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Nuclear Magnetic Resonance in Condensed Matter

11th meeting: “Biomolecular NMR and related phenomena”
July 7 – 11, 2014

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Part I

Lectures
Direct observation of Majorano fermions in superfluid $^3$He

Yury Bunkov$^{1,2}$, Rasul Gazizulin$^{1,2}$

$^1$MCBT, Institut Neel, Grenoble, France
E-mail: yury.bunkov@grenoble.cnrs.fr
$^2$Kazan Federal University, Kazan, Russia

Introduction

The Majorana fermion, which acts as its own antiparticle, was suggested by Majorana in 1937. While no stable particle with Majorana properties has yet been observed, Majorana quasiparticles (QPs) was suggested at the boundaries of topological insulators, like superfluid $^3$He-B. Here we report the direct observation of Majorana QPs by precise measurements of superfluid $^3$He-B heat capacity. We have succeed to separate the temperature dependence of the bulk Bogolyubov fermions and the surface Majorana fermions heat capacity. We have found that in the conditions of our experiments at the limit of extremely low temperature as 0.12 mK the Majorana fermions constitute a part of about 15% of bulk $^3$He-B heat capacity. The heat capacity was measured by two different methods.

Experimental results

The experiments were done in the cell which consists of a closed copper box with a small orifice. The box is immersed in superfluid $^3$He-B with the temperature about 0.1 mK. The temperature inside the box was measured by the Vibrating Wire Resonators (VWRs) which Q-factor is determined by a density of Bogolubov QPs. The QPs density is exponentially related with the temperature. After some heating event the density of QPs and temperature inside the box suddenly rises, and then go back to its initial temperature by thermalisation via the orifice. The extremely low specific heat of $^3$He-B at ultra-low temperatures makes it possible to measure the increase of the temperature inside the box after the releasing the small amount of energy (down to 1 keV). As the heating events, the neutron capture reactions with $^3$He and the VWR heating pulses were used. The heat capacity of $^3$He-B in the box was measured by two different methods. One was the measurements of QPs density jump just after the calibrated heating pulse. The results are shown in Fig. 1. The second method was the measurements of the recovering time constant of the box [1]. In the last case the time constant of temperature recovering depends on the full energy, deposited on Bogolubov and Majorana QPs, see Fig. 2. In a both cases we have seen the deviation of the heat capacity from the pure Bogolubov case. This deviation corresponds well to a predicted density of Majorana particles.

Plans for future

The existence of Majorana QPs is confirmed in a first time in described experiments. In a future we are planning to investigate the Majorana QPs by a coherent magnetic resonance. The technics of Q-ball, described in our other lecture, will be applied.

![Figure 1](https://example.com/fig1.png)

**Figure 1.** The deviation of heat capacity from a bulk one. The circles show the heat capacity, measured after a VWR heating pulse. The boxes shows the heat capacity measured after a neutron capture reaction which releases energy of around 764 keV.

![Figure 2](https://example.com/fig2.png)

**Figure 2.** The recovery time after heating pulses. The straight line corresponds to a recovery time if only Bogolubov QPs are involved. The covered line corresponds to a time constant when the heat capacity of Majorana QPs, measured by first method, is included.

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Spin superfluidity and Bose-Einstein condensation of magnons
Yury Bunkov$^{1,2}$, M. Tagirov$^2$

$^1$MCBT, Institut Neel, Grenoble, France
E-mail: yury.bunkov@grenoble.cnrs.fr
$^2$Kazan Federal University, Kazan, Russia

Introduction

The Spin Supercurrent and Bose-Einstein condensation (BEC) of magnons, similar to an atomic BEC, was discovered in superfluid $^3$He-B, which is characterized by absolute purity.

Later this phenomenon were observed in a few magnetically ordered materials with different types of impurities. In this lecture we will review the properties of magnon BEC in a presence of impurities and defects.

History

The conventional magnon BEC, the phase-coherent precession of magnetization was discovered for the first time in superfluid $^3$He-B in 1984 [1]. It manifests itself by a region, where the magnetization is deflected on a large angle and is precessing coherently even in an inhomogeneous magnetic field. The transverse component of magnetization is described by the single wave function $S_\perp e^{i\omega t+\phi}$. It possesses all the properties of the spin superfluidity. The spatial gradient of phase $\phi$ leads to a spin supercurrent which transports the magnetization. There were observed: phase slip processes at the critical current; spin current Josephson effect; spin current vortex; Goldstone modes etc. The long standing quest of nontrivial magnetic relaxation in superfluid $^3$He have been resolved. The comprehensive review of spin superfluidity in $^3$He-B one can find in [2].

New results, Q-ball of magnons

There are many new physical phenomena related to the Bose condensation of magnons, which have been observed after the discovery of Homogeneously Precessing Domain (HPD). There was found 5 different magnon BEC states in superfluid $^3$He. These include in particular compact objects – coherently precessing states trapped by orbital texture [3]. At small number $N$ of the pumped magnons, the system is similar to the Bose condensate of the ultracold atoms in harmonic traps, while at larger $N$ the analog of the $Q$-ball in particle physics develops. The $Q$-ball is a rather general physical object, which in principle can be formed in condensed matter systems. At the quantum level, this $Q$-ball is a compact object formed by magnons – quanta of the corresponding $\Psi$-field. At low temperatures the condensate can be formed only in a trap, similar to that in atomic gases, and the $Q$-balls are either formed in these traps or dig their own trap.

Magnon BEC in solid antiferromagnets

The magnon BEC in terms of coherent spin precession has been discovered in a monocrystals of CsMnF$_3$ and MnCO$_3$. The experiments demonstrated the formation of magnon BEC as by CW NMR technics so by pulsed NMR experiments. The last one was performed by a new technique. In this method the BEC is formed by a very long RF, while the single BEC state is created. One can see a nice induction decay signal without beats after the switching off of the RF pulse. The details of experiments with CsMnF3 and MnCO3 one can find in Ref. [4]. Indeed, the length of this signal strongly depends on the quality of the crystal. The signal is 10 times longer in a new sample of better quality. Definitely, the quality of the sample plays a crucial role for observation of a BEC in solid antiferromagnets. We will present the last results of these experiments, where we have observed the BEC signal with duration significantly longer then the echo signals. It means that the BEC switches of even the homogeneous broadening of the magnetic system.

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References

Novel high resolution NMR techniques for elucidation of molecular solution-state structure and dynamics

Vyacheslav A. Chertkov,1, Dmitriy A. Cheshkov1,2, Tatiana A. Ganina1, Sergey S. Nechausov1, Kirill F. Sheberstov1,3, Alla K. Shestakova4

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

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.

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 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”) used to get best fit of experimental and calculated SSCC values.

Results

Advantages of the technique developed demonstrated on a series of monosubstituted cyclobutanes, trans-1,2-dihalocyclopetanes, tetrahydrofurane, tetrahydrothiophene, tetrahydrothiophene-1-oxide, pyryridine, 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 tetrahydrofurane and terahydrothiophene are twists T3 and T4, for pyryridine – envelope E with equatorial NH-bond, for terahydrothiophene-1-oxide – envelopes E3 and with axial oxygen and for proline – envelope E5 with axial COOH-group. 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


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Static and MAS $^{13}$C NMR techniques as well as $^{13}$C spin-lattice relaxation are used to investigate the interaction of CO and CO$_2$ as well as water molecules with the host structure of the MOFs Cu$_3$(btc)$_2$ and Cu$_{2.97}$Zn$_{0.03}$(btc)$_2$. $^{13}$C chemical shift anisotropy and isotropic chemical shift were studied over a wide temperature range from 10 K to 353 K. Above 30 K an increasing fraction of mobile carbon monoxide is detected (isotropic line for CO) [1].

To investigate the local motion of the adsorbed molecules in more detail, $^{13}$C nuclear spin-lattice relaxation of $^{13}$CO and $^{13}$CO$_2$ molecules adsorbed in the MOFs is investigated over a wide range of temperature and at different resonance frequencies. In all cases a single-exponential relaxation function is observed and the $^{13}$C spin-lattice relaxation times ($T_1$) reveal minima in the temperature range of our measurements. In comparison to the results from the line shape analysis, this suitable experimental situation allows a more detailed analysis of local motion and the exchange dynamics. The conclusions about the thermal motion of the adsorbed molecules are also compared with recently published NMR self-diffusion studies on these systems. The results will also be discussed in relation to the structure of the MOFs [2].

$^1$H MAS NMR measurements allow us to derive subtle information about the specific interaction of water molecules with the Cu metal sites in the MOFs and the intracrystalline and intercrystalline exchange dynamics [3].

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Modern methods of NMR data collections and spectra processing
Vladislav Yu. Orekhov
Swedish NMR Centre, University of Gothenburg, Sweden
E-mail: orov@nmr.gu.se

The invention of multidimensional magnetic resonance (MR) experiments 40 years ago led to success of the modern MRI and NMR spectroscopy in medicine, chemistry, molecular structural biology, and other fields. The approach, however, has an important weakness: the detailed site-specific information and ultimate resolution obtained in two and higher dimensional experiments are contingent on the lengthy data collection required for systematic uniform sampling of the large multidimensional space spanned by the indirectly detected spectral dimensions [1]. The number of measured data points increases polynomially with the spectrometer field and the desired spectral resolution, and exponentially with the number of dimensions. The problem of lengthy sampling compromises or even prohibits many applications of multidimensional spectroscopy.

Fortunately, the advent of “fast” NMR spectroscopy offers a number of solutions. The time-consuming systematic sampling of the signal on the entire multidimensional Nyquist grid describing the indirect dimensions is replaced by acquiring FIDs for only a relatively small number of grid points, while preserving all essential information that would be present in the full data set. Two distinct approaches can be traced back to the early years of multidimensional NMR spectroscopy. The former is based on the spectral projection theorem and Fourier Transform [2], and applied for example in the ACCORDION experiment 30 years ago [3]. In the second approach, the positions of the measured points are not constrained and often selected randomly [4]. Both approaches require novel analysis tools and non-standard processing methods, often resulting in significantly increased calculations times, and making them only recently a practical approach.

References

The study of the co-diffusion of gases through a microporous solid and the resulting instantaneous distribution (out of equilibrium) of the adsorbed phases is particularly important in many fields, such as gas separation, heterogeneous catalysis, etc. Classical $^1$H NMR imaging is the best technique for the visualisation of these processes, but it requires that each experiment be performed several times under identical conditions, and each time with only one not completely deuteriated gas. For this reason we have devised a new NMR technique where the magnet is displaced vertically, step by step, relative to the bed during the adsorption of the gas; the detector is a very thin coil. The bed is assumed to consist of $n$ very thin layers of solid, and the region probed is limited to each layer; the variation of the concentration of gas absorbed at the level of each layer is obtained as a function of time.

This technique allows the determination of:

- the gas diffusion coefficient profiles $D_{\text{intra}}$ and $D_{\text{inter}}$ against time $t$ at each level of the zeolite bed;
- the intercrystallite concentration profiles, $C(z,t)$, versus time $t$ for different values of the position $z$ in the bed;
- the concentration profiles, $Q(t,X,z)$, in zeolite crystallites located at different positions $z$ in the bed, and $X$ in the crystallites, for different times $t$.

In contrast to classical NMR imaging, this technique gives a signal characteristic of the adsorbed gas. It can therefore provide directly, at every moment and at every level of the crystallite bed, the distribution of several gases competing in diffusion and adsorption. As a first example we show the co-diffusion of benzene and hexane gases through a bed of ZSM5 zeolite.
Local NMR spectroscopy in MRI experiments with small laboratory animals

Yury A. Pirogov
Faculty of Physics, Lomonosov Moscow State University, Russia
E-mail: yupi937@gmail.com

Introduction
On the base of new MRI methods, developed in the Research Magnetic Tomography and Spectroscopy (CMTS MSU) [1-6], some pre-clinic investigations were carried out of small laboratory animals by 7-T biospectroscopy scanner Bruker BioSpec 70/30 URS. The aim of that was to study possibilities of medicine targeted delivery to oncological and ischemia cerebral affection sites [4] and to determine lesion power according to NMR spectrum without surgical intervention in vivo [5, 6].

Local NMR spectroscopy
Tumor experiments
First of these problems was solved with help of liposome containers provided with specific biomarker oriented to tumor cells of C6 glioma and Gd ions as a contrast material. Inside the container was developed by academicians Vladimir Chekhonin preparation suppressing C6 glioma tumor cells of C6 glioma and Gd ions as a contrast material. Effectivity of preparation therapy action was established previously by in vitro experiments. Then the next successful MRI investigations on the rats in vivo confirmed positive medical prognosis.

Ischemia therapy by stromal cells
The other experiment was dedicated to therapy of ischemia brain lesions with help of mesenchymal stromal cells by academician Veronika Skvortsova’s method [6]. Ischemia formation was created by middle brain artery occlusion. Marked (for visualization) by paramagnetic Fe ions stromal cells were injected to the healthy brain hemisphere. After that, the stromal cells percolated to neighbor hemisphere and surrounded ischemia region. Whole month MRI observation for this animal shown some times reducing of ischemia lesion, restoration of behavior functions and brain activity.

Multi nuclear local NMR spectroscopy
Interesting results were found by combined application MRI and NMR spectroscopy options. The last option can be realized in the 7-T BioSpec scanner not only on protons but on the number of heavy nuclei - ¹³C, ¹⁹F and ³¹P. Thanks to their using, interesting tissue voxel is localized in the volume with 2.5-3 mm transverse size and realize measurements of NMR spectra on protons and heavy nuclei in this site. Positions of spectral lines in the spectrum (chemical shift) correspond to characteristic metabolites of tissue. Their distribution reflects the tissue ischemia power, tumor type, allows to measure in real time in vivo local metabolite portrait and internal organs temperature [5-7]. This approach of join MRI and NMR spectroscopy application (that is local NMR spectroscopy) presents noninvasive analogues of biopsy, metabolomics and intra-tissue thermometry.

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References
Laws of volume elasticity in physical processes of formation of phase states and properties

Peter I. Polyakov

Institute For Physics of Mining Processes, Donetsk, Ukraine
E-mail: polyakov@mail.fti.ac.donetsk.ua

Current development of science using highly sensitive methods of the studies has resulted in division of theoretical substantiations into a number of directions without account of generalizing regularities of the physical processes changing the states of the structures under the effect of wide-ranging temperature, magnetic field and hydrostatic pressure [1].

For instance, when analyzing a separated area of research in a wide spectrum of magnetic fields H at a fixed temperature, a statement has been made along with quantum mechanical conception that the linear part of the presented regularities is a result of magnetic field structure disturbance due to magneto-elastic stresses, because even diamagnetic structures demonstrate strictional properties. As a consequence, a linear law is present in high fields at a fixed temperature, together with priority of magneto-elasticity, square law of evolution, competition of thermal and magnetoelasticity.

Wide-area high-pressure testing is a determining method of the impact on the state of the atoms within a structure through the energy of volume elasticity that fixes a physical process by experimental methods.

A definite mechanism of the distribution of thermal elastic stresses takes place in physical processes of exchange transition of the electrons of inner atom shells at the stricture sites with participating semifree valence electrons.

A question emerges, if the process of the effect of parameters can be analyzed, being based on the structure state determined by the 0-temperatures, magnetic fields and pressures? Thermal elastic expansion weakens the stress of the state from the 0-temperatures, the minimum volume, bond energy. The process of heat supply is a weakening of the bond of semifree valence electrons where the conductivity is reduced and the volume and the resistance are increased.

0-pressures at a fixed temperature evoke volume reduction, increase in the stress of the bond energy, increase in density. The jumps of the volume are phase transitions, structural transformations.

0-magnetic fields provoke the magnetic uncompensated state through the temperature and magnetoelastic stresses in the structure that is fixed by magnetostriction. Structure deformation and reconstruction modifies uncompensated state of spins. The introduced stresses are additional sources of the changes of volume, density, form of the structure, “cooling effect” [2].

The studies of simple and complex structures in physical processes under three thermodynamical parameters are the most demonstrative, so they expand the information basis and allow a generalizing analysis.

The analysis of the experimental data has shown that the impact of three parameters is revealed as linear changes in resistive, magnetic properties and the dynamics of the evolution of phase transition regularities.

We should take into account that the effect of all parameters results in the volume change, so the causing role of the volume elasticity is a determining one in cross-effects (thermal, magnetic, baric elasticity).

We shall estimate the energy of Coulomb interactions as \(1\times10^3\) eV, the influence of the crystal field as \(0.1\pm1\) eV, spin-orbit relationship as \(10^{10\pm10^5}\) eV, spin-spin (magnetic) bond as \(10^{4}\) eV, electron-nuclear bond as \(10^{5\pm10^5}\) eV. According to our estimations, the energy of elastic stresses with taking into account the coefficient of compressibility is \(1\times10^3\) eV. We should take into account that quantum mechanical forces forming the magnetism are of short range in fact, so deep understanding of the regularity if interaction is necessary for the estimation of this process. The elastic energy is an immediate energy of long range. These are elastic stresses in the structure that form the linearity of the magnetization regardless of important details of microscopic interactions. By definition, atoms and molecules have small magnetic moments of non-compensation. The structure is the totality of molecules and atoms brought into the sites of the structure (several atoms and molecules) and bound in the lattice by the compatibility of valent and free electrons. These are the approaches of the analysis that permit to define the causal role of the laws of bulk elasticity in the formation of the magnetism as well as their leading role in the first and second order structural phase transitions.

A reversible deformation change of the state of a solid under the effect of outer parameters is a consequence of the fundamental principles of thermodynamics and a prerequisite of the hypothesis of the causing role of volume elasticity in formation of the changes of properties and phase states.

References

Water exchange in biological cells studied by pulsed NMR techniques

**Vitaly I. Volkov, Irina A. Avilova, Lubov’ V. Rimareva, Ludmila D. Volkova**

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

1*Russian Scientific Research Institute of Food Biotechnology, Moscow, Russia*

2*Russian State Agrarian University-Moscow Timiryazev Agricultural Academy, Moscow, Russia*

**Introduction**

The self-diffusion measurement especially the techniques using the pulsed field gradient NMR following by Fourier transforms is the he unique methods for direct structural and dynamic studies in systems with the fast ionic and molecular transport. Water transport in biological systems is important for cellular physiological reactions, osmotic pressure of tissue and drying process of biological materials. 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. This presentation is mainly devoted to investigations of ionic and water transport in biological cells (chlorella, yeast and erythrocytes). 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 Biomateryl Science and Engineering, Graduated School of Life Science and Biotechnology, Korea University, Seoul, Korea.

**Synthetic membranes as model systems**

Sulfo-, carboxyl-, aminogroups containing ion exchange membranes and pore track etched 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 [1]. The quantitative relations of structural and motion parameters were derived from the percolation theory. 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.

**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 [2].

The typical spin echo PFG NMR attenuation obtained at different diffusion times t_0 for water in yeast cells Saccharomyces cerevisiae is shown as example in the figure.

Scaling approach and two compartment exchange model were applied to calculate cell sizes and permeabilities. 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^{-5} 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**

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**References**


Modeling a system with intrinsic disorder: an NMR/MD study of peptide-protein encounter complex

Tairan Yuwen¹, Yi Xue¹,², Fangqiang Zhu³ and Nikolai R. Skrynnikov¹,⁴*

¹Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette IN 47907-2084, USA
²Current address: Department of Biochemistry, Duke University School of Medicine, Durham, NC 27710, USA
³Department of Physics, IUPUI, Indianapolis IN 46202, USA
⁴Laboratory of Biomolecular NMR, St. Petersburg State University, St. Petersburg 198504, Russia
*E-mail: nikolai@purdue.edu

Intrinsically disordered proteins (IDPs) are widely involved in signal transduction. In this role, they bind to their (structured) targets; in doing so they themselves acquire a measure of structural order. The salient feature of the binding mechanism is that it often relies on electrostatic interactions. Initially, the IDP is pulled toward its target by long-range electrostatic forces, forming what is termed an electrostatic encounter complex (a transient state where the IDP is loosely anchored in the vicinity of the binding site). Starting from this point, it quickly finds the correct conformation and tightly binds to the target. From this perspective the encounter complex can be likened to a folding intermediate on the pathway from a random state (free IDP) to a fully structured state (bound IDP).

![Fig. 1: MD snapshots representing Sos peptide in complex with (a) wild-type and (b) Y186L/W169F mutant of c-Crk N-SH3. The latter serves as a model for electrostatic encounter complex](image)

To obtain insight into the structure/dynamics of the electrostatic encounter complex, we choose to study the binding of the proline-rich Sos peptide (which serves as a minimal model for an IDP) to the c-Crk N-SH3 domain. The original system is altered by introducing two point mutations into hydrophobic grooves of the SH3 domain, Y186L and W169F. This abrogates tight binding and shifts the equilibrium toward the intermediate state (i.e. the encounter complex, which is held together by electrostatic interactions between charged residues). The resulting increase in the population of the encounter complex makes it amenable to an NMR study using conventional NMR parameters such as chemical shifts, relaxation rates, and paramagnetic restraints.

