sergey

Saint Petersburg State University Saint Petersburg Russia serkurnikov@gmail.com

Kuzmichev Pavel Konstantinovich

Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry RAS Moscow Russia kouzmitch.mipt346@gmail.com

Kuzmin Viacheslav

Laboratoire Kastler Brossel, ENS Paris France *slava625@yandex.ru*

Lapina Olga

Boreskov institute of catalysis Novosibirsk Russia *olga@catalysis.ru*

Lebedev Vasily Timofeevich

Petersburg Nuclear Physics Institute Gatchina Russia vlebedev@pnpi.spb.ru

Likhachev Ilya Vyatcheslavovitch IMPB RAS Tula Russia *ilya_lihachev@mail.ru*

Loskutov Valentin Valentinovich

Mari State University Yoshkar-Ola Russia *val_losk@rambler.ru*

Makarova Katerina

Medical University of Warsaw Warsaw Poland *katerina.makarova@gmail.com*

Markelov Denis Anatolivich

Saint Petersburg State University Saint Petersburg Russia markeloved@gmail.com

Matveev Vladimir V. Saint Petersburg State University Saint Petersburg Russia vmatveev@nmr.phys.spbu.ru

Mazur Anton, Stanislavovich

Donetsk Institute for Physics and Engineering n.a. O.O. Galkin NAS of Ukraine Donetsk Ukraine antonstanislavovich@gmail.com

Mehrotra Gopal Krishna

MNNIT Allahabad Allahabad India gkmehrotra@mnnit.ac.in

Meier Thomas

University of Leipzig, Institute for Experimental Physics II Leipzig Germany thomas.meier@physik.uni-leipzig.de

Mershiev Ivan

Immanuel Kant Baltic Federal University Kaliningrad Russia *ivan.mershiev@gmail.com*

Michel Dieter

University Leipzig, Faculty of Physics and Earthsciences Leipzig Germany *michel@physik.uni-leipzig.de*

Mikhailova Mariya Evgen'evna

Department of Polymer Physics Faculty of Physics Saint Petersburg State University Saint Petersburg Russia mari1978@mail.ru

Minasyan Nune Sergo

Molecule Structure Research Center of STC OPC of NAS, RA Yerevan Armenia nunemin@gmail.com

Molchanov Vitaliy

Immanuel Kant Baltic federal university Kaliningrad Russian Federation *wi-m@yandex.ru*

Mozzhukhin Georgy Gebze Institute of Technology

Gebze Institute of Technology Istanbul Turkey mgeorge@yandex.ru

Nagarajarao Suryaprakash

Indian Institute of Science Bangalore India nsp@nrc.iisc.ernet.in

Naumova Anna

Saint Petersburg Electrotechnical University "LETI" Saint Petersburg Russia anyanaumova@ya.ru

Nikolaev Boris Petrovich

Institute of highly pure biopreparations Saint-petersburg Russian Federation *nikolaevhpb@gmail.com*

Nunes Rita, Gouveia

Univ. de Lisboa Lisbon Portugal *rgnunes@fc.ul.pt*

Oteju Adeleke Qudus

Ikorodu, Lagos Nigeria adebayodemilade70@yahoo.com

Padlyak Bohdan Volodymyrovych

Institute of Physical Optics of the Ministry of Education and Science of Ukraine Lviv Ukraine bohdan@mail.lviv.ua

Paluch Piotr

Center of Molecular and Macrolomecular Study PAS Łódź Poland *ppaluch@cbmm.lodz.pl*

Paradowska Katarzyna

Medical University of Warsaw Warsaw Poland katarzyna.paradowska@wum.edu.pl

Parshina Victoria

Saint Petersburg State University Saint Petersburg Russia parshenn@mail.ru

Pawlak Tomasz

Centre of Molecular and Macromolecular Studies, Polish Academy of Science Lodz Poland tpawlak@cbmm.lodz.pl

Pleshakov Ivan

Ioffe Physical-Technical Institute of the Russian Academy of Sciences Saint-Petersburg Russia *ivanple@yandex.ru*

Podrecca Manuel

UMONS - Dept of Human Biology and Toxicology Mons Belgium manuel.podrecca@umons.ac.be

Polyakov Peter

Institute For Physics of Mining Processes Donetsk Ukraine poljakov@mail.fti.ac.donetsk.ua

Popova Maria V.