As a first step, the experimental data have been acquired for the complex of the Sos peptide with the wild-type (wt) c-Crk N-SH3 domain. At the same time 3 µs MD trajectory of Sos:wtSH3 complex has been generated with the help of the GPU-based computers. The simulations have been conducted in explicit solvent using Amber 11 ff99SB*-ILDN force field. The comparison of the experimental and simulated results demonstrated that MD simulations tend to overestimate the strength of salt-bridge interactions involving four Arg residues from Sos and six Glu/Asp residues in wtSH3. As it turns out, this problem is endemic for the modern advanced force fields. To address this issue we have implemented an empirical correction whereby van der Waals distance for nitrogen-oxygen pair across the salt bridge has been scaled up by 3%. The modified force field was used to record a new 3.2 µs trajectory of Sos:wtSH3 complex, leading to an excellent agreement with experimental data. Furthermore, using this approach we were able to successfully simulate the entire binding process beginning with Sos randomly placed in the vicinity of wtSH3 and ending with the bona fide Sos:wtSH3 complex whose coordinates are within 1.5Å of the crystallographic structure.

Armed with this improved modeling tool, we have analyzed the experimental data from the complex between Sos and the double mutant of SH3, which serves as a model for the electrostatic encounter complex. The binding affinity of the Sos:dmSH3 complex proved to be relatively low, $K_D = 200 \mu M$, reflecting the dynamic nature of the peptide-protein interaction. As a consequence, the NMR sample contains ca. 10% of the free Sos peptide, which has been accounted for in our analyses. The appropriately corrected experimental data were then compared with a series of MD simulations representing Sos:dmSH3. A number of trajectories demonstrated excellent agreement with the experimental results. Although the MD model in this case cannot be deemed exhaustive, the observed dynamic scenarios are fully consistent with the experimental data. As anticipated, Sos hoovers over the surface of the SH3 domain, loosely anchored via electrostatic interactions (see Fig. 1). These results demonstrate how the protein system with substantial degree of conformational disorder can be successfully characterized via a combination of NMR measurements and MD simulations.

Acknowledgement

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Part II

Oral Reports
Magnetic Resonance features of HIV-associated opportunistic infections of the CNS

A. A. Drozdov, V. M. Cheremisin, I. G. Kamyishanskaya

Saint-Petersburg State University, The Faculty of Medicine, 21 line V.O., 8a
Mariinskaya hosp. Liteyniy, 56
E-mail: a_a_drozdov@mail.ru

Introduction

The Central Nervous System (CNS) is a common site of involvement in patients with AIDS, brain lesions are detected in up to 90% of patients at autopsy. A variety of infections may be diagnosed in these patients. The most common infections include HIV encephalopathy, toxoplasmosis, cryptococcosis, mycobacterial, PML, CMV and Herpes. Detection and differential diagnosis are important medical problems today.

Methods

At Radiology Department of Mariinsky Hospital, St. Petersburg, Russia more than 3000 patients with HIV were diagnosed by MRI in the last 6 years. Some patients had MRI before and then after the treatment, in goals of treatment efficiency assessment.

HIV Encephalopathy

HIV encephalopathy is the most common neurologic manifestation of HIV infection. The etiologic agent is Human Immunodeficiency Virus itself. This virus is neurotropic and causes vacuolation of the white matter, with areas of demyelination and multinucleated. Diffuse atrophy is the most common manifestation of HIV encephalopathy of the brain on MR studies: a diffuse pattern of increased signal in the deep white matter or multiple small punctate white matter lesions on T2WIs are the most common findings.

Toxoplasmosis

Toxoplasmosis is the most common opportunistic CNS infection in AIDS, occurring in about 1/3 of patients with CNS complications. A necrotizing encephalitis usually results, with the formation of thin-walled abscesses. The typical MR appearance of CNS toxoplasmosis is that of multiple ring-enhancing mass lesions with surrounding vasogenic edema. The lesions are usually of increased signal on precontrast T2WIs. Unlike bacterial abscesses, toxoplasmosis lesions are not high in signal on DWI.

Cryptococcosis

Cryptococcosis is the most common fungal infection, causing meningitis as the most common presentation. Imaging studies are usually normal, diagnosis is made by the CSF analysis.

Progressive multifocal leukoencephalopathy

Progressive multifocal leukoencephalopathy (PML) is a viral opportunistic infection, caused by JC virus. The incidence of PML in AIDS patients is approximately 10%. The infection causes demyelination and necrosis, primarily involving white matter. MR reveals focal lesions of increased signal on TIRM and T2WI and decreased signal on T1WIs within the subcortical and deep white matter.

CMV

CMV infection usually does not result in frank tissue necrosis. MR features are divers or absent. CMV meningoencephalitis is occasionally imaged as areas of increased signal on T2WIs in the periventricular white matter.

Mycobacterial CNS infection

Mycobacterial CNS infection is a relatively rare disease among AIDS patients. Most of these patients are intravenous drug abusers with pulmonary tuberculosis. Most patients present with meningitis. Tuberculomas are present in approximately 25% of HIV-patients with CNS tuberculosis.

Results

MRI has the highest sensitivity and specificity for detection infectious disease of the Central Nervous System in HIV-infected patients among other imaging methods. Brain MRI results are essential for effective pharmacological treatment of HIV-associated diseases.
Heteronuclear Dipolar NMR Spectroscopy

Sergey V. Dvinskikh

Royal Institute of Technology, Stockholm, Sweden
Laboratory of Biomolecular NMR and Institute of Physics, St. Petersburg State University, St. Petersburg, Russia
E-mail: sergeid@kth.se

Valuable structural information in solids, soft solids and anisotropic fluids such as, for example, nanostructured composites and biological membranes, can be obtained through the determination of dipolar couplings. Heteronuclear dipolar interactions between rare and abundant spins are measured using Separated Local Field (SLF) experiment where dipolar coupling are correlated to the chemical shifts of the rare nuclei [1].

Popular SLF approaches, which can be applied under stationary and magic angle spinning sample conditions, include (i) monitoring of the single quantum coherence evolution of either rare or abundant spins and (ii) observation of the polarization exchange in the rotating frame. Latter technique typically involves the spin exchange of the spin-locked magnetization components during cross polarization. In another approach, multiple pulse homonuclear decoupling sequence is applied and the magnetization is spin-locked along the effective rf field direction. For efficient spin exchange, the same sequence is synchronously applied in the second frequency channel [2].

It has been demonstrated that the superior resolution in the broad range of the dipolar coupling values is obtained with the proton detected local field (PDLF) technique where the evolution of the single quantum coherences of the abundant spins is indirectly observed [3]. For accurate measurements of large dipolar coupling the rotating frame approaches are competitive [4]. In the technique based on synchronous homonuclear decoupling in two channels the polarization transfer can be achieved for arbitrary magnetization component and experiment can be applied to uniformly or partially labelled samples [2].

In this contribution, an account will be given of recent applications of the SLF technique to study molecular mobility, hydrocarbon chain conformational dynamics, and phase transformations in advanced mesocomposite materials [5-8].

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References
Introduction

ω-hydroxy-4-hexyloxy-4′-cyanobiphenyl (HO-6OCB) and 4-heptyloxy-4′-cyanobiphenyl (7OCB) are two nematic liquid crystals (Fig. 1). The first one can form hydrogen bonds between terminal groups by the virtue of its OH group. Another molecule was chosen for the comparison, as it has similar length and cannot form H-bonds.

Figure 1. Structure of HO-6OCB (top) and 7OCB (bottom)

Conformational structure

Fully-atomistic molecular dynamics simulations can provide important information on the structure of the material under study. Main results on local structure of HO-6OCB and 7OCB such as radial or cylindrical distribution functions, hydrogen bonds formation and their lifetimes can be found in our paper [1]. This report focuses mainly on conformational structure of the above mentioned liquid crystals.

The analysis of dihedral angles distributions shows that the rotational isomeric model can be applied. Odd-even effect is also observed in our simulations affecting dihedral angles distributions as well as aliphatic chains conformations. The all trans conformation of the chain is more typical for 7OCB liquid crystal and is the most frequent (25.8% of all conformations), while HO-6OCB is more likely to have gauche± at the end of the chain (13.2% for each conformation). Another appearance of the odd-even effect is that almost every odd carbon atom (counting from central oxygen atom) is in trans position.

Unfortunately thesis format don’t give us the possibility to introduce our results in sufficient manner, but all the moments will be discussed at the conference in details.

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References

Compact nuclear magnetic relaxometer to express - condition monitoring of liquid and viscous media

Anton Karseev, Vadim Davydov

St. Petersburg State Polytechnical University
E-mail: antonkarseev@gmail.com
1E-mail: davydov_vadim66@mail.ru

Introduction

In the modern world there is a steady deterioration of the ecological state of water objects. Humanity pollutes water objects banks and the water by various hazardous substances. Timely detection of hot spots allows for a set of measures to clean up the coast and the water in time. This prevents more serious ecological disaster. In most cases, the most effective type of environmental monitoring of small water objects is collecting samples and express analysis on a place for detection of existence of pollution. Further samples are transported in stationary laboratory and are exposed to the full analysis. Only trials in which was revealed the suspicion of dangerous impurities presence exposed a complete analysis.

In such a situation, quite effective tool for express control is compact nuclear - magnetic (NMR) relaxometer. Moreover, this instrument can be used for quality control of products and liquid (e.g. milk or beer) or viscous (e.g. engine oil or linseed oil) products.

Registration of the NMR signal

In the proposed design of the portable nuclear - magnetic relaxometer the container with liquid placed into a magnet, which also serves the function of the polarizer and analyzer. Dimensions of the magnetic system were chosen so that the device could be easily transported by hand. For registration of the NMR signal in a weak magnetic field \( B_0 = 0.55 \) mT, we developed autodyne detector scheme (generator weak vibrations). It was based on the differential amplifier cascade, which ensures stable operation of the device and good suppression of common mode interference.

We developed a scheme for the control and processing of the NMR signal, which was based on a microcontroller STM32. It allows to provide optimal conditions for the registration of the NMR signal - high signal/noise ratio (S/N), and to automate the measurements. The microcontroller controls the autodyne generation level for maximize S/N ratio and automatically adjusts the frequency of autodyne detector depending on the magnetic field induction \( B_0 \). To ensure the S / N ratio greater than 5, the microcontroller provided the signal accumulation. Using this scheme allowed to register the NMR signal from liquids with \( T_1 > 0.005 \) s.

Measurement technique

The NMR signal from tap water at \( T = 17.4 \) °C is shown in Fig. 1.

![Figure 1. NMR signal](image)

The shape of the NMR signal decay (dotted line) is determined by the time \( T_2 \) (Fig. 1). \( T_1 \) measurements performed by varying the frequency modulation of the field \( B_0 \). Comparing the \( T_1 \) and \( T_2 \) with the reference values (at a given temperature), you can instantly identify the deviation from the natural state of the medium.

Using microcontroller allowed to control the frequency modulation and modulation field amplitude. It is able to measure the transverse relaxation time \( T_2 \) of the order of 2.5 seconds or less. In the case of large transverse relaxation times, the presence of impurities can be determined by observing the NMR signal on the laptop screen, which records the measurement results.
Molecular mobility in nanostructured mesocomposites studied by dipolar NMR spectroscopy

Boris Kharkov$^{1,2}$, Sergey Dvinskikh$^{1,2,3}$

$^1$Department of Chemistry, Royal Institute of Technology - KTH, SE-10044 Stockholm, Sweden
$^2$Department of NRPM, St. Petersburg State University, St. Petersburg 199034, Russia
$^3$Laboratory of Biomolecular NMR, St. Petersburg State University, St. Petersburg 199034, Russia
E-mail: kharkov@kth.se

Introduction

Nanostructured mesoporous materials have attracted considerable interest during past decades. Unique physical properties of these materials make them indispensable in various industrial applications, i.e. as adsorbents for water remediation, chemical sensors, and filters with high sensitivity to the penetrant molecule size. Nowadays, surfactant-templating synthesis strategies are widely employed for mesocomposites production in both industrial and fundamental research applications. Studying the organic component that is periodically arranged within inorganic matrix of the composite can provide valuable information on the molecular origin of the confinement effects and surface interaction and reveal its affect on the structural and dynamic properties of organic molecules.

Various experimental and computational techniques have been applied to study dynamical and structural parameters of organic molecules adsorbed and confined in the galleries of mesoporous solids. Unlike diffraction and imaging techniques, such as SAXS, TEM, and AFM, NMR spectral and relaxation parameters are sensitive to the local environment and are capable of delivering the structural and dynamical information on atomic and molecular level. Two-dimensional $^1$C separated local field NMR spectroscopy provide quantitative model-independent information on molecular dynamics in anisotropic systems in a wide range of molecular mobility. In a typical SLF experiment, residual heteronuclear dipolar couplings are probed in indirect dimension of 2D experiment, while carbon chemical shifts, measured in the direct dimension, preserve high chemical resolution. In the experiment, dipolar spectra with splitting proportional to C-H bond order parameter $S_{CH}$ are obtained for each resolved carbon position.

SLF in nanocomposites

In the present work, we apply SLF spectroscopy to study nanostructured organic-inorganic mesocomposites. The organic component often exhibits complex phase behaviour with phases characterized by different types of molecular motions.

![Figure 1. a) Schematic representation of a mesolamellar nanocomposite; b) simulated representative C-H dipolar spectra in adsorbed surfactant molecules for three motional models: immobilized molecule, rotator phase, and rotating molecule with fast conformational dynamics](image-url)

As an example, the schematic structure of clay-based layered composite is shown in Figure 1a. The organic double layer is formed by surfactant molecules. The composite exhibits three phases clearly distinguishable by dipolar spectra’s shapes (Figure 1b). Motional modes were identified from the analysis of the order parameter profiles.

Nanocomposites of different geometry [1, 2] and its comparison to lyotrophic mesophases [3, 4] will be discussed in the presentation.

Acknowledgements

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References

Diffusion-Weighted MRI of the body in oncologic practice: method, comparison with PET/SPECT and prospects

T. V. Makurova¹, D. A. Zinkevich¹, V. M. Cheremisin¹,²,
I. G. Kamyshanskaya¹,²

¹Faculty of Medicine, Saint-Petersburg State University, 21 Liniya 8a, Saint Petersburg
²Mariinskaya Hospital, MRI Department, Liteinii prospect 56, Saint Petersburg

The number of patients with cancer has increased significantly for the last 10 years. In 2012, cancer has killed about 8.2 million people according to WHO [1]. In Russia, each year 20.8 new malignancies are diagnosed per 100 thousand population [1]. Unfortunately, in 60% of cases neglected tumors on III – IV stage are detected [1]. Therefore, early diagnosis of the primary tumor and visualization of metastases are essential for the timely and proper patient management.

Nowadays the special place among modern methods of radiation diagnostic imaging of cancer is occupying by CT and MRI.

However, functional and metabolic pathological changes are not usually conjoined with anatomic changes, thus standard CT imaging can’t identify them. Furthermore, using CT isn’t enough for assessing results of the therapy, that is why functional methods of visualization such as SPECT and PET are used to supplement anatomic methods of visualization [2].

In the early 90s diffusion-weighted MRI (DWI) had appeared in medicine, being used to diagnose the cerebrovascular accident. [2] With the advent of superconducting MR- tomographs, it became possible to conduct whole-body DWI [2, 3].

Not only pathologically high glucose uptake characterizes cancer cells, but also high cellularity, so the restriction of water diffusion is hallmark of tumor cells. Modification of the H₂O diffusion, caused by the pathophysiological processes leading to impairment of cell membrane permeability, can be detected by DWI and characterized by maps of apparent diffusion coefficient (ADC). The last notion reflects the mean square distance that molecule of water passes per unit time [3, 4].

Signal intensity on DWI reflects the extent of freedom of the H₂O diffusion in the voxel of the object. In terms of scale relativity it means that tissue with limited diffusion will give hypointensive signal, while tissue with less limited diffusion will be hypointensive. The reverse is true for ADC map: if diffusion is more limited, the meaning of ADC will be lower and accordingly the intensity will be also lower [5].

Recent years usual DWI has been evolved into whole body DWI (WB-DWI), which becomes comparable with PET-CT.

DWI is hold as well as SPECT-CT and PET-CT using the same scanner without unnecessary patient’s shifting, that reduces the chance of a mismatch slices.

PET-CT and SPECT-CT are associated with X-ray exposure and patient’s gamma irradiation, the tracer production. They are more time-consuming and costly methods. Moreover, sensitivity and specificity of isotope tomographic methods depend on tumor’s histology and used radiopharmaceuticals [6].

With reference to WB-DWI, this method allows to assess either on the molecular level, and using inverted scale by type “negative” are visually similar to PET-CT. In addition, DWI method isn’t required opacifying injection or using radiopharm drugs, being cheaper than SPECT and PET.

Simultaneously with the advantages of this technique, there are a number of drawbacks and limitations: the influence of values T2 and T1 (limited opportunities for focuses with short T2 values, with short T1 values focuses visualized as a high-intensity zones); motion and streams artifacts; insufficient resolution, which reduces sensitivity to small focuses [6].

Almost one of the major drawbacks of DWI associated with occurrence of artifacts in breathing, is eliminated with using the program DWIBS, which eliminates the coherent motion of water [2].

Prospectively, early made DWI (after 1st or 2nd course of chemotherapy), supplemented by accounting and modification values of ADC before and after, permits to predict tumor response at the end of treatment.

In conclusion, WB-DWI can be good alternative in searching for the primary tumors and more important, for metastases, their number and location, the extent of the positive response to treatment. WB-DWI is a safe method of diagnosis and can be used repeatedly for monitoring chemo- and radiotherapy.

References

Method development to study heavy crude oils using NMR Imaging joined with Cold Finger testing in situ

Evgeny V. Morozov, Oleg N. Martyanov

Kirensky Institute of Physics SB RAS, 660036 Akademgorodok 38/50, Krasnoyarsk, Russia
E-mail: morozov_if@mail.ru

1Boreskov Institute of Catalysis SB RAS, 630090 Pr. Acad. Lavrentieva 5, Novosibirsk, Russia

Introduction

One of the most critical challenges facing oil industry today is assuring crude oil flow through complex long pipelines. Pipeline failures are extremely costly and potentially disastrous to the environment. Failures can occur in for a variety of reasons, but the most widely spread is n-paraffin (wax) deposition [1]. It occurs along the pipe walls when the temperature of produced fluids falls below the cloud point (the point at which the first wax crystals start to precipitate out of solution [2]). The most commonly used method to study wax deposition tendency in crude oil is Cold Finger testing. The basic concept of this testing is that a surface (cold finger) is placed in a sample of heated crude oil, and cooling fluid is circulated through the interior of the cold finger. Wax deposition on cold surface is measured against the time (it’s accompanied by cold finger removing and weighting).

The deep inside into the mechanisms of deposit formation could be provided by NMR Imaging application to Cold Finger testing, making it possible to visualize the deposits and temperature distribution as well as measurement rates of growth in non destructive manner (in situ). Therefore the aim of this work was to develop the methodology of MRI application to Cold Finger testing including equipment implementation and conducting the model experiments.

Experimental

Experimental installation was consisted of NMR imaging system based on Bruker AVANCE DPX 200 (field 4.7 T, probe PH MINI 0.75, RF coil diameter being 38 mm) and homemade Cold Finger device adjusted into the magnet system (Fig.1).

Results and discussion

In results the experimental installation was implemented and successfully tested on model samples. The temperature profiles measured along the radius (t-profiles were evaluated using calibration curves $T_2 = R(t)$ measured previously) for model glycerol sample revealed a good agreement with theoretically predicted t-profiles based on heat conduction equations.

Installation is able to generate wide range of steady-state temperature gradients (the strongest is 10/80°C where 10°C – the temperature of cold walls and 80°C – the temperature of hot ones). Given temperature gradients were visualized (Fig.2, $T_2$-weighted images are presented) and the action of these gradients on oil samples was studied. So, crude oil stratification and light fractions transport were observed; deposit outgrowth formation was visualized directly.

Conclusion

New method developed seems to be promising for study heat and mass transfer in crude oils, providing the deep insight into the mechanisms of deposit formation.

Acknowledgements

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References

Two frequency nuclear quadrupole resonance for lines identifications

G. V. Mozzhukhin$^{1,2}$, J. Barras$^3$, B. Rameev$^{1,4}$, G. Kupriyanova$^5$

$^1$Gebze Institute of Technology, Istanbul Str. 101, P.B. 141, 41400 Gebze-Kocaeli, Turkey
$^2$Kazan State Power Engineering University, 420066 Kazan, Russian Federation
$^3$Department of Mechanical Engineering, King’s College London, Strand, London WC2R 2LS, UK
$^4$Kazan Physical-Technical Institute (KPhTI), 420029 Kazan, Russia
$^5$Baltic Federal State University, 320014 Kaliningrad, Russian Federation

**Introduction**

In single crystal the preferred direction in nuclear quadrupole resonance(NQR) is defined by quadrupole principal axis, but in powder there is no preferred direction for one frequency NQR. However in the case of two and three frequencies signals the relative directions of the coils have important meaning, because the maximum probabilities of the signal on $\nu_0$, $\nu_1$ and $\nu_2$ frequencies are associated with quadrupole principal axis X, Y and Z. In our work we study two and three frequencies signals for one coil multifrequencies probe and for case of different angles between exciting coils. We also studied the exciting of two transition by one pulse in the system with small asymmetry parameter $\eta \leq 0.2$ and for high asymmetry parameter $\eta \geq 0.2$.

**Modeling and experiments**

Our theory is based on following approach: the durations of pulses are considered to be much shorter than the relaxation time of the quadrupole system. We use the matrix density approach for calculations of transition NQR signal, neglecting the relaxation terms [1].

Firstly we studied the application of the single pulse in the case of small asymmetry parameter $\eta$ (i.e. the bandwidth of excitation pulse is enough to excite both $\nu_1$ and $\nu_2$ transitions). This pulse produces the signal on both transitions $\nu_1$ and $\nu_2$. We carried out calculations of the case of excitation two transitions by two pulse on different transitions. The results for a single crystal for different orientation of coils to principal axis EFG were carried out. We modeled the behavior of the signal for different polar angle $\theta$ and $\phi$. The results of the modeling show that there are two- and three- frequency signals for one coil excitation. Although the signal on the third frequency is smallest, the probability of the detection of this signal is comparable to other signals. In this situation, we suppose that the range of resonance of coil circuit is very wide including all resonance frequencies. However, in powder, there is no unique direction in the laboratory frame defining the quantization axis of the sample, but the axis of the radiofrequency coil defines the preferred direction in the sample. For instance, in work [2] the effective radiofrequency component is defined by the projection of radiofrequency magnetic field on the axis of spin quantization. Some results presented in fig.1.

The average value of $\langle I_z \rangle$ projection on one coil in powder is equal to zero.

Also, we studied the case of two coils with different resonance frequencies $\nu_1$ and $\nu_2$ in powder and variable angle between these coils.

NQR experiments have been performed on Tecmag Apollo NQR/NMR console (0.1-100 MHz) (with two-channel transmitter and one-channel receiver modules for GIT (Gebze Institute of Technology) group and single channel for King’s college group). The sample of our studies was carbamazepine ($\text{C}_{13}\text{H}_{15}\text{N}_{2}\text{O}$, 5H-Dibenzo[b,f]azepine-5-carboxamide) produced by Sigma-Aldrich Company Ltd.

![Figure 1. One frequency (blue) and two frequencies (red) experiments for carbamazepine at room temperature in one coil. $F_1 = \nu_1$, $F_2 = \nu_2$.](image)

**Conclusion**

We investigated some aspects of two frequency method for application in one and two coil experimental setup. The first important conclusion is following: in the case of one coil probe and two coils probe the signal at third frequency after two-frequency excitation is not observable in powder. We need two coils for excitation and third coil for receiving the signal on the third frequency. Thus, use of three-frequency signal for detection of the compounds requires three orthogonal coils experimental setup in powder. The second important conclusion includes the application of two-frequency method for line identification of NQR spectra in one coil probe. We showed that both one coil probe and two coils probe are effective for line identification in the case of carbamazepine.

**Acknowledgements**

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**References**


Possibilities of the MRI in a complex assessment of cardiac diseases

I. N. Petrov, V. M. Cheremisin, I. G. Kamyishanskaya

Saint-Petersburg State University, Medical faculty, 21 line V.O., 8a
Mariinskaya hosp. Liteyny, 56
E-mail: ivan-petrov90@bk.ru

The cardiac MRI, commonly used in cardiology-specialized centers, is rarely applied in general hospitals. While the percentage of cardiac pathology is one of the biggest among other diseases. That is why it is a significant problem for a cardiology and radiology. Together with other modalities, cardiac MRI has a large field for research and scientific work. It caused by the fact that the MRI is one of the most accurate and least invasive methods in cardiac imaging. Sometimes the MRI is an irreplaceable modality in a difficult diagnostic case, when others are not reliable enough or related with unjustified risk for the patient. MRI provides the detailed assessment of the cardiac morphology and function. The using of ECG-gating gives a possibility to avoid the artifacts, caused by cardiac motion. And the right slice positioning due to oblique (in relation to body axes) cardiac axes – gives anatomically-correct pattern of the cardiac structures.

Historically, there are two principal types of sequences. The “dark-blood” sequences are based on the spine echo, where the contrast between the myocardium and the blood is low, but a good visibility of the myocardial edema, whereas the “bright-blood” sequences are based on the gradient echo and have the best contrast to noise ratio and the most clearly view of the endocardial border. Unlike the geometrical assumption in Echocardiography, the evaluation of the cardiac function by MRI allows an accurate quantification of the cardiac chambers volumes, the ejection fraction and other most important indicators of the myocardial function. Furthermore, even the moderate decrease of the local (or global) contractility can be visualized by the myocardium tagging technique with the inversion pre-pulses.

Quantification of the blood flow volumes, velocities and other intracardiac hemodynamic values are enable via the phase-encoding technique. It is actively used to determine indications for surgery in patients with congenital heart disease.

In spite of the higher resolution given by CT in coronary angiography, MRI is an alternative for patients with allergy to the iodine contrast agents. MR-coronary angiography is improving and probably will be able to compete with CT-angiography soon.

MRI is a great modality in visualization of the myocardial ischemia and infarction. MR-perfusion has the best tissue sensitivity. Combined with the stress-test, it gives accurate results in detecting ischemia zones, myocardial necrosis and, which is particularly important, hibernating/stunning myocardium and determines the need of the revascularization.

Delayed contrast-enhanced MRI gives a possibility to reveal myocarditis, sarcoidosis, hypertrophic cardiomyopathy, myocardial scar. Moreover, myocardial mapping enables to quantify these lesions.

Despite of high sensitivity, specificity and accuracy of the abovementioned MR-methods, occasionally the real clinical situation is so difficult, that even MRI don’t enables to determine the right diagnosis. It forces to use the complex examination of the patient, from physical examination to hi-tech modalities and to improve the current diagnostic imaging techniques.
The study of hydration properties of functional groups of glycine and beta-alanine amino acids by nuclear magnetic resonance and quantum chemical calculations

Sevastyan O. Rabdano\textsuperscript{1,2}, Alexey V. Donets\textsuperscript{1}

\textsuperscript{1}Faculty of Physics, St. Petersburg State University, St. Petersburg, Russia
\textsuperscript{2}Laboratory of Biomolecular NMR, St. Petersburg State University, St. Petersburg, Russia
E-mail: sevastyan@rabdano.ru

Most of organic molecules adapted to function exclusively in aqueous environment. Protein-water interactions shape the free energy surface that governs structure, backbone dynamics and protein folding. Functions like enzymatic catalysis, recognition and binding accompanied with specific interactions involving individual water molecules in hydration of solute. Kinetics of these processes constrained by mobility of water in hydration spheres. Hence the study of microstructure and dynamics of solvent is an important question because the primary events in most biological processes take place at the protein-water interface.

Detailed elaboration of present hydration models is not sufficient to capture the hydration of hydrophilic and hydrophobic functional groups of organic molecules. New approach of study of distinct hydrations of functional groups is necessary to correctly describe the solvation of amphiphilic molecules.

We report the technique for study of hydration properties of distinct fragments of organic molecules by nuclear magnetic resonance on \textsuperscript{2}H nuclei. It is based on model of additive contributions from hydrations of functional groups in observed nuclear magnetic relaxation rate. Relaxation rate of the solvent nuclei should be calculated as a sum of contributions of each substructure. In the case of fast exchange of deuterons between all substructures, the spin-lattice relaxation of the solvent nuclei in the investigated system is given by simple formula.

With use of new technique it was established that rotational correlation times of water molecules near methylene group of glycine and \(\beta\)-alanine is 2.8-3 times lower, than one for pure solvent. Ratio of correlation times is remain unchanged in wide temperature range and don’t depends on solution concentration. The increase of water molecules mobility in hydration of amino and carboxylic groups versus pure solvent is observed. At low temperatures difference in mobility is maximum. At high temperatures mobility of water molecules in hydration of amino and carboxylic groups is the same as in pure solvent. Moreover it was established that energy of activation of motion of water molecules in hydration of methylene group is almost equal to activation energy for bulk water. Activation energies of motion of water molecules in hydration of hydrophilic carboxylic and amino groups is 1.2 times lower than in bulk water.

The study of chemical exchange of water and glycine amide deuterons was made. Also quantum chemical calculations of clusters constructed from amino acids and large number of water molecules were performed. The coordination numbers of functional groups, primary orientation of water molecules with respect to organic molecules fragments, hydrogen bond length, Mulliken partial charges of atoms of solute molecule, Mayer bond orders and quadrupole coupling constants of deuterons of water in solutions of glycine and \(\beta\)-alanine were calculated.

Acknowledgements

NMR studies were performed at the Centre for Magnetic Resonance, St. Petersburg State University. pH measurements were performed at the Centre for diagnosis of functional materials in medicine, pharmacology and nanoelectronics, St. Petersburg State University. Quantum chemical calculations were performed at the Resource Center “Computer Center SPbU”, St. Petersburg State University.
Unusual scenario of temperature evolution of magnetic state in novel (Au, Co) doped carbon-based nanomaterials

V. A. Ryzhov1,2, A. V. Lashkul2, V. V. Matveev3, M. V. Mokeev4, P. L. Molkov5, A. I. Kurbakov1,3, K. G. Lisunov3,6, I. A. Kiselev1, D. Galimov2,5, E. Lähderanta2

1Petersburg Nuclear Physics Institute, NRC "Kurchatov Institute", Orlova Coppice, Gatchina, Leningrad province, 188300, Russia
2Department of Mathematics and Physics, Lappeenranta University of Technology, PO Box 20, FIN-53851 Lappeenranta, Finland
3Faculty of Physics, Saint Petersburg State University, Saint Petersburg, Russia
4South Ural State University, 454080 Chelyabinsk, Russia
5Institute of Applied Physics ASM, Academiei Str., 5, MD 2028 Kishinev, Moldova
6Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia
E-mail: ryzhov@omrb.pnpi.spb.ru
E-mail: erikki.lahderanta@lut.fi
E-mail: vmatveev@nmr.phys.spbu.ru

Carbon-based nanomaterials are a novel exciting class of ferromagnetic (F) materials which do not contain any F metals [1]. They attract considerable interest in recent years due to high-temperature F behavior accompanied by a field hysteresis and a remnant magnetization. This makes them catching for applications not only in techniques but in biology and medicine due to their low toxicity through small concentrations of metallic elements [1, 2]. Magnetic properties of a few carbon-based compounds were studied by magnetization measurements in [3]. Nevertheless, many important details (local and long-range structures, character of F ordering over samples) remain unclear. In this work we have studied carbon-based compounds doped by Au (S-Au) and Co (S-Co), which have been prepared and studied earlier in [3]. We have obtained data on their structure and magnetic properties using a few independent physical techniques, which clarify some above mentioned details.

Neutron diffraction data reveal amorphous character of the structure in the both samples that correspond to the well known conceptions on organization of carbon-metal nanocomposites, having nanoporosity. The S-Co sample exhibits a more regular distribution of pores and probably larger average size of material between them in comparison with that in the S-Au sample. This is accompanied by more homogeneous short-range magnetic arrangement and by formation of ground state with long-range F order.

NMR data indicate that both samples are the products of partial carbonization of initial aromatic compounds and these products did not reach the state of glassy carbon.

The main result of the magnetic investigations of the composite samples doped with Au and Co is establishing of their inhomogeneous phase-separated magnetic state, which depends on temperature. This state contains the system of the FM clusters and the magnetic matrix. The latter is formed by paramagnetic centers located outside the FM clusters. The magnetic characteristics and their temperature behavior, as well as structure of the compounds depend appreciably on the doping material. In the sample doped by nonmagnetic Au, the onset of the matrix ordering occurs at lower temperature ($T_C \approx 210$ K) whereas in the Co-doped sample such ordering takes place at higher temperature above 350 K. The S-Co sample exhibits the remanent magnetization and the coercive force, which exceed considerably those of the S-Au sample. In addition, the Co-doped sample displays inhomogeneous magnetic properties on the long-range spatial scale, characterized by larger magnitude of the mean magnetic moment. The complex temperature behavior of the magnetization in the Au-doped sample suggests changing of a mutual arrangement of magnetic moments of the matrix and the FM cluster system from an almost opposite orientation below $T_C$ to an almost parallel one at low temperatures. Only the last stage of this process has been observed in the S-Co sample within the investigated temperature interval. This stage is accompanied probably by formation of an almost homogeneous FM state, as follows from the neutron diffraction investigations.

Generally, the results obtained by different techniques permit us to clarify the peculiarities of the structure and to obtain important information about delicate processes of the magnetic arrangement of carbon-based porous nanomaterials doped by Au and Co.

References

Magnetic resonance study of atomic hydrogen and deuterium stabilized in solid $H_2$ and $D_2$ matrices below 1 K

Sergey Sheludiakov$^1$, Janne Ahokas$^1$, Jarno Järvinen$^1$, Otto Vainio$^1$, Denis Zvezdov$^{1,2}$, Sergey Vasiliev$^1$, Vladimir Khmelenko$^3$, Shun Mao$^3$ and David Lee$^3$

$^1$Department of Physics and Astronomy, University of Turku, Finland  
E-mail: seshel@utu.fi  
$^2$Kazan Federal University, 420008, 18 Kremlyovskaya St, Kazan, Russia  
$^3$Department of Physics and Astronomy and Institute for Quantum Science and Engineering, Texas A&M University, College Station, Texas 77843, USA

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 an important role. Light impurities such as atomic $H$ or $D$ stabilized in solid $H_2$ and $D_2$ may move through the lattice by means of tunnelling and at low enough temperatures behave similar to an ideal gas where collective quantum phenomena related to Bose-Einstein Condensation (BEC) can be observed. On the other hand, effects of exchange interaction in the system are expected to appear at high enough densities of $H$ atoms. In our recent work [1] we succeeded in reaching record high densities of atoms: $n_H = 4 \times 10^{19}$ cm$^{-3}$.

In this work we present our results of electron spin resonance (ESR) and electron nuclear double resonance (ENDOR) experiments with atomic hydrogen and deuterium stabilized in solid $H_2$ and $D_2$ films in 4.6 T magnetic field at temperatures below 1 K.

![ESR spectra](image1)

**Figure 1:** ESR spectra of $D$ and $H$ atoms stabilized in solid $H_2;D_2$ matrix at 300mK. Solid line corresponds to thermal population of the hyperfine levels, dashed line: polarized sample

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-$H_2$ (ortho-$D_2$) onto a cold (<1 K) surface of a quartz microbalance, which served also as a mirror of a 128-GHz Fabry-Perot resonator; 2) we dissociated part of the molecules in the film by running an RF discharge in the miniature helical resonator located nearby [2]. The ESR study was performed using a cryogenic 128-GHz heterodyne spectrometer [3] 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 of $H$ atoms ($f=910$ MHz) and running RF-discharge in the sample cell. An additional varactor-tuned coil ($f=140$ MHz) was arranged near the sample to carry out ENDOR studies of $D$ atoms.

Results

We observed quantum isotopic exchange reactions $D+H_2=H+HD$ and $D+HD=H+D_2$, which effectively increase the concentration of atomic hydrogen in $H_2;D_2$ mixture films. ENDOR measurement provided information on the trapping condition of the $H$ and $D$ atoms in the molecular matrix. The presence of $D_2$ molecules in vicinity of $H$ and $D$ atoms was supported by observation of the holes in both ESR spectra of $H$ and $D$ atoms during pumping the positions of the satellite lines. These satellite lines appear when simultaneous spin flips of the electron of the atom and the deuteron on a neighbour $D_2$ molecule take place. We found efficient dynamic nuclear polarization (DNP) of $H$ in $D_2$ matrices via both Overhauser and solid effects. We suggest that interaction of electrons of the $H$ atoms with magnetic moments of ortho-$D_2$ molecules greatly enhances probabilities of forbidden transitions. In addition, pumping the center of the $H$ spectrum created negative DNP, the effect not seen before in magnetic resonance experiments. We anticipate that this phenomenon may be related with strong exchange effects of $H$ atoms.

References

Part III

Poster Session
Introduction

Liquid crystalline compounds with strong polar fragments are of great interest for electro-optic materials. Earlier the 4-hexyloxy(1) and 4-(ω-hydroxyhexyloxy)-4'(2,2-dicyanoethenyl)azobenzenes (II) were synthesized and studied [1,2].

Two strong polar cyano groups result in increase in dipole moment in comparison with monocyanosubstituted azobenzenes and biphenyls. Moreover hydroxyl group in molecule II can result in intermolecular H-bonded complex formation and physicochemical properties modification. The both compounds (I,II) are the monotropic liquid crystals.

This work was devoted to theoretical and experimental study of these compounds structure by \(^{13}\)C NMR spectroscopy and quantum-chemical calculations.

Experimental and computational

The computations were carried out in the frame of density functional by program PCGAMESS/Firefly. The method B3LYP/6-311G(d, p) was used. The shielding terms \(^{13}\)C were calculated by GIAO method. Chemical shifts were obtained from shielding terms. Chemical shifts of rapidly exchanging \(^{13}\)C nuclei were averaged out. The \(^{13}\)C NMR spectra of I,II solutions in CDCl\(_3\) were obtained with use of spectrometer Bruker Avance III-500.

Results

The optimization of molecular geometry I,II was carried out, dipole moments, polarizability, its anisotropy and theoretical \(^{13}\)C NMR spectra were calculated.

\[ y = 0.985x - 4.4198 \]
\[ R^2 = 0.9957 \]

\[ y = 0.9872x - 4.3238 \]
\[ R^2 = 0.9945 \]

![Figure 1](image)

The durable correlation between calculated and experimental data was observed in the case of trans-conformation of aliphatic substituents (Fig. 1).

Acknowledgements

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References

Co\(^{2+}\) and Fe\(^{3+}\) EPR study of magnetic ZnO nanoparticles for its potential use in cancer cell treatment

Sergey I. Andronenko, Sushil K. Misra

Institute of Physics, Kazan Federal University, Kazan, 420008, Russia
E-mail: sergey.andronenko@gmail.com

1Physics Department, Concordia University, Montreal, QC, H3G 1M8, Canada
E-mail: skmisra@alcor.concordia.ca

Introduction

Nanoparticles are being increasingly recognized for their potential use in biological applications including nanomedicine for cancer treatment. The response of normal human cells to ZnO nanoparticles under different signaling environments was investigated previously and compared to the response of cancerous cells. As a result, ZnO nanoparticles exhibit a strong preferential ability to kill cancerous T cells, compared to normal cells [1, 2]. This ability is enhanced with transition metal ions doping. Therefore careful investigation of local environment and magnetic state of these ions is very important in the study of potential use of ZnO nanoparticles for cancer cell treatment.

Experimental results

An EPR study of ZnO nanoparticles, doped with Fe ions, prepared using acetate method, was recently carried out [3]. Here we present the results of EPR investigations on two types of ZnO nanoparticles, prepared using chemical hydrolysis methods, in diethylene glycol (NL), and in denatured ethanol solutions (QJ), respectively, doped with 0.5 – 10 % Fe\(^{3+}\) and Co\(^{2+}\), which were carried out at X-band (9.5 GHz) at 5 K. To interpret the experimental results, EPR spectra were simulated by exact diagonalization of the spin-Hamiltonian matrix, in order to identify the presence of Fe\(^{3+}\) and Co\(^{2+}\) ions at different magnetically active sites in these samples. The simulation of EPR spectra for NL samples revealed that they contained (i) Fe\(^{3+}\) and Co\(^{2+}\) ions, which substituted for Zn\(^{2+}\) ions, exhibiting axial Co\(^{2+}\) EPR spectrum in crystalline ZnO; (ii) low intense EPR signals in the samples with Co concentration more than 0.5% and less that 5%; (iii) EPR spectrum due to surface oxygen defects; and (iv) FMR (ferromagnetic resonance) from ferromagnetically ordered area, producing very broad signal. Fe\(^{3+}\) and Co\(^{2+}\) EPR lines are broadened due to wide distribution of oxygen defects near surface. Both the paramagnetic Fe\(^{3+}\) and Co\(^{2+}\) ions and the ferromagnetic components are present in NL and QJ samples. EPR linewidth of Co\(^{2+}\) in QJ samples is much larger, than in NL samples.

Origin of ferromagnetism

Recently, Coey et al. [4] suggested new mechanism for ferromagnetism nature, based on charge transfer in defected oxides. They involved the model of Stoner ferromagnetism for explanation of ferromagnetism origin. In this model paramagnetic impurity ions are not ordered and ferromagnetism arises due to defect band electron structure of semiconducting ZnO. In this model, Fe\(^{3+}\) and Co\(^{2+}\) ions and ferromagnetically ordered area exist separately. This model can be applied to semiconducting ZnO.

Conclusion

The main conclusions of our EPR investigations of ZnO nanoparticles are as follows:

(i) The observed EPR spectra provide clear evidence for the presence of both paramagnetic localized Fe\(^{3+}\) and Co\(^{2+}\) ions exhibiting sharp lines, as well as FMR lines, due to ferromagnetically coupled area, producing very broad signal. Fe\(^{3+}\) and Co\(^{2+}\) EPR lines are broadened due to wide distribution of oxygen defects near surface. Both the paramagnetic Fe\(^{3+}\) and Co\(^{2+}\) ions and the ferromagnetic components are present in NL and QJ samples. EPR linewidth of Co\(^{2+}\) in QJ samples is much larger, than in NL samples.