Saint Petersburg State University Saint Petersburg Russia mariavpopova@mail.ru

Privalov Victor Ivanovich

Kurnakov institute of general and inorganic chemistry of RAS Moscow Russia privalov@igic.ras.ru

Privalov Alexei Institute für Festkörperphysik Darmstadt Germany alexei.privalov@physik.tu-darmstadt.de

Rabdano Sevastyan

Saint Petersburg State University Saint Petersburg Russia sevastyan@rabdano.ru

Razumovski Andrean

University of Leiden Leiden Netherlands andreanr@gmail.com

Riabchun Filipp

Saint Petersburg State University Saint Petersburg Russia fryabchun@gmail.com

Ruzheva Svetlana, Alexandrovna

Immanuel Kant Baltic Federal University Kaliningrad Russia fotinija_89@mail.ru

Rykov Ivan

Saint Petersburg State University Saint Petersburg Russia ivan_rykov@nmr.phys.spbu.ru

Ryzhov Vyacheslav Anatolievich

St. Petersburg Nuclear Physics Institute, NRC Kurchatov Institute Gatchina Russia ryzhov@omrb.pnpi.spb.ru

Samoson Ago

NMR Institute and Tallinn University of Technology Estonia ago.samoson@gmail.com

Schäfer Max

Institut of solid matter, TU-Darmstadt Alsbach-Hähnlein Germany oexen@web.de

Severin Evgeniy

Immanuel Kant Baltic Federal University Kaliningrad Russian Federation seadrake88@gmail.com

Shalamova Ekaterina

Lomonosov Moscow State University Moscow Russia katya2006-91@mail.ru

Sheberstov Kirill Fedorovich

Lomonosov Moscow State University Moscow Russia *kirillsheb@gmail.com*

Sheludiakov Sergey

University of Turku Turku Finland seshel@utu.fi

Shelyapina Marina

Saint Petersburg State University Saint Petersburg Russia shelyapina@nmr.phys.spbu.ru

Shestakova Alla Konstantinovna

State Research Institute of Chemistry and Technology of Organoelement Compounds Moscow Russia *alla@nmrcenter.ru*

Shevtsov Maxim Alexeyevich

Institute of Cytology of the Russian Academy of Sciences Saint Petersburg Russia shevtsov-max@mail.ru

Shishmakova Elena Vyacheslavovna

Saint Petersburg State University Saint Petersburg Russia sunflower46@yandex.ru

Sibgatullin Timur Anvarovich

Kazan Institute of Biochemistry and Biophysics Kazan Russia *timsdance@mail.ru*

Skripov Alexander Vladimirovich

Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences Ekaterinburg Russia *skripov@imp.uran.ru*

Skrynnikov Nikolai R.

Purdue University West Lafayette USA *nikolai@purdue.edu*

Smolyak Svitlana

G. Kurdyumov Institute for Metal Physics NAS of Ukraine Kyiv Ukraine sssmolyak@mail.ru

Soloninin Alexey Viktorovich

Institute Metal Physics Ekaterinburg Russia alex.soloninin@imp.uran.ru

Stefaniak Olga

Medical University of Warsaw Warsaw Poland *olga.stefaniak@wum.edu.pl*

Sukharzhevskii Stanislav

Saint Petersburg State University Saint Petersburg Russia stas@nmr.phys.spbu.ru

Tagirov Murat

Kazan Federal University Kazan Russian Federation *murat.tagirov@kpfu.ru*

Tupikina Elena

Saint Petersburg State University Saint Petersburg Russia *elenatupikina@gmail.com*

Tutukin Konstantin Victorovich

Saint Petersburg State University Saint Petersburg Russia kos101@mail.ru

Uskova Alina

Saint Petersburg State University Saint Petersburg Russia *linka_ss@mail.ru*

Vasil'ev Sergey

Institute of Problems of Chemical Physics Chernogolovka Russia viesssw@mail.ru

Vasilenko Tatyana Anatolievna

Institute for Physics of Mining Processes Donetsk Ukraine tvasilenko@mail.ru

Vasiliev Sergey Aleksandrovich

University of Turku Turku Finland *servas@utu.fi*

Vezo Olga

Saint Petersburg State University Saint Petersburg Russian Federation olgakuz-ko@mail.ru

Viryasov Sergey

Obolensk Russia lab71@mail.ru

Volkov Vitaly

Institute of Problems of Chemical Physics Chernogolovka Russia vitwolf@mail.ru

Volkov Vladimir Ya.

Moscow State University for Equipment Engineering & Informatics Serpukhov Russia volkovobolensk@mail.ru

Vorontsova Anna

Saint Petersburg State University Saint Petersburg Russia

annavorontsova@msn.com

Vyvodtceva Anna

Saint Petersburg State University Saint Petersburg Russia annavyvod@gmail.com

Zagorodny Yuriy

G. Kurdyumov Institute for Metal Physics NAS of Ukraine Kyiv Ukraine *yuryzagorodny@yahoo.com*

Zhernovoy Alexander

Saint Petersburg State Technological Institute Saint Petersburg Russia azhspb@rambler.ru