(ii) EPR signal, due to surface oxygen defects, was clearly observed in NL samples, but not in QJ samples. This explains the smaller magnetic moment observed in NL samples, where not all oxygen defects involved in ferromagnetic ordering. QJ samples, on the other hand, exhibit intense FM resonance signals, suggesting that all oxygen defects in them are magnetically coupled. This accounts for their stronger ferromagnetism.

Acknowledgements

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References

Registration of magnetic resonance from nuclei other than protons on 0.5 Tesla MRI scanner

Nikolay V. Anisimov, O. Pavlova, M. Gulyaev, A. Samoylenko, Yu. Pirogov

Faculty of Fundamental Medicine, Lomonosov Moscow State University, Moscow, Russia
E-mail: anisimovnv@mail.ru

Introduction

In this paper we report on additional technical capabilities that were found in a typical MRI scanner – Bruker Tomikon SS0 (0.5 T). These may be employed for a wide range of NMR applications – high resolution NMR spectroscopy (MRS), MRI and NQR. The main attention is directed to detecting fluorine (19F) signals. Interest in this nucleus consists in prospects to use perfluorocarbons as blood substitutes and MRI contrast in medicine [1].

Materials and methods

This study was initially focused on registering fluorine nuclei. It turned out that the resonant circuit, which includes a built-in magnet gap transmitter coil, is tuned only on the proton NMR frequency (21.08 MHz). It can be not returned on the fluorine NMR frequency (19.83 MHz). Therefore, we were looking for other options for the transmitter coil and adopted firm resonator intended for the study of the knee. By modifying its electronic components it has been transformed to work as a transceiver. Measurements were preceded by experiments using the homemade transceiver probeheads. As a result we have gained experience registering MRS not only from the proton 1H and fluorine 19F, but other nuclei - phosphorus 31P, carbon 13C, deuterium 2D. Their resonant frequencies are respectively, 8.53, 5.30 and 3.24 MHz. For some nuclei other than protons (19F and 31P), technique to obtain MRI images was debugged. In addition, 35Cl NQR signal from powdered KClO3 placed outside of the polarizing magnet was successfully registered.

Results

By optimizing the parameters of the transceiver coils (design and location), MRS is possible without the long-term accumulation of signals. A large number of scans (~103 or more) is required only for nuclei with low natural abundance - 13C, 2D. The MRS and NQR from other above mentioned nuclei were recorded with a single scan. The same applies to isotopically enriched nuclei. Examples of MRS and MRI are shown in Figure 1.

Left: the 19F MRS and MRI (one of 5 slices in two projections) from a cylindrical vessel (H/Ø = 4/2 cm) filled with perfluorocarbon. These MR images were obtained in 1 minute using multiple spin-echo - TR/TE\textsubscript{min} = 470/12.5 ms, ETL = 8, (in-plane resolution 1 mm, slice thickness 1 cm).

Center: 13C MRS of ethanol after 1.5 hours signal accumulation, Right: 35Cl NQR spectrum from from powdered KClO3 after one scan.

Discussion

It is interesting that according to firm documentation, the MRI transceiver tract is not suitable for registration of nuclei other than protons. Indeed, an output RF amplifier LPPA 2120 (Dressler) and a preamplifier HPPR (Bruker) equipped with filter X-BB31P have the bandwidths declared: 19-22 and 12-32 MHz respectively. Really their bandwidths are much broader. Probably the MRI manufacturer is interested only in narrowly targeted use of its products. Therefore it declares only those characteristics that lead away from the temptations to use the equipment for questionable applications. May be that’s why transmitter coil was specially designed so that it cannot be tuned to 19.83 MHz.

Conclusion

We revealed significant potential for use of the MR scanner for multi-nuclear magnetic resonance applications. The results obtained by MRI and MRS fluorine nuclei give reason to hope that the registration of these nuclei can be carried out and not only in studies of laboratory animals, but also man. Obviously the registration of the NMR spectra in weak fields (0.5 T) is of only methodological interest. MRI is of interest in any field. But registration of nuclei other than protons and fluorine in weak fields is while not widespread due to insufficiently high sensitivity of the method. As for NQR, this method is now little used in structural studies, not at least because of the lack of specialized equipment. MRI and NMR spectroscopy equipment can be adapted to solve this problem.

References


Figure 1. MRI, MRS and NQR spectra which were obtained using 0.5 T MRI scanner. Spectrum widths are 3.2, 2, 40 kHz
Whole-body NMR spectroscopy as a tool to assess human body composition

Nikolay V. Anisimov, E. Shalamova, K. Volkova, M. Gulyaev, A. Samoylenko

Faculty of Fundamental Medicine, Lomonosov Moscow State University, Moscow, Russia
E-mail: anisimovnv@mail.ru

1Semenov Institute of Chemical Physics, Moscow, Russia

Introduction

Methods for evaluating the content of fatty tissue in the human body are described. They are based on the analysis of MR images and recording the NMR spectra of the whole body. Particular attention is paid to the spectroscopic method, where the evaluation is made by analysis of the intensities ratio of water and fat peaks. Early measurements were performed on mice by a high field NMR spectrometer [1]. Interest in such measurements is due to the fact that they are easy to implement and take little time. But the main thing is that there is correlation between the intensity ratio of peaks and the content of fat in the body of an animal. The aim of our work was to adapt the method used on small laboratory animals to human studies.

Materials and methods

The measurements were performed on a standard (horizontal bore magnet) 0.5 Tesla MR scanner (Bruker Tomikon S50). NMR spectra were recorded from all parts of the body, and then summed. In the total spectrum, peaks of water and fat were defined - figure 1. The analysis of peak intensities (I_W and I_F) gave information about the content of fat in the human body.

Results

The measurement results for the 8 test subjects (6 females and 2 males) are presented in the table below.

<table>
<thead>
<tr>
<th></th>
<th>f1</th>
<th>f2</th>
<th>f3</th>
<th>f4</th>
<th>f5</th>
<th>f6</th>
<th>m7</th>
<th>m8</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ</td>
<td>960</td>
<td>985</td>
<td>997</td>
<td>1000</td>
<td>1014</td>
<td>1016</td>
<td>1045</td>
<td>1175</td>
</tr>
<tr>
<td>I_f/I_w</td>
<td>0.97</td>
<td>0.84</td>
<td>0.93</td>
<td>0.77</td>
<td>0.63</td>
<td>0.61</td>
<td>0.31</td>
<td>0.42*</td>
</tr>
<tr>
<td>V_f/V</td>
<td>-</td>
<td>0.46</td>
<td>0.42</td>
<td>-</td>
<td>0.32</td>
<td>-</td>
<td>-</td>
<td>0.27</td>
</tr>
</tbody>
</table>

One can notice that both parameters I_f/I_w and V_f/V are approximately linearly dependent on average density of the body. In particular it indicates to correlation between fat content in human body and intensity of fat peak in the whole body NMR spectrum.

The problem connected with low magnetic field (0.5 T) was revealed. Width of the lines appeared to be comparable with the distance between them. It leads to the difficulties not only of measuring integrals of spectral lines but also the differentiation of peaks. Because of this in low field one can obtain a doubtful result for a very lean subject – see value I_f/I_w for m8 (marked with an asterix) in the table.

Conclusion

Measurements indicate a correlation between the average density of body and fat in it. It is consistent with the results of work [1]. It is preferable to perform spectroscopic measurements at a stronger magnetic field (1.5 T and more) to obtain whole body high resolution NMR spectra.

References

Development of Earth’s field nuclear magnetic resonance (EFNMR) setup for applications in security scanning devices

Erdem Balç, Hakkı Acar, Georgy V. Mozzhukhin, Bulat Z. Rameev, Pavel A. Kupriyanov, Alexander V. Ievlev, Yuri S. Chernyshev, Artur R. Lozovoy, Ruslan V. Archipov

Gebze Institute of Technology, 41400, Gebze-Kocaeli, Turkey
E-mail: erdembalci_05@hotmail.com

1Saint Petersburg State University, 198504 Saint Petersburg, Russian Federation
2Kazan Federal Volga-region University, 420009 Kazan, Russian Federation

Introduction

Recently, there has been a renewed interest in the Earth’s field nuclear magnetic resonance spectroscopy (EFNMR), which has been known for more than 60 years [1, 2]. It has attracted an attention of researchers as inexpensive alternative to the high resolution NMR spectrometers in a number of applications. As early as in 1965, G. Bene et al. showed that it is possible to measure heteronuclear J-couplings in the Earth’s field NMR [3]. It has also been stressed that some information accessible in low fields is hard to obtain in high fields [4], e.g. there are the benefits in the relaxation measurements made at low fields [5-7]. Another important fields for potential EFNMR applications are security scanning devices [8, 9], and the MRI imaging combined with MEG in medicine [10]. However, improvement of the signal to noise ratio (SNR) and spectral resolution (SR) are the crucial points in order to use this technique effectively. Thus, new effective approaches and ideas must be developed in order to increase the low SNR and SR in the EFNMR measurements.

Experimental setup

Our EFNMR setup consists of Magritek low-frequency (0-1 MHz) KEA-2 NMR console. A pulse current source has been constructed to apply the DC current pulses to the polarizing coil. Serially-connected active and passive filters have been developed to filter the low/high frequency noise (i.e., 50 Hz harmonics) and to increase the SNR. The active filter works at a 200 Hz (narrow) band. The cut-off frequency of passive filter (high pass) is 1 kHz.

Experimental results

The transmitting/receiving probe has been constructed as the gradiometer coil. The probe is composed of two coils wound on opposite directions in order to mitigate the noise effect of radiofrequency interference (RFI). The probe was placed in the 7 mm thick aluminium box and additionally a double copper-aluminium metal folio was wrapped around the probe to decrease further the SNR. All these measures have resulted in about 65 dB of the RFI. As additional measure to increase the SNR, the pre-polarization technique has been used. In this technique, a polarizing magnetic field of 100 Oe, orthogonal to the Earth’s field, is applied to the sample. As result of pre-polarization technique the SNR is increased by factor of 250. The pre-polarization coil consists of 3 layers, each of 125 turns wound with 1 mm thick copper wire on a tellon cylindrical frame. In the standard laboratory conditions the uniformity of Earth’s magnetic field is usually low due to presence of magnetic materials around the EFNMR setup (e.g. due to iron items in the lab and in the construction wall). Therefore, the shimming should be applied to compensate the gradient of the Earth’s magnetic field and to obtain the better SR. For that we constructed a shimming system, consisting of a 3 sets of paired coils for each orthogonal axes of x, y and z. A wood box of cubical shape (outside of aluminium shielding box) has been used as a fixture for the coils (Fig. 1).

Experimental tests of the EFNMR setup have been performed on H2O and Fluorine samples. The long decay time of free induction decay signal of the H2O sample reveals rather good homogeneity of the Earth’s magnetic field (Fig. 2).

Conclusions

We have developed and tested the EFNMR system, consisting of KEA-2 NMR unit, polarizing coil, the gradiometer RF probe, RF shield box, a metal folio wounded around coil and shimming coils. It has been demonstrated that the system improves the SNR and the SR for several orders of magnitude. Further research is planned to apply the constructed EFNMR setup in the studies of various compounds and to develop the security scanning system.

Acknowledgements

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References

Application of magnetic resonance spectroscopy in the diagnostics of multiple sclerosis

Yu. V. Bogachev, V. A. Fokin¹, O. A. Cherdakov, D. Yu. Sugonyako

Department of Physics, Saint Petersburg Electrotechnical University "LETI"
¹S.M. Kirov Military Medical Academy

Introduction

The modern development of MR-spectroscopy has provided an opportunity to study certain chemical compounds or metabolites in a variety of pathologic processes affecting CNS in vivo. In addition to traditional MRI proton MR-spectroscopy (1H-MRS) has significantly shed light on understanding of the pathophysiology of multiple sclerosis (MS) and response to therapeutic treatment. With the help of MRS biochemical changes and their course in time can be analyzed. In acute plaques choline and lactate increase at demyelinating process early, reflecting inflammation and demyelination, which is followed by reduction of NAA in most foci. That reflects damage or loss of axons (Dong-Hyun Kim, 2012). The peak of NAA is perhaps the most informative spectral value, and the level of losses in NAA reflects severity of damage of axons and correlates with the level of disability in the late phase (Ponnada A. Narayana, 2005). A partial or full restoration of NAA might happen with time [1].

Experimental Methods

Proton MR-spectroscopy of the brain was performed on a MR scanner Siemens «Magnetom Symphony» with a magnetic field strength of 1.5 Tesla. MRI examination included following steps:

- positioning the patient under examination;
- performing of traditional MRI;
- conducting MR spectroscopy on hydrogen;
- performing of MRI of the brain after intravenous administration of contrast agent;
- spectrogram analysis, constructing of parametric and colored maps of metabolite distribution and their ratios.

In this paper we have analyzed data of 6 patients suffering from multiple sclerosis. Thus, changes in metabolites in 16 MS plaques were studied.

In order to get MR spectra the methodology of Multi Volume Spectroscopy (MVS) was used. 64 MR-spectra were obtained for each patient.

Results and Discussion

The following metabolites were determined in the MR-spectrum: N – acetylaspartate (NAA), choline (Cho), creatine (Cr) (Fig. 1).

In all patients, the lactate peak (Lac) and lipids (Lipid) were not detected in the spectrum.

Additionally, according to the data provided by MRI with contrast enhancement only one plaque out of 16 investigated accumulated the contrast agent as on the diffuse type.

The results show that average concentration of NAA in MS plaques decreased by 14.5% compared with the norm. The average concentration of Cho in MS plaques increased by 9.9% compared to the norm.

The ratio of NAA / Cr in the plaque of multiple sclerosis decreased compared to the same area in the healthy hemisphere by 15.5%. At the same time the ratio of Cho / Cr increased by 2.3% in the demyelination sector (Fig. 2).

Subsequent MRS showed changes in absolute and relative concentrations of the metabolites in plaques of multiple sclerosis in a patient. The ratio NAA/Cr in the first demyelination focus increased by 77% compared to the initial examination. In the second focus it increased by 52%, in the third – by 38%.

In this paper, we confirmed that according to MR spectroscopy on hydrogen one can follow the development of the MS disease and determine therapeutic effect.

References

NMR spectroscopy of benzimidazole derivatives synthesized in subcritical water

Sergey N. Borisenko¹, Anna V. Lekar¹, Elena V. Vetrova¹, Sofya L. Srabionyan, Svetlana N. Sushkova¹, Gennadii S. Borodkin¹ and Nikolay I. Borisenko²

¹Research Institute of Physical and Organic Chemistry, South Federal University, Russia, Rostov-on-Don
²Ecological-Analytical Center, South Federal University, Russia, Rostov-on-Don
E-mail: boni@ipoc.rsu.ru

Introduction

The purpose of this study was to develop and study of experimental schemes of organic synthesis in subcritical water to give a yield of the comparable or better compared with traditional methods of synthesis. As a test reaction was chosen synthesis of 2 - (2-pyridyl) benzimidazole started from 1,2-phenylenediamine, and pyridine-2-carboxylic acid.

Experiment

Sub-and supercritical water (t $\leq$ 350 °C, p $\leq$ 218 bar - subcritical water; t $> 350$ °C, p $> 218$ bar - supercritical water) has recently attracted attention as a universal medium for chemical reactions. A characteristic feature of these reactions is that the sub-and supercritical water acts as a non-toxic solvent with good varying physicochemical properties (due to changes in pressure and temperature) [1].

In the present study we explored the possibility of using the synthesis as static installations and flow diagrams, consisting of a high-pressure pump (up to 300 atm). Especially constructed for the purpose of high-pressure cell - stainless steel extractor, a pressure regulator, a stove, providing temperature control with temperature range up to 320 °C [2].

The effect of reaction parameters, such as temperature, pressure, flow rate and the reaction time of the reaction was studies.

Analysis of the reaction products was performed by NMR spectroscopy. Depending on conditions of synthesis in the reaction product observed the compounds 1, 2 and 3 in various proportions.

These results indicate that the proposed pilot scheme may be used for environmentally friendly (Green chemistry) organic synthesis of benzimidazole derivatives in subcritical water. The benzimidazole derivatives synthesized in the subcritical water could used for created the new “low-dose drug” based on glycyrrhizic acid [3].

Acknowledgements

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

References

Synthesis and NMR study of the novel class of tellurazoles – 2-sulphur-functionalized benzotellurazoles

Inna G. Borodkina1, Gasan M. Abakarov2, Gennadii S. Borodkin1, A.-M. M. Ali3, Igor S. Vasilchenko1, P. A. Ramazanova3, Pavel B. Chepurnoi1, Svetlana B. Zaichenko1, Yuriy F. Mal'tsev4, Anatoliy S. Burlov5, Vladimir I. Minkin1

1Institute of Physical and Organic Chemistry, Southern Federal University, Stackhi pr. 194/2, 344090, Rostov-on-Don, Russia, E-mail: nmr@ipoc.sfedu.ru
2Dagestan State Technical University, Shamiya str. 70, 367015, Dagestan Republic, Russia
3Dagestan State University, Gadjiava str. 43a, 367000 Makhachkala, Dagestan Republic, Russia
4Physical Faculty of Southern Federal University, Zorge str., 5, Rostov-on-Don, 344090, Russia

Introduction

Chalcogen containing compounds are a matter of the great interest [1, 2]. From the other hand modern data on the heterocyclic tellurium-containing are comparatively scarce [3]. In continuation of our investigations of organoselenium and organotellurium derivatives we have obtained and studied by NMR novel sulphur-functionalized benzotellurazoles 1-3.

Results and Discussion

Compound 1 was synthesized according to the following Scheme 1:

H2N
H

Scheme 1

This derivative can exist in two forms (Scheme 2):

\[ \text{Scheme 2} \]

IR spectrum of the solid sample of 1 demonstrates bands at 1315 and 3105 cm\(^{-1}\) which may be assigned to the stretching of C=S and N-H groups respectively. It may point to the realization of the form 1b in the solid state.

NMR spectra of 1 registered on the AVANCE-600 spectrometer in DMSO-d\(_6\) show (ppm) the next signals (atom labeling see on Fig. 1): 1H - 7.09 (1H, dd, H-C5), 7.27 (1H, dd, H-C6), 7.36 (1H, dd, H-C4), 7.73 (1H, dd, H-C7), 13.36 (1H, s, HN); 13C - 114.73 (C4), 120.78 (C8), 123.86 (C5), 127.21 (C7), 132.14 (C6), 146.64 (C9), 195.41 (C2); 15N - 199.40; 125Te - 990.15.

The final conclusion on the existence of 1 in solution in the form 1a was made on the base of the correlation spectrum \(^1\)H,\(^{15}\)N HMBC demonstrating distinct cross-peak \(^1\)H,\(^{15}\)N.

Alkylation of 1 may occur by two pathways (Scheme 3):

\[ \text{Scheme 3} \]

\[ \text{Figure 2} \]

Interesting feature of the \(^1\)H NMR spectrum of 3 is inequality of proton signals of aminogroup that may be caused by participation of one proton in the formation of hydrogen bond.

\[ \text{Figure 1} \]

Acknowledgements

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

References

Heteronuclear and 2D NMR Investigation of Pyrazole-Quinoline Ligand and its Zn and Cd Complexes


1 Institute of Physical and Organic Chemistry, Southern Federal University, Stachki pr. 194/2, 344090 Rostov-on-Don, Russia E-mail: nmr@ipoc.sfedu.ru
2 Institute of Physics of Southern Federal University, Stachki ave. 194, Rostov-on-Don, Russia
3 A. N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Leninskii ave. 31/4, Moscow 119991, Russia
4 Southern Scientific Centre of Russian Academy of Sciences, Chekhova ave. 41, Rostov-on-Don, Russia
5 National Research Centre “Kurchatov Institute”, Academician Kurchatov sq. 1, Moscow, Russia
6 A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova str. 28, Moscow 119991, Russia
7 Southern Federal University, Sadovaya str. 105/42, Rostov-on-Don 344006, Russian Federation
8 Physical Faculty of Southern Federal University, Zorge str., 5, Rostov-on-Don, 344090 Russia

Introduction

Zinc complexes of azomethine ligands are the matter of interest as active layers for OLED devices owing to their thermal stability with high temperature of vitrification, light sublimation during formation of amorphous films, variability of structures, comparative simplicity of their synthesis, good photo- (PL) and electroluminescent (EL) properties and electron-transfer characteristics.

Chelate complexes containing quinoline fragment are the matter of the great interest. Tang and Van Slyke [1] used tris(8-hydroxyquinolinato)aluminum, playing double role both as light emitter and electro-transfer material, in construction of the first OLED device working at low temperature.

In continuation of the efforts on the search of the advanced PL and EL materials, usable for construction of OLED devices, we have obtained novel aminomethylene derivative of 1-phenyl-3-methyl-4-(quinolyl-3-methyleneamino)-1-H-pyrazole-5-one with 3-aminoquinoline (I) and synthesized zinc and cadmium complexes (II, III) on its base.

Results and Discussion

Compound I as it shown by IR (vNH) and NMR spectra data (double =CH- and –NH- signals) exists in ketimine form (Fig. 1) both in solid and solution.

Zinc and cadmium complexes were obtained by coupling the ligand with metal acetates in methanol. Disappearing the NH stretching band in IR spectra and NH signal (as is singlet character of CH signal) in 1H NMR spectra of complexes point to the deprotonation of the ligand molecule under complexation.

Signal of H(6) proton in III is doublet (J_{H(6)-Cd} = 34.5 Hz) and signal of 113Cd (δ = -580.71 ppm) is triplet that is comparatively seldom in registration of 113Cd NMR spectra of cadmium metallochelates.

So, we have obtained novel zinc and cadmium metallochelates of pyrazole-quinoline containing ligand – potential working elements for OLEDs.

Acknowledgements

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

References

The application of the NQR relaxometry for the study of phase transitions in the molecular crystals

Philipp Dolinenkov¹, Irina Korneva¹,², Nikolay Sinyavsky¹,²

¹Immanuel Kant Baltic Federal University, A. Nevsky St. 14, 236041 Kaliningrad, Russia
²Baltic State Academy, Molodiazhnaya St. 6, 236029, Kaliningrad, Russia

Introduction

The polymorphic transitions are the phase transitions causing regrouping of molecules in crystals. Thus there are serious problems with the offer of mechanisms which could explain, that actually occurs with molecules in time and in space.

The purpose of the present work is researching of the phase transitions in paradichlorobenzene by NQR relaxometry methods with use of Laplace transformation inversion [1]. The choice of the paradichlorobenzene as a sample is caused by that this substance was studied by a wide range of experimental methods including NQR. However, the mechanisms of phase transitions in p-C₆H₄Cl₂ not been clarified in detail to the present time.

Results and discussion

The experiments were performed on the Tecmag Apollo NQR spectrometer with TNMR software. The well-known pulse sequences were used to measure the relaxation times. Kinetics Exp TNMR script was used at studying processes in time. The program RILT described in work Iari-Gabriel Marino [2] was used for inversion of Laplace transformation. The polycrystalline samples were obtained from the melt. The crystalline phase of the sample was identified using known temperature dependences of ³⁵Cl NQR frequencies for different paradichlorobenzene phases.

Conclusion

It is established, that after hardening of p-C₆H₄Cl₂ from the melt only β-phase is formed which in time spontaneoulsy turns into a stable α-phase. In the porous material preliminary impregnated with the molten sample, spontaneous phase transition does not occur and β-phase is kept steadily.

Acknowledgement

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References
A reduction of concomitant magnetic fields effect through the optimization of the gradient magnetic system

Viatcheslav Frolov, Oksana Ilina
Faculty of Physics, Saint Petersburg State University
E-mail: vfrolov@bk.ru

Introduction

MRI at low field (as EFNMR) and very low (less than the Earth field) more and more become widespread subject of research. In this aspect it is useful to consider effect of concomitant fields for a concrete gradient system. It is known the appearance of gradient of certain component of potential field produces inevitably gradients of other, orthogonal, components [1]. Magnetostatic field is potential, hence this effect is inherent to procedure of getting NMR-image [1]. This effect is negligible for practical MRT, nevertheless it can be important in low field experiments: The less a magnetostatic field strength is and the more a gradient and the sample volume are, the more concomitant gradients effects exhibit [2, 3].

The optimization of NMR-imager gradient magnetic system

An analysis of the contribution of concomitant gradient magnetic fields to quality of magnetic resonance imaging is made. Their revealing in the concrete gradient system, namely in the system of two coaxial coils is considered as an example. A design of such systems supposes the best linearity of the magnetic field dependence on a coordinate along the axe. in explored volume. But taking into account the concomitant gradient effect requires to modify the design parameters. The direct calculation of magnetic field spatial distribution generating by a such system was performed. The conditions of the smallest distortion are determined.

Calculation methods

The calculations of the magnetic field components out the axe of a gradient system have carried out with known integral formulas based on Bio – Savart – Laplace low [4]. An optimization of the coil interspacing are made according to the criterion of standard deviation minimum for dependence of the field total module from a straight line. The numeric computations have performed with the environment MathCad 14.

Results

Results of the concomitant gradient analysis will be presented. The optimum parameters depend both on relation of the maximum field generated by gradient system in sample volume to the main static field, and on dimensions and position of the sample.

Conclusion

It is shown a magnetic field concomitant with a longitudinal gradient enhances the nonlinearity of coordinate dependence of the field. This misrepresents MRI because of scale variations within investigated object. To minimize the harmful effect, it is necessary to change parameters of the system generating magnetic field gradients. For example, in system from two coils the distance between the coils should be incremented in comparison with Maxwell position to 1.35 coil radius. In so doing in the worst extreme case when the main homogenous magnetic field is negligible, the standart deviation from linearity within object in the size about of half-radius of coils will make no more than 4 %.

References

Opportunity to enhance the contrast of MRI images using dynamic nuclear polarization in low magnetic fields

Dmitry M. Furman, Viatcheslav V. Frolov
St. Petersburg State University, 1 Ulyanovskaya st., Petrodvorets, 198504, St. Petersburg, Russia
E-mail: dm.furman.nmr@mail.ru

Introduction
Dynamic polarization of nuclear using Overhauser effect (DNP) is new and promising direction in the application of magnetic resonance imaging (MRI). Researches in the application (DNP) in low magnetic fields gained widespread popularity the past 15 years. Application of this technique in MRI remains a scientific problem and it is not beyond the scope of individual experiments.

Theoretical assumption
Using the method of dynamic nuclear polarization, based on the Overhauser effect can be increased intensity of the NMR signal. However, the frequency of the polarizing pulse for most MRI scanners (more than 1 T) is equal to a few hundred gigahertz, which destroys many organic substances and dangerous for living organisms. The use of weak fields on the order tens of mT allows you to use the polarizing pulse order of hundreds of MHz, which is more secure.

Experimental review
Now most of the experiments conducted in fields of 1 Tesla. Experiments DNP in MRI (OMRT) are able to pass under normal temperature conditions without strong cooling investigated object of study. Observed improved signal / noise ratio, as well as the ability to use both the spin echo (SE) and gradient echo (GRE) for space encoding. In the experiment, nitroxyl radicals as contrast agent (TEMPO (C9H18NO)), due to their good stability over time. Method contrast is that the places where the application of this radical DNP MR image is more intense signal (from the hydrogen nuclei). DNP method is applicable to the nuclei $^{13}$C, $^{15}$N, $^{31}$P and $^1$H.

![Figure 1. OMRI protocol (from [1])]()

Scientific prediction
The DNP by Overhauser effect is able to occur in the low magnetic fields. DNP can be applied in the case of these fields. OMRT can be used to improve the quality of the MRI image, and to more accurately tissue staining. The use of low magnetic field will produce an in vivo MRI.

References
Nicotinamide solvation in aqueous ethanol: $^{15}$N NMR study

G. A. Gamov$^1$, S. V. Dushina$^1$, V. V. Aleksandiiskii$^{1,2}$, V. A. Sharnin$^1$

$^1$Research Institute of Thermodynamics and Kinetics of Chemical Processes, Ivanovo State University of Chemistry and Technology, Ivanovo, Russia
E-mail: kax504@isuct.ru
$^2$Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia

Introduction

3-pyridinecarboxamide (nicotinamide, B3 vitamin, PP provitamin) as well as nicotinic acid is an antipellagric agent. In the living tissues both of compounds participate in synthesis of NAD and NADP coenzymes. Furthermore, nicotinamide has a number of additional functions. It influences protein and RNA formation, synthesis of some other bioactive molecules, etc.

On the other hand, 3-pyridinecarboxamide is a promising compound which could be used as basis for synthesis of metal complexes with greater biological activity than in case of non-bound ligand. Nicotinamide is known to form the coordination bond with d-metal ions donating them a lone electron pair of nitrogen heteroatom. The solvation state of donor centre greatly affects the complexation thermodynamics. Therefore, the solvation of this molecular fragment should be studied in details.

Experimental

The HMBC $^{15}$N-$^1$H spectra of nicotinamide solutions (0.2975-0.3025 mol/kg) in aqueous ethanol were recorded on Avance III Bruker 500 NMR spectrometer with operating frequencies of 50.701 MHz at the 298.2 K temperature. A 5 mm 1H/31P/DNBBzN Triple Resonance Broad Band Probe (TBI) was employed. Nitromethane was used as external standard.

An experimental error of chemical shift measuring did not exceed 0.1 ppm. The temperature maintaining using temperature unit BVT-3000 was ±0.1 K.

![Figure 1. Dependence of $^{15}$N nicotinamide heteroatom chemical shift on aqueous ethanol solvent composition. Chemical shift values are given with respect to $\text{CH}_3\text{NO}_2$.](image)

The nicotinamide of extra pure grade was used without additional purification. The deaerated bidistilled water was used for every solution preparation. The ethanol was purified via distillation at atmospheric pressure. Water content in the alcohol was controlled by densitometry (3.98 mass. %) and was taken into account when the binary solvents were made. The results of HMBC $^{15}$N-$^1$H study of nicotinamide solutions are given in Fig. 1.

Discussion of the results

The chemical shift of heterocyclic nitrogen increases smoothly depending on the aqueous ethanol solvent composition (Fig. 1). It probably means the nearly uniform replacing of H-bonded complexes of heteronitrogen with water by that with ethanol in the overall interval of binary solvent composition.

Nevertheless, we should note the more significant changes in the nitrogen shielding at some ethanol concentrations. When going from mixed solvent with $X_{\text{EtOH}} = 0.16$ m.f. to that with $X_{\text{EtOH}} = 0.25$ m.f., the variation of $^{15}$N$_{\text{heter}}$ chemical shift is 0.8 ppm, but when going from solvent with $X_{\text{EtOH}} = 0.25$ m.f. to that with $X_{\text{EtOH}} = 0.3$ m.f., i.e. organic component content increases by 0.05 m.f., the chemical shift gains 1 ppm. In the interval of binary solvent composition of $X_{\text{EtOH}} = 0.16 – 0.3$, the replacing of heteroatom nitrogen H-complexes with water by that with ethanol seems to pass in the greater degree than it occurs at other concentrations of organic solvent.

It was shown in our previous works [1, 2] by means of $^1$H and $^{13}$C NMR spectroscopy that the maximal changes in the solvation of heterocyclic fragment occur at $X_{\text{EtOH}} < 0.3$. This data is in accordance with the presented results of $^{15}$N NMR spectroscopic study. However, chemical shifts of nitrogen atom give no possibility to calculate the equilibrium constant of its resolvation process. The thermodynamics of nicotinamide heteronitrogen transfer from water to aqueous ethanol was determined from $^{13}$C NMR experiment [2].

Acknowledgements

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References

Signal Denoising in Earth’s Field Magnetic Resonance
Ilknur Gunduz¹, Ivan Mershiiev, Erdem Balci¹, Galina Kupriyanova², Georgy Mozzhukhin¹,³, Bulat Rameev¹
¹Gebze Institute of Technology, P.K.141,Gebze-Kocaeli, 41400 Turkey
²Physics-Technical Faculty, Baltic Federal State University, Kaliningrad, 236014, Russia
³Physics department, Kazan Power State Engeering Ubiversity, Kazan, Russia
E-mail: ilknurgunduz34@gmail.com

Introduction
The identification of chemical compounds by a low field NMR includes detecting NMR relaxation parameters for the selected material [1]. Earth’s Magnetic Field NMR (EFNMR) has some perspectives for application like analytical method in mobile systems. However, the Signal to Noise Ratio (SNR) of the NMR signal in Earth’s magnetic field is very small in comparison of high field NMR [2]. Outside interference has very high level compare to EFNMR signals. We analyzed of EFNMR signals and applied the wavelet processing technique for EFNMR signal de-noising.

Statistical analysis of signals in EFNMR spectrometer
In main methods of the gain of SNR it is usually accepted that noise is Gaussian (“white”). Thus the first important question is following: what is statistics of the noise signal? May it is possible to accept (use) the Gaussian distribution for the noise? We studied statistical properties of the noise in EFNMR spectrometer. For this purpose we compared the statistical properties of the noise signal and model noise signal. Usually we also suppose that noise model signal is a “white” Gaussian noise. Then we compared the experimental noise in our spectrometer and model noise signal.

In our measurements, SNR was measured by relation of the maximum amplitude to noise dispersion. SNR after quadrature detector is close to Rayleigh-Rice distribution. It means that the noise signal distribution is normal. Thus we can conclude that the noise in our experiments is “white”. Minor distortions from the fit could be found, however in first approximation, it is clear that the noise distribution is “normal”.

The application of wavelet analysis to EFNMR de-noising
Two ways of the signal representation are usually applied: time domain and frequency domain. In fact the wavelet transform gives a possibility for the two-dimensional representation of the signal amplitude in both time and frequency dimensions. For simplicity in our analysis we use only figures where the amplitude is shown as function of one parameter only (frequency or time). We used two approaches for the signal de-noising: a) first approach is based on the wavelet filtering of a signal in the frequency domain; b) second one is based on de-noising of a signal by Donoho-Johnstone method [3] with the next restoration of the signal in the time domain. For wavelet filtering of a signal in the frequency domain Matlab Wavelet ToolBox has been used. Different levels of decomposition and various modifications of wavelet filtering were applied to obtain the best SNR. The results of the application of wavelet transform reveal that de-noising using both Symlet and Doubeshi wavelets work well for our EFNMR spectra. It should be however noted here that a genuine signal has rather high SNR of about 10. Therefore wavelet filtering in the frequency domain was enough to obtain rather good results. The application in time domain based on Donoho-Johnstone method shows effective denoising too. However, comparison of Symlet wavelet with Dobeshi wavelet reveals that the last one gives slightly better results.

Conclusion
We applied the wavelet methods for time domain and frequency domain. Use of both Symlet and Doubeshi wavelet produces the similar results in the frequency domain, while Doubeshi wavelet decomposition to level 4 and 8 gives better results in the time domain. Thus we demonstrated that various variants of wavelet transform could be used for successful denoising of the EFNMR signal. Also we applied wavelet transform approach in signal processing for recognition of a priory known signals (i.e. for identification/detection of substances) as well as for denoising of the spectra of mixtures or fine structure of spectra of EFNMR signals.

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References

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The structure connectome: a review

Oksana Ilina, Viacheslav V. Frolov

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

Introduction

The human brain has between 50–100 billion nerve cells or neurons that constantly interact with each other. Mapping the human brain is one of the great scientific challenges of the 21st century. This review is about a connectome, the complete map of the neural connections in a brain.

History of connectomics

A field of neuroscience that analyzes neuronal connections is called the connectomics. Connectomics actually started before the word existed. For example a nearly complete cellular connection map of the nematode Caenorhabditis elegans was represented in 1986 [1]. The term “connectome” was first defined in 2005 by O. Sporns as “a comprehensive structural description of the network of elements and connections forming the human brain” [2]. Independently and in parallel, in 2005 in his Ph.D. thesis P. Hagmann coined the term “connectomics”, defined as the study of the brain’s set of structural connections [3]. In 2009 the five-year Human Connectome Project (HCP) was launched. The purpose of this project is to characterize brain connectivity and function and their variability in healthy adults.

Connectome construction

Methods

Several methods are used in obtaining connectivity information: electroencephalography (EEG), magnetoencephalography (MEG), positron emission tomography (PET), single-photon emission computed tomography (SPECT), electron microscopy techniques (EM) and other modalities. But the main methods for mapping the connectome are the functional magnetic resonance imaging (fMRI) and the diffusion MRI. These methods allow to obtain functional and structural connectomes, respectively. The analysis of structural and functional connectivity between different regions of the brain provides a comprehensive insight into its underlying organization.

Structural connectome construction

It was observed that white matter exhibits reliable anisotropic properties and that it is possible to infer fiber tract trajectories using diffusion MRI (Diffusion Tensor Imaging). But DTI was unable to resolve multiple fiber bundle orientation inside an imaging voxel. The methods that allow to solve this problem are Diffusion Spectrum Imaging (DSI) and High Angular Resolution Diffusion Imaging (HARDI) techniques. Challenges and perspectives of these methods and the structural connectome construction were reviewed.

References

**Analysis of the identity and quality of peptide-based drugs by quantitative $^1$H NMR spectroscopy (qNMR)**

V. A. Ivlev, G. A. Kalabin, V. G. Vasil’ev

Peoples’ Friendship University of Russia, Moscow, Mikluho-Maklay st., 10/2
E-mail: chemistron@mail.ru

**Introduction**

Quantitative $^1$H NMR spectroscopy is the primary method of quantitative measurements [1]. Through a combination of unique opportunities (short measurement time, accuracy and precision, no need for standards and calibration, nondestructive and conclusiveness, no need to extract the analyte from a mixture, determination of the complete molecular structure) qNMR as the differential isotope method has no analogues for the analysis of pharmaceuticals and their metabolome, various natural objects and complex mixtures.

**Typical problems solved by qNMR in pharmaceutical chemistry**

- Identification of the structure of drug substances;
- Quantitative determination of the active substance;
- Identification and quantitative determination of residual solvents and impurities;
- Determination of stability and structure changes of medicines during the storage;
- Getting of a “fingerprint” of multicomponent systems (extracts, infusions, etc.);
- Determination of composition of multicomponent drugs;
- Determination of isomeric composition, relationship of diastereoisomers and enantiomers (using chiral solvents and complexing agents).

**Objects of study**

In this work, possibilities of the method are applied to the analysis of substances and medicines developed in Russia - thymodepressin(A), sedatin(B) and imunofan(C).

Monographs dedicated to the analysis of transbuccal films were developed for medicines A u B (substance concentration - 0.037 g/ml and 0.7 mg/ml, respectively) and for the medicine (B) – in the form of injection solution (50 mg /ml).

Quantitative determination was held by comparing integral intensities of inputted reference compound and signals marked with symbols “*” in the formulas. A typical spectrum of peptide drugs is shown on an example of thymodepressin as transbuccal film in Figure 1.

![Figure 1](image_url)

The active compound content in the weighed portion calculated by the following equation:

$$m(X) = m(IS)/M(IS) \cdot (I(X)/N(X))/(I(IS)/N(IS)) \cdot M(X)$$

where X - the active compound, IS - internal standard, m - mass, M - molar mass, I - the integral intensity of signals, N - the number of protons.

**References**

NMR-complex for diagnosis and control of cure of kidney scarcity decease
R. S. Kashaev, A. S. Kopilov
Chair of Instruments and Automated Drive, Kazan State Power Engineering University
E-mail: kashaev2007@yandex.ru
Kazan State Medical Academy

Introduction
Medical ordinary clinics need cheap complexes, able to determine the decease stage and control of its cure, in particular kidney scarcity (KS). It can be done using dependences of nuclear (proton) magnetic resonance (NMR) structure-dynamical parameters from physical-chemical parameters of blood and plasma changes, which always accompany sharp and chronic kidney scarcity. To realize such approach corresponding device must be elaborated and NMR relations must be revealed.

NMR-relaxometer for decease diagnosis
Was elaborated portable relaxometer NMR, presented at fig.1 and defeated by RF patents №67719, №2319138, №73486. Power supply is autonomous – from accumulator or grid. Control and data processing – by Notebook. Used magnetic system from NdFeB alloys. Magnetic field inhomogeneity is less, than 4⋅10⁻⁷ B₀. Inhomogeneity of B₀ < 2% in 75% of its coil volume.

Dependence of NMR-parameters from blood phys-chemical properties
Last decades NMR-tomography is widely used for deceases diagnosis. In Zavoisky Kazan Physical-Technical Institute was elaborated and produced NMR-tomograph, successfully exploited in several medical centers. Using NMR-relaxation parameters of blood, plasma or urea of patients, diagnosis, control of their treatment can be done using NMR data, which on the example of cancer diagnosis demonstrated its powerfullness. However practically were not established correlations for KS. Interesting also to study by NMR the influence of hemodialysis on blood structure.

Up to contemporary times discussed the influence of hemodialysis on rheological properties of blood [1]. Majority of the works are devoted to study of influence of hemodialysis on aggregation of eritrocites and trombocites and the prognosis of KS terminations stages are made on clinic laboratory statistics and histomorphology data. NMR-tomography was used for qualitative-quantitative analysis of kidney toomographs and spin-lattice relaxation times T₁, protons density, intensity of NMR-signals on NMR-tomograph BMT 1100 (Bruker) [2].

According to Asaba H. [3] at pathological stages of KS appear sufficient amount of peptides with molecular mass 300-5000 dalton – so called substances of the middle molecular mass (MMM), which are the products of the peptide leasing and which work as secondary endotoxines. Appeared also the communications about spectrophotometric method of determination of intoxication index and catabolic pool of MMM in plasma from absorbance at the wave length λ = 238-258 nm. Was confirmed, that pool of MMM in blood is stable and is determined by organism state [4].

We revealed the relations between stage of KS and NMR-parameters. Relaxation times measurements were done using Carr-Parcell-Meiboom-Gill method in blood plasma. Spin-echo envelope had two components with different relaxation times, but in the blood could be extracted up to three components with error ± 4%.

Measurements results
Was revealed linear relation between $T_{2\lambda}$ and мочевина concentration $M$, normalized to peptide concentration in blood. For creatinin $K$ exponential relation between $T_{2\lambda}$ and its concentration. Correlations are described:

$$M = 54 - 0.033T_{2\lambda}$$

(1)

$$K = 4.7 \exp(-T_{2\lambda}/C)$$

(2)

Sensitivity $S$ of relation $M(T_{2\lambda})$ equals $S = 33$ (unit/sec)
Constant $C$ in equation (2) correspond to the shortest relaxation time $C = 577$ ms, probably corresponding to terminal stage of the kidney decease, at which $K = 4.7$.

Obtained results can be explained by the increase of the “middle weight substances” (MWS), having short relaxation times due to increasing restriction of molecular motions. Beeing the products of peptide leasing, they, probably act as secondary endotoxines.

References
NMR – study of the water molecules on the microbial cell surface at microbial growth process

R. S. Kashaev, A. S. Kopilov

Chair of Instruments and Automated Drive, Kazan State Power Engineering University
E-mail: kashaev2007@yandex.ru

Introduction

Biological processes are controlled by molecular dynamics on the surface, because the structure of water, surrounding cell, determines the membrane ability to provide substrate and energy exchange with environment. NMR-method gives opportunity for study of mentioned problems. It is the most powerful analytic method for quantitative investigations of phases in microbial oil/water dispersions in-vivo [1-2].

Apparatus and methods

Measurements of the NMR-parameters: spin-spin relaxation times $T_2$ and proton populations $P_{sw}$ were performed using Carr-Purcell-Mayboom-Gill pulse sequence on the elaborated relaxometer NMR, defeated by RF patents №67719, №2319138 [3], №73486. Power supply is autonomous – from accumulator or grid. Control and data – by Notebook. Coefficient of sensitivity is $K = v_0^2 D^3 [\text{MHz}\text{cm}^2]$ $= 2700 - 4150$, where $v_0 = 10-12$ MHz – frequency of proton magnetic resonance, $D = 10-30$ mm – diameter of the coil. Power $< 15$ VA. Weight $< 15$ kg.

Samples of microbial bacteria Pseudomonas Putida and Rhodococcus Robopertinctus were sited on saturated by oil polymer carrier in retort with nourishing solution and cells suspension. Cultivation of oil bacteria communities was processed by professor of Kazan State University Naumova R.P. As a source of substrate were used sulphurdev Devon Romashkinskaya oil (Republic of Tatarstan), which have density $\rho = 880$ kg/m$^3$ with heavy black mineral oil (BMO) fraction with $S = 3\%$ and CH$_3$/CH$_2 = 5.6$. Concentration of microorganism in suspension was measured by light absorption ($\lambda = 580$ nm).

Experimental results

Measurements of relaxation time dependences from bacteria concentration on fig. 1 showed that spin-echo envelopes has two components for nourishing bulk water media with the relaxation times $T_{2A}$ and $T_{2A}$, measured using NMR-parameters: $T = 6$ s, $\tau = 400$ $\mu$s, $N = 4000$, $n = 5-10$; and two components for near microbial cells water protons with the relaxation times $T_{2B}$ and $T_{2B}$, measured using parameters: $T = 2$ s, $\tau = 200$ $\mu$s, $N = 1000$, $n = 50$. Last impulse sequence gives opportunity to measure mainly amplitudes, regarding to $T_{2B}$ and $T_{2B}$ relaxation times. $T_{2B}$ is attributed to protons of water molecules that form solvate envelope as a result of interaction of water OH-groups with NH$_3^+$ and COOH- groups of amino acids of cell membranes, peripheral proteins.

Figure 1. Upper Dependence of proton populations $P_i$ of different relaxation times from $N_i$ concentration in bacteria suspension. $\bullet$ - $T_{2A} = 1.72 \pm 2$ s, $\nu - T_{2A} = 1 \pm 1.2$ s, $o - T_{2B} = 500$ ms, $\Theta - T_{2B} = 120$ ms

The explanation of results can be based on the ability of water molecules to form macromolecular structures or conglomerates of water [4-5] in cell's solvate covers. In order to estimate correlation times of water protons in solvate covers we use the results of NMR relaxation theory of the proton relaxation in solutions in the presence of diamagnetic ions [2]. The relaxation rate $(T_{2s})^{-1}$ in solvate cover will be determined by the contributions from intra, inter molecular interactions and from non averaged proton interactions $(T_{20})^{-1}$ in solvate cover:

$$T_{2s}^{-1} = (1 - P_{or})(T_{2s}^{-1} + T_{2\text{inter}}^{-1}) + P_{or}T_{2\text{or}}^{-1}$$

(1)

Contributions are averaged by proton exchange.

From (1) can be determined $P_{or}$ if all relaxation times are known:

$$P_{or} = 0.296T_{2B} - 0.078$$

(2)

Calculations show, that when $T_{2sw}$ decrease from 700 ms to 300ms the percentage of structured water protons rise from 0.345 to 0.909.

References

Water dynamics in the aqueous solution of the B1 domain of immunoglobulin-binding protein L. A molecular dynamics simulation study

Ekaterina A. Krylova, Andrei V. Egorov

Faculty of Physics, Saint Petersburg State University
Ulianovskaya 1, 198504, Saint Petersburg, Russia
E-mail: krylovaea2803@mail.ru

Introduction

Understanding the properties of water in biological systems is a problem of fundamental interest in chemistry and biology. Studies of protein hydration dynamics in solution have been an active field of research for years [1]. In this context, computer simulations, capable to provide a detailed molecular-level description of solution structure, should be very fruitful for further investigation of this issue. In the present study the water dynamics in the hydration layer around the B1 domain of immunoglobulin-binding protein L [2] (Fig. 1) at normal conditions has been treated by classical molecular dynamics simulations.

Figure 1. Structure of the B1 domain of immunoglobulin-binding protein L (PDB code 2PTL)

Molecular Dynamics simulations

MDynaMix package [3] was used in the present study. A solution of 1 protein molecule (963 atoms) among 7404 H2O molecules was simulated. Molecular dynamics simulations were carried out in an isothermal-isobaric (NPT) ensemble in a cubic periodic cell at 1 atm and 25°C. Water was simulated with the rigid SPC/E model [4]. To describe water interactions with protein molecule the force field was simulated with the rigid SPC/E model [4].

Introduction

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Figure 1. Structure of the B1 domain of immunoglobulin-binding protein L (PDB code 2PTL)

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Results

A detailed view on the water dynamics around the protein can be given through the reorientational correlation functions:

\[ C^\alpha = \langle P(e^\alpha(t) \cdot e^\alpha(0)) \rangle, \]

where \( P \) is the first rank Legendre polynomial, and \( e^\alpha \) is the unit vector pointed along the \( \alpha \) axis in the molecular frame of each water molecule. The correlation time, \( \tau^\alpha \), can be obtained by fitting the correlation functions using the following expression:

\[ C^\alpha = e^{-t/\tau^\alpha}. \]

In our analysis we have used three different axes: the H-H vector, \( R_{HH} \), the molecular dipole, \( R_D \), and the normal to the plane of the molecule, \( R_P \).

In the present study the motions of water molecules in protein hydration layer have been evaluated and compared with the bulk water data.

Acknowledgements

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References

Introduction
The study of NMR relaxation in biological tissues gives us the important information not only about the dynamics of the molecular structure but also about the motion of its individual fragments. Such information can be extracted from the study of spin-lattice and spin-spin relaxation time \(T1, T2\), and the nuclear Overhauser effect, as all of these characteristics are determined by the spectral density function of fluctuating magnetic, which are directly related to the structural parameters of the molecules and correlation times of molecular motion. If several types of interactions give the contribution to the relaxation of the nuclei then correlation relaxation mechanisms may occur. The most interesting data on the movement of individual fragments can be obtained from the relaxation data of \(\text{CH}_2\) groups [1, 2].

Experimental details
In this work, the samples of adipose tissues with different deuterium content (300 ppm, 800 ppm, 1000 ppm, 5000 ppm) were investigated by \(^{1}\text{H}, ^{13}\text{C}\) and \(^{2}\text{H}\) NMR. The spectra and relaxation measurements were performed on a spectrometer VARIAN 400MHz. Correlation experiments COSY (\(^{1}\text{H}, ^{13}\text{C}\)) were carried out to identify signals in \(^{13}\text{C}\) and \(^{1}\text{H}\) NMR spectra. Particular attention was paid to the \(^{1}\text{H}\) and \(^{13}\text{C}\) NMR relaxation of \(\text{CH}_2\) groups in terms of defining the model of rotational motion and the exchange mechanisms between protons and deuterium. Standard inversion recovery experiments and spin echo techniques were used to measure the longitudinal relaxation and the transverse relaxation times correspondingly. NOESY experiments were carried out to elucidate the mechanisms of exchange between protons and deuterium with increasing deuterium concentration in the samples.

Theoretical details
Preliminary investigations showed that the \(^{1}\text{H}\) NMR spectra of all samples of adipose tissue have characteristic peaks. It was found that the intensity of the signals referred to \(\text{CH}_2\) groups is different for the sample with different deuterium concentration. More significant differences in the structure of the spectra of different samples is observed in \(^{13}\text{C}\) NMR spectra in the region assigned to the \(\text{CH}_2\) groups. To interpret the experimental results the operator equations describing the relaxation of each component of the \(^{13}\text{C}\) triplet of \(\text{CH}_2\) groups were used. It was found that the longitudinal relaxation rates of each line in the spectrum of the nucleus \(^{13}\text{C}\) scalar coupled with two protons are individual and equal

\[
R^0 = R_0 - \lambda_s, \quad R^{\pm 1} = R_0 + \lambda_s \pm \mu.
\]

Here \(R^0\) is the relaxation rate of the central component, \(R^{\pm 1}\) is the relaxation rate of extreme components. The autocorrelation contributions from the dipole interaction (DD), chemical shift anisotropy of the nucleus (CSA) \(^{13}\text{C}\) are included in \(R_0\), \(\lambda\) is DD(C-H1)-DD(C-H2) cross-correlation term, \(\mu\) is CSA-DD cross-correlation term. The difference in the decay rates of extreme spectral components arises in the presence of CSA \(^{13}\text{C}\)-(CH) and CSA (H)-D (HH) cross-correlations. The various models of internal molecular motion such as the rigid molecule model and model of rotational jumps in the area bounded by a certain angle are used [2, 3].

Results
The studies have shown that adipose tissue samples have a significant difference in quantity and mobility of the \(\text{CH}_2\) groups. The model of rotational jumps in a bounded area is more suitable for the interpretation of experimental data on the \(^{13}\text{C}\) NMR relaxation \(\text{CH}_2\) group belonging to the chain \((\text{CH}_2)_n\) in the sample contained deuterium. It was found that the exchange process between deuterium and protons involves protons, not only \(\text{OH}\) groups, but also the \(\text{CH}_2\) groups belonging to the chain \((\text{CH}_2)_n\). This effect was observed in samples in which the deuterium concentrations are 5000 ppm, 1000 ppm.

References
Increasing signal/noise in the NQR measurements using composite pulse

Galina Kupriyanova, Ivan Mershiev, Filip Dolinenkov, Valeriy Sabirekian
Physics-Technical Faculty, Baltic Federal State University, Kaliningrad, Russia
E-mail: galkupr@yandex.ru

Introduction
In recent years the physical properties research with change of the matter particle size has causes considerable interest. Earlier it was experimentally shown that longitudinal and transverse relaxation times of a nuclear quadrupole resonance (NQR) depend on the size of microparticles of a sample [1, 2]. In microcomposite structures it was obtained that longitudinal relaxation times \( T_1 \) have unimodular distribution, but transverse relaxation times have multimodal distribution [3]. However, for the complex samples of the molecular crystals with impurities, for micro-powders, micro-composites, porous media due to different intermolecular interactions, relaxation time distribution is continuous and requires a multi-exponential inversion as for \( T_1 \) and \( T_2 \) [2]. For the purpose of increase in the measurement accuracy of relaxation times and obtaining detailed information on the internal factors influencing distribution of relaxation times, we carried out the study of composite pulses action on the NQR line width, the ratio signal/noise and relaxation parameters.

Experimental details
In this work the powder samples with various sizes of granules were investigated. Fractions were allocated with the sizes: > 1000 microns, 500-600 microns, 300-350 microns and 200-250 microns. The sizes of particles and their distribution were determined by an electronic microscope with using of the special software Image J. NQR signals on \(^{13}\text{C} \) were registered on NQR/NMR spectrometer Tecmag with Apollo console. Potassium chlorate KClO\(_3\) was chosen as a sample for study by \(^{35}\text{Cl} \) NQR: asymmetry parameter \( \eta = 0 \), a quadrupole constant \( e^2Qq = 1.058 \) MHz at \( T = 299 \) K, NQR frequency \( \nu = 28,954 \) MHz at \( T = 77 \) K. NTNMR software was used for composite pulses generation and processing of measurements results.

Three composite pulses intended to compensate for the effects associated with the inhomogeneous of sample excitation and the imperfection of \( 90^\circ \) pulses were selected for the experiments [4]. The following sequences of composite pulses were used: 45\(^\circ\)\_135\(^\circ\); 90\(^\circ\)\_300\(_{\text{90(0)}}\), 315\(_\text{(0)}\)\_225\(_{\text{180(1)}}\)\_90\(_\text{0(0)}\) for relaxation experiments.

Results
Our study showed that the use of composite pulses leads to narrowing of NQR linewidths and to increase in the signal/noise ratio. The greatest strengthening of NQR signals was reached with using a composite pulse 90\(_\text{0(0)}\)\_300\(_{\text{90(0)}}\) for the samples containing 200-250 microns fractions. The use of composite pulses for carrying out relaxation measurements allowed us to obtain more detailed information on relaxation times distribution in the samples containing small granules (Fig.1). It was proved that distribution of longitudinal relaxation times \( T_1 \) and transverse relaxation times \( T_2 \) has multimodal character. Especially essential distinction in relaxation times distribution was received for samples with sizes of granules from 300 to 350 microns and 200-250 microns.

Conclusion
The use of composite pulses for recording NQR signals in powder containing different sizes of microparticles allowed us to achieve linewidth narrowing and to increase the signal-noise ratio. Elimination of the effects associated with the inhomogeneous irradiation of the sample and the imperfection of 90\(^\circ\) - and 180\(^\circ\) pulses by applying composite pulses enabled us to extract more detailed information on relaxation times distribution.

References
Introduction

Understanding transport in heterogeneous media is important in various disciplines ranging from materials science, to porous catalysts, to oil recovery, to biophysics. The complexity of the microscopic structure of the object, such as heterogeneity in diffusive properties and restrictions on molecular motion, results in non-Gaussian evolution of particle displacements. In particular, the effective self-diffusion coefficient $D(t)$ itself becomes time-dependent and shows a decrease from the value of the bulk self-diffusion coefficient $D_0$ to a constant value $D_\infty$ in the long time limit. In the present work, we find an analytical expression for the self-diffusion coefficient $D_\infty$ of diffusing molecules in a 2D heterogeneous medium.

Theory

Inspired by the structure of the cell membrane and the adjacent membrane cortex, we consider a particle diffusing in 2D in presence of a meshwork with permeable barriers characterized by a mean mesh size $R$. Over a macroscopically long period of time $t$ a diffusing molecule covers, as a result of the Brownian motion, a distance $L$ (diffusion displacement) in. The square of this diffusion displacement $L^2$ is a sum of squares of diffusion displacements $l^2$ of this molecule in all meshes this molecule has visited during time $t$. Hence, the average value of the square of the diffusion displacement of molecules in the medium under consideration over time interval $t$ is as follows:

$$\langle L^2 \rangle = k \langle i^2 \rangle = 4 D_\infty(R) t,$$

where $k >> 1$ is the average number of passages from one mesh to another during time $t$, $D_\infty(R)$ is the long-time self-diffusion coefficient, and $\langle i^2 \rangle$ is the average square of the molecule diffusion displacement for the time period between two consecutive entries into neighboring meshes. Previously it has been shown [1] that the dependence of the self-diffusion coefficient on the geometry of the heterogeneous medium can be described by the expression

$$D_\infty(R) = D_0 \exp(-P_\sigma(R)),$$

where $D_0$ is the self-diffusion coefficient of the bulk liquid and $P_\sigma(R)$ is the probability of “steric interaction” with a barriers which generally depends on the size and shape of the mesh, permeability of the barriers, and size of diffusing particles.

Comparison with Computer Simulations

Recently, the effect of membrane microheterogeneity on anomalous subdiffusion in cell membranes was studied by Monte Carlo simulations of two-component (DMPC/DSPC) lipid membranes coupled to a model membrane cortex [2]. It was found that the long time diffusion coefficient shows a pronounced reduction decrease with an increase in the filament pinning density (Figs. 1 and 2).

References

NMR Studies of intermolecular interaction in polymer melts
A. Lozovoy\textsuperscript{1}, N. Fatkullin\textsuperscript{1}, S. Stapf\textsuperscript{2}, C. Mattea\textsuperscript{3}

\textsuperscript{1}Kazan Federal University, 420000, Kremli str. 18, Kazan, Russia
E-mail: Artur.r.Lozovoy@gmail.com
\textsuperscript{2}Technische Universität Ilmenau, 98693, Ehrenbergstraße 29, Ilmenau, Germany

Introduction
In the recent theoretical papers \cite{1, 2} it was shown that intramolecular and intermolecular contributions to the dipole-dipole interaction in polymer melts have different time dependences and generally one cannot neglect intermolecular part as it was done before.

Theoretical predictions
For polymer melts with $T_2 \geq \tau_1$ (terminal relaxation time) the expression for intermolecular contribution into the transverse relaxation rate is as follows:

$$\frac{1}{T_2} = \frac{\pi}{10} \sqrt{\frac{R_g}{M}} \exp \left( -\frac{4h^2n_s}{DR_g} \right)$$

(1)

For polymer melts with $T_0 < \tau_1$, approximation of the transverse relaxation decay should be done with the use of that expression:

$$g(t) = \exp \left\{ -\frac{2}{\sqrt{3\pi}} \frac{36\pi(1 + \beta)}{5(2 - 3\alpha)(4 - 3\alpha)} \left( \frac{4h^2t^2n}{M} \right)^{\frac{3}{2}} \right\}$$

(2)

This works in the case of anomalous diffusion with relative mean-squared displacement time dependence of this type:

$$< r^2(t) > \geq At^\alpha,$$

(3)

where $\alpha < 2/3$.

Polyisoprene transverse relaxation study
Transverse relaxation was measured with the use of Hahn echo pulse sequence in cis-polyisoprene-1,4. The molecular mass dependence of $T_2$ relaxation time is shown on the Fig. 1.

For samples with molecular mass larger than 22000 $\tau_1 >> T_2$. So curves of the transverse relaxation decay for samples with $M = 7100, 13200$ and 22000 were studied with the use of the expression (1). The results of calculated intermolecular contribution to the transverse relaxation rate and measured transverse relaxation rate are gathered in the table 1.

![Figure 1. Dependence of $T_2$ relaxation time on the molecular weight](image)

Table 1. Comparison of experimental transverse relaxation rate and the theoretical calculation of intermolecular contribution

<table>
<thead>
<tr>
<th>M</th>
<th>$\frac{1}{T_2}$, s\textsuperscript{-1}</th>
<th>$\frac{1}{T_2}$, s\textsuperscript{-1} inter</th>
<th>Relative contribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>7100</td>
<td>110</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>13200</td>
<td>281</td>
<td>83</td>
<td>29</td>
</tr>
<tr>
<td>22000</td>
<td>384</td>
<td>210</td>
<td>55</td>
</tr>
</tbody>
</table>

It is clear that contribution of intermolecular interactions are not negligible while concerning nuclear magnetic transverse relaxation.

Acknowledgements
Financial support from Deutsche Forschungsgemeinschaft (DFG) through grants STA 511/13-1 and RO 907/15 and 907/16 is gratefully acknowledged.

References

Composite pulses for $^{14}$N NQR with minimal phase distortion

Ivan Mershiev, Galina S. Kupriyanova

Institute of Physics and Technology, Immanuel Kant Baltic Federal University, Kaliningrad, Russia
E-mail: IMershiev@kantiana.ru

Introduction

Since their introduction in the late 70s [1], composed pulses proved itself as a useful tool for compensating RF field inhomogeneity and pulse length imperfections, especially in spin-echo NMR experiments. In the past few years, activity in this area of research increased due to using of composite pulses in NMR quantum information processing [2]. In this work, we present broadband composite pulse sequences for NQR with limited phase shift.

Composite pulses in NQR

In NQR composite pulses usually used to compensate RF field inhomogeneity and frequency offset effects. To design NQR composite pulses, different methods were used: perturbation approach, numerical calculations and quaternion algebra [3]. Calculation of composite pulses effects in NQR is generally more complex than similar ones in NMR, because of SU(3) symmetry group of spin I=1 nuclei and effects of excitation averaging in powders and amorphous substances. Because of that, pulse lengths correspond to maximum signal amplitude and spin inversion is usually referred as “pseudo-90°” and “pseudo-180°” pulses. Their actual length, comparing to NMR pulse, is 119.5° and 257° accordingly. Another downside of averaging effects is complex behavior of signal phase after excitation with composite pulse.

Optimization goals and constraints

Composite excitation in NQR can reduce NQR line broadening, increase signal magnitude, and increase effective excitation range for remote detection.

Studying the effects of composite pulses, we could not explore many composite pulse sequences due to hardware limitations. Our NQR spectrometer, Telemag Apollo, is capable to 32-step phase modulation only (multiple to 11.25°). Another issue is that many composite pulse sequences is prone to strong phase distortion. Abrupt phase changes may result in “holes” in excitation profile at corresponding pulse lengths. In this case, minimization of phase distortion would be beneficial.

Our goal was to design composite pulses with discrete set phase modulation, broadband excitation, limited phase variance, and capable to phase cycling. For theoretical calculations, we used fictitious operator approach by Vega and Pines [4]. Numerical calculations performed with mixed discrete-integer optimization using genetic algorithm. All calculations were performed for on-resonance case.

Results

Fig. 1 shows simulated nutation curves for single excitation pulse and proposed composite pulses. Simulation takes into account effects of powder averaging.

Figure 1. Nutation curves of NQR signal magnitude after excitation with single pulse and proposed composite pulses. Composite pulse sequences are shown in table 1

Composite pulses can provide uniform excitation of the sample in a wide range of radiofrequency field intensities or varieties of pulse lengths. Limited and smooth phase variation allows straightforward use of these composite pulses in NQR experiments.

Table 1. Composite pulse sequences and limits of phase variance

<table>
<thead>
<tr>
<th>Composite pulse</th>
<th>$\Delta \phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A $0.150(180°)-0.250(157.5°)-0.350(225°)$</td>
<td>$\pm 7°$</td>
</tr>
<tr>
<td>B $0.170(247.5°)-0.500(67.5°)-0.260(180°)$</td>
<td>$+0.2°, -7°$</td>
</tr>
<tr>
<td>C $0.540(90°)-0.550(213.75°)-0.270(236.25°)$</td>
<td>$+6°, -0.4°$</td>
</tr>
</tbody>
</table>

References

Non resonance signal suppression in pulse NQR

Georgy Mozhukhin¹,², Galina Kupriyanova³, Bulat Rameev¹,⁴, Bekir Aktas¹

¹Gebze Institute of Technology, 41400 Gebze-Kocaeli, Turkey
²Kazan State Power Engineering University, 420066 Kazan, Russian Federation
³Baltic Federal State University, 320014 Kaliningrad, Russian Federation
⁴Kazan Physical-Technical Institute (KPhTI), 420029 Kazan, Russian Federation

E-mail: mgeorge@yandex.ru

Introduction

There is growing interest to the studies of non-standard configurations of nuclear quadrupole resonance (NQR) technique. For instance, a kind of the NQR parametric detection, using irradiation of the sample by a carrier high (microwave) frequency, has been proposed recently [1]. Another example, which has been already verified experimentally, is a broadband NMR/NQR setup with non-resonant probe [2]. In our case we have studied an effect of additional low-frequency radiation on the parameters of higher frequency NQR signal.

Experiments and discussion

Two-channel NQR spectrometer on the base of Tecmag Apollo console with two-frequency probe and two Tomco amplifiers have been used. RDX (C₃H₆N₆O₆ – 1,3,5-trinitrohydro-1,3,5-triazine) and sodium nitrite (NaNO₂) have been used as the samples in our experiments. One channel has been used for detection of spin echo signal and the second one has been used for non resonance irradiation of the sample. Two frequency RF probe consisted of two mutually orthogonal coils, each tuned to the own resonance frequency.

The non-resonance attenuation of the echo signals has been observed in the case of irradiation at the second frequency. A pulse at the non-resonant frequency in the range of 80 kHz – 800 kHz has been applied between 90° and 180° echo pulses. The value of attenuation depends from the pulse duration, frequency and amplitude of RF magnetic field induction B₁, acting at the second channel (see Fig.1). The linewidth broadening has been observed also in the free induction decay (FID) experiments. In this case non-resonant irradiation pulse has been applied before and during the RF pulse. Our experiments reveal that: a) the application of powerful radiofrequency pulse destroys the spin coherency that in turn produces the attenuation of the echo signal; b) irradiation pulse at the second frequency results in broadening for 30% of FID signal; c) both echo and FID effects are decreasing with the frequency.

Two mechanisms may be responsible for disappearing of the echo signal and broadening of FID signal. The first, obvious mechanism is Zeeman effect of the oscillating RF field on the quadrupole system. It is known [3] that application of the static or low-frequency magnetic field results in the broadening of powder NQR spectra. Another possible mechanism is related to the effect of the electric field component on piezoelectric crystals, like NaNO₂.

Conclusion

It has been shown that application of the secondary low-frequency irradiation suppresses the NQR echo signal and results in broadening of FID signal. The effect may be practically utilized in the two frequency RF probes of explosive detection devices to discriminate between the NQR and spurious signals.

Acknowledgements

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References

Preclinical in vivo MR Imaging using the mouse model

Maria S. Muravyeva, Alexandr A. Khrapichev, Marina V. Shirmanova, Elena V. Zagaynova

1Lobachevsky State University of Nizhni Novgorod, Nizhni Novgorod, Russia
E-mail: masha-muravyeva@mail.ru
3Nizhny Novgorod State Medical Academy, Nizhni Novgorod, Russia

Introduction
Currently, significant attention is focused on the preclinical research and the number of applicable experimental techniques is constantly extending. Magnetic Resonance Imaging (MRI) is one of the most promising in vivo techniques due to non-invasiveness and absence of the harmful radiation. The image contrast could be based on parameters specific to MRI such as T1 and T2 as well as on biological properties of tissue such as water content, blood flow and diffusion, etc. Another option is to use specific contrast agents to highlight the region of interest.

Equipment and techniques
The laboratory in the University of Nizhny Novgorod is equipped with state of the art preclinical MR spectrometer, 9.4T superconducting wide bore magnet is driven by Agilent DDR2 console (Fig. 1). The main directions of research Nizhny Novgorod would be the functional imaging (fMRI) – measurement of temporal changes of blood flow in the different parts of the brain [1]; the diffusion tensor imaging (DTI) – measurement of localized diffusion anisotropy to determine the fiber structure of the brain [2]; the angiography (ASL) – mapping the distribution of blood flow in the brain [3]. In addition, we are going to use one of the most advanced MR techniques the chemical exchange saturation transfer (CEST) – enchantment of the contrast based on the magnetization transfer of highly diluted contrast agent weak signal to strong water signal, which signal can be registered directly [4].

Preliminary results
The research in the MRI lab is still on the preliminary stage. Significant work is devoted to the installation of various scientific equipments. The main focus of research is going to be on the development of new contrast agents for tumor detection. As preliminary results, we are demonstrating here the first ever in vivo MR images taken in Nizhny Novgorod. Anatomical T2*-weighted images of mouse brain are shown in Fig. 2 (experimental parameters: FOV = 40x40mm, matrix = 128x128; slice thickness = 1mm; echo time = 2ms; repetition time = 40ms; total experimental time = 50s).

References
Possibilities of the MRI in a complex assessment of cardiac diseases

I. N. Petrov, V. M. Cheremisin, I. G. Kamyshanskaya

Saint Petersburg State University, Medical faculty, 21 line V.O., 8a
Mariinskaya hosp. Liteyniy, 56
E-mail: ivan-petrov90@bk.ru

The cardiac MRI, commonly used in cardiology-specialized centers, is rarely applied in general hospitals. While the percentage of cardiac pathology is one of the biggest among other diseases. That is why it is a significant problem for a cardiology and radiology. Together with other modalities, cardiac MR has a large field for research and scientific work. It caused by the fact that the MRI is one of the most accurate and least invasive methods in cardiac imaging. Sometimes the MRI is an irreplaceable modality in a difficult diagnostic case, when others are not reliable enough or related with unjustified risk for the patient. MRI provides the detailed assessment of the cardiac morphology and function. The using of ECG-gating gives a possibility to avoid the artifacts, caused by cardiac motion. And the right slice positioning due to oblique (in relation to body axes) cardiac axes – gives anatomically-correct pattern of the cardiac structures.

Historically, there are two principal types of sequences. The “dark-blood” sequences are based on the spine echo, where the contrast between the myocardium and the blood is low, but a good visibility of the myocardial edema, whereas the “bright-blood” sequences are based on the gradient echo and have the best contrast to noise ratio and the most clearly view of the endocardial border. Unlike the geometrical assumption in Echocardiography, the evaluation of the cardiac function by MRI allows an accurate quantification of the cardiac chambers volumes, the ejection fraction and other most important indicators of the myocardial function.

Furthermore, even the moderate decrease of the local (or global) contractility can be visualized by the myocardium tagging technique with the inversion pre-pulses.

Quantification of the blood flow volumes, velocities and other intracardiac hemodynamic values are enable via the phase-encoding technique. It is actively used to determine indications for surgery in patients with congenital heart disease.

In spite of the higher resolution given by CT in coronary angiography, MRI is an alternative for patients with allergy to the iodine contrast agents. MR-coronary angiography is improving and probably will be able to compete with CT-angiography soon.

MRI is a great modality in visualization of the myocardial ischemia and infarction. MR-perfusion has the best tissue sensitivity. Combined with the stress-test, it gives accurate results in detecting ischemia zones, myocardial necrosis and, which is particularly important, hibernating/stunning myocardium and determines the need of the revascularization.

Delayed contrast-enhanced MRI gives a possibility to reveal myocarditis, sarcoidosis, hypertrophic cardiomyopathy, myocardial scar. Moreover, myocardial mapping enables to quantify these lesions.

Despite of high sensitivity, specificity and accuracy of the abovementioned MR-methods, occasionally the real clinical situation is so difficult, that even MRI don’t enables to determine the right diagnosis. It forces to use the complex examination of the patient, from physical examination to hi-tech modalities and to improve the current diagnostic imaging techniques.
Pulse magnetic field control of NMR signal in a ferrite domain walls

Pavel S. Popov, Ivan V. Pleshakov

1Saint Petersburg State Polytechnic University, 195251, St. Petersburg, Russia
2Ioffe Institute, 194021 St. Petersburg, Russia
E-mail: ivanple@yandex.ru

Introduction

Magnetic field pulses acting on nuclear spin echo, excited in magnetically ordered material, may be regarded as an additional method for study of the substance, [1]. Recently this technique was developed for such cases, as, for example, domain walls investigation in poly- and single crystals of magnetic oxides, [2, 3]. Except of the use of the method in physical search, it can be utilized in experimental equipment elaboration and other branches of engineering. The possible application belongs to functional electronics [4], when a medium operates as a signal processing unit. It is well known that the NMR in ferrites can be exploited by this way in so called echo-processors, when the echo regarded as an output signal of a system, [5]. Being promising, such devices posses, however, a problem of spurious signals, forming as responses of sample to the excitation by the radio frequency (RF) pulses from different sequences (crossed echoes).

Here we discuss the suppression of the spurious echoes from interacting two-pulse trains by long magnetic field pulse, overlapping in time the second RF sequence and the interval, where the multiple responses appear.

Experimental method

As an operating medium in this work a lithium-zinc ferrite (Li$_{0.425}$Fe$_{2.425}$Zn$_{0.15}$O$_4$) was used, where the nuclear spin echoes of $^{57}$Fe were excited by two series of RF pulses ($S_1$ and $S_2$, including A, B and C, D pulses correspondingly). An additional pulsed magnetic field with amplitude $h_M$ was applied to the sample during the time of $S_2$ action and echo formation interval $\tau$. This scheme is illustrated by Fig. 1, where the time diagrams of the pulse sequences with the necessary notations are shown. As it is seen from the figure, the combinations of RF pulses from $S_1$ and $S_2$ produced (by two-pulse and stimulated mechanisms) a number of responses, masking the desired signal (echo from two pulses in every series).

Results

Fig. 1 demonstrates the effect of pulsed magnetic field onto the set of sample responses: the entire ensemble of cross echoes was completely suppressed when $h_M$ was high enough, while the signals excited by AB- or CD-pulses persisted. The nature of the phenomenon is connected with the fact that the NMR was observed from the domain walls, which could be displaced by the external magnetic field. If the latter has a form of pulse, shown in Fig. 1, and overlapping the interval, where the response of the spin system onto the action of $S_2$ series is excited and registered, the spins, involved to the formation of the echo signals from $S_1$ and $S_2$ belong to the spatially separated areas. It means that the different pulse trains no longer interact, and cross echoes cannot arise.

The relationship of the suppression value with $h_M$ confirmed the model: the intensities of crossed echoes decreased with the increasing magnetic pulse amplitude, obeying the different dependencies for two-pulse and stimulated responses.

Acknowledgements

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

References

Introduction

Recently extensively investigated the isotopic D / H reactions exchange on different physiological and pathological processes in biological objects, especially in the blood. However, so far not studied features of deuterium exchange in human breast milk and oral fluid, which is important for the development of non-invasive diagnostic methods, including the monitoring of environmental safety in the population.

Materials and methods

Determination of deuterium concentration in water, blood plasma, human breast milk (HBM) and oral fluid (OF) were performed using nuclear magnetic resonance spectrometer (NMR) JEOL JNM-ECA 400MHz at the Center for collective use "Diagnostics of the structure and properties of nanomaterials" in Krasnodar State University (Krasnodar). Spectra were recorded at the corresponding resonance frequency of deuterium nuclei, 61.4 MHz. The recording parameters were acquisition time, 6.7 s; relaxation delay 20 s; x-pulse, 5.6 µs; and 0.15 hz resolution). The recording temperature was 25 s at a stabilization accuracy of 0.2 s. The measurements were performed using ampoules 5 mm in diameter, inside of which sealed capillaries were rigidly fixed. The latter contained mixtures of deuterated and nondeuterated dimethylsulfoxide (DMSO), calibrated in the concentration scale under determination. This yielded a 2D NMR signal in the region of 3.4 ppm (with respect to (CD$_3$)$_2$Si) with the D NMR signal of HDO lay in the field of 4.7 m.d. (with respect to (CD$_3$)$_2$Si). The obtained spectra were processed by determining the ratio of the integral intensities of the D NMR signal of HDO in the investigated sample with respect to the D NMR signal of DMSO-D$_2$, the density of which was in turn determined under the same conditions relative to standards (samples of water with precisely determined deuterium contents of 3.7, 51, 150 ppm). The measurements for each sample were performed repeatedly to reduce the experimental error. The error of determination for the deuterium content in blood plasma was ±1 ppm [1]. Indicators D / H exchange were studied in biological substrates in two groups of women in childbirth, were examined in the Municipal Budget Institution of Health "Maternity" (Krasnodar). In group 1 (n = 14) were included women receiving an ordinary diet, group 2 (n = 8) were included women receiving, besides the usual diet, deuterium depleted water (60 ppm) in a volume of 1.5-2 liters per day for 25-30 days before the test. Statistical processing was performed using the R Development Core Team, (2008), the difference was considered significant at p <0.05. For evaluation of correlations used Pearson's coefficient (r).

Deuterium content in biological fluids

The studies found that under man physiological conditions there is a gradient of the deuterium content (OF >> plasma >> HBM) and the last indicators in biological fluids differ significantly, as represented in the table below:

<table>
<thead>
<tr>
<th>Index</th>
<th>Plasma</th>
<th>OF</th>
<th>HBM</th>
</tr>
</thead>
<tbody>
<tr>
<td>D, ppm</td>
<td>144,3±0,6</td>
<td>159,8±0,4</td>
<td>141,6±0,4</td>
</tr>
</tbody>
</table>

It is known that the indicators of deuterium in natural conditions under water, proteins, lipids, carbohydrates are differ significantly, due to different speeds of isotope (D / H) exchange reactions in various chemical bonds in biomolecules:-OH, -SH, -NH$_2$ (=N-H) n –R$_2$C-H. Therefore, in order to clarify the causes of the above described isotopic D / H gradient was carried out a correlation analysis of the relationship between deuterium content in biological fluids and biochemical composition of plasma, OF and HBM.

As a result, it was found that there was a direct correlation relationship between the content of water in the biological fluids and deuterium parameters: r = 0,85 (p <0,05), whereas between the content of organic components in biological fluids and deuterium content there is inverse relationship: for proteins r = -0,45, carbohydrates r = -0,61, lipids r = -0,96 (p <0,05), it should be considered in designing algorithms noninvasive assessment of heavy nonradioactive isotope in body, including deuterium, since the biochemical composition of biological fluids can be quite variable depending on the person's lifestyle (diet, physical activity and other factors) [2]. In blood plasma of women who consume deuterium depleted water, there was a significant deuterium decrease at 19.7% (p <0,05). At the same time serum indicators also decreased in OF and HBM, but the presence of isotopic D / H gradient (OF >> plasma ≥ HBM) survived. Thus, on the basis of our studies found that in human biological fluids there is an isotopic D / H gradient: OF >> plasma > HBM, the presence of which is due primarily by features of the biochemical composition of the plasma, OF and HBM. The highest negative correlation (r = -0,96) noted between deuterium concentration and lipid content in the appropriate biological fluids.

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References

Structure and stability of lanthanide cryptates in solutions

 Alla K. Shestakova¹, Vyacheslav A. Chertkov²

¹State Research Institute of Chemistry and Technology of Organoelement Compounds, sh. Entuziastov 38, 111123 Moscow, Russia
E-mail: alla@nmrcenter.ru
²Department of Chemistry, Moscow State University, Leninskiy Gory 1/3, 119992 Moscow Russia
E-mail: chertkov@org.chem.msu.ru

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. Of special interest is their superb hydrolytic cleavage of biocidal phosphate esters, DNA and RNA. There are not many structural investigations with such systems (see e.g. [1, 2]).

Results and discussion

We have studied the complexation of MX₃ (M = La, Eu and Pr; X = Cl, NO₃ and SO₃CF₃) with 1,10-diaza-18-crown-6 with R = H at N (I), R = n-C₁₅H₃₂ (II), [221]cryptand (III) and [222]cryptand (IV). The ¹H and ¹³C NMR spectra revealed for the complexes different types of coordination sphere for the lanthanide ions. The nature of solvent is important for controlling the ligature type. In classical inner-sphere complexes, metal atom binds to all co-ordination sites of the ligands (first of all N-atoms). Complexation leads to dramatic effect on conformation of the ligand, which studied by detailed analysis of multiplet structure of high resolution ¹H NMR spectra and supported for the most important cases by X-Ray studies. ¹³⁹La NMR provides important information on the structure of first co-ordination shell of the lanthanide complexes in solutions. Complexation with monocyclic ligands I and II leads to deshielding effect of ¹³⁹La nuclei by 30 ppm, while co-ordination with bicyclic IV (D₈ᵥ-symmetry complex) enlarges shielding by 100-130 ppm. The inner-sphere complexes of host-guest type are rigid on the NMR time scale. Their structure analysis was performed using the whole magnitude of NMR spectral information, first of all the spin-spin coupling network for the diamagnetic La(III) complexes. Comparison of the chemical shifts for the diamagnetic La(III) and paramagnetic Eu(III) and Pr(III) complexes provides a contact and pseudocontact shielding terms for both ¹H and ¹³C nuclei, which also allows the geometry interpretation.

Monocyclic ligands I and II form complexes with C₂ᵥ – symmetry and cis-conformation in weak solvating solvents (chloroform, acetonitrile, methanol), which supported also by X-ray data of complex between lanthanum nitrate and macrocycle I [1]. The complexes with [221]cryptand are highly stable even in water solutions. We show, that complexes with the [222]cryptand of the type EuX₃L (X = Cl, NO₃ and SO₃CF₃; L = IV) exist in the two forms: with D₃h and C₂ᵥ-symmetry. In contrast to monocyclic ligands, lanthanide cryptates are formed slowly on NMR time scale (see e.g. [2]). We present here results of the kinetics studies of their formation for europium chloride and triflate in methanol solution. X-ray diffraction data revealed the structure of inner-sphere almost C₂ᵥ-symmetrical complex with [221]cryptand and hydrated lanthanum triflate. A series of ECP quantum chemical calculations (Lanl2dz approach) supports the structure of complexes under study. Experimental vicinal spin-spin coupling constants between protons of neighboring CH₂-groups for complexes of lanthanum salts with macrocyclic ligands I and III in solutions (CDCl₃, CD₃OD and CD₃CN) are in good agreement with the ab-initio calculated ones (PFT DFT with UB3LYP and 6G/311(d) basis set, see e.g. [3]). 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.

References

Magnetic biosensing of experimental glioblastoma targeting with superparamagnetic nanocarriers tagged to heat shock protein Hsp70

Maxim A. Shevtsov¹, Boris P. Nikolaev², Ludmila Y. Yakovleva², Yaroslav Y. Marchenko², Vyacheslav A. Ryzhov²

¹Institute of Cytology of the Russian Academy of Sciences (RAS), Russia, St. Petersburg
E-mail: shevtsov-max@mail.ru
²Research Institute of Highly Pure Biopreparations, Russia, St. Petersburg
²Petersburg Nuclear Physics Institute, NRC Kurchatov Institute, Russia, Gatchina

Introduction
Heat shock protein Hsp70 is known to stimulate anti-tumor immune response and thus could be applied for immunotherapy in neuro-oncology [1]. Previously, it was reported that targeted delivery of Hsp70 to the glioblastoma could be achieved by implication of magnetic nanoparticles (MNPs) [2]. Further analyses of magnetic conjugates distribution in vivo by MR imaging and magnetometry is highly important for optimizing therapy.

Materials and Methods
Superparamagnetic nanoparticles were coupled to carbodiimide modified Hsp70 (Hsp70-SPIONs) as reported earlier [2]. The biodistribution of conjugates was analyzed in the model of intracranial glioma C6 in rats. On the 20th day following tumor implantation conjugates were intravenously administered. After 24 hours animals were sacrificed and tissue samples were obtained for magnetometry. The methods of longitudinal nonlinear response to a weak ac magnetic field and registration of electron magnetic resonance were used for detail study of the Hsp70-SPIONs in tissues [3]. The tumor selectivity of MNPs was analyzed in the MRI scanner at 11 T.

Results
Synthesized SPION-Hsp70 conjugates had the properties of the negative MR T2-contrast agents. Intravenous administration of the conjugates resulted in accumulation of the particles in the glioma that was detected by MR scans (Fig. 1).

Further magnetometry of tissue samples confirmed the preferential accumulation of the Hsp70-SPIONs in tumor with distribution in other tissues as follows: glioma > liver > lungs > heart > muscle > brain > skin. The magnitude of signal was calibrated and represented in relative units as measure of magnetic material in samples. The high content of magnetic conjugates was found in glial tumor in comparison to surrounding normal brain tissues thus proving the tumor retention of the nanoparticles (Fig. 2).

Conclusions
1. The applied magnetic biosensing is sensitive method for measuring the magnetic conjugates in tissues.
2. Hsp70-SPION conjugates could be accumulated in glioblastoma in high dosage.

Acknowledgements
Authors thank A. V. Dobrodumov, A. M. Ischenko, I. N. Voevodina for support of the study.

References
Spin-lattice relaxation of hydrogen nuclei in dilute solutions of carbosilane dendrimers of the 5th generation with integral mesogenic groups attached by ethyleneglycol spacers

E. V. Shishmakova

Department of physics, St. Petersburg State University, Ulyanovskaya street 1, Petrodvorets, St. Petersburg, 198504, Russia
E-mail: leshishmakova@nmr.phys.spbu.ru

Introduction

Dendrimers are a relatively new class of polymer systems with unique properties, which have applications in various areas of polymer chemistry, biology and medicine. In this work the method of nuclear magnetic resonance is applied for studying the rotational mobility of atoms, which included in the internal part (the kernel) dendrimers and beyond the kernel (spacer or limit the group) for carbosilane dendrimers of the 5th generation, containing end groups butyl hydroxyphenyl ether of hydroxybenzoic acid, attached to the matrix via ethyleneglycol of the spacer.

The chemical and structural formulas of the dendrimer are shown in Fig. 1.

![Chemical and structural formulas of carbosilane dendrimers of the 5th generation (Peg-But)](image)

The main task of the work was a detailed comparison of the temperature dependences of rates of the spin-lattice NMR relaxation of hydrogen nuclei (1/T1) for different groups of dendrimers of the 5th generation (Peg-But).

The experimental part

The studied systems were solutions of dendrimers in the deuterated chloroform (CDCl3) with concentration of about 3% wt. The measurements of 1H NMR spectra were carried out with the spectrometer AVANCE 400 and AVANCE 600 (Bruker, relaxation measurements - spectrometer AVANCE 400).

The choice of the temperature range of research (225 K ± 320 K) was determined by the boiling and freezing points of deuterochloroform.

Results and discussion

The work was directed to build the temperature dependences of the relaxation rates in the temperature range T = 228 – 318 K and to determine the main parameters, such as the activation energy and the correlation time.

Figure 2 shows the temperature dependence of the relaxation rate for carbosilane dendrimers of fifth generation and its approximation.

![Temperature dependence of the relaxation rate of carbosilane dendrimers of the 5th generation (Peg-But)128](image)

It was obtained that not all lines have a bell-shaped form as in Fig. 2. Most of the lines were presented in a more complex form, which was impossible to handle the exponential curve.

For the theoretical description of the expected temperature dependences the standard function was taken:

\[
\frac{1}{T_1} = A_0 (1/(\omega_0 T) + \frac{\tau_{cor}(T)}{1+(\omega_0 \tau_{cor}(T))})
\]

where, \(E_a\) is the activation energy, \(\omega_0\) is the resonance frequency, \(\tau_{cor}\) is the correlation time. Table 1 presents data processing relaxation rates for 1 and 3 lines of dendrimers.

![Table 1. The results of processing of the experimental dependences of the relaxation rates for 1 and 3 lines of the investigated dendrimers](image)

Conclusion

As it follows from the temperature dependences, only the lines relating to the core of dendrimers ("internal" line) demonstrate a simple bell-shaped form, the corresponding dependence (1) with one correlation time. The majority of the remaining lines show more complicated temperature dependence, which can be described as a combination of two or more dependence of the type (1). Apparently, this type is explained by the superposition of several types of reorientation, when there is a large number of the degrees of freedom involving these groups.
**Introduction**

The intermetallic compound Ti₃Al having the hexagonal DO₁₉-type structure shows excellent mechanical properties and oxidation resistance. The alloy is also a candidate for light hydrogen-storage material. Since hydrogen absorption may lead to strong changes in properties of an intermetallic [1], it is important to have a clear microscopic picture of the hydrogen effects in the Ti₃Al-H system. The aim of the investigation is to obtain experimental information on H-sites, hydrogen mobility and hydrogen-induced changes in the electronic structure. In this work we report the results of a nuclear magnetic resonance (NMR) study of the Ti₃AlHₓ system over wide range of concentrations (0 ≤ x ≤ 4.3).

**Results and discussion**

The intermetallic compound Ti₃Al was charged with H₂ gas at a pressure of about 1 bar using a Sieverts-type vacuum system and the hydrogen content was determined from the pressure change in the calibrated volume of the system. According to x-ray diffraction analysis, two samples with hydrogen content of x = 0.31 and x = 0.51 are solid solutions, but other samples with H content of x = 1; 2; 4.32 have different crystal structures. Lattice parameters and the crystal structures are presented in table 1.

**Table 1.** Lattice parameters of studied samples Ti₃AlHₓ

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (hexagonal)</th>
<th>β (b.c.c.)</th>
<th>γ (f.c.c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a, Å</td>
<td>c, Å</td>
<td></td>
</tr>
<tr>
<td>Ti₃Al</td>
<td>5.8</td>
<td>4.66</td>
<td>-</td>
</tr>
<tr>
<td>Ti₃AlH₀.₃₁</td>
<td>5.8</td>
<td>4.65</td>
<td>-</td>
</tr>
<tr>
<td>Ti₃AlH₀.₅₁</td>
<td>5.8</td>
<td>4.65</td>
<td>-</td>
</tr>
<tr>
<td>Ti₃AlH₁</td>
<td>5.76</td>
<td>4.9</td>
<td>3.28</td>
</tr>
<tr>
<td>Ti₃AlH₂</td>
<td>-</td>
<td>-</td>
<td>3.29</td>
</tr>
<tr>
<td>Ti₃AlH₄.₃₂</td>
<td>-</td>
<td>-</td>
<td>3.27</td>
</tr>
</tbody>
</table>

The measured spin-lattice relaxation rate T⁻¹₁ of H and ²⁷Al is the sum of several contributions. In metal-hydrogen system, the main contributions to T⁻¹₁ are the hyperfine interaction between nuclear spins and conduction electrons (T⁻¹ₑ₁) and the dipole-dipole interaction of nuclear spins modulated by hydrogen motion (T⁻¹₁ₑ). At low temperatures, the T⁻¹₁ₑ contribution is negligible, and the T⁻¹ₑ₁ contribution is determined directly from T⁻¹₁. The electronic contribution is proportional to temperature, T⁻¹ₑ₁ = A + CₑT. The values of A and Cₑ obtained from the linear approximation are listed in table 2. Cₑ is proportional to the square of full density of electron states at the Fermi level, N(E_F), and a comparison of Cₑ for ²⁷Al and ¹H nuclei in Ti₃AlHₓ shows an increase in N(E_F) in the compounds with increasing hydrogen content. Large value of A for ¹H can be explained by the significant impurity concentrations.

**Table 2.** Values of A and Cₑ obtained from the low-temperature data on T⁻¹₁ of nuclei ¹H at 90MHz and ²⁷Al at 23 MHz

<table>
<thead>
<tr>
<th>Sample</th>
<th>A, s⁻¹</th>
<th>Cₑ, s⁻¹K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>²⁷Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti₃Al</td>
<td>0.01</td>
<td>0.0084</td>
</tr>
<tr>
<td>Ti₃AlH₀.₃₁</td>
<td>~0.00</td>
<td>0.229</td>
</tr>
<tr>
<td>Ti₃AlH₀.₅₁</td>
<td>~0.00</td>
<td>0.475</td>
</tr>
<tr>
<td>Ti₃AlH₁</td>
<td>~0.00</td>
<td>1.45</td>
</tr>
<tr>
<td>Ti₃AlH₂</td>
<td>~0.00</td>
<td>0.253</td>
</tr>
<tr>
<td>Ti₃AlH₄.₃₂</td>
<td>~0.00</td>
<td>0.368</td>
</tr>
</tbody>
</table>

Figure 1 shows the temperature dependence of the spin-lattice relaxation rate of ¹H in Ti₃AlHₓ at 23.8 MHz. Significant T⁻¹₁ deviations from the linear behavior were detected only above 300 K at 23.8 MHz for samples with x ≥ 1. These deviations can be attributed to H mobility. The hydrogen mobility in Ti₃AlHₓ with x≥1 is likely to be due to the occupation of the tetrahedral interstitial sites by H atoms.

**References**

NMR research into H$_2$O-H$_2$O$_2$-D$_2$O system

Nikolay S. Vasilyev$^2$, Denis V. Kashaev$^1$

$^1$Physics and engineering department, Kuban state university, 149, Stavropolskaya st., Krasnodar, Russia, 350040
$^2$South Scientific Centre of Russian Academy of Sciences, 41, Chehova st., Rostov-on-Don, Russia
E-mail: nikolasvs@mail.ru

Introduction

In this report we discuss results from our study of the H$_2$O-H$_2$O$_2$-D$_2$O system with different concentration D$_2$O and H$_2$O$_2$. It is known that H$_2$O, H$_2$O$_2$ and D$_2$O molecules play an important role in a variety of different biochemical reactions and biophysical processes of live cells. We compared the results of studies of the spin-lattice relaxation time, chemical shift (HD) of H$_2$O-H$_2$O$_2$-D$_2$O and H$_2$O-D$_2$O systems.

Experiment

Measurements were carried out on a NMR spectrometer JEOL JNM-ECA 400. It was used the distilled water with resistance 300 kOm/sm and D$_2$O (enriched to 99.8% in deuterium). The water samples for the deuterium measurements were prepared with different concentrations of D$_2$O (C), lay in the range of 7 – 97 %. The peroxide samples for the deuterium measurements were prepared with different concentrations of H$_2$O$_2$ lay in the range of 0 – 100%. The point 0% means that the sample contains only H$_2$O$_2$ (37% of peroxide and native concentration of deuterium) and the point 100% is equal the net D$_2$O (enriched to 99.8% in deuterium). The spin-lattice relaxation times (T$_1$) were measured at 61.4 MHz. The pulse sequence used was 180° - τ - 90°. The temperature in the probe was controlled with the accuracy of ±0.5 K. The uncertainties of the derived T$_1$ values was estimated to be 2 %.

Results and discussion

The concentration dependence of the HD spin-lattice relaxation time in H$_2$O-D$_2$O and H$_2$O-H$_2$O$_2$-D$_2$O liquids present in figure 1. T$_1$ is determined at 293 K. Results indicates, that the spin-lattice relaxation time dependence has the polynomial form. Curve approximations are shown on the figure 1. The upper curve corresponds to the H$_2$O-H$_2$O$_2$-D$_2$O system, the lower curve - H$_2$O-D$_2$O system. The figure 1 shows that the curves differ from each other. Extremes of polynomial functions are located in different places in the concentration range. Function (H$_2$O-H$_2$O$_2$-D$_2$O) has a maximum and a minimum (H$_2$O-D$_2$O system). We used the expression obtained in [1] for the relaxation time, to determine the parameters that change when you add the peroxide in the H$_2$O-D$_2$O system. We conclude that these parameters are the activation energy (related to the correlation time) and the so-called parameter of asymmetric. Specified parameter describes the structure of a nonuniform electric field (deviation from axial symmetry) [2]. The spin-lattice relaxation time has a polynomial quadratic dependence on the parameter of asymmetric. The activation energy varies linearly with increasing concentration of deuterium in the H$_2$O-D$_2$O system.

Also it was found [1] that the deuteron relaxation times can be explained by considering only two contributions to T$_1$. One of them was associated with the breaking of hydrogen bonds and another with the rotational relaxation of single water molecules. It is possible that the both contributions define polynomial concentration dependence of the HD spin-lattice relaxation time. Experimental NMR measurements of the deuterium in neat D$_2$O water indicated that the motion of water is anisotropic [3].

Consequently, an increase in deuterium concentration in the H$_2$O-H$_2$O$_2$-D$_2$O system increases the intensity of competition of the exchanging processes between the water and the peroxide molecules. In addition, we obtain the time-averaged data on relaxation processes. This leads to an increase in relaxation time and the availability of near maximum concentration (33%).

References

Testing of cigarette filters by low-field NMR method

Vladimir Y. Volkov¹, Ekaterina V. Sosunova²,³

¹Moscow State University for Equipment Engineering & Informatics, Moscow 107996, Russia
²Central Research Institute of Tuberculosis, Russian Academy of Medical Sciences, Moscow
³DNA Synthesis LLC, Moscow 127238, Russia

E-mail: volkovobolensk@mail.ru

Introduction

More than 400 billion cigarettes per year are produced in Russia. To reduce the harm to health of the smoker, as a rule, is used smoke filters. In this report the method for checking the quality of filtration by using a low-field NMR is proposed.

Experiment

Cigarettes “Yava classic” (10 mg tar per cigarette according to data on pack), “Next Rose” (3 mg/cig) and “Pall Mall” (1 mg/cig) were studied. Cigarette was smoked after conditioning in desiccators with relative humidity of 60% for one week. Smoking was carried through the usual or elongated mouthpiece (Fig.1). Cigarette quenched up 5-7 mm before filter. Then filters were carefully separated from the unburned tobacco and immediately placed in glass vials of 10 mm in diameter with a tight lid. Cigarette smoking was carried out by using of simple pump with a puff volume of 35-50 cm³, do not more than one puff per minute.

Figure 1. One or two more filter sticks (F1, F2) were inserted to mouthpiece with elongated nozzle to determine the breakthrough of smoke particle through the cigarette filter (F0)

NMR relaxometer “Hromatek-Proton-20M” with resonance frequency 20 MHz, duration 90°-pulse 2.2 µs, and “dead time” 10 µs, was used for measurements. One multi-pulses sequence like CPMG, but at step by step increasing intervals τᵢ between 180°-pulses [1], was used to measuring full FID curve (FID plus echo’s amplitudes):

\[ 90°-\text{FID}_{\tau₁}(180°-\text{echo} _{-\tau₁})_{n₁}\cdots(180°-\text{echo} _{-\tau₂})_{n₂} \cdots, (1) \]

where \( \tau_{i+1} = (\tau_i + \Delta \tau_i) \), \( i = 1, 2, 3, \ldots \)

Full FID’s, recorded by this method (Fig. 2), are well described by the sum of three groups of exponents. The first Gaussian exponent relates to the protons of cellulose acetate, of that is made a cigarette filter, has the largest amplitude (\( A_{\text{acetate}} \)) and time \( T_{2A} = 15 \pm 19 \) µs. Second wide spectrum of exponents has \( T_2 = 0.1 \div 3 \) ms and refers to the protons of smoke water that was condensed on the filter. Third, the slowest exponent has time \( T_2 \) more than 20ms, and refers to the protons of crude tar that was captured on the filter.

Figure 2. Full FID’s (FID plus echo’s amplitudes) for pure and smoked filters of Yava cigarettes

Relationship \( A_{\text{water}}/A_{\text{acetate}} \), \( A_{\text{tar}}/A_{\text{acetate}} \), and \( (A_{\text{water}}+A_{\text{tar}})/A_{\text{acetate}} \) respectively refers to the amount of condensed water, amount of tar and the total amount of smog delayed by filter. So, the measurement data is automatically normalized to the proton density of pure dry filter and can be converted to the weight of the filter.

Figure 3. Components of tobacco smog were absorbed by cigarette filters

Presented on Fig. 3 experimental data show that the tested cigarette filters captures only a part the harmful components of tobacco smog. Half or more pollutants may penetrate through the cigarette filter depending on the depth and frequency of puffs. Thus, the proposed method can be used to assess the quality of cigarette filters.

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List of Participants

Alexandriysky Viktor V.
Ivanovo State University of Chemical Technology
Ivanovo, Russia
nmr@isuct.ru

Andronenko Sergey
Kazan Federal University
Kazan
Russia
sergey_andronenko@gmail.com

Anisimov Nikolay Viktorovich
Faculty of Fundamental Medicine, Lomonosov Moscow State University, Moscow, Russia
anisimovnv@mail.ru

Balci Erdem
Gebze Institute of Technology
Gebze-Kocaeli, Turkey
erdembalci_05@hotmail.com

Borisenko Nikolay Ivanovich
Southern Federal University
Rostov-on-Don, Russia
bon@ipoc.rsu.ru

Borodkin Gennadii
Institut Neel, CNRS
Grenoble, France
nmr@institut-neel.fr

Borodkina Inna
Institute of Physical and Organic Chemistry
Southern Federal University
Rostov-on-Don, Russia
nmr@ipoc.rsu.ru

Bunkov Yury
Institut Neel, CNRS
Grenoble, France
yury.bunkov@grenoble.cnrs.fr

Cherdakov Oleg
Department of Physics
Saint Petersburg Electrotechnical University “LETI”
Saint Petersburg, Russia
chedakov@bk.ru

Cheremisim Vladimir Maksimovich
Faculty of Medicine
Saint Petersburg State University
Saint Petersburg, Russia
vm_cher@mail.ru

Chernyshev Yuri Sergeevich
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
cher@nmr.phys.spbu.ru

Chertkov Vyacheslav
Department of Chemistry Moscow State University
Moscow, Russia
vchertkov@hotmail.com

Chizhik Vladimir Ivanovich
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
vchizhik@mail.ru

Dolinenkov Philip
IKBFU
Kaliningrad, Russia
dolinenkov@mail.ru

Donets Alexey V.
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
aldonets@mail.ru

Drozdov Aleksandr Andreevich
Faculty of Medicine
Saint Petersburg State University
Saint Petersburg, Russia
a_a_drozdov@mail.ru

Dvinskikh Sergey V.
Royal Institute of Technology
Stockholm, Sweden
sergeid@kth.se

Egorov Andrei
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
egorov@nmr.phys.spbu.ru

Fedyukina Galina, Nikolaevna
FBIN State Research Centre for Applied Microbiology and Biotechnology
Obolensk, Russia
galafed@mail.ru

Fraissard Jacques Paul
university P. and M. Curie, ESPCI
Paris
France
jacques.fraissard@upmc.fr

Frolov Viatcheslav
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
vfr0lov@bk.ru

Gamov George Aleksandrovich
Ivanovo State University of Chemistry and Technology
Ivanovo, Russia
kax504@isuct.ru

Gerts Egor
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
gerts-e-d@yandex.ru

Gunduz Aykac Ilknur
Gebze Institute of Technology
Kocaeli, Turkey
Ilknur_gunduz34@gmail.com

Ilina Oksana
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
oxana.ilina@gmail.com

Izhev Vassily
Peoples’ Friendship University of Russia
Moscow, Russia
chemistry@mail.ru

Jena Vinod
ICFAI University Raipur
BHILAI
INDIA
jena_vinod02@gmail.com

Jurga Stefan
Adam Mickiewicz University Poznan
Poznań
Poland
centrum@amu.edu.pl

Kamyshanskaya Irina Grigor’evna
Faculty of Medicine
Saint Petersburg State University
Saint Petersburg, Russia
irina_k@mail.ru

Karseev Anton Yuryevich
Saint Petersburg State Polytechnical University
Saint Petersburg, Russia
antonkarseev@gmail.com

Kashaev Rustem Sultan-Hamit
Kazan State Power Engineering University
Kazan, Russia
kashaev2007@yandex.ru

Kharkov Boris
Department of Chemistry, Royal Institute of Technology - KTH
Stockholm, Sweden, Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
kharkov@kth.se

Komolkin Andrei V.
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
komolkin@nmr.phys.spbu.ru

Krylova Ekaterina
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
krylova_ea2803@mail.ru

Kupriyanov Paul
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
p.kupriyanov@nmr.phys.spbu.ru

Kupriyanova Galina
I. Kant Baltic Federal University
Kaliningrad, Russia
galkupr@yandex.ru

Lavrov Sergey
Faculty of Physics
Saint Petersburg State University
Saint Petersburg, Russia
aze4h@rambler.ru

Litov Konstantin
Ivanovo State University of Chemistry and Technology
Ivanovo, Russia
SEVERUS_87@mail.ru

Loskutov Valentin Valentini
Mary State University
Yoshkar-Ola, Russia
vval_losk@rambler.ru